INTERACTIONS BETWEEN
ORGANIC POLYMERS AND
CEMENT HYDRATION PRODUCTS

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THESIS SUMMARY

Organic substances, particularly polymers, are finding increasing use in modifying the properties of cements and concrete. Although a significant amount of research has been conducted into the modification of the mechanical properties of cements by polymers, little is known about the nature of the interface and interactions taking place between the two phases. This thesis addresses the problem of elucidating such interactions.

Relevant literature is reviewed, covering the general use of polymers with cements, the chemistry of cements and polymers, adhesion and known interactions between polymers and both cements and related minerals.

Although several polymer systems were studied, two in particular were selected, as being well characterized. These were : - 1) polymethyl methacrylate (PMMA), the polymer derived from methyl methacrylate (MMA), and 2) an amine-cured epoxy resin system. By this approach, a methodology was developed for the examination of other polymer/cement interactions.

Experiments were conducted in five main areas : -

1) polymer-cement adhesion and the feasibility of revealing interfacial regions mechanically,
2) chemical reactions between polymers and cements,
3) characterization of cement adhesion surfaces,
4) interactions affecting overall polymerisation rates, and
5) studies of polymer impregnated cements.

The following conclusions were reached : -

1) The PMMA/cement interface contains calcium methacrylate as an interfacial reaction product, water being a reactant. Calcium methacrylate is detrimental to the properties of PMMA/cement composites, being highly water-soluble.

2) The pore surface of cement accelerates the polymerisation of MMA, leading to a decreased molecular weight compared to polymerisation of pure MMA, minerals in hydrated cement powders having the opposite effect.

3) The investigation of reaction products presents a number of experimental problems, selection of appropriate techniques depending upon the system studied. For the two systems examined in detail, ion chromatography proved particularly useful; DTA, IRS and XPS indicated reactions, though the data was hard to interpret; XRD proving inconclusive.

4) It is impractical to reveal interfacial regions mechanically, but may be accomplished by chemical means.

KEY WORDS : - Interface; bonding; cement; polymer; methyl methacrylate.

To my grandparents : -

Robert Mackison McNaught and **Bessie Collins McNaught**

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1 INTRODUCTION AND AIMS

Polymer-cement systems, where polymers act as binders, reinforcing agents or modify the properties of fresh cement have been investigated for many years. Significant improvements in strength, decrease in absorption characteristics and improved durability have stimulated considerable international interest and research into these novel composite materials.

1.1 TYPES OF INTERACTION BETWEEN CEMENTS AND POLYMERS

Interactions between cements and polymers may occur in a number of ways depending upon the application. For the purposes of this project it was convenient to consider all polymer/cement interactions as one of two types - either where monomers come in contact with hydrated cements and are then cured, or where monomers or polymers are added to fresh cement before or during its hydration.

The two types of interaction may be subdivided into six categories as follows : -

1) Adhesives and surface coatings
2) Polymer concrete (PC)
3) Polymer impregnated cement (PIC)
4) Admixtures
5) Polymer portland cement concrete (PPCC), and
6) Macrodefect-free cement (MDF).

Explanation of the strength modification of cements incorporating polymers have been interpreted by reference to simple models, requiring the assumption that the two materials making the composite have the same properties within the composite as they do in bulk. In most cases this has been shown not to be true, the increase in strength being greater than predicted by assuming the proportions of each component contribute to the composite's properties directly, i.e. polymer / cement composites do not always obey the rule of mixtures. An explanation of this has been to suggest that polymers heal microcracks or blunt the crack tips, such that more energy is needed to propagate the cracks, hence strengthening the material.

1.1.1 POLYMERS USED WITH HYDRATED CEMENT

The first subdivision includes resins used as adhesives in the construction industry and as repair materials for patching decaying or damaged concrete. Such resins may also be used for crack injection. Surface coatings are used on concrete, not only to improve their abrasion resistance, general wear properties and permeability, but also as decorative finishes in many indoor and outdoor applications. The paint industry has developed many such products for application to surfaces of cement articles.

It was found that certain polymers are able to penetrate deep into cement pore systems, rather than just the outer few millimetres. These PIC articles are attracting increasing interest as it has been shown that impregnation greatly improves the strength and durability of cements. It is hoped that the corrosion of reinforcement in concretes may be reduced if impregnation succeeds in reducing their permeability.

A further application of polymers uses resins as an analogy to concrete : In these materials an aggregate is mixed with a binder and the composite allowed to cure. In concrete, cement is the binder, but in these PC materials it is a resin.

1.1.2 POLYMERS USED WITH HYDRATING CEMENTS

This group of interactions concern the effects of polymers and other organic compounds on cements during hydration, thus facilitating the processing, hydration kinetics and final properties of fresh cement. Such substances are known as admixtures.

The polymer in PPCC is also sometimes considered an admixture, because it is often added as an emulsion to the fresh cement. This assists both hydration and the final properties after curing.

A further development has led to the quite remarkable MDF cements. In these materials highly polar, water-soluble polymers are added to hydrating cements, the polymers binding the hydration products. After special processing involving rolling and pressing, the materials produced are of very high strength, to the extent of being strong in tension as well as compression, unlike ordinary cements.

1.1.3 OTHER RELATED MATERIALS

A closely related field relevant to this whole area of study is that of dental and orthopaedic materials. A considerable amount of research has been conducted into the problems of developing very strong adhesives of low toxicity and very high durability that may be cured in contact with living human tissues with the minimum of distress to the patient and damage to other tissues. Such preparations are used for dental fillings, repairs and bone-bonding agents. Although some lines of enquiry involve exotic and expensive adhesive materials, the problems are basically the same as in polymer/cement systems i.e. the bonding of organic polymers to inorganic substrates composed of calcium salts.

1.2 SCOPE OF KNOWLEDGE ABOUT POLYMERS USED WITH CEMENT SYSTEMS

There has been a considerable amount of work conducted into the nature of polymers used with cements. Many types are recognised, and the mechanisms by which they polymerise, together with how this may be accomplished, are well understood.

Mechanical testing to failure as well as providing figures of ultimate strengths of materials can yield interesting information as far as the locus (or path) of failure is concerned : this is of interest in assessing whether the failure is through the cement, polymer, interfacial or a combination of these. Only a small amount of work has been done in this area. Also, because polymer/cement composites are relatively new, only a small amount of work has been conducted into durability studies.

The diffusion mechanisms of polymers and their nature within a pore structure has attracted some attention, authors relating polymer chain lengths to pore size distributions. However, there are some anomalies, and only a small amount known about the kinetics of polymerisation in porous media.

Interaction products from surface reactions have proved hard to detect, some inconclusive work having been carried out on specific polymers.

Elementary measurements have determined the amount of polymer that may be incorporated in cements by impregnation, and there are numerous publications on the strengthening of cements by polymers. Abrasion resistance studies have been carried out, together with assessments of the adhesive properties of polymers and polymer

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concretes to fresh cement and concrete surfaces. Studies have also been carried out on the plasticising effects of polymers together with their effects on hydration kinetics.

1.3 OTHER AREAS OF INTEREST TO THIS PROJECT

Some areas are less well studied and could be considered as the 'finer points' of the field. In many ways, as far as the civil engineer is concerned, the fact that polymers modify cements in useful ways is of greater interest than how this occurs : the development of new and better building materials attracting more research interest than the mechanisms by which this is achieved. Nevertheless, a theoretical understanding of polymer/cement interactions could lead to better selection of materials and the anticipation of certain problems before they arise.

1.3.1 EXAMINATION OF POLYMER INTERFACES

Many practical problems are associated with the study of polymer/cement interfaces : these arise from the fact that interfaces are seldom flat planes between identical materials that can be separated exactly at the boundary. These problems make interfaces rather elusive, their nature being inferred from other associated investigations, for example the study of interfacial interaction products. Bearing this in mind, it is possible to develop models of interfacial adhesion, identifying those features that would be useful to study.

The simplest model would be where polymer bonds to a cement surface without reacting as such, and where negligible diffusion has taken place *(fig 1.1)*. The nature of the bonding would depend particularly on the flow properties of the monomer, its contact angle with, and the roughness of the cement surface. With such a model, near interfacial fracture could be envisaged during mechanical testing.

Developing the model further we would take into account the fact that diffusion into the cement would probably occur, and equally diffusion of certain soluble cement phases into the polymer could also be envisaged *(fig 1.1)*. In this model, pore size and penetration would be important, particularly if the pores were of compatible size to the monomer molecules. Capillary driving pressure and diffusion would govern the penetration of polymer. Also, any changes in the density of the polymer would introduce stresses and change the pore structure of the cement.

Finally, the possibility of reaction layers must be taken into account. Reactions could take place simply between cement and monomer, the adhesion surface being subjected

to the heat and products of the reaction as well as the heating effects from the polymerisation itself *(fig 1.1)*. As with the polymer, if the reaction products have different densities than their component reactants then stresses could be set up within the pore structure of cements.

All these possibilities are useful areas of study when considering polymer/cement interactions.

1.3.2 SCOPE OF THIS PROJECT

As can be seen above there are many different polymer/cement systems available for study, each having a large number of variables in itself; cementitious building materials are made with widely differing compositions including concretes, mortars, slags, PFAs, these being made with different water/cement and water/solids ratios, cured under a number of different regimes for different times. Polymers too have very different physical and chemical properties requiring different curing conditions and application techniques. Most polymer types may be blended together to modify the properties of the mixture, there being thousands of different blends commercially available.

Clearly it was necessary to restrict the number of variables - this being done in two ways :- First by restricting investigations to interactions taking place between polymers and hydrated cements only, polymer effects on cement hydration being excluded. Secondly, limiting the choice of materials to OPC pastes of different water/cement ratio and cure time, restricting the inorganic components. The polymers used almost exclusively in this work were polymethyl methacrylate and an amine-cured epoxy system. The latter were chosen as 'typical' polymers used with cement systems; methyl methacrylate being well characterised, and epoxy a common repair material.

Because the study of interfaces of this kind presents certain potential problems it was decided that a wide range of techniques would be used in the hope of establishing a methodology for approaching polymer/cement interactions that could be applied to other polymers and cementitious materials.

The project was conducted along the following lines :-

1) Polymer was cast against hydrated cement surfaces to allow mechanical testing of the interface in order to examine the locus of failure. Attempts were also made to assess the strength of the adhesive bond between polymer and cement.

2) Bulk reaction products were investigated, the interfacial area being maximised by using hydrated cement powders.

3) Interfacial as opposed to bulk reaction products were studied together with visual observations of near-interfacial areas produced by the mechanical testing.

4) Interactions affecting the kinetics of polymerisation were studied in both powdered and impregnated cements.

5) Polymer / cement interactions in polymer impregnated cements were studied in terms of pore filling models and the structure of the polymers within the cement pore system.

FIGURE 1.1
TYPES OF INTERFACE

SIMPLE	DIFFUSIONAL	COMPLEX
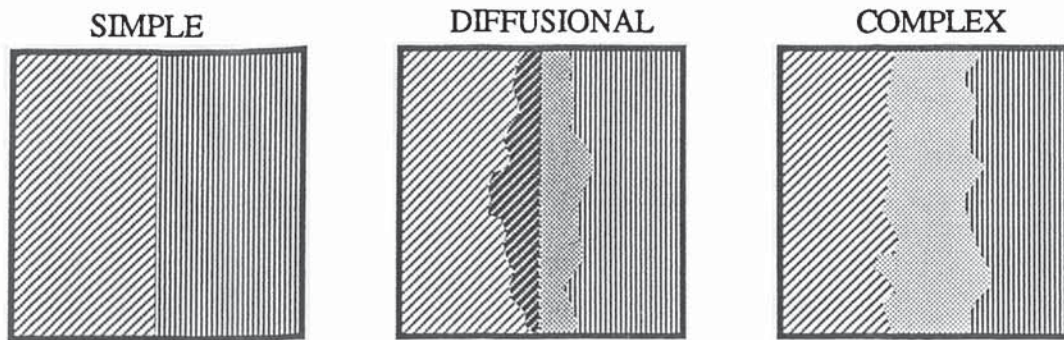
SIMPLE - One component is in contact with the other with
negligible diffusion or reaction.
DIFFUSIONAL - Each component diffuses across the interface into the other.
COMPLEX - A zone of reaction products are formed at the interface.

DETAIL OF POLYMER / CEMENT INTERFACE

pore —→

Void—

Pore partially filled
with polymer

CEMENT

Void filled
with polymer

POLYMER

Line of
cement
surface
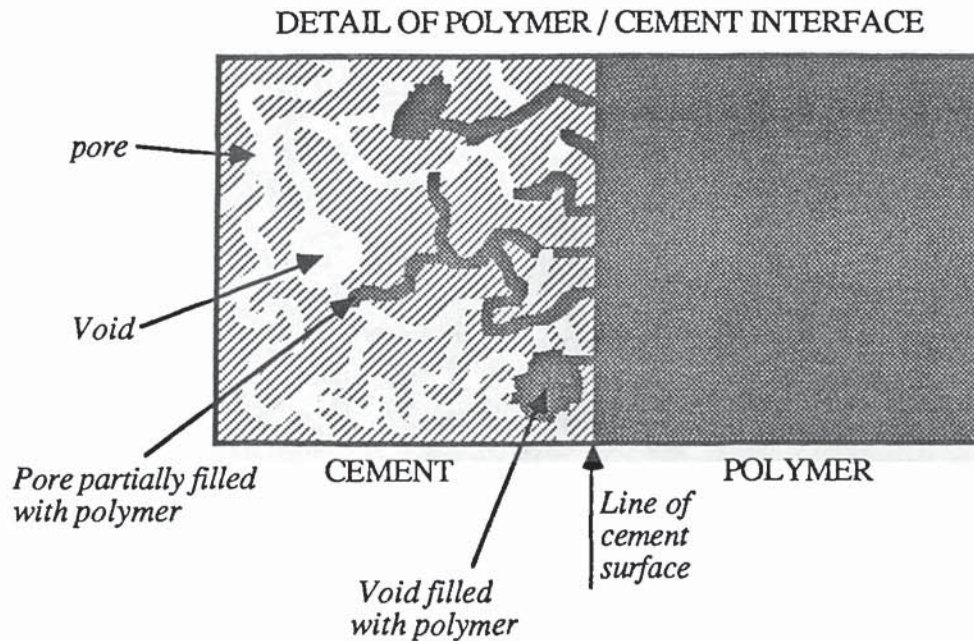
The interface formed by polymer in contact with cement surfaces
is blurred by diffusional effects, drawing the polymer into the cement
pore structure, and may be complicated further by interfacial reaction products.
Thus the interface is not planar even with machined cement surfaces.

2 LITERATURE REVIEW

2.1 THE USE OF POLYMERS WITH CEMENT SYSTEMS

In recent years there has been an increasing interest in the use of polymers to modify the physical and chemical properties of cement systems. Polymers may be used as coatings to enhance the surface properties of cement units, or may be incorporated in the body of a cement in a number of ways, forming a family of new composite materials. Both of these applications attempt to remedy basic problems inherent in cement systems, for example, the poor resistance to chemical attack, rapid freeze-thaw deterioration, low tensile and shear strengths, air voids and shrinkage cracking *(ref 1)*.

2.1.1 SURFACE COATINGS AND PATCH MATERIALS

Coatings are applied to cements to increase their durability and prolong their useful lifetimes. As a preventative measure, coatings are useful to limit the permeability of cements particularly to such species as Cl^- which is a major factor in the corrosion of steel in concrete. Penetration by water, CO_2 and SO_2 is also limited by coatings, hence their use in limiting carbonation and sulphate attack *(ref 2)*.

Several classes of coating have been established, these include:-

a) Thermoplastic - plastics which soften on heating,
b) Thermosetting - plastics which set once irreversibly,
c) Solutions - surface treatments dissolved in suitable solvents,
d) Emulsions - dispersions of treatments in suitable liquids, and
e) Sheets - preformed surface wrappings.

Selection of the most appropriate coating for a particular application requires assessment of many factors - These range from environmental and dimensional considerations, through the physical properties (strength, elasticity, viscosity, creep, thermal expansion, permeability etc.) of the coatings themselves, to economic considerations of film thickness, pot life, application method and cure times.

A vast range of products are available for use as coatings including:-

a) silicones, polyethylene, asphalt and waxes (thermoplastics),
b) epoxies, neoprene and urethane (thermosets),

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c) silicates and flourosilicates in solution,

d) polyvinyl acetate, acrylics and bituminous emulsions, and

e) rubber and resinous sheeting *(ref 3)*.

Coatings are also used in the repair of concrete structures following the appropriate mapping and preparation of the repair surfaces. Where damage has occurred from corrosion of steel in concrete structures, repair is affected by restoring the original alkaline environment of the cement, or by providing a physical barrier to air and water *(ref 2)*.

After identification of the affected area, the first stage in the repair process is to cut back all the unsound cement until a clean, firm surface is exposed. The steel is similarly cleaned to remove any rust or scale that has developed during corrosion. Where steel is badly corroded it is cut out and fresh steel welded in as bars or a mesh. Resin or cementitious mortar is then applied in layers 15-25 mm thick, this providing a coating for the reinforcement. Several coats are used to build up the repair, a final decorative coat being used to make the repair blend in with the rest of the structure *(ref 2)*. Polymers are also used as sealants for cracked or damaged concrete, various commercial epoxies and polyurethanes being employed. Recent work has also demonstrated the use of high molecular weight polymethyl methacrylate in this context *(ref 4)*.

In some applications the fire resistance of the repair may need to be taken into account, since charring of polymer mortars may result in a loss of strength at the repair. Fire can also present problems from the combustion products of polymers. These are usually acrid, accompanied by dense smoke and often toxic.

2.1.2   POLYMER / CEMENT SYSTEMS

Properties of cement systems can be further modified by the incorporation of polymers to the bulk of the cement itself. The resulting polymer/concrete composite systems have been developed to modify concrete in three main ways:-

a) To adjust the rheology of the freshly mixed concrete,

b) To develop strength during the setting process, and

c) To improve the ultimate properties of the hardened concretes *(refs 1 & 4)*.

For most purposes it is this last facility that is of most interest. Improvements particularly in mechanical properties can be directly related to the filling of the pore and microstructures of the cement with load-bearing polymers. These improvements are a function of:-

a) The extent of the pore filling,

b) The load-bearing characteristics of the polymer used,

c) The amount of monomer to polymer conversion, and

d) The type of concrete and its precasting method *(ref 1)*.

The incorporation of polymers may be accomplished in a number of ways, giving rise to a number of classes of polymer-concrete composites.

2.1.2.1 POLYMER CONCRETES (PC)

These consist of a polymer as binder for some sort of aggregate, with the polymer as the continuous phase. The overall properties of the composite will depend mostly upon the mechanical behaviour of the polymer *(ref 6)*. Ductility tends to be greater in these materials than in other polymer/cement systems and creep can also be substantial especially at high temperatures. Strength may be improved by the use of chemical coupling agents which increase the bonding (see later). The proportion of polymer to aggregate also affects strength; some studies recommending the use of additional cross-linking agents. Poor hydrothermal durability has also been noted and cracking problems sometimes occur due to internal stresses generated by thermal expansion of polymer *(ref 6)*.

Many substances have been used as the aggregate in PC, one ecologically interesting application using re-cycled waste. Problems of bleeding may occur if the aggregate concentration is too low or of too low density. Excessive vibration should also be minimised during the forming process as this too can cause bleeding and segregation.

Polymers typically used in PC include polyester, polyester-styrene, epoxy-furan and epoxy with dibutyl phthalate. PCs for use at higher temperatures employ such binders as acrylonitrile, styrene-divinylbenzene and methyl methacrylate.

Polymerisation of the monomer may be accomplished by use of an initiator by itself, or an initiator and promotor; hardeners and coupling agents are used for epoxies.

2.1.2.2 POLYMER PORTLAND CEMENT CONCRETE (PPCC)

This class of composite involves addition of polymer material to a cement before it has undergone its initial hydration. The polymer may be in the form of a thermoplastic monomer (for subsequent polymerisation) or as a thermoplastic polymer emulsion of particle size 0.05-1.0 mm *(ref 7)*. In the finished composites there is no overall polymer network formed. Polymer emulsions surround cement grains inhibiting the formation of a supersaturated solution of hydration products, thus acting as hydration retarders. As hydration proceeds, water from the emulsion becomes incorporated in the hydrating cement and is also removed through capillary pores. There is therefore a transfer of polymer from the emulsion to the solid phase, affecting the physical properties of the cement. Generally, polymer additives are used to increase the strength of the final composite. Typical polymers include natural rubber latex, neoprene latices, styrene-butadiene rubber latices, polyvinyl esters and polyacrylics, although alkaline degradation of the latter two has been noted *(ref 7)*.

Other applications aim to modify the rheological properties of the cement mix by introducing flocculation of the cement paste. Such substances as polyurethanic acid, cellulose and starch esters have shown potential for many years, although perhaps better considered admixtures *(ref 1)*. Assessment of rheological properties on site has been done by consideration of the spreadability of the mix, and is mainly related to cement/polymer and water/cement ratios *(ref 8)*.

Investigations of the bonding in polyester-styrene / siliceous aggregate mixtures show hydraulic instability of the carboxylic ester groups. Such degradation can be minimised by the addition of beta-Ca_2SiO_4. This releases Ca^{2+} in an aqueous environment leading to the formation of ionic bonds between Ca^{2+} and the carboxylic anions of the ester *(ref 5)*.

Research has been conducted into the use of chemically cured polymers added to hydrated cement mixes. Typical is the use of water-dispersable epoxies due to their greater cross-linking ability and faster setting times than other latices. They are also less susceptible to chemical attack. Work also continues into chlorosulphonated polyethylenes, phenol-formaldehyde, urea-formaldehyde and polyurethane additives. With the exception of the ester-modified concrete 'Estercrete', such materials are not yet economic to produce *(ref 5)*.

2.1.2.3 POLYMER IMPREGNATED CONCRETE (PIC)

PICs (as the name suggests) are composites where a hardened cement article suitably prepared is impregnated with liquid monomer which is subsequently polymerised.

The history of such materials dates back to work conducted into impregnation of wood with polymers *(ref 5)*. This was directly applicable to cements requiring low viscosity monomers for impregnation, polymerisation being accomplished by one of three methods:-

a) Thermal catalytic,
b) Promoted catalytic, and
c) Radiation induced.

All three processes result in the formation of free radicals, and polymerisation proceeds via chain reactions. Thermal catalytic polymerisation uses an initiator to produce free radicals at elevated temperatures (60-100°C typically) *(ref 9)*, whereas promoted catalytic polymerisation employs a promotor to produce the free radicals at ambient temperatures. Production of free radicals is easier with a promotor, but much less controlable - thus the required depth of penetration must be achieved before substantial polymerisation (and hence thickening) has occurred.

Radiation polymerisation was developed as a result of work done by the United Kingdom Atomic Energy Authority on nuclear waste storage *(ref 5)*. The process involves free radical production by gamma-ray bombardment. Radicals are produced at ambient temperatures, but the large thicknesses of biological shielding needed for handling such penetrating sources, together with their cost and slow polymerisation times, can be somewhat disadvantageous.

Although most PICs involve low viscosity monomers for free-radical polymerisation, studies have been carried out on impregnation with hot epoxy resins *(refs 10 and 11)*. Viscosity of the resin/hardener mix is reduced at higher temperatures (105°C for example) and allows substantial penetration of the liquid. Evaporation losses are not significant with epoxy resins, but as the impregnation temperature approaches the degradation temperature for the polymer, the forming process involves some difficulty.

Techniques for producing PIC have been developed over many years. Basically they involve casting the initial cement article and allowing it to cure for an appropriate time.

This is then oven-dried and saturated with monomer, initiator and promotor as appropriate. Once a satisfactory depth of monomer penetration has been achieved, polymerisation can be carried out by an appropriate technique *(ref 12)*, for example by irradiation. Drying is often carried out at around 150°C, although temperatures of up to 400°C have been tried. Impregnation is often carried out at atmospheric pressure, although high pressure soaking preceded by evacuation provides a greater depth of penetration *(ref 5)*. Some studies have shown that penetration rate is proportional to the square root of the time of soaking and also proportional to the applied pressure *(ref 1)*.

It has been demonstrated that PIC has greater strength, better surface properties, corrosion resistance, abrasion resistance and freeze-thaw durability than ordinary cements *(ref 13)*. Study of the microstructure of PIC show a lack of microcracking after loading, compared to that expected from ordinary cements. In addition, it has been found that poorer grades of aggregate may be used in PIC if the impregnation is substantial *(ref 14)*.

Gebauer et al *(ref 15)* published optical and scanning electron photomicrographs showing methyl methacrylate and styrene impregnated samples in thin section with the polymer partially or wholly filling the pore structure and capillaries of the cement. It was concluded that methyl methacrylate and styrene impregnation leads to vast improvements in strength and corrosion resistance by this process.

Polymers typically used in PIC include acrylonitriles, methacrylates, vinyl chloride styrenes and divinylbenzene with initiators of benzoyl peroxide and azobisisobutyronitrile. Promotors include dimethyl toluidine, dimethyl aniline and cobalt napthenate.

In spite of the relatively high monomer costs, PIC remains one of the most promising uses of polymers in cement. It has already seen use in bridge decks, baths and flooring slab applications *(refs 9 and 16)*, and to improve the bonding of smooth steel bars to concrete *(ref 17)*.

2.1.2.4 MACRODEFECT-FREE CEMENT (MDF)

The search for new high-strength materials has produced certain novel ceramic materials, one of the most interesting being MDF cements. Birchall *(refs 18 and 19)* reviews a number of new high-strength composite materials finding MDF cements of comparable bending strength to aluminium. Ceramics are not generally thought of as

particularly strong in tension or bending, but as Birchall points out, in the appropriate context or with the right processing, this need not be the case. For example, the shells of sea creatures are both light and very strong, being composed of a matrix of calcium carbonate crystals. If this were one solid crystal then its strength properties would be far less impressive. Similarly, with the appropriate processing cements can be made incredibly strong. It was noted that in ordinary cements the strength is determined mostly by their porosity. Thus cements of a low W/C ratio are stronger than those of a high W/C ratio because they contain less voids. Using a Griffiths model of cement strength, all the voids are potential crack-initiation sites. Voids are however an unavoidable part of ordinary cements, but by adding a polymeric binder and rolling the cement under high shear it is possible to knead out the majority of the voids and consequently increase the strength of the cement. Studies of the microstructure of MDF cements compared to OPCs by Alford *(ref 20)* showed almost identical fine microstructures, but the absence of larger pores in MDF cements. For this reason such composites are 'macrodefect'-free, rather than 'defect'-free cements. Although the use of such materials is not yet widespread, their potential was demonstrated by Birchall *(ref 21)* who produced an effective MDF spring.

Polymeric materials typically used in MDF cements are water-soluble polymers such as polyvinyl acetate (PVA) and polyacrylamide. A typical procedure as described by Sinclair *(ref 22)* involves mixing powdered polymer with unhydrated cement and water in the ratio of 10:100:12, this being mixed and sheared between rollers. During the processing the polymer begins to bind the cement and also lubricates the grains to assist rolling. The resulting material was left to harden for 12 hours under moderate pressure then dried at 80°C for four hours.

The use of MDF cements although highly promising as building materials is associated with certain practical problems. For large-scale work the polymers used are relatively expensive and the rolling and pressing needed in the processing is relatively sophisticated. Dimensional stability also presents difficulties where MDF cements are used in aqueous environments. The problem arises from the fact that the polymers and the cations cross-linking them are both water-soluble, this leading to leaching, strength reduction and swelling problems on long exposure to water *(ref 23)*.

2.2 CHEMISTRY OF CEMENT MINERALS

2.2.1 HYDRATION CHEMISTRY OF ORDINARY PORTLAND CEMENTS

The chemistry of cement hydration is highly complex, receiving a vast amount of world-wide study. For the purposes of this project setting reactions themselves are of only background significance, since it is interactions between hydrated cements and polymers that are of most interest. However, hydration chemistry is very important in that it predicts the mineral assemblage, aspects of the morphology and pore system that polymers will encounter when used with hydrated cements.

The following account illustrates the chief minerals and major reactions occurring during hydration. It has been assembled from publications by Lea *(ref 24)*, Lea *(ref 25)* and Soroka *(ref 26)*.

All the minerals in cement clinker are anhydrous. The addition of water causes many of the cement minerals to react very rapidly, forming supersaturated solutions of hydration products from which the solid hydration product crystallise. Ideally, the individual minerals would achieve an equilibrium between reactant and product dependent upon the amount of water present. Water (itself being a reactant) affects the balance of the equilibrium, thus the amount of hydration products formed will depend upon the amount of water present. The hydration reaction are also time-dependent, some occurring much faster than others, the mineral composition of cements changing with time. Theoretically speaking, complete hydration can only be achieved in infinite time, however most of the reactions approach completion within about a year.

2.2.2 CHIEF MINERALS IN OPC

Four main minerals can be identified in unhydrated OPC. These are as follows : -

  a) Tricalcium Silicate (C_3S), closely related to the mineral alite,
     this being a substituted C_3S.
  b) Dicalcium Silicate (C_2S),
  c) Tricalcium Aluminate (C_3A), and
  d) Tetracalcium Aluminoferrite (C_4AF) belonging to the solid solution
     series $C_6(AF_2,A_2F)$.

On the addition of water to the cement, all the minerals begin to hydrate at once. In spite of mutual interactions that may occur between different minerals, it is convenient to treat the hydration of each mineral separately.

Tricalcium silicate and alite

Initial hydration is fast, forming a gelatinous mass around the C_3S grains. This is a calcium silicate hydrate (C-S-H) gel from which crystals of calcium hydroxide (Portlandite) form. C_3S hydration very rarely goes to completion, crystals of hydrated C_3S being seen under the microscope as small centres surrounded by a gelatinous mass from which white hexagonal prisms of Portlandite grow.

Dicalcium silicate

Four main forms of this mineral have been identified, these being the α, α', β and γ forms. Only the β (or possibly the γ) are seen to any major extent in OPC. Hydration is slow, again forming Portlandite from the C-S-H gel, however, replacement of CaO by K_2O results in much higher hydration rates.

Tricalcium aluminate

In water alone C_3A hydrates very quickly to form small radiating needles of C_3AH_6, the hydrate of C_3A. When the hydration is taking place in a saturated solution of calcium hydroxide, the hydration is much slower. The final products are C_3AH_6 or C_4AH_{11} (tricalcium aluminate hydrate).

Tetracalcium aluminoferrite

Hydration of this mineral is again fast, the reaction consuming calcium hydroxide. Final reaction products are C_3AH_6 and C_3FH_6.

OTHER CEMENT MINERALS

It is worth also considering the effects on the hydration of the above minerals with two other commonly occurring cement minerals. These are gypsum (hydrated calcium sulphate) and calcium chloride.

Gypsum

This has no effect on the hydration of C_3S and C_2S. It does however react with C_3A to form plates and needles of C_3AH_6 which are soon overgrown with radiating needles of calcium sulphoaluminate. The practical effect of this action is to slow down the hydration of C_3A. There is an analogous reaction with the ferrite phase to form a hydrate of the solid solution series $(C,A,F,(CaSO_4)).31H_2O$.

Calcium chloride

Both C_3S and C_2S react with solutions of $CaCl_2$. The action of the chloride is to speed up the hydration reactions, particularly that of C_2S which (as mentioned above) is relatively slow. C_3A also reacts with chloride to form calcium chloroaluminates, this having the effect of binding chloride. As before, Portlandite crystallises as hexagonal plates from the C-S-H gel formed during the hydration.

2.2.3 COMPOSITION OF CEMENTS

The four main component minerals of cements are present in different abundances depending upon the composition of the raw materials used in the firing of the unhydrated cement. The composition may be determined by mineralogical, spectroscopic or chemical techniques. Where chemical techniques are used to determine the relative abundances of elements in cements, this is expressed in terms of their percentage weight as oxides, and is related to the mineral composition. The general formula used to calculate this was developed by Bogue. The mineral composition, calculated from the Bogue formula, of the OPC used extensively in this project is given in the experimental section *(see table 3.1)*.

A certain amount of research has also been conducted into the estimation of the amount of cement minerals in mixtures, for example slag and polymer impregnated cements. Various preparations have been tried to dissolve hydrated and unhydrated cement minerals, leaving the other components of the mixture relatively untouched. Kondo *(ref 27)* and Luke *(ref 28)* examined a number of such preparations. Several alcoholic solutions of salicylic acid were tried with some success (60-90% of cement minerals being dissolved), the most effective preparation being a mixture of EDTA, triethanolamine and sodium hydroxide, this dissolving over 95% of cement minerals. The possibility of even more effective preparations was discussed, these using metal complexing agents more effective than EDTA.

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2.2.4 STIFFENING AND SETTING OF OPC

Physical explanations of the behaviour of setting cement pastes are difficult to arrive at. Thus it is hard to define exactly the point at which a cement has actually 'set'. Generally the problem is looked at in the following terms ; when a cement sets it changes from a fluid to a rigid state. This constitutes the establishment of a coagulation-crystallisation network. Hardening may be seen as the further development of the crystalline structure to a rigid, unalterable network. The terms 'initial' and 'final' sets have been coined to mean respectively the time from mixing for the cement to partially lose plasticity, and the time needed for the cement to achieve the firmness to resist a certain defined pressure *(ref 26)*.

Relating the physical changes to the chemical changes on hydration cannot be done with much certainty - however, we can say that hydration of C_3A and C_4AF is very fast, the products of C_3A being of little structural use. The hydration of C_3S and C_2S is much slower, taking about a year to approach completion. It is these minerals that are thought to be responsible for the major strength developments in cements.

2.2.5 COMPOSITION OF PORE SOLUTIONS

The processes involved in forming cements proceed by crystallisation of hydrates from a super-saturated solution. As mentioned above, hydration reactions would in theory take infinite time to go to completion, and thus ions are in solution throughout the whole hydration process. Polymers used in PPCC, MDF cement and admixtures interact with these ions, so a knowledge of their chemistry is important in the study of setting reactions.

Deposition of hydrates after the initial set takes place on the pore walls of the cement. Thus, if polymers were to come in contact only with pore walls (by impregnation for instance), then it would be important to know the composition of the surface of the pore walls. This would represent the last phases to be deposited by the pore solution, and could be predicted partially by a knowledge of the composition of the pore solution from which they were deposited.

The chemistry of pore solutions is highly complex, and has attracted a considerable amount of research interest. Shin *(ref 29)* and Diamond *(ref 30)* indicate that Ca^{2+}, Al^{3+}, Na^+, K^+, SO_4^{2-}, Cl^- and OH^- go into solution on the addition of water to the

unhydrated cement. In particular Na^+ and K^+ remain in solution throughout the majority of the hydration, these being countered primarily by OH^-, pore solutions being consequently highly alkaline. Complex equilibria are set up between the different ions in solution and the solid phases, these all being affected by initial concentrations of unhydrated cement phases and temperature. It would normally be expected that pore walls of dried cements would be rich in potassium and sodium hydroxides, since it is these ions that are abundant and highly soluble in the pore solution.

2.3 DEVELPOMENT OF CEMENT MATRIX STRUCTURES

One of the most important physical processes involved in the setting of cements is the development of a pore structure. This is an unavoidable part of cement morphology, and is often detrimental. The reasons for this are twofold : - 1) that the pore structure permits ionic diffusion deep into cements, potentially corrosive ions such as Cl⁻ gaining access, and 2) that all pores may be regarded as defects in the cement structure, each a potential crack-initiation site. For these reasons, a low porosity is desirable, and may be achieved by 1) using a low W/C ratio, 2) processing to remove defects (as in MDF cements), or 3) using polymers to block or line the pore structure, and thus remedy the deficiencies that it imparts.

Measurements of the porosity of cements shows that the range of pore sizes is great, and depends both on W/C ratio and cure time. A number of models and classifications have been put forward to explain pore structure development. The basic facts that these models have to explain are as follows : -

> a) When cement powder is mixed with water the phases hydrate at different rates to produce an interlocking crystalline mass with water in the spaces between crystals.

> b) Even at low W/C ratios there is still a considerable proportion of pores <5 nm in diameter.

> c) Oven drying cements shows that some of their water is evaporable, and some is not.

> d) Cements adsorb different amounts of water at different relative humidities and temperatures, some of the water not always being recoverable.

The key factor in these considerations is the role of water in the developing structure. Water of course brings about hydration, the majority of voids being water-filled, the remainder due to air trapped on mixing. Many researchers however, believe it is an oversimplification to consider the role of water in cements simply as hydrates and free water. There is general agreement that cements contain the following *(refs 31 & 32)* : -

> a) Unhydrated cement grains,
> b) hexagonal calcium hydroxide crystals,

c) hexagonal or cubic aluminates or sulphoaluminates,

d) empty or water-filled pores,

e) poorly crystalline calcium silicate hydrate (CSH) gel, and

f) some aluminates and ferrites.

The earliest model was formulated by Powers *(ref 31)* who classified pores by size, 'gel' pores being less than 1.5 nm in diameter, 'capillary' pores being much larger. In the model water is in three environments : -

a) as hydrates,

b) water absorbed in the CSH gel, and

c) free water in capillary pores.

This model was developed by Ishai to provide explanations of volume and moisture content changes on loading cements. The role of water was thought to be five-fold, between undulating crystal layers.

a) As hydrates,

b) water in capillaries outside the range of surface forces,

c) water adsorbed onto the surface of hydrates,

d) water between two layers of hydrates, and

e) monolayers of water caged between CSH gel layers as part of the crystal structure (a 'zeolite' structure).

Ishai's model was refined in a structural sense by Feldman and Sereda (ref 31), who considered the morphology of hydrates to be 'crumpled sheets' enclosing water in the roles described by Ishai.

These models go some way to explain the basic observations about pore structure development : all models draw a distinction between free water and water in hydrates. Ishai, Feldman and Sereda's models also draw attention to sorbed water in several different environments. Adsorption/desorption can account for differences in moisture content under different conditions, and if damage to the structure occurs trapping water then some would be unrecoverable.

2.3.1 ASSESSMENT OF PORE STRUCTURES

Mercury intrusion porosimetry (MIP)

By far the most commonly used technique for pore structure determinations is that of mercury intrusion porosimetry. The technique involves forcing mercury under pressure into dried cement chips. There is a relationship between pore diameter and the pressure needed to force mercury into a pore of that size, mercury only poorly wetting a cement surface. By measuring the volume of mercury forced into the cement at different pressures, it is possible to plot the volume of pores of different diameters. The accumulated volume is the connected porosity.

Oven drying

A rough estimate of pore volume may be gained simply by measuring the change in mass of a cement on oven drying. This assumes that all the pores filled with water are connected and all water is evaporable - which is not the case. However, because the proportion of adsorbed water is relatively small, a reasonable indication of the porosity may be gained.

Density measurements

The porosity of a material is related to the density of the material and to the density of the solid phases present. The density of dried cement chips may be determined via a density bottle full of mercury, mercury not significantly wetting or penetrating the cement surface. Crushing and sieving the cement allows a second density measurement to be taken, this being the density of the solid phases. The difference between these two values allows calculation of the void volume of the original cement i.e. its porosity *(ref 33)*.

Resaturation techniques

Porosity values obtained via oven-drying are usually subject to errors when used for determinations in real cements due to partial evaporation of water from pores before testing. However, by oven-drying above 100°C it is possible to drive off the majority of the remaining water. Soaking such specimens in unreactive low viscosity liquids allows practically all the connected pore structure to be re-filled. Knowing the density and mass of liquid taken up on soaking, it is possible to calculate the volume of the

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connected pore structure. Liquids commonly used include distilled water, isopropanol and methanol.

Exchange techniques

There is evidence that oven-drying cements damages the finer pore structure. Thus resaturation techniques are subject to this problem. It is possible to minimise these effects by allowing an unreactive solvent to exchange with the pore water. By carrying out density measurements of cement saturated in water and then saturated in an unreactive solvent it is possible to calculate the connected pore volume.

Pore surface area determination

Brunauer, Emmett and Teller developed a technique (the BET technique) for determining the area of the pore surface by measuring the adsorption/desorption behaviour of an inert gas onto the pore surface. Again oven-drying is used to remove water from the pore structure prior to testing. Typically water vapour or nitrogen is used, the method requiring relatively sophisticated equipment capable of sensitive measurements.

2.3.2 COMPARISON OF TECHNIQUES FOR ASSESSING PORE STRUCTURES

Assessment of pore structures in cements is performed predominantly by MIP Although there is evidence to suggest that high pressure mercury damages the finer pore structure, it remains the only commonly used technique that gives an estimation of the distribution of pore sizes *(ref 31)*.

Resaturation and exchange techniques give very similar values for cement pastes, but blended cements are less consistent. There is also evidence that methanol reacts slowly with calcium hydroxide, making it less suitable than other low alcohols for use with cements.

The BET method involves certain errors, particularly when water vapour is used, since the sorption/desorption behaviour of cements is complex and not always reversible.

Porosity values obtained by density measurements involving crushed and sieved samples differ from those obtained by the other techniques in that they are total porosity

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measurements, the others being measures of the connected porosity. However, the latter is generally a more useful quantity.

Finally, most techniques involve oven-drying which has been shown to damage to the pore structure to some extent. Although other techniques are available they are often slow, and can involve complex equipment. For some applications, polymer impregnation for instance, oven drying is carried out as part of the processing anyway. In terms of percentage porosity this damage is relatively small, and bearing in mind the simplicity of the technique, oven-drying remains the most widely used drying technique.

2.3.3 MODIFICATION OF CEMENT PORE STRUCTURES BY POLYMER IMPREGNATION

Polymer impregnation of cement with suitable monomers leads to vast improvements in strength, durability and corrosion resistance. These properties result from the filling of the pore structure of cements by polymers *(ref 34)*. The largest increases in mechanical properties are obtained by impregnation of low porosity samples i.e. those with low water/cement ratios, for example W/C = 0.25 *(ref 35)*. Simple examination of the pore structure shows three types of pore, these being a) voids, b) gel pores and c) capillary pores *(ref 36)*. Not all of the pore space in cements is available for filling as the process relies on the interconnection of the pores. Different studies have indicated different values for the amount of pore space available for filling : the figure ranges from about 70% *(ref 36)* to about 80% *(ref 37)* in OPC. These figures represent the volume of pores in the interconnected network not still filled with water. For this reason cement samples for impregnation are often oven-dried beforehand.

Complete impregnation was claimed by Bright*(ref 38)* in the special case of a particular silica-modified OPC. This had a very low permeability under normal conditions, becoming highly permeable above about 200°C rendering it unsuitable for high temperature applications. Thus it was decided to impregnate with high temperature polymers to block the pore structure. Impregnation was effected at 400°C using both a two-part resin and a mixture of 70% methyl methacrylate, 30% trimethylolpropane-trimethacrylate with benzoyl peroxide initiator. This proved to be highly effective in blocking the pore structure.

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2.3.3.1 PORE FILLING

Hastrup *(ref 37)* concluded that pore filling with MMA is probably accomplished by two routes, a) micropores are filled by the formation of layers of polymer on the pore's internal surfaces, until the walls meet, and b) by capillary condensation, that is to say the condensation of MMA vapour by a lowering of its vapour pressure due to surface interactions. In the case of MMA, MIP data indicated that (contrary to expectation) fine pores develop after impregnation. The cause was thought to be either capillary condensation of MMA in the pores followed by the 20% volume change that accompanies the change of MMA to PMMA, resulting in the formation of new pores by cracking of the PMMA, or by capillary condensation giving an equal coating thickness of polymer to all pore walls. The result being that smaller pores are blocked and larger ones are diminished in size. Identical behaviour to this was found when analysing the structure for porous vycor glass *(ref 37)*. Scanning electron microscopy has confirmed some of these findings, pores being seen lined or filled with polymer. One study however showed MMA in pores developing as a fibrous mass of radiating needles *(ref 35)*.

Further electron microscopy by Mikhail *(ref 39)* relating cement age to maximum polymer load found four basic stages affecting the loading, due to the curing of the cement. Of course the actual time the different stages are active is partially dependent on the nature of the cement and cure conditions.

Thus in order to maximise the polymer load (and hence the modification by the polymer), it is necessary to impregnate cement at a suitable age.

A useful parameter that can be obtained from pore extractions is the 'polymer loading' of cements. This is a measure of the polymer content of the impregnated cements expressed as a percentage. It is defined as : -

Polymer load (%) = $((W_i - W)/W) \times 100\%$

Where : -
W_i = Impregnated weight, and
W = Unimpregnated weight

Comparison of different monomers indicates that with styrene monomer, polymer load does not seem to be a function of water/cement ratio in specimens of values 0.25 - 0.7.

However, with MMA changes in polymer load are noticeable either side of the critical water/cement ratio of 0.4. This may be connected with a volume change that occurs on the conversion of MMA to PMMA *(ref 39)*, (see later). Higher polymer loads may be obtained with MMA than styrene because it was thought MMA penetrates the pore network further than styrene *(ref 39)*.

2.3.3.2 MODIFICATION OF CEMENT PROPERTIES IN TERMS OF THE MIXTURE RULE

When a porous substance is impregnated, according to the Reuss mixture-rule its overall mechanical properties should be a combination of the mechanical properties of the matrix and impregnant in isolation. This will be in ratio of the volume fractions of each. Young's modulus has been examined in this way, the combined value being expressed as : -

$$E_c = 1 \ / \ [\ (V_1/E_{01}) + (V_2/E_{02})\ ] \quad \text{Where : -}$$

E_c = Young's modulus for the composite,
E_{01} = Young's modulus for the matrix at zero porosity,
E_{02} = Young's modulus for the impregnant at zero porosity,
V_1 = volume fraction of the matrix, and
V_2 = volume fraction of the impregnant.

Certain systems have been tested to demonstrate the validity (or not) of the rule. Porous glass and hardened cement paste impregnated with both molten sulphur and MMA have been studied *(ref 40)*. Solid volume fractions were determined by helium comparison pycnometry and by weighing in methanol. Logarithms taken of hardness (determined by microhardness measurements) and elasticity moduli were found to have a linear relationship, the gradient being different for different materials.

It was concluded that the interface between sulphur and cement, and PMMA and cement was sufficiently good to allow modification of the mechanical properties of the cement, but in the case of MMA impregnation did not completely eliminate porosity. Water vapour was able to penetrate some samples causing swelling and cracking.

The assumptions of the mixture rule were found to hold for sulphur impregnation, but not for MMA. The phase change in the solidification of sulphur has a different effect to the polymerisation reaction in cement pores *(ref 40)*. Also, the mixture rule requires that

the component substances have the same properties in the composite as they do in bulk - this may not always be the case.

2.3.3.3 ANALYSIS OF POLYMERS FROM PIC

Extraction of polymers from polymer impregnated cements is usually accomplished by the technique of soxhlet extraction.

For PMMA and polystyrene extraction is accomplished using a number of solvents. Mikhail *(ref 39)* successfully used acetone refluxed for 24 hours, followed by precipitation of the polymer with methanol. Chlorinated organic compounds such as chloroform, methyl ethyl ketone, benzene and many other aromatics are also suitable solvents for these polymers, although greater care is needed in handling them from a safety point of view. In spite of the effectiveness of the solvents, the extraction technique is not always efficient, only 20% extraction from some cements being possible *(ref 37)*.

Molecular weight of addition polymers may be determined after pore extraction. It has been found that higher molecular weights of polymers are obtained from cements with a relatively higher proportion of larger pores. This is in accordance with what would be expected on steric grounds *(ref 39)*. The relationship between pore size and average molecular weight has been shown to be linear *(ref 41)*. In addition, average molecular weight of PMMA in impregnated cements has been shown to decrease with higher polymerisation temperatures, but is not significantly affected by the depth of penetration. For this reason, the polymer is easier to extract by the soxhlet technique the higher the polymerisation temperature used *(ref 39)*.

2.3.4 IMPREGNATION OF OTHER POROUS MATERIALS

Analysis of the pore structures of birch wood, hardened cement paste and porous glass after vacuum impregnation with MMA in the gas phase was carried out by Hastrup *(ref 37)*. The study was intended to determine how different pore structures are modified by MMA. It was found that Birch wood was virtually impenetrable, while the cement and glass samples could be substantially impregnated. Soxhlet extraction was used to obtain polymer from the pores, 100% extraction being possible for the glass, but only 20% for the cement.

2.4 REVIEW OF COMMON RESIN SYSTEMS AND THEIR INVESTIGATION

2.4.1 POLYMERISATION PROCESSES

The process of polymerisation involves chemical reactions between the monomer molecules that results in their combination. There are two basic ways in which this can be accomplished ; a) Reactions between monomer molecules that result in the combination of monomer molecules with the elimination of some simple molecule like water - so called 'step' polymerisation, and b) by the activation of some of the monomer molecules such that they react with ordinary monomer molecules, again resulting in bonding between the two, but with the replication of the active site - so called 'addition' polymerisation *(ref 42)*. These two processes are sometimes called 'condensation' and 'free-radical chain' polymerisation respectively, this leading to some confusion ; step polymerisation is almost always a condensation reaction i.e. one that eliminates water specifically, and addition polymerisation is almost always a free-radical chain reaction - but exceptions are sometimes found!

2.4.2 COMMON RESIN SYSTEMS

The paint and plastics industries have conducted a vast amount of research into the formulation and properties of resin systems to be used as adhesives or surface coatings. Many resins are suitable for use with cements because of their physical and chemical properties. It should be noted that many resin systems may be blended with one another to achieve certain characteristics. A few of the the most common systems are discussed below *(refs 43 & 44)*: -

2.4.2.1 ALKYD RESINS

These resins are amongst the cheapest and most widely used, being the product of reactions between polybasic organic acids and polyhydric alcohols. Water is eliminated between acid and alcohol groups, the product being a polymeric ester. Such resins can be called 'polyesters', but this term has come to mean a specific class of resins itself (see later). Alkyds are seldom used in their pure polyester forms, but are modified by reaction with other substances, boiled vegetable oils for example. Oils of this type are themselves esters of glycerol and fatty acids, boiling them being a method of breaking oils into these constituents. When the fatty acids are liberated they may be polymerised with the polyhydric alcohol of the alkyd, thus introducing fatty acid chains (and their oil properties) into the polymer itself.

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Many oils have the property of drying by cross-linking C=C bonds in the fatty acid chains with oxygen, this being a useful feature to include in the alkyd itself.

Typical reactants are phthalic anhydride (a dibasic acid) and glycerol (a trihydric alcohol) reacted together with boiled linseed oil (a drying oil.)

2.4.2.2 EPOXY RESINS

It is the three-membered epoxide ring that is the functional group in this type of resin. Incorporated into a molecule it can perform additions or condensations leading to polymerisation. Additions occur readily with -OH or -NH groups, the latter often being part of a low molecular weight polyamide commonly known as a 'hardener.'

Condensation reactions occur when water molecules add to epoxy groups to produce diols. These in turn preform condensation reactions with polybasic acids as in the case of alkyds - in fact they may be regarded as upgraded alkyds.

2.4.2.3 ACRYLIC RESINS

Acrylic acid and its derivatives polymerise by addition of monomer molecules with opening of their C=C bonds. The groups containing C=C are called vinyl (CH_2=CH-) or vinylidene (CH_2=C) groups, the former giving rise to the classification 'vinyl' polymers and 'vinyl' polymerisation. Different groups may be attached to the vinyl or vinylidene groups to give the final polymer special characteristics: e.g. -COOH (acrylic acid) is water-soluble and ionisable, -Cl (vinyl chloride) is a flexible rubber-like material and -C_6H_5 (styrene) is a hard, brittle plastic.

Acrylic adhesives based on 2-cyanoacrylate esters are enormously powerful, setting seconds after application. Recently they have been marketed as 'superglues' because of their versatility. The polymerisation reaction is catalysed by water and inhibited by air. Therefore, since most substrates have a small amount of adsorbed surface moisture, this is almost always sufficient to catalyse the polymerisation. The adhesive may remain unpolymerised in a sealed container partially filled with air for several months.

It is thought that polymerisation proceeds via an ionic mechanism, OH- from the dissociation of water being the initiator.

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2.4.2.4 POLYESTER RESINS

The term 'polyester' in a strict sense describes the bonding formed by the reaction of polybasic acids with polyhydric alcohols involving the elimination of water molecules. An important distinction is made between those polybasic acids that contain C=C bonds and those that do not. The former leads to 'unsaturated' polyesters, the latter to 'saturated' polyesters - the basis of alkyd resins. Introducing C=C bonds into the backbone of the polymer allows the possibility of cross-linking with acrylic monomers which themselves polymerise by opening of the C=C bond. It is in this context that the term 'polyester' is commonly used, i.e. a moderate molecular weight condensation polymer containing an unsaturated backbone that is cross-linked with acrylic monomers.

Typical formulations of polyesters would include such reactants as maleic acid (an unsaturated dibasic acid) reacted with glycerol (a trihydric alcohol) to form a resin by condensation reactions eliminating H_2O. This would be dissolved in an acrylic monomer (e.g. styrene) with some initiator and promotor to cause polymerisation and the cross-linking of the two resin components.

Polyester resins are hard, tough and solvent-resistant and may be cured in minutes at room temperature.

2.4.2.5 POLYURETHANE RESINS

The functional group giving rise to polymerisation in polyurethane resins is the isocyanate group -N=C=O. This performs three major reactions that lead to polymerisation : -

a) Isocyanate groups perform addition reactions with -OH groups. Thus they are compatible with oils and alkyds that also contain -OH groups, causing cross-linking at those points. The linkage formed by this reaction is formally known as a 'urethane' linkage (see below.)

$$-N=C=O \;+\; HO- \;\longrightarrow\; \begin{array}{c} -N-C-O- \\ |\;\;|| \\ H\;\;O \end{array}$$

    isocyanate   urethane
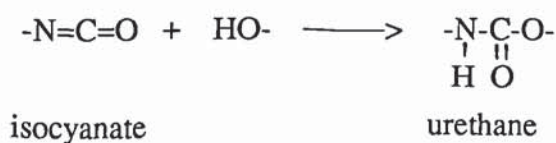
b) Reactions can occur between two isocyanate groups and a water molecule resulting in a condensation reaction producing CO_2 (see below.) The most commonly used starting material for such reactions is a substance called tolylene diisocyanate (TDI).

$$-N=C=O \ + \ H_2O \ + \ O=C=N- \longrightarrow \ \overset{\displaystyle \overset{H}{|} \quad \overset{H}{|}}{-N-\underset{\underset{O}{||}}{C}-N-} \ + \ CO_2$$

isocyanate   isocyanate
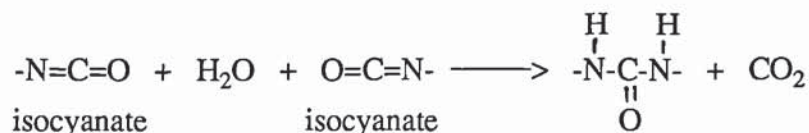
c) Isocyanates sometimes react reversibly with certain molecules, for example phenol. At room temperature phenol adds onto isocyanates, but at 150°C reverts back to phenol and the isocyanate group. Thus an isocyanate may be 'blocked' by phenol, i.e. activated to perform polymerisation reactions only at elevated temperatures. This allows urethane resins to be cured at an appropriate time and not immediately on mixing.

Isocyanates have very good adhesive properties, cure at low temperatures, high durability and chemical resistance, but suffer from the problems of producing CO_2 on moisture curing, and are all highly toxic.

2.4.2.6 SILICONE RESINS

Silicon, being in the same group of the periodic table as carbon can perform some similar chemical reactions. Of particular interest is the ability that some silicon compounds have to form polymers.

A typical starting material for polymer formation is dichloro dimethyl silane which undergoes hydrolysis to form dihydroxy dimethyl silane. Water may be eliminated between -OH groups resulting in polymerisation. Such substances are commonly used as coupling agents where the silicon-containing molecule also has organic functional groups. Typically epoxide rings and -OH groups are used allowing one part of the molecule to bond to inorganic substances and the other to bond to organics.

Silicones are rarely used by themselves due to their cost, but in conjunction with other resin systems provide good chemical resistance, better wetting of inorganic surfaces than organic resins, high water resistance and useful coupling properties.

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2.4.2.7 OTHER RESIN SYSTEMS

Phenols may be made to react with formaldehyde by condensation reactions in acid or alkaline conditions. Such resins are known as 'novolacs' and 'resoles' respectively, the latter being more common, and extensively used in the plastics and paint industries.

Many formulations of nitrogen-containing resins have been developed, the most common types being urea/formaldehyde and urea/melamine resins. Amine resins of this kind are often used in conjunction with acrylic monomers. By co-polymerising an acrylic monomer (e.g. styrene) with an amine-containing acrylic monomer (e.g. acrylamide), the resulting polymer will have the potential to cross-link with amine resins. Nitrogen-containing resins produce hard, durable corrosion-resistant coatings suitable for outdoor applications.

In the 40's, various attempts were made to develop cheap synthetic rubbers. The most successful of these involved the polymerisation of dienes and their subsequent cross-linking. Typical dienes used included buta-1,3-diene ($CH_2=CH-CH=CH_2$) and chloroprene ($CHCl=CH-CH=CH_2$). Pure diene polymers have similar structures to natural rubbers, with many C=C bonds. It is at these sites that cross-linking may be performed. In general it is the cross-linking substance that mostly determines the properties of the material. Some of the more common types include styrene-butadiene rubber (SBR), nitrile-butadiene rubber (NBR) and chloroprene rubber (CR).

2.4.3 RESINS USED IN THIS PROJECT

Although there is a wide range of resin systems used with cements and concrete, this project has been restricted mostly to two polymer systems. One was typical of those used in the construction industry (an amine-cured epoxy resin), the other simple and well characterised (polymethyl methacrylate). The chemistry of these two systems will therefore be described in detail.

2.4.3.1 EPOXY RESIN

The resin chosen for this project is cured by a hardener via reactions between the two resulting in substantial cross-linking. Both components set rigid in a matter of hours after being mixed together.

The resin itself is made by the reaction between 'bisdiphenol' and epichlorohydrin in alkaline solution. The presence of OH⁻ in solution tends to remove protons from the -OH groups on the bisdiphenol, allowing attack at the -O- sites by the epichlorohydrin. The resulting intermediate chlorohydrin compound reacts with more OH⁻ to reform epoxide rings at the ends of the molecule. This constitutes the resin (or 'liquid cement'), the name 'epoxy resin' deriving from the epoxide rings on the molecule *(ref 42)*. The substance itself is a transparent yellowish liquid with a moderately high viscosity and pungent odour *(ref 45)*. Polymerisation of the resin results in the formation of a tough, slightly yellowish substance, insoluble in most organic solvents.

Triethylene tetramine is the hardener in the system, undergoing reactions between the epoxide rings of the resin and its own amine groups. The result is a massive cross-linking of the two components. Resin and hardener are mixed in the proportions of 10:1 respectively, these being the proportions recommended by the manufacturers. Curing is complete when all the epoxide rings have reacted and therefore maximum bonding obtained*(fig 2.1)*. It is rarely possible to determine chain lengths in these sorts of polymers due to their extensively cross-linked structures.

2.4.3.2 POLYMETHYL METHACRYLATE (PMMA)

This is one of the most common polymers used in the impregnation of cements and was used extensively in this project. The monomer itself, methyl methacrylate (MMA), is the methyl ester of methacrylic acid, and is a clear, volatile liquid of boiling point $101^{o}C$ with a pungent odour, soluble in many organic solvents. Polymerisation results in formation of PMMA which is a tough, clear and chemically resistant compound known more commonly by its trade names of Perspex, Plexiglas and Lucite *(ref 42)*.

Polymerisation of MMA

MMA is highly susceptible to polymerisation, this being possible by the action of heat, light radiation and catalysts. Of most interest to this project was the polymerisation at elevated temperatures by the catalyst benzoyl peroxide (BP), although other catalysts such as azobisisobutyronitrile have an identical effect. Different authors recommend different proportions of monomer to catalyst. Vogel *(ref 46)* and Waddington *(ref 47)* recommend 10-20 mg BP to 10 cm³ MMA, other workers employing a mixture of 40 g BP to 2 kg MMA with 12 g dimethyl para-toluidine promotor. As mentioned above, the polymerisation reactions of MMA must result in combination of the activated molecule

with an ordinary monomer molecule, with replication of the active site. The reactions in this case proceed as free-radical reactions, and are summarised in *fig 2.2 (ref 42)* : -

Chain initiation by BP

BP molecules decompose into free-radical species at a rate dependent upon temperature. These radicals interact with monomer molecules to cause combination and the replication of a free-radical site. Thus chains are initiated, and grow by the process described above *(fig 2.2)*.

Chain termination

The free-radicals that cause additions to the chains are eventually destroyed by two mechanisms : either they combine to form a single bond, thus joining two chains together and terminating both, or two free-radical species disproportionate by one abstracting the free electron from the other.

Action of promotors

Promotors are additives to monomer/catalyst mixtures that result in the polymerisation reactions occurring at lower temperatures than are required by catalysts by themselves. This project investigated the use of dimethyl para-toluidine as a promotor, though dimethyl aniline would have had the same effect *(ref 5)*. These substances catalyse the decomposition of BP, and hence lead to substantial chain initiation without the need for elevated temperatures.

Curing

Chain lengths by addition reactions of this sort are dependent on temperature (related to molecular diffusion) and the concentration of the reactants : it is easy to see that if there is only a low concentration of catalyst then few long chains will form and vice versa. At 60°C with 2% BP, polymerisation is usually completed within about an hour.

FIGURE 2.1
PREPARATION OF EPOXY RESIN

'bisdiphenol'

epichlorohydrin

chlorohydrin intermediate + NaCl

reformation of epoxide rings + NaCl + H_2O

further reactions increase chain length to an average
molecular weight of 700, with the above repeated unit.

REACTION WITH HARDENER

$-OCH_2CH\ CH_2 + NH_2- \longrightarrow -OCH_2CHCH_2NH-$

epoxy groups of the resin react with amine groups
of the hardener forming the above linkages.

49
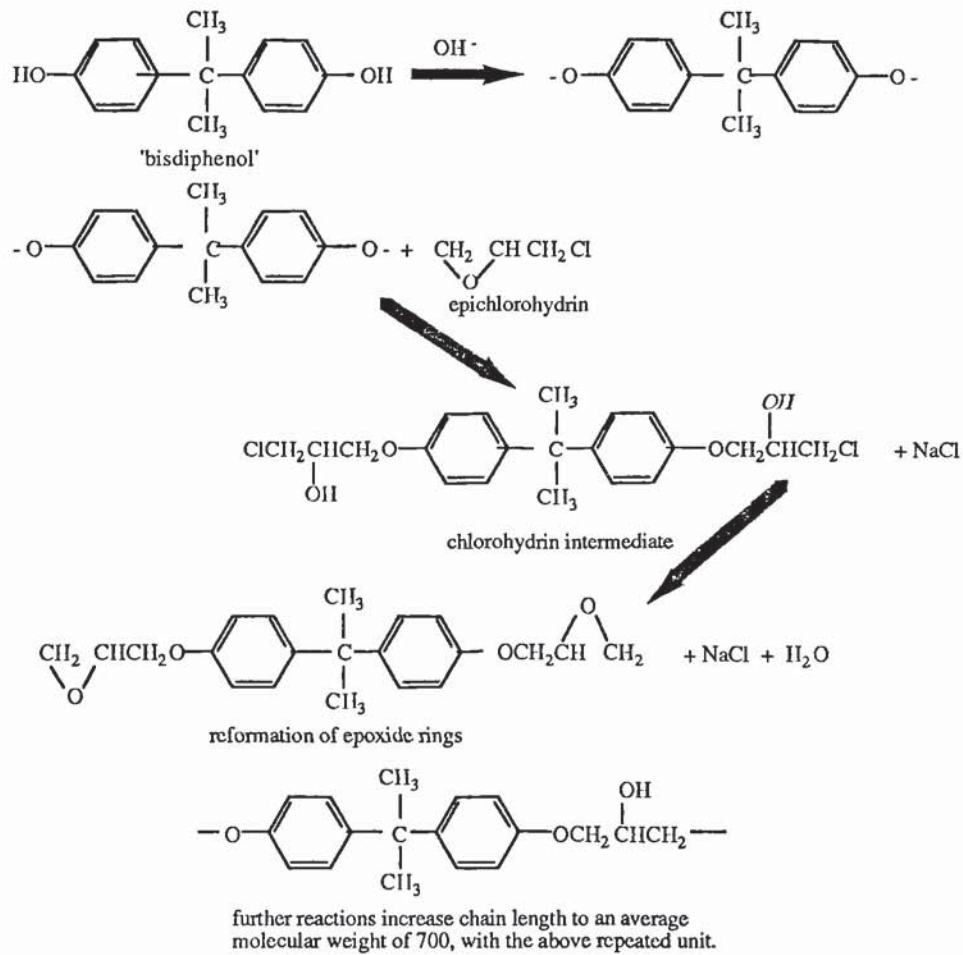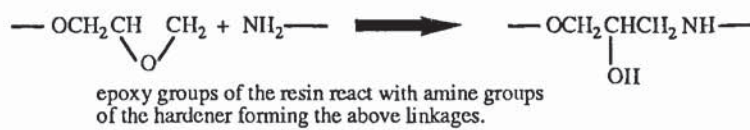
FIGURE 2.2
POLYMERISATION OF MMA

CHAIN INITIATION

benzoyl peroxide

methyl
methacrylate

CHAIN PROPAGATION

| end of growing polymer chain | methyl methacrylate | polymethyl methacrylate |
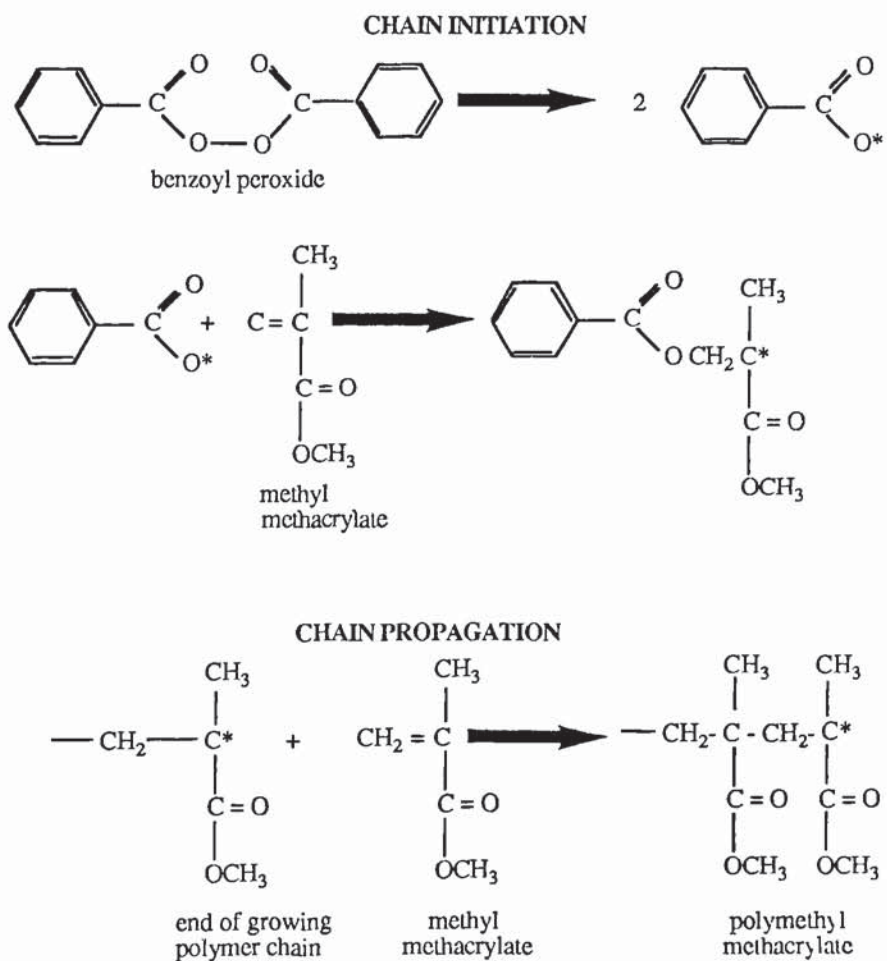
2.4.4 INVESTIGATION OF POLYMERS

Many different properties may be studied covering a whole range of chemical and physical phenomena. Information gained by studying these properties is useful for identification and characterisation purposes, as well as detailing polymerisation histories. It is this latter area in particular that would most readily indicate that reactions have taken place between cements (or related minerals) and polymers. Many of the features that can be studied are interrelated, the major ones being listed below : -

2.4.4.1 GENERAL MECHANICAL PROPERTIES

Polymers, like any other material may be characterised by assessment of their mechanical properties, these being related to the monomer type and processing. Such quantities as strength, abrasion resistance, fatigue, creep and durability may be explored.

2.4.4.2 THERMAL PROCESSES

When polymers are heated various chemical and physical changes occur. A commonly measured feature is the glass transition which occurs at a specific temperature and represents a major change in the physical properties of the polymer from a glassy to a plastic state. At higher temperatures actual melting may occur, with its associated oxidation and general degradation of the polymer.

2.4.4.3 CRYSTALLINITY

This term is slightly misleading in that polymers do not belong to any crystal system, and in that sense are amorphous. However, many polymers do have definite structure below the glass transition temperature. Polymer chains tend to cluster into microscopic balls by intermolecular forces, these being known as 'spherulites.' Straining also effects crystallinity in that it re-orientates chains parallel to the straining direction. At a molecular level, attraction between chains depends both on the type of groups attached to the polymer backbone, and to their position. In a linear polymer with a carbon backbone there are two distinct orientations per carbon atom. Polymers with a completely random distribution of groups between the two orientations are known as 'atactic;' those with the groups in only one orientation 'isotactic;' and those with groups alternating between the two positions 'syndiotactic.' As well as affecting the mechanical properties, tacticity also effects the crystallinity of polymers.

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Since it is intermolecular attractions between linear polymers that cause spherulite formation, in general it is only addition polymers that form spherulites.

2.4.4.4 DEGREE OF POLMERISATION

This area of study applies more to the processing of polymers than to the final materials themselves. It is clearly a useful quantity to determine, since the mechanical properties and general reactivity of polymers vary with the degree of polymerisation. For example, a polymer to be used as a surface coating for a porous material may require a certain viscosity to allow it to penetrate the surface pores.

2.4.4.5 CHAIN LENGTH DISTRIBUTION

As well as having some effect on mechanical properties, the chain length distribution gives a record of the polymerisation history i.e. the number and length of chains that have been formed in the polymerisation reaction. It is possible to predict mathematically the spread of polymer chain lengths from the concentration of reactants and thermodynamic data - put simply, at higher temperatures more chains will be initiated so the average chain length will be small, and vice versa.

Is should be pointed out that usually chain lengths are only determinable in linear polymers, these generally being addition polymers.

2.4.4.6 KINETICS OF POLYMERISATION

An understanding of the kinetics of polymerisation is necessary in order to design the apparatus needed for their processing. Particular problems are encountered at any scale of production if polymerisation is allowed to proceed too quickly. Many polymerisation reactions have a natural tendency to accelerate, and if this gets out of hand can lead to local overheating, bubbles in the final material, boiling and pressure explosions! Needless to say, care must be taken to avoid these eventualities.

Kinetic studies can also be used to identify interactions that interfere with polymerisation processes. Some minerals, for instance, have the effect of accelerating polymerisation, others inhibiting polymerisation.

2.4.5 TECHNIQUES FOR THE INVESTIGATION OF POLYMERS AND POLYMERISATION MECHANISMS

Many techniques are available for studying different aspects of polymeric materials, some of which have been used by this project. Some of the more general techniques are detailed below *(ref 48)* : -

2.4.5.1 SPECTROSCOPY

Of particular importance are the techniques of infrared, ultraviolet and nuclear magnetic resonance spectroscopy, these yielding information about the chemical environment and bonding of the different species in polymers - it is sometimes possible to determine chain shapes from such data. Mass spectrometry, giving information about different ionisable polymer fragments sometimes after pyrolysis, is probably only of use in the fingerprinting polymers, and for determination of their empirical formulae.

2.4.5.2 CHROMATOGRAPHY

Techniques of chromatography are good at separating polymer mixtures. In the gas phase polymer vapours may be examined by gas liquid chromatography, while aqueous extracts of anions such as Cl⁻ from epoxies are accessible via ion chromatography. High performance gas chromatography is useful for substances that may be volatilised but are too heavy for gas chromatography. By far the most important technique is gel permeation chromatography of polymer solutions, being able to determine the spread of polymer molecular weights. Finally, thin layer chromatography of polymer mixtures though very easy to perform has been superseded by the other techniques.

2.4.5.3 THERMAL ANALYSIS

Differential thermal analysis and differential scanning calorimetry give roughly similar results when applied to polymers. Peaks at the glass transition temperature, melting point, oxidation stage and degradation stage are characteristic of many polymers. This allows for fingerprinting and the following of some polymer reactions. Thermogravimetric analysis has been used successfully for quality control of polymers, and can be used to determine aspects of their microstructure.

2.4.5.4 SURFACE ANALYSIS

Three recently developed techniques are highly effective in the determination of surface chemistry i.e. the chemistry of the first layer of atoms on a surface. X-ray photoelectron spectroscopy (XPS) is most effective in the detection of surface chemistries, as is secondary ion mass spectroscopy (SIMS), but with deeper surface penetration. Inelastic electron tunneling spectroscopy (IETS) has been applied to the examination of polymers adsorbed by surfaces, particularly metal ones.

2.4.5.5 KINETIC MEASUREMENTS

The effect that different substances and conditions have on polymerisation rates may be studied by a number of techniques, some requiring regular sampling and others requiring continuous monitoring. Of the former, standard chemical techniques may be used to follow the disappearance of reactants. For example, acid/base titrations to determine the acidity of extracts at different times from an alkyd resin reaction mixture would show a decrease as the polymerisation reaction proceeded.

Two techniques have been used successfully for continuous monitoring of polymerisation reactions, these being calorimetry and shrinkage : as many polymerisation reactions proceed heat is liberated and the mixture contracts slightly. These phenomena may be related directly to the polymerisation rate.

Similar techniques have been used to follow the individual processes in the overall polymerisation of monomers, in particular the decomposition of initiator molecules, and hence the initiation rate *(ref 49)*.

2.4.5.6 PROPERTIES OF DILUTE POLYMER SOLUTIONS

Information about polymer chain lengths may be gained by the study of dilute polymer solutions (<2%), using relatively unsophisticated equipment. Viscosity, osmotic pressure and light scattering may be related mathematically to the average chain length of the polymer solute. By careful fractionation of polymer solutions it is possible to determine average chain lengths for all the fractions of a sample, thus obtaining an approximation to the overall spread of chain lengths. Bulk polymerisation processes are somewhat random, distributions of chain lengths approximating to gaussian curves. This behaviour can be explained in a simple way by considering two extremes; First, if the concentration of initiated chains is very high then they will all propagate a little before terminating. The vast majority of chains will thus be short. Second, if the concentration of initiated chains is low then they will continue to propagate, the

proportion of monomer molecules to chains steadily decreasing. As this proceeds, the probability of chains terminating rather than propagating steadily increases, the final polymer having a very broad spread of chain lengths. Real situations are more complicated, but not substantially different.

Chain length determination using viscometry

The apparent viscosity of a polymer solution is determined at a number of concentrations. By plotting the apparent viscosity against concentration a straight line is obtained that may be extrapolated to zero concentration. This point is the intrinsic viscosity of the solution. This value is used in the following equation to obtain chain average chain length *(refs 50 & 51)*.

$$M = A \times B \, [\, \eta \,]^{c}$$

Where : - η = Intrinsic viscosity

M = average molecular weight

$A, B \, \& \, c$ = constants.

2.5 THE SCIENCE OF ADHESION

The term 'adhesion is often used indiscriminately to describe the strength of the bond between two phases. More rigorous descriptions of adhesion assess the bonding in various ways : Souheng *(ref 52)* gives definitions of the more commonly observed types of adhesion. He first defines adhesion itself as "the state in which two dissimilar bodies are held together by intimate molecular contact such that mechanical force or work can be transferred across the interface". The more specific definitions are as follows :-

> a) Thermodynamic adhesion - the equilibrium forces or energies associated with a reversible process,
> b) Chemical adhesion - adhesion involving chemical bonding at the interface,and
> c) Mechanical adhesion - adhesion from the mechanical interlocking of two phases.

A distinction is also drawn between adhesive strength and cohesive strength, the latter being associated with failure in the bulk of one phase rather than at the interface. Similar definitions to that of Souheng have been proposed ; ASTM D907-70 defines adhesion relating to adhesives as "the state where two surfaces are held together by interfacial forces which may consist of valence forces (i.e. those associated with electrostatic forces) or interlocking forces (i.e. those associated with mechanical interlocking) or both" *(ref 53)*.

2.5.1 FORMATION OF THE ADHESIVE BOND

When two phases are brought into contact, bonding may occur between them in a number of ways. Of most importance to this project is obviously the bond between polymers and cements, liquid that will become polymer coming into contact with the solid cement before setting. In such samples bonding occurs in three stages : -

> a) Interfacial molecular contact by surface wetting,
> b) surface diffusion to achieve adsorptive equilibrium at the interface, and
> c) chemical reactions at the interface.

At a sharp interface, the attraction is mainly by Van der Waal forces. Thus the two phases must get very close for this to become significant, i.e. within about 0.5 nm.

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Wetting of the surface is therefore very important to get any adhesion at all. Bonding is aided if phases are used with strong polar interactions, or that form chemical bonds. Alternatively, with a diffuse interface where substantial diffusion has occurred, strong bonding is possible via the Van der Waal forces alone.

The effect of chemical bonding is obvious in that it prevents molecular slip and increases the fracture energy of the interface. Good adhesion is promoted generally by the following: -

  a) Strong atom-atom bonding,
  b) low amounts of stress near the interface (for example some coatings introduce stresses at the interface on drying),
  c) absence of easy modes of deformation (i.e. the theoretical strength of a material is much higher than that seen in practice because of deformation and fracture processes limiting strength), and
  d) absence of long term degradation modes - adhesion strength may be lost in certain systems by long term processes like fatigue *(ref 54)*.

When the two phases making up an adhesive joint are brought into contact different interactions occur. Mattox *(ref 54)* classifies these possible interactions in five different ways : -

  a) Mechanical - Physical interlocking on a rough surface,
  b) monolayer-monolayer (abrupt) - non-diffusional, possibly with a lack of mutual solubility between the phases,
  c) compound - compound layer formed by chemical interactions,
  d) diffusional - gradual concentration change due to diffusion at the interface,
  e) combinations of these.

2.5.2 SURFACE WETTING

It is usually very important to achieve substantial wetting of the adhesion surface. Incomplete wetting leads to interfacial defects and reduces the work of adhesion, and hence the bond strength. Typical causes of incomplete wetting would be surface oxidation, dust, grease and differences in surface texture. Scantlebury *(ref 55)* demonstrated that the amount of surface wetting is dependant partly on the nature of the phases, but also on the surface topology. For peel tests (see later) on coatings carried out on smooth and rough surfaces it was found that the rate of change of revealed

surface area (related to adhesion strength) is directly proportional to the surface roughness.

Thus for a rougher surface the bond is stronger if the surface can be substantially wetted. If this is not the case then adhesion is actually reduced by surface roughness. This idea can be developed further by considering the penetration of surface pores by the liquid phase. Clearly the more penetration that can be achieved, the better the bonding will be. Packham *(ref 56)* derived equations for the depth of penetration of liquids into cylindrical pores. However, these were an over simplification of the real situation, since most surface pores are not cylindrical. A more realistic pore shape described is the "ink pot" or re-entrant pore, these having a small neck and larger chamber.

Determination of penetration depth versus contact angle for the two geometries shows that penetration into ink pot pores is much lower than that for cylindrical pores. In addition it was found that with increasing time penetration was similarly increased *(ref 56)*. Penetration may be improved generally by the following : -

     a) *Lowering the contact angles,*
     b) lowering the viscosity,
     c) increasing the setting time of the polymer, and
     d) increasing the external pressure.

2.5.3 FAILURE IN ADHESIVE JOINTS

The failure of an adhesive joint can be looked at in two ways : either as the force required to cause failure or in terms of the location of the failure. Both are of interest to this project, the latter leading to the concept of 'locus' (or path) of failure.

Experimental determination of failure strengths yields values that are about a magnitude lower than expected by theoretical calculation of simple interfacial bonding. Two theories have been put forward to explain this *(ref 57)* : - First, the discrepancy could be explained in terms of Griffiths cracks; that is to say that thermodynamically, all materials have a finite number of flaws and cracks that can initiate failure at stresses much lower than those predicted from theory. More specifically, even the best prepared cement samples are full of voids, all of which are potential crack-initiators. On this theory, impregnation of cements with polymers will improve the properties of cements by sealing these voids, thus rendering them unsuitable as crack-initiation sites *(ref 58)*.

The second explanation was put forward by Bikermann *(ref 52)*, and although it has come in for much criticism concerning the nature of the proofs he offered for it, has some interesting implications.

2.5.3.1 BIKERMANN'S DOCTRINE

Examination of the locus of failure of adhesive joints shows that failure very seldom occurs actually at the interface of materials. Bikermann's Doctrine put forward the idea that 'failure is rare at the interface, usually occurring through thin boundary layers of atomic dimensions. In the absence of these layers, then failure occurs through the weaker of the two phases' *(ref 52)*. Evidence for these weak boundary layers comes from a number of sources : Souheng *(ref 59)* used polyethylene dissolved in oleic acid to stick aluminium ribbon to a glass substrate. Once the polymer had set it was possible to peel the ribbon off, and a 4 mm layer of polyethylene was left on the ribbon - failure was not at the interface. Development of a boundary layer was thought to be connected with differing solvent concentrations through the layer, and to the movement towards the interface of lower molecular weight polymer chains *(ref 57)*.

Other examples of boundary layers include those formed by heat-aging of phenolic or epoxy resins set against aluminium ribbon. The aging process was carried out at 288°C for 100 hours. Boundary layers were thought to be formed by the aluminium-catalysed oxidation of the polymer at the interface.

Bikermann *(ref 60)* defines several types of weak boundary layer that can be formed when coatings are applied to metal surfaces. Failure could occur due to weaknesses in any of the possible layers. Criticism of Bikermann's proposals was in terms of the proofs he offered for the Doctrine. These were as follows :-

> a) The probability of a crack advancing along an interface via n unlike atoms is $(1/3)^n$, i.e. very small indeed,
>
> b) the attractive force between two unlike atoms is intermediate in magnitude between those for like atoms, according to the London theory of forces,
>
> c) strength at the interface is greater than within the bulk of the two materials since the volume of the interface is very small in comparison. Thus the probability of flaws in the volume of the interface is much less than that in the bulk of the materials themselves, and
>
> d) the probability of a crack following a tortuous path (i.e. that of the interface) is negligible.

These were disputed by Souheng *(refs 52 and 59)*, but the concept of weak boundary layers remains.

2.5.3.2 EXAMINATION OF THE LOCUS OF FAILURE

Examination of the locus of failure is possible by various techniques *(refs 52 and 61)*, some of which have been employed in this project. They include contact angle measurement, optical microscopy, scanning electron microscopy (SEM), transmission electron microscopy (TEM), infrared spectroscopy (IR), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), probe analysis, X-ray fluorescence (XRF), ion scattering spectrometry (ISS), and secondary ion mass spectrometry (SIMS).

2.6 ADHESION OF POLYMERS TO CERAMIC MATERIALS

A number of polymer/ceramic systems have been studied in recent years. Certainly the bonding of polymers to cements is attracting more and more interest, though work on the bonding of polymers to hard tissues is becoming increasingly studied in the medical field.

2.6.1 FACTORS AFFECTING AGGREGATE ADHESION

Several factors have been identified that affect the macroscopic behaviour of polymer-cement systems. Physical aspects (i.e. the keying of the polymer to the ceramic substrate in a purely mechanical sense) results in adhesion without any consideration of chemical bonding. The geometry of the substrate is of importance in the above consideration, curing conditions, binder content, aggregate size distribution and nature are the other major factors important in affecting adhesion *(ref 62)*.

2.6.2 POLYURETHANE COATINGS FOR CEMENT

Several polymer/cement systems have been studied in terms of bond strength and durability, this being of great economic interest in the repair of concrete structures. In particular, waterproofing membranes for bridge decks are being developed that can be applied to wet or dry concrete surfaces. These have been shown to have much higher adhesive strengths than traditional bituminous and roofing felt coverings *(ref 63)*, and are also much easier to apply.

Assessment of the adhesion of polyurethane rubber to concrete (as used for covering bridge decks) has been examined by the use of peel tests *(fig 4.1) (ref 63)*. Sections of cement appropriately cured and prepared were treated with urethane monomer and subsequently polymerised. The resulting rubber coatings were then peeled off using a tensometer apparatus, the force required to do this being a measure of the bond strength.

The properties of this rubber coating may be modified by certain additives. These were used for both chemical and economic reasons : zeolite minerals were added to absorb water when the polymer was set against a wet surface, and coal tar added to dilute the polymer greatly increasing its volume without significant loss of bond strength. The exact nature of the chemical bond is however, not known.

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2.6.3 THE ROLE OF POLYMER IN PIC

Gebauer *(ref 64)* studied modification of the strength of cements by polymer impregnation. He concluded that the strength of such materials was not so much concerned with the adhesive properties of the polymers, but more on their reinforcing properties. A contrary conclusion was reached by Liu *(ref 65)* who inferred strong interfacial interactions between polymer and cement.

Both agree that the strength of PIC composites can be increased by using a polymer of high Young's modulus, this being retained to high temperatures if the glass transition temperature is high, i.e. the temperature at which the polymer converts from a rigid to a plastic form is high. Liu found that the glass transition temperature was raised in the pore system of cements, this being related to polymer/cement bonding.

2.6.4 POLYMER ADHESION TO HARD TISSUES

There is a significant quantity of literature on the subject of bonding polymers to human hard tissues i.e. bones and teeth. Several polymers show potential for bone-bonding agents and dental repair treatments. Hard tissue structures are similar to cements in that they are porous calcic ceramics.

2.6.4.1 BONE BONDING AGENTS

Since the war, many adhesives have been examined to assess their potential as bone-bonding agents. Many were rejected simply on adhesive grounds, others for being carcinogenic, toxic or of too long cure times. Two showed particular potential, PMMA and cyanoacrylates *(ref 66)*. Tests involving bone samples fractured transversely with an osteotome were glued together using the adhesive being studied, prior to testing to destruction on an Instron tensile testing machine.

PMMA was found to bond mechanically by 'keying', the monomer having penetrated between the bone trabeculae (or fibres) before curing. Cyanoacrylates required nucleophiles such as alcohol or water to initiate polymerisation, thus they did not bond to desiccated bone samples. Where bonding did occur it was essentially 'adhesive', that is to say by interfacial chemical reactions; the thinner the layer, the stronger the bond.

2.6.4.2 SURFACE PENETRATION OF DENTAL SPECIMENS

As mentioned earlier, the adhesion of polymers to dental or orthopaedic specimens is closely related to the study of the adhesion of polymers to cements, both being porous calcic ceramics.

Nakabayashi *(ref 67)* examined the adhesion of polymers to teeth with the aid of a surface etchant. Those studied were phosphoric, acetic and citric acids in concentrations of 10-30%. These suitably modified the topology of the adhesion surfaces to allow strong and durable bonds to be formed suitable for dental applications. It was also found that use of the weaker acids (citric acid for instance) resulted in the greatest increase in bond strength, stronger acids destroying the tooth structure.

Examination of the adhesion surface was carried out by dissolving the tooth adhering to the polymer with HCl and studying the resultant structures using an electron microscope. These showed that etching of the tooth surface had revealed the biological structure of the tooth i.e. a well-ordered series of pits that had become filled with polymer.

Many adhesives have been tried for use as dental cements, a comparison of several commercially available composite resins showing those containing functional methacrylate groups as exhibiting the strongest bonds *(ref 68)*.

2.6.4.3 DENTINE BONDED WITH 2-CYANOACRYLATE ESTERS

A further study by Brauer *(ref 69)* examined the bonding of dentine to 2-cyanoacrylate ester cements. These were of particular interest due to their ability to bond to wet surfaces. The isobutyl and amyl homologues were found to exhibit the strongest bonding, and durability tests in water showed less than 30% disbonding after immersion in water for over one year. Polymerisation rate (although not necessarily ultimate strength) was increased by treating the adhesion surface with dimethyl p-toluidine promotor. Again it was concluded that weak organic acids are very useful as etchants for adhesion surface preparation, the study using phosphoric acid.

The experimental procedure involved mounting a tooth in resin then cutting a surface for adhesion with a water-lubricated rock saw. It was then dried and a surface treatment applied if required. The surface was again dried and a drop of monomer added. A

weighted PMMA rod was then placed on the surface and polymerisation achieved by ultraviolet light. The finished specimen was then ready for tensile testing.

2.6.4.4 ADHESION OF GLASS IONOMER CEMENTS TO DENTINE

Glass ionomer cements are materials made from ion-leachable aluminosilicate glasses and polymeric acids, these setting to hard translucent materials within minutes of mixing. These materials have found extensive use as dental cements, Graham *(ref 70)* describing tests to measure their adhesive capabilities in dental applications. It was found that etching dentine substrates with 50% citric acid improved bonding between the two materials.

2.6.5 CHEMICAL COUPLING AGENTS

These are molecules having an affinity at one end for the substrate and at the other for the polymer *(ref 71)*. These provide convenient linking molecules between substrate and polymer, and as a consequence the bonding and adhesion are improved *(ref 72)*. A wide variety of coupling agents have been developed, with appropriate functional groups for the phases concerned. In bonding to cements, ceramics and glasses the most commonly used coupling agents are silanes *(ref 73),* although fatty acids (e.g. stearic acid) have been shown to improve bonding to limestone *(ref 74)*. The functional group in the case of silanes bonds directly to surface silicon atoms, whilst acid groups bond via acid/base interactions.

pH is an important factor in choice of coupling agent. This affects the nature of the surface groups by changing the potential of the substrate surface. It is therefore important to suitably adjust the pH of a surface that is to be treated with a coupling agent.

Coupling agents may be applied in a number of ways : -

        a) Surface treatment,
        b) Added to the monomer prior to polymerisation ,
     or c) Sprayed onto the aggregate prior to use.

Different processing and materials demand different application techniques - clearly it is more appropriate to add coupling agents to the mix of a PC than to use a surface application on the adhesion surface. Where coupling agents are added to PCs there is an

optimum concentration that gives a maximum increase in mechanical properties. A greater or lesser concentration decreasing the strength of the material.

It is possible to assess the increase in bond strength by use of coupling agents in two ways : First, by examination of the mechanical properties of a PC before and after addition of modifying additives it is possible to assess any change in macroscopic properties, for example hardness. Secondly, if there is an interface of suitable geometry, mechanical testing of the interface is possible, for example by tensile testing of the interface.

2.7 POLYMER/CEMENT CHEMICAL INTERACTIONS

Interactions between polymers and oxide surfaces has been considered in a number of ways. Many workers in recent years have found it convenient to consider the interactions in terms of London forces, dipole forces, induced dipole forces, hydrogen bonds and acid-base Bronstead interactions. The latter is probably better expressed as Lewis acid-base interactions in terms of electron donors and acceptors *(ref 75)*.

Chemical examination of ceramic surfaces shows three major features : -

    a) Silicate surfaces are as the oxide,

    b) these oxides can be hydrated and dehydrated at elevated
        temperatures,

and c) the resultant hydroxyl-rich surface adsorbs and retains layers
        of water.

2.7.1 ACID-BASE INTERACTION AT OXIDE SURFACES

Oxide surfaces of a silicate can undergo both hydration and dehydration reactions. In an analogous way to organic chemical mechanisms, we can represent 'acidity' and 'basicity' of the -OH groups by the general equation : -

$$X\text{-}OH + H_2O \leftrightarrows X\text{-}O^- + H_3O^+$$

$$X = \text{underlying silicate structure}$$
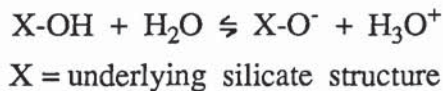
The acidity of the compound being hydrated is a measure of the degree of dissociation it undergoes in water.

2.7.1.1 SURFACE DEHYDRATION

Several factors affect the ability of a surface to become hydrated or dehydrated, the most important being pH. A general reaction scheme is as follows : -

$$\overset{H^+}{-XOH_2^+ \cdots\cdots OH_2} \leftrightarrows -XOH + H_2O \overset{OH^-}{\leftrightarrows} -XO^- \cdots\cdots HOH$$
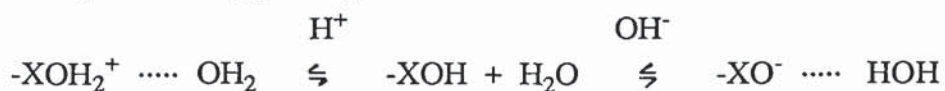
    X = Underlying silicate structure

    $\cdots\cdots$ = hydrogen bonds

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It can be seen that oxide surfaces are surrounded by water molecules via hydrogen bonding in high or low pH environments. Bonding is between different parts of the water molecules and the surface, but in the mid-range of pH dehydration occurs.

2.7.1.2 SURFACE INTERACTIONS WITH POLAR ORGANIC MOLECULES

Again, in a similar way to surface dehydration/hydration, interactions with organic compounds can lead to bonding via acidic or basic mechanisms. These are as follows : -

Acidic mechanism

$$-XOH + HOR \longrightarrow -XO \cdots HR \rightleftharpoons -XOH_2^+ \cdots -OR$$

with H above the HR.

HOR could be a carboxylic acid for instance

Basic mechanism

$$-XOH + NH_2R \longrightarrow -XOH \cdots NH_2R \rightleftharpoons -XO^- \cdots NH_3^+R$$

NH$_2$R could be an amine for instance
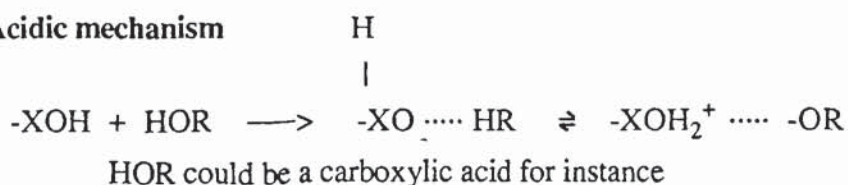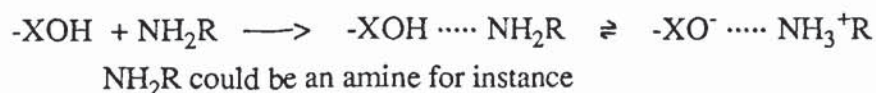
The mechanism applicable to a particular surface will depend upon the surface potential. With a low potential, the surface will tend to be a proton acceptor and hence will favour the 'acidic' mechanism, and with a high surface potential will tend to be a proton donor and hence favour the 'basic' mechanism.

2.7.1.3 WATER DISPLACEMENT MECHANISMS

As we have seen above, surface reactions occur with water and polar organic molecules. When both are present there is competition for the surface bonds expressed by : -

Acidic mechanism

$$-XO \cdots HR + 2H_2O \rightleftharpoons -XO^- \cdots H_2O + H_2O \cdots HR$$

with H above XO and above the right-hand XO.

Basic mechanism

$$-XOH \cdots NH_2R + 2H_2O \rightleftharpoons -XOH \cdots OH_2 + HOH \cdots NH_2R$$
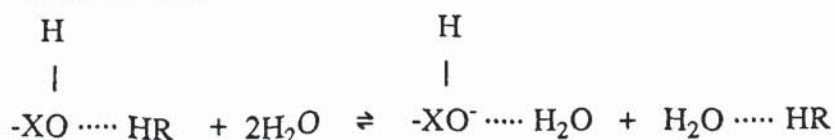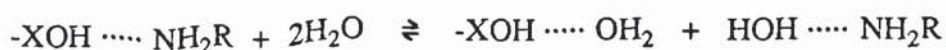
Competition of this kind limits the choice of compounds suitable for use as adhesion promotors, only strong acids and strong bases tending to be of much use, these forcing the equilibria right to left. It has also been found that orientation of groups (i.e. steric considerations) and optimum concentrations are also factors in forcing the displacement equilibria in favour of the promotor-surface bonds.

2.7.2 CHEMICAL REACTION BETWEEN POLYMERS AND CEMENT MINERALS

The chemical compositions of hydrated cements are highly complex. Thus studies have tended to consider reactions of polymers with specific compounds. Of course, cements themselves have been studied, the diversity of their chemistry making interpretation somewhat harder.

2.7.2.1 STUDIES OF PIC INTERACTIONS

A number of papers have been published concerning polymer/cement interactions. The most widely used technique in these studies is that of thermal analysis, particularly differential thermal analysis (DTA).

Gebauer *(ref 15)* studied reactions of hydrated cement with methyl methacrylate and styrene monomers in impregnated cement specimens. The polymer was cured by gamma-radiation and promoted-catalytic means, wrapping the specimens in foil to minimise monomer evaporation.

DTA analysis was carried out in a nitrogen atmosphere, it was noted that characteristic peaks from calcium hydroxide at 530°C were absent in methyl methacrylate impregnated samples. This was not true in the case of styrene. A reaction between calcium hydroxide and PMMA/MMA was thus inferred.

Ausken *(ref 76)* investigated possible products of the reaction, the applicability of DTA in the study of these reactions being questioned by Ramachandran *(ref 77)* and Ishizaki *(ref 78)*. They postulated that polymer/cement reactions are masked by other thermal effects during the DTA run itself. These reactions are discussed in detail in section 5.2.1.

Madruga *(ref 41)* demonstrated that two types of PMMA could be extracted from PIC. By using soxhlet extraction with benzene followed by precipitation with methanol, PMMA could be extracted from the pore space of the impregnated cement. Treating the residue with a saturated solution of salicylic acid in methanol the silicates in the cement could be dissolved, leaving the PMMA unaffected. A subsequent extraction from the new residue with benzene and methanol-induced precipitation resulted in a second crop of polymer. Since all the polymer was not extracted from the initial sample with a good solvent, it was suggested that a chemical interaction between -COO⁻ and Ca^{2+} as Lewis acids and bases takes place. The species extracted the second time were thought to be charge-transfer intermolecular complexes formed in the capillary pores at lower polymerisation temperatures. With their formation, glass transition temperature was increased due to the more restricted molecular movement they caused.

The initial yield of polymer increases with increasing polymerisation temperature, the average molecular weight of this fraction always being lower than that extracted the second time. Similar behaviour was noted for the PMMA/MMA - $ZnCl_2$ system, this reducing the polymerisation rate with increasing $ZnCl_2$ content. As expected, the more initiator added to the monomer, the lower the average molecular weight of polymer formed, since more chains are started.

2.7.2.2 INTERACTIONS IN POLYMER PORTLAND CEMENT CONCRETE AND ADMIXTURES

In many systems where polymer is added to cement while still liquid and hydrating, it would be hard to draw distinctions between PPCC and admixtures as far as the interactions are concerned. The distinction depends largely upon the effect desired : it could be said that the polymer in PPCC is used to modify the properties of the hardened cement, whereas admixtures are used to modify the properties of the cement during setting. Of course, to form a PPCC it is necessary to have a polymeric component - admixtures need not involve polymers.

This survey has been restricted to polymeric additives, the distinction between PPCC and admixtures being unimportant as far as interactions are concerned.

Chandra *(ref 79)* discussed the whole field of the effects that polymers and admixtures have on cement hydration. He discussed various chemical interactions particularly those of styrene/methyl methacrylate dispersions where bonding was detected between the polymers and calcium ions from the cement. It was thought that the bonding arose from

the acrylic acid residues left in the polymer and from conversion of the ester groups in methyl methacrylate to acid groups.

Sugama *(ref 80)* examined reactions between C_3S and its hydration products with vinyl-type monomers. This was studied by infrared spectroscopy, yielding some interesting results : ionic bonding was detected between the $-COO^-$ groups of the polymer and the Ca^{2+} ions from the C_3S.

Eash *(ref 81)* considered the systems of polyvinylidine chloride (Saran) and styrene-butadiene polymer latexes with cements. A latex in this case is a colloidal dispersion of polymer particles that can be made to coat unhydrated cement grains by the use of surfactants. This prevents coalescence of the grains and resists coagulation under the high sheer forces of mixing cement. Anti-foaming agents were used to minimise air entrapment.

The chemistry of hydrating cement pastes was discussed earlier, but can be summarised by the following : -

Cement + H_2O ——> $NaOH$ + KOH + $Ca(OH)_2$ + $CaSO_4$ solution

$NaOH$ + KOH + $Ca(OH)_2$ + Silica form basic surface of cement particles

Basic surface + Ca^{2+} ——> A Calcium Silicate

It was found that the bonding between Ca^{2+} and the polymer was actual chemical bonding, forming a monolayer of polymer over the surface of the cement grain. This was not the case where Na^+ was substituted for Ca^{2+}, no bonding occurring. The nature of the bond is not known, but thought to be either : -

a) reactions with double-bonds in the polymer,
or b) some surfactant reaction.

The result of this monolayering is to allow hydration of cement grains to continue inside the layers, water being able to penetrate but not the polymer particles themselves. The grains swell, increasing their surface area until the polymer coatings coalesce in one continuous phase. In addition, polymer particles tend to migrate towards surfaces

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exposed to the air and coating the cement grains thus exposed. The effect is to inhibit the premature drying of the cement, allowing hydration to continue to a high degree.

Studies of the chemistry of the calcium hydroxide/styrene-methacrylate polymer dispersion system by Chandra *(ref 82)* found that if the mix proportions were less than 4:1 cement to polymer the film-forming ability of the polymer was lost, and calcium hydroxide does not crystallise from the solution - above that ratio it does. The findings were interpreted in terms of ionic bonding between the -COO⁻ groups of the polymer and Ca^{2+} in solution, although this was not thought to be a complete explanation. As a result of this ionic interaction, polymer particles adhere to calcium hydroxide grains as a sort of cement binding them together and causing their precipitation *(ref 83)*.

Thermal stability of PPCC has been shown to be affected by interactions between polymer dispersions and both C_2S and C_3S *(ref 84)*. Interactions were thought to occur between the CaO in the silicates and the $-CH_2-$ groups of the vinyl-type polymers used. The C-S system aided the thermal stability much more than the C-A system, SiO_2, Al_2O_3, Fe_2O_3 and $Ca(OH)_2$ appearing to have no effect.

2.7.2.3 SETTING REACTIONS IN MDF CEMENTS

With the addition of water-soluble polymers to cement systems, two different types of interaction take place depending upon the amount of polymer used. Sinclair and Groves *(ref 22)* give a clear account of such reactions, two systems being studied.

Calorimetry was used to study the reaction between polyvinyl alcohol (with a trace of acetate) and high alumina cement where a significant reduction in the rate of hydration was noted, this effect being at a maximum for the addition of 1.6% polymer. Above this concentration the hydration was less retarded, a new feature appearing on the thermograms attributed to reactions taking place between polymer and cement. This finding was supported by XRD and IR studies, leading to the following reaction scheme : -

a) In the alkaline environment of the cements the acetate groups of
   the polymer hydrolyse, leaving a negatively charged site on the
   polymer and free acetate,

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$$-O\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{C}}} + H_2O \xrightarrow{\ OH^-\ } -OH + HO\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle O}{\overset{\|}{C}}}$$

$$-OH \xrightarrow{\ OH^-\ } -O^- + H_2O$$
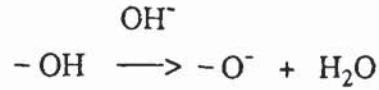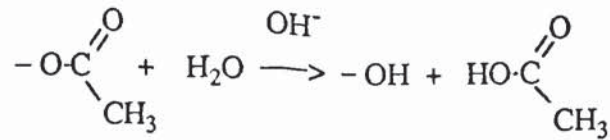
b) metal cations from the cement cross-link these negatively charged polymer sites (see below), and
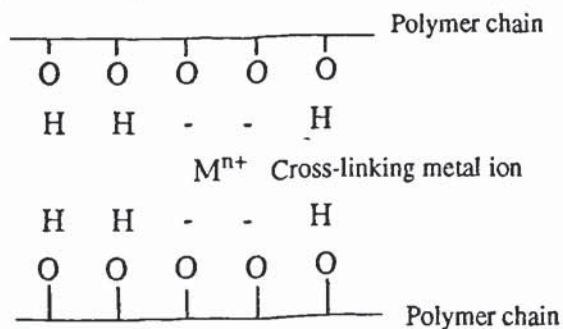
c) rigidity is increased further as the composite drys out.

Polyvinyl alcohol (PVA) as such is hard to use in aqueous systems as it is strongly hydrogen-bonded. However, PVA containing a small proportion of acetate groups which may be hydrated readily assists the overall solution of the polymer.

Similar setting reactions were noted in OPC and polyacrylamide. In this, the amide groups convert to carboxylates and ammonia in the highly alkaline environment, cross-linking occurring with metal cations in solution. After a few hours the material sets rigid. Diagramatically the reactions are as follows : -

$$-\underset{\displaystyle NH_2}{\overset{\displaystyle O}{\overset{\|}{C}}} + H_2O \xrightarrow{\ OH^-\ } -\underset{\displaystyle OH}{\overset{\displaystyle O}{\overset{\|}{C}}} + NH_3 \qquad (ref\ 53)$$

amide + water acid + ammonia

```
                                                    ——— Polymer chain
   |     |     |     |     |
   C     C     C     C     C
  //\   //\   //\   /\\   //\
 O  NH₂ O  NH₂ O  O-  -O  O  O  NH₂

              Mⁿ⁺    Cross-linking metal ion

 O  NH₂ O  NH₂ O  O-  -O  O  O  NH₂
  \\/   \\/   \\/   \//   \\/
   C     C     C     C     C
   |     |     |     |     |
   ————————————————————————————  Polymer chain
```
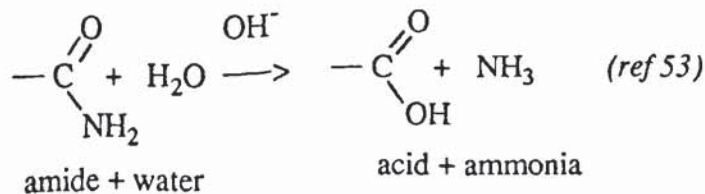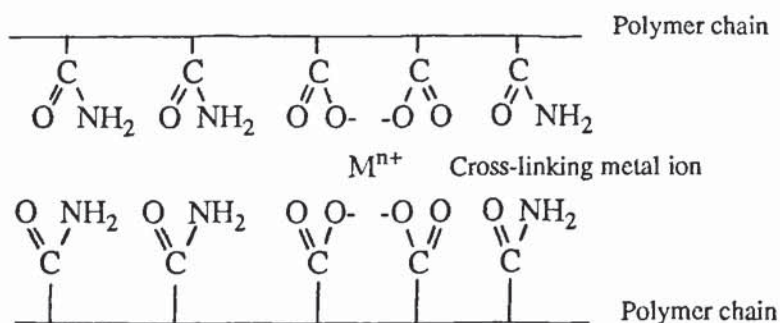
2.7.3 SETTING REACTIONS IN DENTAL CEMENTS

A number of dental materials have been developed which employ components similar to cement minerals with organic substances that are related to those used in MDF cements.

Some of the earliest work in the field was discussed by Wilson *(ref 85)*, who examined reactions between zinc oxide and eugenol (the chief constituent of oil of cloves.) Mixing these together produced a hard translucent substance in twenty minutes or so. Infrared studies showed the presance of $Zn-OCH_3$ bonds indicating chelation of the zinc by eugenol (see below.) Eugenol itself is strongly hydrogen-bonded, the two effects cross-linking eugenol into a rigid solid.

$$
\begin{array}{c}
CH_3 \\
|\\
O- \quad O\\
\nearrow \quad \nwarrow\\
CH_2C=CH_2.H_3C_6 \quad Zn^{2+} \quad C_6H_3.CH_2=CCH_2\\
\searrow \quad \nearrow\\
O \quad -O\\
|\\
CH_3
\end{array}
$$

eugenol   eugenol
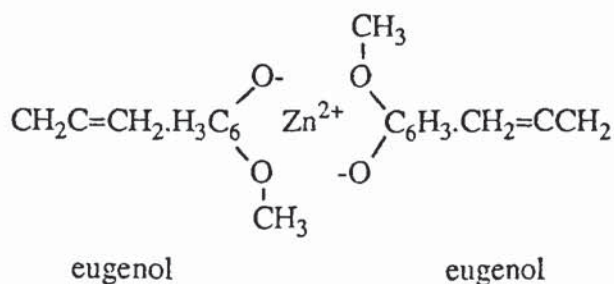
Following this came the development of dental silicate cements. In these, phosphoric acid is mixed with ion-leachable aluminosilicate glass powders *(ref 86)*. The setting reaction was interpreted as : -

   a) conversion of the glass particles to a hydrated gel containing Al^{3+} ions,
   b) at the same time H_2PO_3 produces $H_2PO_4^-$ ions, then
   c) the two ions react to form aluminosilicophosphates.

The behaviour was not observed when Zn^{2+} ions were produced in a gel, the amphoteric nature of Al^{3+} being the likely cause.

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Finally, expanding the principle of dental silicate cements, materials known as glass ionomer cements were developed. In these materials an ion-leachable aluminosilicate glass powder is reacted with a polymeric acid, polyacrylic acid being commonly used *(ref 87)*. Glass ionomer cements set in 2-10 minutes depending upon the materials used, the mix proportions and the temperature.

In the setting reaction pH increases from about 2.0 to 5.5, the process being described by Crisp *(refs 88 & 89)*. as follows : -

  a) Glass particles form rims of hydrated siliceous gel containing Al^{3+} and
    Ca^{2+} ions,
  b) the acid groups of the polymer bind the cations, thus cross-linking
    chains, and
  c) after sufficient diffusion has occurred, the material will have set rigid.

Diagrammatically, the setting reactions in glass ionomer cements are very similar to those proposed for the setting of MDF cements (see above.)

2.7.4 KINETIC INTERACTIONS BETWEEN ALUMINOSILICATE MINERALS AND POLYMERS

Clay minerals have a diverse chemistry, and are essentially aluminosilicate layers with net negative charges balanced by metal cations and water molecules between the layers. Such minerals are of interest because of their chemical similarities to cement minerals.

Clays have been shown to interfere with the polymerisation processes of acrylic monomers. Solomon *(ref 90)* studied the effects that clay minerals have on the rate of polymerisation of styrene and methyl methacrylate. It was found that styrene could be polymerised by the mineral Attapulgite. Chemical methods were used to prove the existence of radicals when the two were mixed. In the case of methyl methacrylate it was found that clays inhibit polymerisation.

This theme was developed by Hiari *(ref 91)* who found it convenient to consider monomers as either electron accepting or electron donating i.e. as Lewis acids or bases. This factor governs their reactions with clay minerals, determining whether they will produce or destroy radicals.

With the proximity of the electrons in the benzene ring to the carbon-carbon double bond, styrene can readily donate an electron from the double bond to form a radical (see below).

$$
\begin{array}{ccc}
\overset{H}{\underset{Ph}{\diagdown}}C=C\overset{H}{\underset{H}{\diagup}} & \longrightarrow & \overset{H+}{\underset{Ph}{\diagdown}}C=C\overset{*H}{\underset{H}{\diagup}} \quad \text{or} \quad \overset{H*}{\underset{Ph}{\diagdown}}C=C\overset{+H}{\underset{H}{\diagup}}
\end{array}
$$

where Ph is a benzene ring and * is an unpaired electron

styrene   radicals
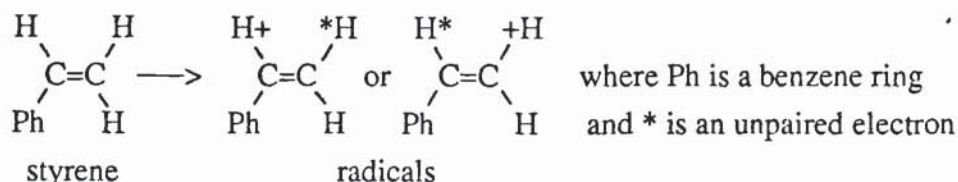
The same cannot be said of methyl methacrylate owing to the relative scarcity of electrons in the proximity of the double bond. More likely is that methyl methacrylate will accept an electron to form radicals (see below).

$$
\begin{array}{ccc}
\overset{H}{\underset{H}{\diagdown}}C=C\overset{CH_3}{\underset{C=O}{\diagup}} & \longrightarrow & \overset{H+}{\underset{H}{\diagdown}}C=C\overset{*CH_3}{\underset{C=O}{\diagup}} \quad \text{or} \quad \overset{H*}{\underset{H}{\diagdown}}C=C\overset{+CH_3}{\underset{C=O}{\diagup}}
\end{array}
$$

methyl methacrylate   radicals
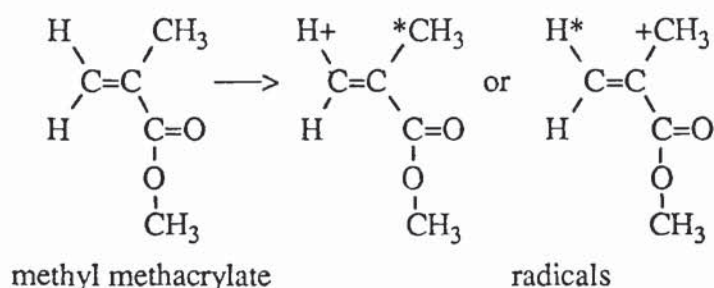
Similar behaviour was found by Godard *(ref 92)* who observed that the rate of polymerisation of methyl methacrylate initiated thermally by benzoyl peroxide was slowed down compared to that in bulk, when it was impregnated into asbestos cement. The opposite was true for styrene.

Sites for electron donation are available in clay minerals. Solomon *(ref 90)* attributed the formation of radical species in styrene to interactions with Lewis acid sites at clay crystal edges containing aluminium. Inhibition of the polymerisation of methyl methacrylate was attributed to electron-transfer reactions occurring at other sites in clay minerals, these processes destroying radicals and so inhibiting polymerisation.

A number of other features were also noted from this work : -

a) that oxygen adsorbed onto minerals accelerates polymerisation, possibly by conversion to peroxides with subsequent decomposition to radicals *(ref 90)*,

b) that adsorbed water speeds up polymerisation by electron-transfer reactions *(ref 90)*,

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c) that the rate of decomposition of benzoyl peroxide initiator is related to the pH of the mineral surface *(ref 92)*, and

d) that the initial interaction between acrylic monomers and clay minerals is complex formation *(ref 91)*.

3 EXPERIMENTAL

3.1   MATERIALS

3.1.1   CEMENTS

All the cement specimens used in these experiments were made from Ordinary Portland Cement (OPC) powders mixed with distilled water. A chemical and physical analysis of the cement used during this investigation (OPC batch 119), was compiled by Blue Circle Industries PLC Research division in July 1985 *(table 3.1)*.

3.1.2   POLYMERS AND RESINS

3.1.2.1   EPOXY RESIN

The product chosen for the experiments involving epoxy resins was selected from the 'Araldite' range available from Ciba Geigy. This consisted of resin AY103 (a liquid cement made by the reaction between bis-diphenol and epichlorohydrin) and hardener HY931 (triethylene tetramine). These were selected because they produce, on mixing, a relatively low viscosity liquid that is workable for up to 2 hours and completely cured within 24 hours, providing excellent adhesion to the cement surface. In fact, Ciba recommend the use of this system for bonding with cements.

3.1.2.2   POLYMETHYL METHACRYLATE (PMMA)

PMMA is a polymer formed by free-radical chain reactions from molecules of the monomer methyl methacrylate (MMA). This is a highly volatile liquid at room temperature, requiring an initiator to accomplish the formation of free-radicals, and hence polymerisation of the monomer. Throughout these experiments the initiator benzoyl peroxide was used, and the temperature of the mix raised to 65°C.

3.1.2.3 MMA PREPOLYMERS

50 g of MMA containing 2% benzoyl peroxide by weight was heated in a large test tube to 90°C using a water bath. The mixture was stirred vigorously with a motor-driven paddle. After about 10 minutes the mixture began to thicken noticeably, then boil. At this point the test tube was cooled with tap water. The resulting prepolymer was stored in sealed tubes at -5°C until use.

3.1.2.4 POLYMERS ALSO USED

Several other polymers were used to a lesser extent in the investigation, these being detailed in *table 3.2*.

3.2 SPECIMEN MANUFACTURE

3.2.1 CEMENT PASTES

All the cement samples used in these experiments were cast using the OPC mixed with distilled water. The appropriate water/cement ratio was selected, and the weight of cement and water necessary for each batch of samples calculated. In general, each batch consisted of about 1.5 Kg of cement, sieved to 300 μm. Mixing was carried out with the appropriate amount of distilled water in an industrial food mixer. The mixer was left to run for about 15 minutes, stopping occasionally to scrape in any cement clinging to the inside of the bowl, out of range of the mixing rotor.

After the mixer had stopped the cement slurry was poured into a plastic jug prior to filling cylindrical plastic containers 76 x 49 mm in diameter. Each container was filled to a depth of about 2 cm with the slurry, taking care not to allow the slurry to segregate. The containers were then placed on a vibrating table until air bubbles no longer came to the surface of the slurry. Care was again taken to avoid segregation owing to the vibration. Once this was complete, a further layer of slurry was added carefully, and the process repeated until all the containers were overflowing. The topmost layer was scraped off and a small piece of polythene sheet placed over the exposed surface. A cap was forced on the top of the container thus sealing the pot. A water jet was used to clean the outsides of the containers, they were labelled and placed in a rotator for 24 hours to prevent segregation during the initial set of the pastes. After 24 hours the cylinders were demoulded and placed in a curing room at 25°C until required.

3.2.2 CASTING POLYMERS

3.2.2.1 EPOXY RESIN

A calculation of the amount of polymer for each experiment was made. The appropriate quantity of resin was then weighed into a small pot on a balance. Hardener was added, and the sample stirred thoroughly with a glass rod for two minutes. The polymer was

then used, any air bubbles trapped during the mixing process rising to the surface within 15 minutes i.e. well before the polymer had substantially cured.

3.2.2.2 POLYMETHYL METHACRYLATE

A calculation of the amount of polymer required was made. Using a glass pipette, methyl methacrylate was weighed into a test tube. The appropriate amount of benzoyl peroxide was then added, a rubber bung fitted and the monomer shaken to dissolve the peroxide. The bung was then removed and a loose tissue plug fitted, as such mixtures have been known to suddenly polymerise explosively! The mixture was then ready for use. Polymerisation was carried out at $65^{\circ}C$ in another loosely stoppered test tube in a water bath. When dimethyl toluidine promotor was employed, polymerisation occurred at room temperature.

3.2.3 PULL-OFF SPECIMENS

A small specially shaped piece of cement was fitted into the lower chamber of the test specimen mould *(fig 3.1)*. Liquid resin was then poured into the upper chamber and left to cure. A light coating of grease was applied to the rubber beforehand to prevent adhesion to the mould. Care was taken not to allow grease onto the cement adhesion surface.

Rubber moulds

A specimen of the desired geometry for the tests was made by gluing together two of the cement members described below. This was placed on a cardboard sheet and coated with a commercial rubber solution compound called 'Mould Master'. Once this was dry a further coat was added and the process repeated until there was a coating some 3-4 mm in thickness over the specimen. Once dry the rubber was peeled off the specimen. This, together with two other moulds was used to set polymer against cement members.

Cement members

The cement units were made by using a water-lubricated rock saw to cut 2 cm slices from cylinders of cement prepared in *3.2.1*, and flats were then cut at right angles to the plane of the disc. Using water-lubricated emery paper (English abrasives paper 166, P400A), the edges were smoothed and the adhesion surface selected. This was then abraded at right angles to the flats, and washed with distilled water. This process

was carried out as fast as practical to minimise further hydration of the cement. Specimens were then carefully dried with a tissue and returned to the curing room until they were needed. These members were made directly after demoulding to allow the maximum time for the specimen to hydrate in its finished form.

Polymer members

Epoxy resin was used with a mix ratio of 10:1 resin to hardener, this being the proportion recommended by the manufacturers. The members were formed in situ by polymerisation of the resin in the upper chamber of the mould, in contact with the cement adhesion surface.

Once the polymer had cured the rubber mould was peeled off, the specimen removed and any loose polymer filed off. The specimen was then ready for testing.

3.2.4 SHEAR SPECIMENS

3.2.4.1 SINGLE INTERFACE SHEAR SPECIMENS

Cement members were prepared as in section *3.2.3* with a thickness of 10 mm. A small mould of internal dimensions slightly greater than *30 x 30 x 15 mm was prepared* in expanded polystyrene. This was placed on the adhesion surface, the region overlapping the cement being sealed from the outside with hot wax. The mould was then filled with epoxy resin and allowed to cure at room temperature. Cement, polymer and mould were then trimmed square using a rock saw. The finished specimen was of dimensions 30 x 30 x 20 mm, consisting of equally sized polymer and cement members *(fig 3.2)*.

3.2.4.2 DOUBLE INTERFACE SHEAR SPECIMENS

A single interface specimen was prepared as above using a disc of cement 2 mm in thickness. After the polymer had cured a second mould was fitted and sealed to the other side of the disc. This too was filled with polymer and allowed to cure. After trimming, a specimen of the same dimensions as a single interface specimen was produced, consisting of a thin layer of cement sandwiched between two polymer members *(fig 3.2)*.

3.2.4.3 ADHESIVE LAYER SHEAR SPECIMENS

Adhesive layer shear specimens were produced by using resins and polymers as adhesives to join two cement discs 10 mm in thickness. A 2 kg weight was used to apply pressure to the adhesive layer until solidification had occurred. Specimens were then trimmed to 30 x 30 mm square.

3.2.5   POLYMER CEMENT EXPERIMENTS

3.2.5.1 DRYING CEMENT SAMPLES

After the appropriate time, hardened cement cylinders were removed from the curing room and broken into small pieces with a hammer and cold chisel. About 50 g were transferred to a pestle and mortar and ground to pass a 300 μm sieve. This powder, together with the remaining chips, was dried by placing in an oven at 105°C for 48 hours. Finally, the powder and chips were labelled and stored in a desiccator until they were needed.

3.2.5.2 POLYMER CEMENTS

Approximately 5 g of dry cement powder was weighed into a test tube. An equal weight of monomer + initiator *(see 3.2.2.2)* was added with a pipette. The test tube was lightly stoppered with a piece of tissue. Using a water bath the test tube was heated   to about 65°C until the mixture began to increase in viscosity. Raising the temperature further than this resulted in boiling of the curing monomer. Care was also taken to mix the sample every five minutes or so to prevent stratification. Once solidification had occurred (40-60 minutes typically) the sample was heated at 100°C for an hour to ensure maximum polymerisation.

On completion, the test tube was removed from the water bath and dried. It was then wrapped in a tissue and the glass broken. The completed polymerised rod was then labelled and placed in a desiccator until further examination.

3.2.5.3 PHYSICAL MIXES

Mixtures were made of hydrated cement and polymer powders sieved to 300 μm. The hydrated cement powders used were those prepared in *3.2.1*, and the polymer powders were made by filing solid polymer samples as prepared in *3.2.2.2*.

3.2.6 THIN SECTIONS OF POLYMER/CEMENT INTERFACES

Samples of PMMA in contact with cements were made by polymerising MMA *(See 3.2.2.2)* monomer in a test tube with small chips of dried hydrated cements. Once the polymer was cured the test tube was broken to remove the specimen. A cut was made at right angles to an interface between polymer and cement, and this set face down on a glass microscope slide using Canada balsam. Another cut was made parallel to the first to leave a slice some 2-3 mm in thickness on the slide. This was further thinned by grinding until the minerals in the cement became transparent. A cover slip was fixed on the slice, and the slide was ready for optical examination. Similar specimens were prepared at different W/C ratios and cure times using both PMMA and epoxy resin. Polymer cement and prepolymer specimens were similarly produced at a variety of controlled temperatures. Thin sections were cut at right-angles to the polymer/cement interface.

3.2.7   PREPARATION OF POSSIBLE POLYMER/CEMENT REACTION PRODUCTS

Reagent grade methacrylic acid was diluted with distilled water to make a 4 mol/l solution. In a similar way, 2 mol/l solutions of calcium chloride and sodium carbonate were made up. Methacrylic acid was added to 50 ml of the carbonate solution through a burette, the reaction liberating carbon dioxide. When the effervescence had just ceased, calcium chloride solution was added to excess. After a minute or so white radiating needles of the methacrylate began to form. The resulting fibrous mass of interlocking crystals were recrystallised from water, filtered and dried with a little ice-cold acetone.

3.2.8 SELECTIVE DISSOLUTION OF PMMA

The polymer in polymer cements, and the polymer in adhesion experiments bonded to cement surfaces were both dissolved away using chloroform ($CHCl_3$). Specimens containing 1-2 g PMMA were immersed in 100 ml $CHCl_3$ at room temperature for 24 hours, swirling occasionally. Crushing was not necessary for the polymer cements, all the obvious polymer residues having gone into solution. Polymer/cement adhesion specimens were transferred directly into a soxhlet extractor and washed with $CHCl_3$ for 6 hours. Polymer cement specimens were swirled then centrifuged, before carefully decanting the polymer solution. Fresh $CHCl_3$ was added, the mixture shaken and centrifuged again. The polymer solution was again decanted, and the process repeated

three times. The residue was then transferred to a soxhlet extractor and washed with $CHCl_3$ for 6 hours, before drying in air at room temperature. All the polymer solutions were combined. Where this was needed for further examination, they were carefully poured onto a polythene sheet and the $CHCl_3$ allowed to evaporate. Films of polymer could thus be recovered.

3.2.9 DECOMPOSITION OF PMMA

About 2 g of PMMA chippings were placed in a test tube with a short piece of neoprene tubing connected to the top. The other end was placed in a flask that was cooled by an ice-bath. Heating the chippings with a bunsen burner caused the PMMA to boil, a heavy white vapour being evolved. This was condensed in the flask, being crude methyl methacrylate.

TABLE 3.1

CHEMICAL COMPOSITION AND PHYSICAL DATA FOR OPC

CHEMICAL DATA		PHYSICAL DATA	
Oxide	%	Specific surface area (M^3/Kg^2)	421
Silicon	20.0	Apparent particle density (Kg/M)	3150
I.R.	0.27	Le Chatelier expansion, (mm)	1
Alumium	5.3		
Iron	3.4	Setting times (Vicat):-	
Manganese	0.06	Standard consistency water (%)	26.3
Phosphorous	0.08	Initial set (mins)	70
Titanium	0.26	Final set (mins)	105
Calcium	64.5	100mm concrete cube compressive	
Magnesium	1.2	strength 0.5 W/C ratio (N^2/mm)	
Sulphur	3.0	Sand : agg. : cement = 1.9 : 2.3 : 1	
L.O.I.	0.9	At 3 days	24.0
Potassium	0.78	At 7 days	32.0
Sodium	0.10	At 28 days	42.5
		MINERALOGICAL DATA	%
Free CaO(%)	2.2	C3S	61.5
L.S.F.	97	C2S	11.9
S/A+F	2.3	C3A	8.3
A/F	1.6	C4AF	10.4

TABLE 3.2

OTHER POLYMERS STUDIED

NAME	TYPE	PREPARATION	SUPPLIER
P38	Styrene cross-linked polyester resin	Peroxide hardener mixed with resin ~1:50 by volume	W. David and Sons ltd
Fastglass	Styrene cross-linked polyester resin	Peroxide hardener mixed with resin ~1:100 by volume	W. David and Sons ltd.
Superglue	Acrylic	Applied to mating surfaces as supplied	Loctite Holdings ltd.
Eve-o-stick	Contact adhesive	Applied to mating surfaces and allowed to dry before contact	Eve-o-stick ltd.
G/P	Saturated polyester	Phthalic anhydride heated with glycerol 3:2 by weight, applied hot	------
G/M	Unsaturated polyester	Maleic acid heated with glycerol 3:2 by weight, applied hot	------

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FIGURE 3.1

PREPARATION AND LOADING OF
PULL-OFF SPECIMENS

Cement cylinder cast

Cyllinder cut into
disc

Faces cut on disc

Cement placed in rubber
mould and resin added

Exploded view of finished
specimen showing square
adhesion surface shaded
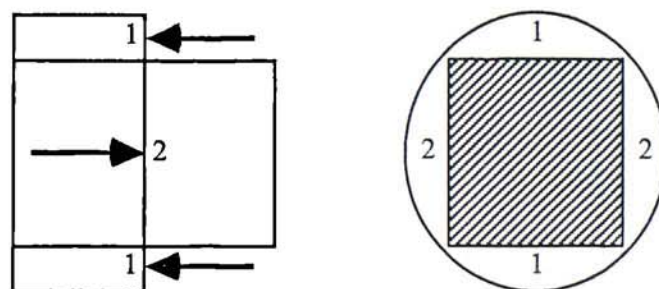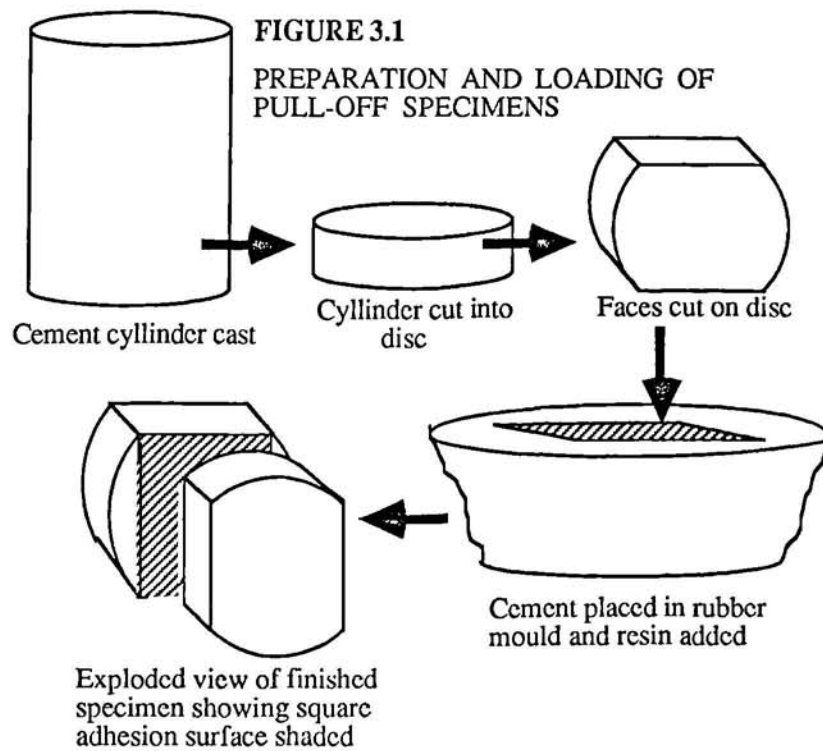
Specimens loaded in direction of arrows. Numbers 1 and 2
represent loading faces on each member, adhesion surface
being shaded.

A PULL-OFF SPECIMEN UNDER TEST
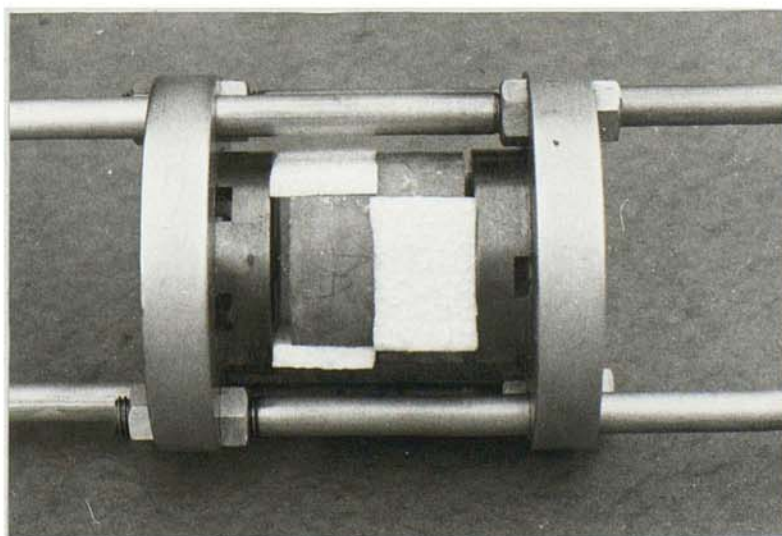
FIGURE 3.2

PREPARATION AND LOADING OF SHEAR SPECIMENS

The following procedure was used to prepare double-interface specimens. Single-interface specimens only required resin adding to one side.

Cement cyllinder cast

Thin disc cut for double-interface specimens

Thick disc cut for single-interface specimens

Polystyrene mould fitted and sealsd with wax

Resin added and allowed to cure

single-interface

double-interface

Finished specimen trimmed to size

Resin added and allowed to cure

Specimen inverted, second mould fitted and sealed with wax

Frame

Adjustable jaw

Locking plate

Specimen

Loading direction

Loading direction

SHEAR SPECIMEN UNDER TEST

3.3 TESTS

3.3.1 PULL-OFF TESTS

A Hounsfield Tensometer fitted with a compression attachment was used for pull off tests, forcing the specimen apart at the cement/ polymer interface *(fig 3.1)*. The stress/strain curve was recorded together with the mode of failure i.e. at the interface or not. Both parts of the failed specimen were stored in a desiccator for further examination.

3.3.2 SHEAR TESTS

Test procedures for single interface, double interface and adhesive layer shear specimens were identical : The specimen under test was fitted into the locking plate and inserted tightly against the lower jaw of the shear apparatus *(fig 3.2)*. The apparatus was tensioned until both jaws were just in contact with the specimen, then adjusted to the plane of the interface. Loading then commenced, the resulting stress/strain behaviour to failure being recorded.

3.3.3   DIFFERENTIAL THERMAL ANALYSIS (DTA)

A small amount of powdered sample was accurately weighed into the sample crucible of the DTA and fitted into the head. Usually the amount used was that necessary to almost fill the crucible after gently tapping it on the bench.

The furnace was carefully lowered into position and the metal sealing ring tightened around its base. A thermometer was lowered onto the head and the temperature within the furnace measured. A ceramic plug was then fitted in the top of the furnace and the chart recorder adjusted to read the temperature just measured. Cooling water for the sealing ring was turned on and the cold junction flask checked to ensure it was still filled with an ice-water mixture. The heating rate, maximum temperature and differential trace were set, and the apparatus switched on. Once at the preset maximum temperature, the machine switched off automatically. The furnace was raised and the sample crucible removed to cool. Finally the residue weight was determined.

Dry powders sieved to 300 μm were used for all DTA experiments. These included pure polymer, pure cement, polymer cements and physical mixes of polymers and cements.

3.3.4 INFRARED SPECTROSCOPY

Molecules irradiated with infrared radiation absorb energy at specific wavelengths related to different vibrational modes of the molecule. Measurement of the absorption of infrared radiation over a range of frequencies produces a spectrum specific to the molecule in question. For this reason, infrared spectroscopy is a commonly used technique for identification of molecules. However, interpretation of spectra also yields structural information: Molecular vibrations can be classed as complex whole-molecule vibrations, or as vibrations specific to different chemical groups. Since groups absorb at roughly the same wavelengths independent of the nature of the whole molecule of which they are part, groups can be identified by their specific peak positions. Whole-molecule vibrations specific to each molecule tend to take place in the region below 1500 cm^{-1}, the region sometimes being referred to as the "fingerprint" region. On the other hand, group vibrations occur (for the most part) above 1500 cm^{-1}.

A detailed description of how absorbencies occur is not relevant to this study, but it is important to explain the conventions and terminology generally used to express infrared data.

On a standard IR spectrum absorbence is plotted as the ordinate, with absorbence increasing in the negative direction. Absorbencies are generally scaled with the aid of a computer to maximise peak heights. Units are not usually quoted, relative intensities of peaks (0-100%) being the important feature. Wavelength is plotted as the abscissa increasing left to right. For numerical reasons it is plotted as the reciprocal of wavelength in cm^{-1}, often from 4000-220 cm^{-1}. The scale often has two regions from 4000-2000 cm^{-1} and 2000-220 cm^{-1}. This is not strictly necessary, but makes the spectra compatible with those from earlier instruments that required a scale change for mechanical reasons.

Tabulated IR data expresses absorbence in four ways:- a) absorbence values in cm^{-1} or nm, b) groups assigned to the absorbence, c) peak intensity and d) vibrational mode. Peak intensities are often described as strong, medium, weak, broad or variable. Six vibrational modes for specific chemical groups are defined, these being symmetrical stretch, asymmetrical stretch, bending, rocking, twisting and wagging.

A Perkin Elmer 1710 infrared fourier transform spectrometer was used exclusively for these experiments. The apparatus used a laser beam to scan the 4000-220 cm^{-1} region of

the infrared, absorbencies due to molecular vibrations being detected at specific, well defined wavelengths.

3.3.4.1 SOLID SAMPLE PREPARATION

A few milligrams of the sample to be tested was placed in a hard agate mortar with a microspatula. Three or four spatula ends of I.R. grade potassium bromide powder were added and the mixture ground to a fine uniform powder. This was then carefully sprinkled into a 1 cm die using the spatula again, until the powder just covered the surface of the dye in an even layer. The top of the die was inserted, and the assembled unit fitted into a press. A vacuum line was connected, and the pressure on the die pumped to 2 tons. After 30 seconds or so this was carefully increased to 10 tons, and the pressure maintained for 2 minutes or so. At the end of this time the pressure was released and the vacuum line disconnected. A thin disc was formed and fitted into a sample holder for the spectrometer.

Potassium bromide is virtually transparent to infrared light of the wavelengths used, so absorbencies encountered in scanning the disc were attributed to the sample only. However, potassium bromide does absorb water readily, so it was stored before use at 110°C, discs being used immediately and not stored.

3.3.4.2 LIQUID SAMPLE PREPARATION

Since all the liquids that were studied were non-aqueous, sample preparation was relatively straightforward : - A small drop of the liquid to be tested was placed on a circular sodium chloride plate. A similar plate was placed on top so that a thin film of the liquid was produced between the two plates. A metal jig was used to clamp the plates together, allowing them to be fitted into the spectrometer. Sodium chloride is also virtually transparent to infrared light of the wavelengths used, absorbencies therefore being attributed to the sample liquid only. For obvious reasons, aqueous substances are not used with sodium chloride plates, so cleaning had to be done using dried acetone. The plates themselves were stored in a desiccator when not in use.

3.3.5 ION CHROMATOGRAPHY

The process of ion chromatography involves passing an ultra-pure aqueous solution of the sample to be analysed through an ion chromatography column. This contains particles that adsorb the ions in solution. Passing an eluent through the column causes a

gradual exchange of adsorbed ions back into solution. The concentration of these exchanged ions varies with time depending upon the chemical nature of the ions, eluent and adsorbent particles, and also upon the rate of elution. These factors cause the different ions to be washed off the column at different times. Thus by measuring the conductivity of the eluent it is possible to detect the the appearance of the different ions. On calibrating the apparatus with ionic solutions of known concentrations, it is possible to identify the ions in an unknown sample, together with their concentrations.

The apparatus used for ion chromatography was a Dionex 2000i/SP. An AS6 anion column was used for the separation of ions, using a 0.001mol/l $NaHCO_3$ eluent at a flow rate of 0.1 ml per minute. For most of the samples used, the sensitivity of the machine was in the order of 3-30 mS. Data is recorded on a chart recorder with a suitable sensitivity to maximise peak height. This was digitised on a Hewlett Packard 9874A digitiser linked to a BBC computer. Software was developed to calculate peak areas from which concentrations could be derived.

Three types of sample were used in for ion chromatography, these being cements themselves *(see 3.2.1)*, cements refluxed with MMA and polymer cements. The cements used were 0.4 W/C ratio hydrated for 2 and 240 days, and a 0.7 W/C ratio hydrated for 2 days.

Pure cement samples were used as controls in the experiment, these being available as an oven-dried powder sieved to 75 μm. About 4 g was shaken with 100 ml of distilled water for 30 minutes, then filtered. The filtrate was made up to 250 ml, this needing no further dilution for injection into the Dionex.

In a similar manner, the refluxed cements were prepared for injection by refluxing about 4 g with 50 ml of distilled MMA for 1 hour. The MMA was removed by distillation, and the cement residue shaken with water, filtered and the filtrate made up to 250 ml. This was then injected into the Dionex.

Polymer cements were prepared as described in section *3.2.5.2*. As with the other types of sample they were crushed and sieved, shaken with water, filtered and the filtrate made up to 250 ml. This was injected into the Dionex.

A series of anion standards were prepared from the appropriate sodium salt. The concentration of each was accurately determined, and about 0.02 mol/l. These standards were further diluted and mixed to obtain standards with similar peak sizes in the same

Dionex sensitivity range. The salts used were chloride, sulphate, bicarbonate, benzoate, silicate, aluminate and methacrylate.

Quantitative determination of methacrylate

Samples of refluxed and polymer cements of 0.4 W/C ratio were prepared as described in section *3.2.5.2*, except for the addition of water. Five samples were produced of water contents 0, 25, 50 and 100% of the original water content before the cement was oven-dried. A further specimen was prepared by refluxing MMA with cement powder immediately after further oven drying at 105°C overnight. Water extracts of all samples were prepared as described above.

3.3.6 X-RAY DIFFRACTION (XRD)

A Phillips diffractometer using $CuK_{\alpha 1}$ radiation of wavelength 0.15406 nm was employed.

Using the samples of polymer and cement powders described in *3.2.1* and *3.2.5*, a set of physical mixes of different polymer/cement ratios were made up. This was done by weight on an accurate balance, the ratios being from 100% cement to 100% polymer. It was necessary to prepare about 1g of each mixture, this being enough to fill the sample holder on the diffraction set.

Powders of polymer cements were prepared as in *3.2.5*. Again, about 1g of sample was needed to fill the sample holder on the diffraction set.

3.3.7 X-RAY PHOTOELECTRON SPECTROSCOPY (XPS)

XPS is one of the most powerful techniques for surface examination, producing chemical information about the upper few nm of the surface. The procedure involves bombarding surfaces in an ultra-high vacuum with monoenergetic X-rays of low penetrating power, then sorting the emitted electrons in terms of energy. By plotting the number of electrons emitted against energy, an XPS spectrum is produced. Characteristic peaks occur attributable to each element present on the surface, and the different chemical environments within which the elements are found. Two major physical effects produce XPS spectra, the 'photoelectron' and 'auger' processes. In the photoelectron process, incoming X-ray photons cause ionisation of electrons in lower orbitals. A relaxation process then occurs, involving the transfer of electrons from

higher energy orbitals to fill the vacancies left in lower orbitals. The energy thus liberated can be imparted to higher energy electrons, causing their emission. This is known as the 'auger' process.

Although electrons from both processes are present throughout the excited region, most are readily absorbed. It is only those produced in the upper few nm that can escape from the surface. For this reason, XPS spectra produced in this way are representative of the actual upper layers of the surface, and not the bulk composition.

The spectrometer used was a Kratos XSAM 800 interfaced with a computer using DS 800 software. The radiation used was Mgk_α of energy 1253.6 eV.

Cement specimens were prepared either by machining with a water-lubricated diamond rock saw, or by chipping with a cold chisel. The maximum permissible size for insertion into the vacuum chamber was 15 x 7 x 2 mm. Specimens were oven dried at 105°C for 24 hours, being transported to the vacuum chamber in a desiccator. In a few cases drying was accomplished either under vacuum, or by saturation with isopropanol followed by evaporation at room temperature in a desiccator.

For adhesion surfaces, cement specimens were prepared as above, then placed in MMA propolymer in a sealed container. Final polymerisation was accomplished by heating at 40°C in a water bath for 24 hours. This was subsequently removed by dissolution in $CHCl_3$ *(see 3.2.8)*. Some cement specimens were refluxed with MMA for 1 hour, followed by its evaporation in an oven at 105°C for 24 hours.

3.3.8 OPTICAL MICROSCOPY

Thin sections as prepared in *3.2.6* were examined at different magnifications using a Vickers M41 photoplan microscope. Both plane-polarised and cross-polarised light were employed.

3.3.9 INVESTIGATIONS USING CALORIMETRY

A Wexham isothermal calorimeter was used for all the calorimetry experiments. The apparatus consists of two calorimeter cells maintained at constant temperature in a large water-bath. Inside the cells there was an aluminium can with lid, containing a measured volume of transformer oil - usually 50 ml. Into this was placed the sample container, the lid was closed and the can fitted onto a thermopile attached to an aluminium

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heatsink in the bottom of the cell. Several types of sample container were used, depending upon the nature of the sample; For polymers and polymer cement experiments, 2 ml heat-sealed ampules or 2 ml stoppered sample bottles were used; for polymer impregnation experiments, dried impregnated cement disks were wrapped in aluminium foil, dipped in wax and coated with a plastic film.

The lid of the cell helped press the can firmly onto the thermopile, and with wires connected to a calibration heater within the can, and to the thermopile itself, the cell could be lowered into the waterbath. Once isothermal conditions were established, measurement of the e.m.f. of the thermopile with time was commenced, this being related to the heatflow through the thermopile.

On the completion of each run, i.e. when there was negligible heatflow through the thermopile, the calibration heater within the can was switched on. Subsequent measurement of the E.M.F. response against time together with the heater power enabled scaling constants to be derived for the particular run just completed. These constants were then used to compute the rate of heat output during the run, and also the total heat output.

The mathematical treatment of these results necessitated the use of a BBC microcomputer, data being assembled by digitising chart recorder output using a Hewlett Packard 9874A digitiser.

3.3.10 KINETICS OF DECOMPOSITION OF BENZOYL PEROXIDE

Benzoyl peroxide molecules decompose into two free-radical fragments at a rate dependent upon temperature and concentration of promoters. It is possible to determine the number of free-radicals that have been formed with time photometrically, by allowing them to react with the highly coloured free-radical compound diphenyl picryl hydrosyl (DPPH). By plotting log transmitted intensity (i) against time, the relationship is linear whilst the DPPH is being consumed. By adding hydrated dried cement powder to a BP/DPPH solution, any modifications of this rate would indicate interactions with the cement.

About 0.2 g DPPH and 2 g BP were weighed accurately into a 500 ml graduated flask and made up with toluene. 30 g cement powder sieved to 75 μm was placed in a large round-bottomed flask. 250 ml of the solution was transferred to the flask, and the time recorded. This, together with the remnants still in the flask were transferred to a water

bath at 40°C. At 15 minute intervals, 10 ml of the solution containing cement was centrifuged to sediment any particles prior to measuring on a spectrophotometer. This was set to measure absorbence at 428 nm, the maximum absorbence for DPPH. Similarly, the other solution was also measured and the time recorded. The process was repeated at 15 minute intervals until the intense purple colour of the DPPH was lost from both solutions (6-8 hours). Concentration of DPPH with time was determined by plotting log i/i_0 against time, i_0 being the initial transmitted intensity.

3.3.11 SCANNING ELECTRON MICROSCOPY (SEM)

Both cements and polymers were examined using this technique, the preparation being the same in each case: Specimens about 5 mm square for examination were glued to SEM stubs using polystyrene cement. Polymer samples needed no pre-treatment, whereas cements required drying in an oven an 105°C for at least 24 hours. Stubs were then placed in an oven for 24 hours to ensure complete evaporation of the solvent in the glue. Once this was completed they were irrigated with a conducting film spray and left by a dryer for a few minutes. The stub was then fitted in the sample holder of the SEM, the door closed and vacuum pump started. After 15 minutes or so vacuum was sufficiently good to allow the examination to start. Photomicrographs were taken of the features of interest.

3.3.12 POLYMER MOLECULAR WEIGHT DETERMINATION BY VISCOMETRY

1-2 g PMMA recovered by selective dissolution or as polymerised in bulk was accurately weighed into a 100 ml graduated flask and made up with $CHCl_3$. After mixing, 75 ml of the resulting solution was pipetted into another 100 ml flask and made up with $CHCl_3$. Three further serial dilutions were made, care being taken to allow the last drops of viscous solution to be collected. All the solutions were placed in a water bath at 20°C until use.

The viscometer used consisted of an upper and lower bulb connected via a capillary in a 'U' tube configuration. The lower bulb was marked so it could be filled with an identical volume of solution for each determination. The upper bulb was marked above and below, the time for liquid to drain between these marks and back into the lower bulb being related to the viscosity of the solution.

The lower bulb was filled to the mark with the solution under test. This was flushed through the apparatus a few times, before being pumped into the upper bulb using a

pipette filler. The time for the solution to pass the upper and lower marks was recorded. This was repeated until the values agreed to 2%. The solution was then poured out of the apparatus, which was then cleaned using fresh $CHCl_3$. Each solution was tested in this manner.

3.3.13 LONG IMMERSION STUDIES OF CEMENTS IN MMA AND BP DISSOLVED IN TOLUENE

Cement specimens of different W/C ratio and cure time were oven dried at 105°C to constant weight. Sets of specimens were then immersed in a) undistilled MMA, and b) a solution of 50 g BP in 500 g toluene. Both were maintained at room temperature in airtight boxes for several months. At appropriate times, the specimens were removed and allowed to dry at room temperature for 2 days. These were subsequently weighed, and any residues on the surfaces removed for further examination before immersion again.

4 LOCUS OF FAILURE AND ADHESION MEASUREMENT

4.1 INTRODUCTION

When using polymers for adhesive and repair applications, it is of prime importance that a strong and durable bond is formed with cement and concrete. The aim of this series of experiments was to cause interfacial failure between cements and polymers by mechanical means, thus allowing microscopic examination of the interaction zone. It was not expected that polymers performing strong bonding with cements would fail at the interface totally, though it was hoped that some interfacial or near-interfacial areas would be revealed. Nevertheless, failure wherever it occurs provides information regarding interactions between polymer/cement systems.

Experiments were conducted with the following aims : -

1) To determine the locus of failure of specimens under mechanical loading.

2) To assess the general bonding characteristics of a number of polymer and resin systems with cements.

3) To determine any differences in adhesion and failure characteristics with water/cement ratio and age of hydrated cement.

Although a variety of tests exist to determine bond strength of adhesives and patch repair materials *(fig 4.1)*, in this work specimens and apparatus were investigated to establish those designs that promote failure at or near the interface. It was also hoped that such designs would also be applicable to small-scale testing.

4.2 PREVIOUS WORK

The word 'adhesion' is in general use for a number of phenomena relating to bonding between dissimilar phases. In general, it is applied to configurations consisting of one phase as a coating on the other, or as a layer between two members of the other phase.

The exact meaning of adhesion often depends upon the user! Physicists tend to use the term to mean "the attractive force generated between two phases brought into intimate molecular contact", whereas chemists and engineers would tend to use it to mean "the ability of a coating to stay attached when scratched, slashed, stressed, or otherwise abused" *(ref 93)*.

Theory of adhesive fracture indicates that it is very seldom that the locus of failure actually runs through the interface, but more likely through one or both of the materials that make the interface. It is also thought that there are boundary layers in each material formed on either side of the interface that are of different character to the body of the materials. The locus of failure often runs through these boundary layers causing failure near, but not actually at the interface.

For adhesion measurement it is often useful to form the interface by, in effect, gluing two substrate members together. The 'adhesive' is then as a thin coating between the members. However, comparisons between adhesives are sometimes difficult, since it has been shown that the strength of such joints is generally reduced with increasing film thickness*(ref 94)*, and producing consistent specimens is sometimes difficult. For this reason a statistical approach is generally adopted.

Several tests have been developed to examine adhesion strengths of materials, bearing in mind failure in such joints is very rarely at the interface. The process of producing interfacial failure can be looked on as taking place in two stages 1) initiation of a crack, and 2) crack propagation across the specimen under load. Arnold *(ref 95)* divides all crack-propagation mechanisms into three modes : - 1) cleavage, 2) edge sliding, and 3) tearing.

A number of commonly used configurations for adhesion strength testing employing these modes are given below. Diagrams of several test specimens are also displayed in *fig 4.1*.

FIGURE 4.1

ADHESION TEST PROCEDURES AND SPECIMEN GEOMETRIES

BASIC LOADING MODES

Mode 1 (cleavage)

Mode 2 (edge sliding)

Mode 3 (tearing)

Pull-off (mode 1)

Pull-off (mode 1)

Single-cantilever beam (mode 1)

Double-cantilever beam (mode 1)

Peel test (mode 1)

Angled shear (mode 2)

Lap (mode 2)

Four-point bend (mode 2)

Three-point bend (mode 1)
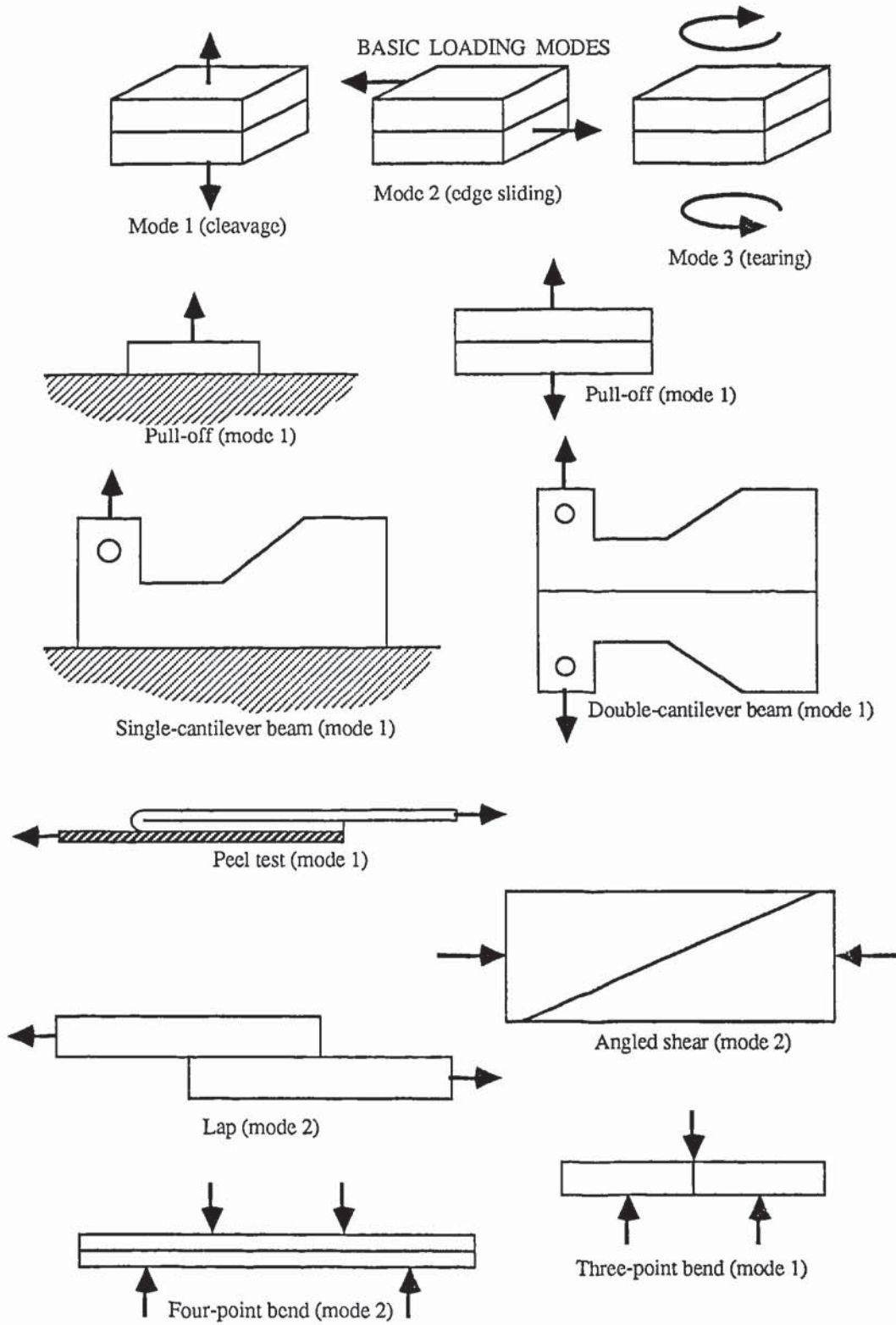
4.2.1 TESTS FOR COATINGS

4.2.1.1 PULL-OFF TESTS

These are adhesion tests where two 'substrate' members of a specific geometry are glued together with the material under test, a cure period elapses, and the members pulled apart until failure occurs. International standards describe one such test procedure (ISO 4624, DIN 53232) for measurement of paint coatings by pull-off tests. Two types of test specimen are described.

Sickfeld *(ref 94)* examined stress concentrations in the two geometries by constructing transparent models and subjecting them to the sort of loading they would get in practice. By the use of holographic interferometry it was possible to see the stress patterns building up in the models. This demonstrated that stress builds up at different points on the samples, particularly around the margin of the interface. As a result there would be differences in the stressing of the interface and therefore differences in the mode of failure between the two.

It was also shown that the stress intensity factor increases with substrate thickness until a critical thickness is reached, then the factor is constant. In steels this thickness is of the order 10-15 mm depending upon the adhesive and conditions used. This itself can be related to bending moments in the substrate.

The other major geometrical factor affecting the mode of failure of the cylindrical specimens used was cylinder thickness, more consistent results being obtained with larger cylinders. Clearly adhesion measurement is a statistical process, the more identical samples tested the better. Sickfeld *(ref 94)* used many identical samples for each coating.

4.2.1.2 SIMPLE PULL-OFF TESTS

Much simpler pull-off tests have been designed - these are not as rigorous as the standard tests described above, but much easier to perform. In the tests plates or washers *(ref 96)* are bonded to coatings. A typical test involves a small metal plate with a wire attached of specific dimensions *(ref 97)*. This is bonded to the substrate with the adhesive of interest. By applying a tensile force to the wire, the force required to pull the plate off the surface may be determined.

4.2.1.3 TENSILE BEAM TESTS

Specially shaped beams may be used for adhesion testing these being glued together with the material under test. These are shaped according to the mathematics of the stresses they will suffer as a crack proceeds through the glued area.

Two such designs were developed from ASTM D3433-75 "Tests for fracture strength in cleavage of adhesives in bonded joints" *(ref 97)*. The two types of specimen developed are as follows : -

The double-cantilever beam constant-compliance specimen

In this design the two halves of the specimen are glued together with the adhesive under examination. Specimens are designed with a slot between the members to allow crack propagation along the interface on loading. These are attached to a tensometer via the holes in each member. The specimen is then loaded as appropriate (i.e. for ultimate tensile stress, for fatigue etc.) By tapering the beams appropriately, compliance (the inverse of stiffness) of the specimen remains the same as the crack propagates *(ref 98)*.

The single-cantilever beam constant-compliance specimen

This design of specimen is very similar to the double beam type, having only one beam glued to a rigid substrate. Similarly to the double-beam specimens a slot is created with a piece of release tape (PTFE for example) placed between the member and the substrate. This runs from the loading end to about 1/3 the way along the interface in order to create a crack at the interface. Subsequent loading causes the crack to propagate along the interface. The test procedures are the same as for the double beam design. Again, the compliance of the specimen remains the same as the crack propagates.

4.2.1.4 PEEL TESTS

Many coatings and films have sufficient flexibility to be assessed by variations of the so-called 'peel' test *(ref 93)*. Two types of test are in common use : - For thinner films (e.g. inks) the film is applied to the substrate and allowed to dry. An appropriate time later, a piece of tape (e.g. Scotch tape) is stuck to the surface and then ripped off as quickly as possible. Some of the coating is removed by the process, the rest remaining stuck to the substrate. The quantity still remaining on the substrate may be determined

photometrically. Data on the adhesion of such coatings allows plots to be made of time after application of ink versus quantity of ink remaining after the test.

The test is both useful and easy to perform, though not quantitative. Information is also obtained on the locus of failure of the coatings under test.

The other basic permutation is for thick flexible films. Test specimens are made by bonding coatings to solid substrates allowing one end to be unbonded to the substrate. This is often done by placing a piece of release paper on the end of the substrate before applying the coating. A tensile force is applied to the loose end of the coating, the substrate being firmly supported. This results in the coating being peeled off the substrate, the force required and speed of peeling being a measure of the bond strength.

4.2.1.5 SHEAR, CREEP AND FATIGUE TESTS

Shear has been employed in adhesion measurement. Test specimens tend to be large-scale yet relatively easy to make. Hugenschmidt *(ref 99)* described several test specimens employing shear. Lap and angled joints demonstrate two geometries of glued specimen, one for compressional the other for tensile testing. Lap tests have been used extensively to test the bond strengths of specialised adhesives in dentistry *(ref 100)* as well as in the fields of mechanical and civil engineering. Angled shear specimen has also been used for measurement of the adhesion of epoxy resins to concrete members *(refs 101 and 102)*.

Creep and fatigue are also of interest for the repair of structures (for example). Hugenschmidt *(ref 99)* also carried out work on bonding 'young' concrete beams to 'old' ones using epoxy resin, allowing curing to be completed then loading the specimens in a four-point bend apparatus. The amount the beams flexed was plotted against number of loading cycles until the sample fatigued. A similar set-up with constant loading was used to determine creep *(ref 99)*.

4.2.1.6 DURABILITY TESTS

The durability of polymer modified mortars is again of interest to the repair of cement structures. Several Japanese studies have examined mortar/resin-modified mortar bond after exposure to the elements. Ohama *(ref 103)* carried out a study of blocks made from styrene-butadiene rubber modified mortar bonded to ordinary mortar as specified in JIS R 5201, that had been left outside for up to ten years. These were then tested to

failure along the interface using a three-point bend test. Graphs were plotted of load at failure versus time of exposure. It was found that there was a more rapid decrease in strength over the first year of exposure, followed by a more gradual decrease until the completion of the test program. Similar test procedures were employed by Tsuruta *(ref 104)* for measuring the bond strength of different aggregates in PIC with ordinary concrete. Here too three-point bend tests were used, the specimens being notched on the upper surface.

A similar study by Konaka *(ref 105)* on resin mortars used in tunnel construction involved test specimens made in a similar way to those described above *(ref 103)* where ordinary mortar was bonded to a resin-mortar, the finished specimen then placed in a water bath at 20°C until needed. Testing involved measuring the force needed to split the specimen at the interface using a three-point bend test according to JIS A 1184.

It was found that aggregates pre-treated with silane coupling agents improved adhesion strength in water, and that pH, curing temperature and quantity of accelerator added were all contributing factors affecting adhesion strength.

Some attempts have been made to standardise test procedures for polymer/cement systems, most experimenters preferring to use tests directly applicable to their own experiments *(ref 106)*.

4.3 RESULTS AND DISCUSSION

4.3.1 DEVELOPMENT OF SPECIMENS AND PROCEDURES

The primary aim of these experiments was to develop specimens that could be fractured so that the locus of failure passed through or very close to the interfacial region. It was not expected that complete interfacial failure would be experienced, this requiring bonding between the phases to be very weak. The 'usefulness' of the tests was assessed in terms of their ability to reveal interfacial regions for further examination. Nevertheless, locus of failure wherever it passes gives some indication of the relative strengths of the two phases and the bond between them.

Specimens

The first design used, simple 'pull-off', was only partially successful in producing near interfacial failure. Often failure was through the cement members since the strength of the polymer/cement interface exceeded the strength of the cement itself. Specimens were also difficult to produce, their moulds suffering damage easily.

It was hoped that the shear tests would remedy these problems first by directing the plane of maximum stress along the interface, and secondly by easier specimen preparation. With 'single-interface' specimens, although the locus of failure started interfacially at the edges of the specimen, it soon passed substantially through the cement. The problem was not alleviated by notching specimens at the interface, although specimens were easier to prepare than pull-off specimens. General bonding characteristics between cement and polymer were assessed using single-interface specimens, partially in terms of strength, but mostly in terms of locus and character of failure. Only one cement was used in order to show differences in failure between the different resins and polymers.

'Double-interface' specimens made use of the fact that failure in shear specimens made with epoxy resin was almost always through the cement member. By sandwiching a thin layer of cement between two polymer members, failure was constrained to the region of the cement layer.

'Adhesive layer' specimens were in a sense double-interface specimens with a thin polymer layer sandwiched between two cement members. It was possible to make the polymer layers much thinner than the corresponding cement layers, but not necessarily

of equal thickness between different polymers. This was not considered an important factor in these experiments because of their qualitative nature. 'Adhesive layer' specimens were used exclusively for polymer/cement compatibility experiments, only one cement being used.

Details of specimen preparation are given in *3.2.3* and *3.2.4*.

Procedures

The apparatus used for these tests was based on a Hounsfield tensometer. For the pull-off specimens, force was applied by a compressional attachment applying pressure to polymer and cement members via hardwood sticks *(fig 3.1)*. This arrangement was relatively easy to set up, stress versus strain for the apparatus alone becoming linear above 0.2 kN.

The shear apparatus was more complicated to set up, being designed to compensate for minor specimen inaccuracies, in particular any lack of squareness after machining, and variations in polymer thickness. Adjustments could be made to the jaws in two ways : - a) by raising or lowering to the desired failure plane (usually the polymer/cement interface), and b) by altering their angle to the exact geometry of the specimen under test *(fig 3.2)*. There was also a locking plate designed to secure specimens to the base plate of the device and thus prevent rotation during loading. This was a development beyond the original design which was to take specimens 20 mm high i:e. the distance between the upper and lower plates *(fig 3.2)*. In practice it was too difficult to make specimens exactly that thickness - specimens thicker than 20 mm could not be inserted, and those thinner rotated under load. The upper and lower plates thus applied substantial force in directions other than along the desired failure plane. By using thin specimens secured by the locking plate, rotation was prevented. Subsequent examination of certain specimens was hampered by the operation of the apparatus : after failure had occurred there was a tendency for the jaws opposite the secured member to grind over the fracture surface for up to 10 mm, making surface examination difficult in that region. Similarly, specimens that fractured into several pieces became jammed between the upper plate and the secured member, some damage to the fracture surface being sustained.

Despite the relative complexity of the apparatus, once loading commenced stress versus strain for the apparatus alone became linear above 0.5 kN.Details of test procedures are given in *3.3.1* and *3.3.2*.

4.3.2 LOCUS AND CHARACTER OF FAILURE

Pull-off specimens

Since the majority of pull-off specimens failed through the cement, little can be deduced about the general character of their interfaces with cement other than the broad observation that they are stronger than the cement itself *(fig 4.2)*. However, those that did fail at the interface showed some interesting features. It was obvious that there were different structures on the adhesion surfaces for different W/C ratios, and this was particularly evident at low magnifications. The 0.5 W/C ratio samples showed a series of polymer rings on the cement adhesion surface, whereas the 0.6 and 0.7 W/C ratio samples showed a pattern of cement particles pulled out of the body of the cement stuck to the polymer and vice versa *(figs 4.3a and 4.3b)*. Immediately after the pull-off test itself the rings on the 0.5 W/C ratio cement surface were noticed to be slightly tacky, setting rigid in a week or so. A large temperature rise was observed during setting of the polymer members, and it seems possible that the rings were connected with a surface reaction. This had the effect of substantially weakening the interface. Some specimens showed scales of polymer adhering to the cement surface as if the original polymer had not completely wetted the cement surface *(fig 4.3a)*.

Double-interface specimens

Stress/strain plots for all the double-interface specimens (compared to the plot for the shear apparatus alone), indicated that there was negligible yielding before failure. The fifteen identical 0.5 W/C ratio 7 day specimens had loci of failure passing almost exclusively through the cement layer *(fig 4.4)*. All fracture surfaces showed darker streaks and circular patches where polymer had penetrated the cement layer. The streaks were associated with polymer that had penetrated hair-line cracks, the origin of the circular patches being uncertain, possibly associated with void filling, some voids being seen lined with polymer *(fig 4.5a&b)*.

Since all the cement layers were cut from different batches of cylinders it might be expected that there would be slight differences in the structure. Indeed, early batches showed more voids than later ones, the former having a slightly higher strength (3.99 kN S.D 0.29 kN compared to 3.71 kN S.D. 0.44 kN). One specimen showed a circular pattern of impregnated cracks, this having the highest strength in the batch

(5.30 kN). These findings could be interpreted in terms of the polymer reinforcing the cement by curing in the region bordering fissures and possibly small voids.

Failure in all double-interface specimens was brittle, and mostly through the cement. All fracture surfaces showed features associated with polymer penetrating the region bordering fissures and small voids. These could be seen as small ridges and domes on one fracture surface, corresponding to channels and dimples on the other. Loci of failure could thus be seen passing through the cement bordering polymer and polymer impregnated regions. There appeared to be no obvious differences in character of the fracture with cure time for the two W/C ratios tested *(figs 4.6 and 4.7)*. With all W/C ratio specimens, ring structures were seen on some fracture surfaces, and there was a tendency to see cracks running from cement to polymer on edges at right angles to the shear directions and interfaces. These were at 30-45° to the horizontal, dipping in the shear directions, and associated with the ridges on the fracture surface *(figs 4.8 and 4.9)*. This suggests that fracture proceeds along a series of planes in the cement inclined away from the shear directions, these sometimes passing into the polymer if both phases are brittle, have similar strengths and their interface is strong. By comparison, failure in pure polymer specimens was in the range 9-10 kN, also occurring as a complex series of inclined planes.

During the production of the double-interface specimens there was no indication of surface reaction taking place as noted in the pull-off specimens.

4.3.3 BONDING CHARACTERISTICS OF DIFFERENT POLYMERS AND RESINS WITH CEMENTS

Of the seven resins and polymers tested by the single interface technique, failure proceeded in one of three ways : - a) brittle failure, fracture substantially in the cement, b) brittle failure, fracture substantially near the interface, and c) yielding and plastic deformation of the polymer member *(fig 4.10)*.

Single-interface specimens

The first category included epoxy, P38 and Fastglass, the cement members in each case fracturing into several pieces. The polymer remained intact, the fracture surface showing large lumps of cement still bonded to it, and smooth areas on the interfacial plane. These would appear to be where the polymer had failed to wet the cement surface, bonding not being possible in those areas *(fig 4.11 a&b)*. With the epoxy and

P38 this appeared to be random, but with the Fastglass was seen as a border 3-4 mm wide around the edges of the specimen *(fig 4.12 a&b)*. This must be related to the geometry of the specimen and must have occurred after the initial hardening of the resin, since the original geometry was circular before trimming to rectangular. Possible explanations include slow deformation effects after the initial set, or some effect connected with the loading. Leaving these speculations aside, strong bonding was achieved with epoxy and styrene cross-linked polyesters, one of the latter being applied with a putty-like consistency, the others as viscous liquids.

The second category included promoted catalysed MMA and the glycerol/phthalic anhydride polyester, both members remaining intact in each case after failure. Problems were experienced in formulating the former - the effect of a too rapid polymerisation resulting in bubble formation at the interface. Failure was interfacial, or just within the cement, a very thin layer still remaining on the polymer fracture surface. With the glycerol/phthalic anhydride resin failure was interfacial or just within the polymer, thin layers being visible clinging to the cement fracture surface. In both cases strengths were relatively poor.

In the third category were promoted catalysed styrene and the glycerol/maleic acid polyester. Both were slightly plastic on testing, and both yielded relatively easily. In the case of styrene the polymer layer buckled on loading, peeled back leaving some still clinging to the cement surface. With the glycerol/maleic acid specimen the whole polymer member slipped without buckling, leaving a thick layer on the cement surface. This proved to be a very tenacious resin : it absorbed water slowly and was observed to creep over a period of days. Although it was sparingly soluble in water, it proved to be very hard indeed to remove from any cement surface to which it was applied.

Adhesive layer specimens

Adhesive layer specimens all appeared to fail in a similar manner - partly through one of the interfaces and partly through the cement members, one generally carrying much more of the fracture *(fig 4.13)*. The interfacial areas could be associated with lack of wetting of the adhesion surface with consequential lack of bonding. Superglue fractured into sheets *(fig 4.14a)*, whilst polystyrene showed dendritic patterns *(fig 4.14b)*. The relatively low strength of Eve-o-stick results from lack of contact between the adhesion surfaces. About ninety percent of the adhesion surfaces showed 'clean' resin, the areas where both sides had touched showing failure through the cement or interfacially *(fig 4.14c)*. This resin shows great potential for bonding cements, because the resin yields,

pulling out as long elastic fibres before failure occurs. Specimens thus bonded can accommodate relatively high strains before failure.

Using these forms of test, all the polymers and resins showed moderate to strong bonding to cement surfaces, the polymers and interfaces often being stronger than the cements themselves. It is impossible to draw too many conclusions from the test because it lacks a statistical analysis, factors of resin thickness were disregarded and exact formulations of some of the resins were not known. However, a number of factors did come to light : -

In all cases except the epoxy resin there was only slight evidence for surface penetration and hence mechanical interlocking of the two phases. Thus if bonding is still strong despite this, some chemical bonding could be invoked. The character of this is somewhat uncertain, but could be an acid/base interaction, cements and cement surfaces being highly basic. Certainly acid groups are present in both the saturated polyesters, and almost certainly the Fastglass and P38 being unsaturated polyesters. Exact formulations of these latter resins were not available, but their general type is commonly known. Both are however cross-linked with styrene, this in itself being shown to bond to cement. The reason for this is uncertain, since styrene possesses no functional groups. Acid/base behaviour is also possible with acrylic polymers since they may contain acid residues. In any case, acrylic esters (MMA and Superglue being examples) can hydrolyse to form co-polymerisable acids.

The physical nature of the resin or polymer has a significant bearing upon the locus and character of the failure. In the case of epoxy, MMA, Fastglass and P38 the polymer was rigid and stronger than the cement, directing failure through the cement. Repairs to cement or concrete structures using such resins would produce joints stronger than the bulk material itself. Superglue and glycerol/phthalic anhydride polyesters have strengths similar or less than cement, thus directing the locus of failure interfacially or into the polymer. Such resins would thus not prove very useful as structural adhesives.

In the case of the glycerol/maleic acid, styrene and Eve-o-stick resins the polymer remains essentially plastic. Since the bond with cement is strong, such polymers can strengthen cements in two ways : - first, cracks passing from cement to polymer would be halted, and second, cements would be held together after cracking by polymer fibres. This latter approach is the basis of fibre-reinforcement, which makes use of the fact that cements are brittle and certain polymers are ductile.

A final point arising from both types of specimen and several of the resin types is the importance to achieve good surface wetting or bonding cannot take place. The excellent performance of the epoxy and Fastglass would seem to be related to their ability to wet the adhesion surface. Bonding between cement with P38 and Eve-o-stick in particular was reduced by lack of surface contact.

4.3.4. RELATIONSHIP BETWEEN STRENGTH AND W/C RATIO

For this experiment pairs of pull-off specimens of W/C ratio 0.5, 0.6 and 0.7 were used. Five out of the six specimens made (two of each W/C ratio) failed close to the interface with loads ranging from 0.27 to 0.73 kN *(table 4.1a)*. One specimen failed through the cement limb.

Examination of the double-interface shear specimen data showed that the force required to cause failure was increased with decreasing W/C ratio. Numerical data is expressed as force required to cause failure of the specimen irrespective of the locus of failure. Averaging the values for identical specimens showed the following trend : - 0.4 W/C ratio 5.57 kN, 0.5 W/C ratio 4.57 kN and 0.7 W/C ratio 2.08 kN *(table 4.2a&b)*. Almost all the specimens tested failed through the cement layer or near interfacially, those with substantial failure through the polymer being regarded as not representative of the general trend, and their strengths disregarded.

4.3.5 RELATIONSHIP BETWEEN STRENGTH AND CURE TIME

Eighteen 0.6 W/C ratio pull-off specimens were prepared. The cement members (two sets of nine) were cured for different times - 2 days and 90 days. Of the two day specimens four failed near the interface at stresses of 0.50 to 0.92kN, and five failed through the cement limbs *(table 4.1b)*. All the sixty day specimens failed through the limbs. This would tend to suggest that the bond is stronger for longer cure times, though there is no significant quantitative data to back this up. This is not what would be expected since the cement at the greater age would be considerably stronger than that at the younger, being able to resist fracture through the cement member more easily.

Double-interface shear specimens showed a general increase in strength with cure time. This was true of both the W/C ratios tested, showing the following trend : - 0.4 W/C ratio 2 day 4.46 kN, 60 day 6.13 kN ; 0.5 W/C ratio 2 day 3.13 kN, 28 day 4.57 kN *(table 4.2a&b)*. The apparent reduction in strength at 0.4 W/C ratio at 28 days probably

reflects a lack of data points rather than any mineralogical change weakening the cement at this age.

Again, failure was almost exclusively through the cement or near interfacially, failures through the polymer being regarded as unrepresentitive and excluded from strength measurements.

4.3.6 INTERPRETATION OF STRENGTH DATA

As strength measurements of this kind require statistical analysis it was hoped that by testing a large number of identical specimens an assessment could be made of the scatter expected from each cement. After testing two sets of nine pull-off specimens it was apparent that failure was generally occurring through the cement members, and not interfacially. Thus the numerical data from such tests only reflect the strength of the cement, and the fact that it was weaker than the polymer and the interface. Pull-off tests were subsequently abandoned because they rarely produced interfacial failure. It was hoped that the double-interface specimens would remedy this problem by directing the locus of failure close to the interface. A statistical analysis was applied to the double interface specimens as follows : - fifteen 0.5 W/C ratio 7 day specimens were produced having a mean strength of 4.01 kN and standard deviation of 0.56 kN. This represents 14% of the mean value, hence the scatter is quite substantial. Since only two identical specimens were tested for each cement, the data cannot be relied upon to give exact numerical predictions of strengths, only general trends *(fig 4.15)*.

Although the trends indicate an increase in strength with increasing cure time and decreasing W/C ratio, the locus of failure was predominantly through the cement rather than at either interface. Thus the trends mostly reflect the inherent strength of the cement rather than adhesion strength. As with the pull-off tests these tests were subsequently abandoned because of their general inability to reveal interfacial areas.

Even if adhesion strengths were measurable in this way, considerations would have to be made of the complex nature of the interface i.e. there would be a strength associated with the interface of the original cement adhesion surface with the polymer, and the impregnated cement with the non-impregnated cement.

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4.3.7 STRENGTH DATA FOR SINGLE-INTERFACE SPECIMENS

This data was not intended to give absolute values of bond strengths, only general trends. In this respect it can be seen that commercial polyesters and epoxy resin have the highest bond strengths. In general, single-interface specimens *(table 4.3 and fig 4.16)* proved to be stronger than the corresponding adhesive layer specimen for each polymer and resin system *(table 4.4 and fig 4.17)*.

4.4 SUMMARY AND CONCLUSIONS

Attempts were made to develop specimens where polymer was bonded to cement such that they could be fractured in the region of the interface between the two phases. Where this occurred, it was possible to examine interfacial regions microscopically. Some qualitative information about bonding between cements and a number of polymers was also obtained by observing the locus of failure between the two phases.

Specimens were prepared for testing in tension and shear. These were as follows : -

1) Pull-off specimens
2) Single-interface shear specimens,
3) Double-interface shear specimens, and
4) Adhesive layer shear specimens.

Examination of the fracture surface produced on failure was carried out using optical and scanning electron microscopy.

The following was concluded : -

1) The locus of failure in cements bonded to epoxy resin passes usually through the cement, though some interfacial failure may be observed. Where it is through the cement, it may be seen passing around voids and cracks impregnated with polymer from the adhesion surface, indicating reinforcement of the matrix.

2) Strong bonding between cements and polymers may be achieved with epoxy resin and polyesters, less so with acrylics. In the case of polyesters, this may be due to the presence of acid groups.

3) Wetting of the cement adhesion surface is of prime importance to bonding.

4) Adhesives that cure to a plastic rather than a brittle state terminate cracks passing from cement to polymer.

5) It was not possible to detect a relationship between bond strength, cure time and W/C ratio using the specimen configurations tested.

FIGURE 4.2
FAILURE IN PULL-OFF AND SHEAR SPECIMENS
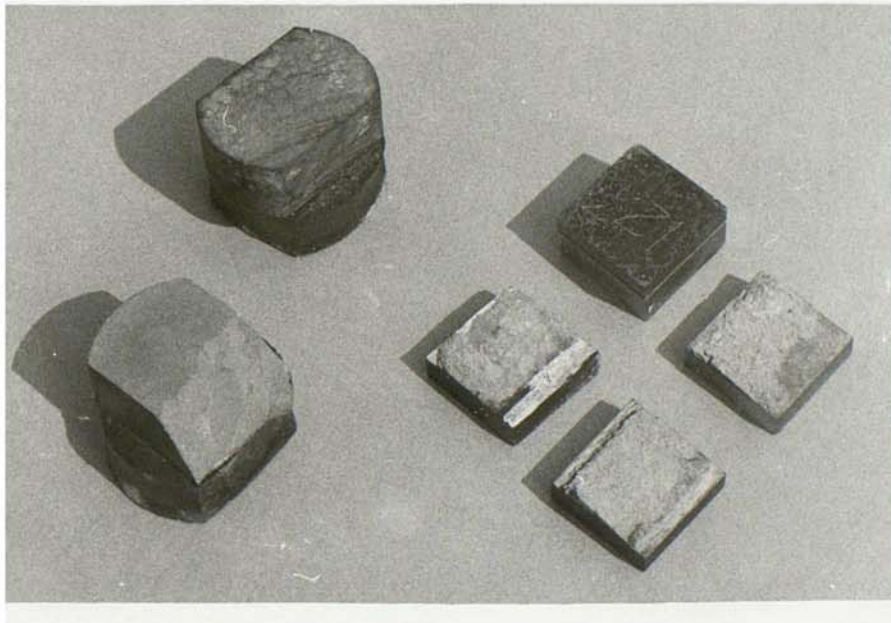
Left-hand side top - Pull-off specimen as produced.

Left-hand side bottom − Tested pull-off specimen with locus of failure passing through cement member.

Right-hand side top - Double interface specimen as produced

Right-hand side right - Tested single interface specimen with locus of failure partially interfacial, but mostly through cement.

Right-hand side middle - Tested single interface specimen notched with PTFE tape, locus of failure mostly through cement.

Right-hand side bottom - Tested single interface specimen notched with saw cuts, locus of failure mostly through cement.

FIGURE 4.3a
RING STRUCTURES PRODUCED AT CEMENT / EPOXY INTERFACE

0.5 W/C ratio 28 day cure cement adhesion surface (SEM).
Horizontal dimension = 5 mm.

FIGURE 4.3b
EPOXY 'SCALES' ON CEMENT SURFACE

0.6 W/C ratio 28 day cure cement adhesion surface showing epoxy 'scales' adhering
(SEM). Note also possible lack of wetting over rest of surface.
Horizontal dimension = 5 mm.

FIGURE 4.4
LOCUS OF FAILURE IN IDENTICAL 0.5 W/C RATIO 7 DAY CURED DOUBLE-INTERFACE SPECIMENS

Note spotted pattern indicative of voids lined by polymer, also dark streaks and ring structures indicative of polymer penetration of cracks. Failure loads for specimens top left to bottom right are as follows (kN) : - 3.38, 3.23, 4.48, 3.89, 3.43, 4.57, 4.05, 3.90, 3.63, 4.00, 3.95, 5.30 and 3.69.

FIGURE 4.5a
TYPICAL TEXTURE ON DOUBLE-INTERFACE SPECIMENS

Note ridges and dimples due to polymer impregnation of 0.5 W/C ratio 7 day cured
cement. Locus of failure passes through cement around these features.
Horizontal dimension = 10 mm.

FIGURE 4.5b
TYPICAL TEXTURE ON DOUBLE-INTERFACE SPECIMENS

Note valleys due to polymer impregnation of 0.5 W/C ratio 7 day cured cement,
corresponding to ridges and dimples on other fracture surfece.
Horizontal dimension = 10 mm.

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Specimens in each vertical column have same W/C ratio, namely (left to right) : - 2, 7, 28 and 60 days. First and second, third and fourth rows are matching fracture surfaces.

FIGURE 4.7
LOCUS OF FAILURE IN DOUBLE-INTERFACE
SHEAR SPECIMENS OF 0.5 W/C RATIO
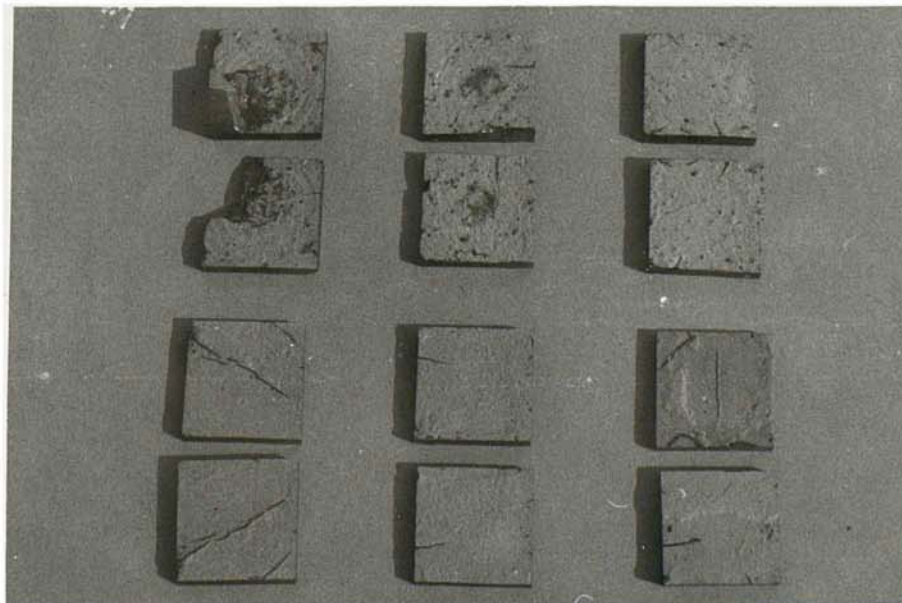
Specimens in each vertical column have same W/C ratio, namely (left to right) : - 2, 7 and 28 days. First and second, third and fourth rows are matching fracture surfaces.

FIGURE 4.8
RING STRUCTURE ON DOUBLE-INTERFACE SHEAR SPECIMEN

Ring structure on fracture surface of 0.5 W/C ratio 7 day cured specimen. This results from polymer reinforcement of the regions bordering circular cracks.
Horizontal dimension = 20 mm.

FIGURE 4.9
DOUBLE-INTERFACE SPECIMEN BORDERING A RING STRUCTURE

Note fracture passing from ring structure into polymer member. Cement was 0.5 W/C ratio 7 day cure. Horizontal dimension = 15 mm.

FIGURE 4.10
LOCUS OF FAILURE IN SINGLE-INTERFACE SHEAR SPECIMENS
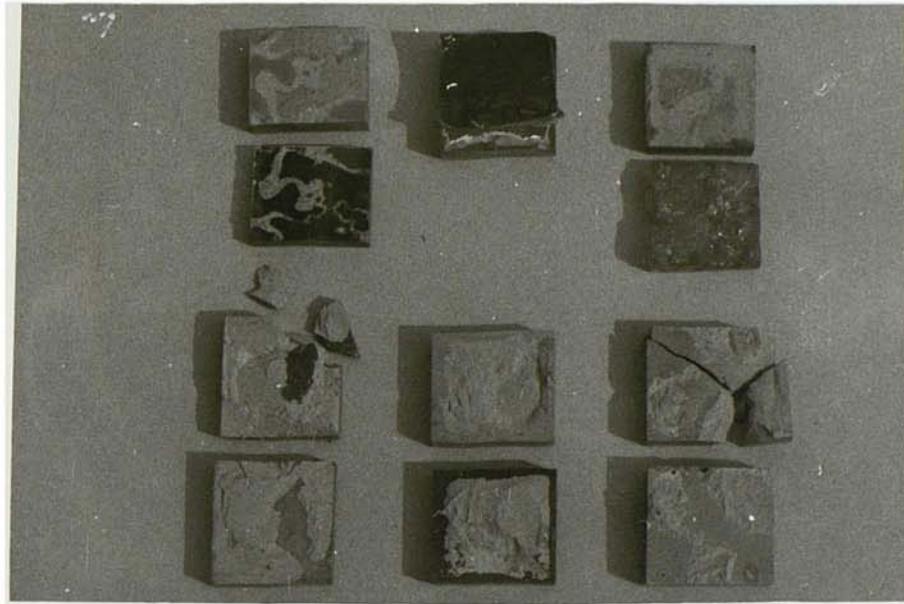
Specimens are (top left to bottom right) : - MMA prepolymer, styrene prepolymer, glycerol / phthalic anhydride polyester, epoxy resin, Fastglass polyester, P38 polyester. First and second, third and fourth rows are matching fracture surfaces, cement members above, polymer members below. Note : -

1) Incomplete wetting of adhesion surface in MMA, G/P polyester and P38.
2) Plastic behaviour in polystyrene.
3) Near-interfacial failure in G/P polyester and border of Fastglass specimen.
4) Fracture of cement members in epoxy and P38.

FIGURE 4.11a
SINGLE-INTERFACE SPECIMENS WITH LOCUS OF FAILURE
PASSING FROM INTERFACE TO CEMENT

0.4 W/C ratio 28 day cure cement with epoxy resin. Polymer is lower region.
Horizontal dimension = 20 mm.

FIGURE 4.11b
SINGLE-INTERFACE SPECIMENS WITH LOCUS OF FAILURE
PASSING FROM INTERFACE TO CEMENT

0.4 W/C ratio 28 day cure cement with P38 polyester. Note regions where polymer has
not significantly wetted cement surfece Horizontal dimension = 20 mm.

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FIGURE 4.12a
LOCUS OF FAILURE OF SINGLE-INTERFACE SPECIMENS
USING EPOXY RESIN

*0.4 W/C ratio 28 day cure cement. Upper and lower halves of picture show
corresponding sides of fracture, locus of failure starting interfacially at border of
specimen before passing into cement. Horizontal dimension = 15 mm.*

FIGURE 4.12b
SINGLE-INTERFACE SPECIMENS WITH FASTGLASS

*0.4 W/C ratio 28 day cure cement. Upper and lower halves of picture show
corresponding sides of fracture, locus of failure starting interfacially at border of
specimen before passing into cement. Horizontal dimension = 15 mm.*

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FIGURE 4.13
LOCUS OF FAILURE IN ADHESIVE LAYER SHEAR SPECIMENS
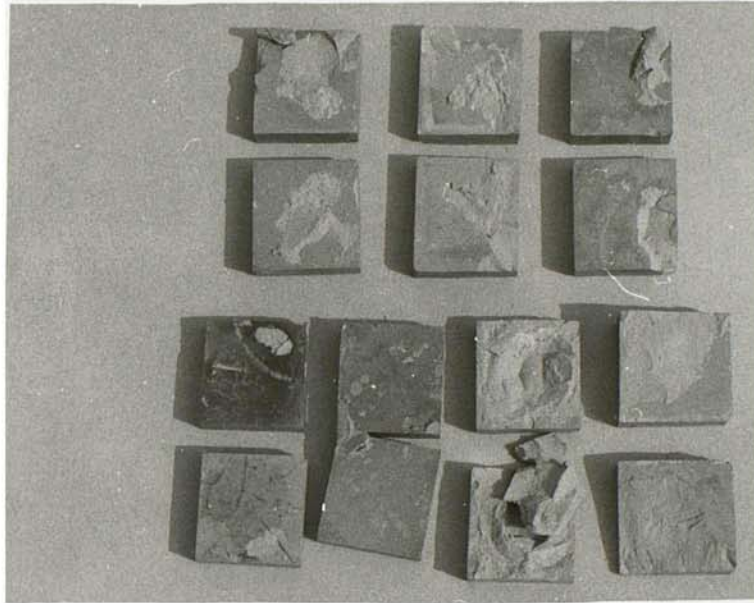
Specimens are (top left to bottom right) : - MMA prepolymer, superglue, styrene prepolymer, epoxy resin, Eve-o-stick, Fastglass polyester, P38 polyester. First and second, third and fourth rows are matching fracture surfaces, cement members above, polymer members below. Note : -

1) Incomplete wetting of adhesion surface in P38.
2) Partial interfacial failure in MMA, superglue and polystyrene specimens.
3) Lack of surface contact in Eve-o-stick, polymer still adhering to both surfaces where contact has occurred.
4) Fracture of cement members in Fastglass.

FIGURE 4.14a
LOCUS OF FAILURE IN SUPERGLUE

Fracture surface in Superglue showing flaking of polymer, locus of failure passing into one cement member (top left). Horizontal dimension = 10 mm.

FIGURE 4.14b
LOCUS OF FAILURE IN POLYSTYRENE

Dendritic polystrene showing some cement crystals pulled from other member. Horizontal dimension = 10 mm.

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FIGURE 4.14c
LOCUS OF FAILURE IN EVE-O-STICK

Upper and lower halves of picture are corresponding sides of fracture surface. Note how only some areas coated with resin have come into contact, those that have remain bonded with elastic strands. Horizontal dimension = 10 mm.

TABLE 4.1a

FAILURE DATA FOR PULL-OFF SPECIMENS

W/C RATIO	AGE (Days)	APPLIED FORCE (kN)	MODE OF FAILURE
0.5	5	0.37	Near interfacial
0.6	5	0.44	Near interfacial
0.7	5	0.46	Near interfacial
0.5	12	0.62	Through cement
0.6	12	0.60	Near interfacial
0.7	12	0.27	Near interfacial

TABLE 4.1b

FAILURE DATA FOR PULL-OFF SPECIMENS OF 0.6 W/C RATIO

AGE (Days)	APPLIED FORCE (kN)	MODE OF FAILURE
2	0.51	Near interfacial
2	0.56	Near interfacial
2	0.50	Near interfacial
2	0.85	Near interfacial
2	0.63	Through cement
2	0.42	Through cement
2	0.53	Through cement
2	0.51	Through cement
2	0.56	Through cement
90	0.67	Through cement
90	0.92	Through cement
90	0.67	Through cement
90	0.57	Through cement
90	0.53	Through cement
90	0.77	Through cement
90	0.46	Through cement
90	0.85	Through cement
90	0.68	Through cement

TABLE 4.2a

FAILURE DATA FOR DOUBLE-INTERFACE SHEAR SPECIMENS

0.4 W/C RATIO		0.5 W/C RATIO		0.7 W/C RATIO	
AGE (days)	FAILURE LOAD (kN)	AGE (days)	FAILURE LOAD (kN)	AGE (days)	FAILURE LOAD (kN)
2	5.30	2	3.13		
2	3.62	2	3.33+		
7	5.73	7	3.90*		
7	6.62	7	4.72*		
28	5.05	28	2.17+	28	1.88
28	6.09	28	4.57	28	2.00
60	6.21			28	2.35
60	6.05			28	2.08

+ *Failure occured substantially through polymer, otherwise through cement*
* *Also used in table 4.16b.*

TABLE 4.2b

FAILURE DATA FOR IDENTICAL 0.5 W/C RATIO DOUBLE-INTERFACE
SHEAR SPECIMENS CURED FOR 7 DAYS

FAILURE LOAD (kN)							
3.38	3.23	4.48	3.89	3.43	5.30	4.05	3.90*
3.63	4.57	3.92	4.72*	4.00	3.95	3.69	

FIGURE 4.15

FAILURE LOADS IN DOUBLE-INTERFACE
SHEAR SPECIMENS
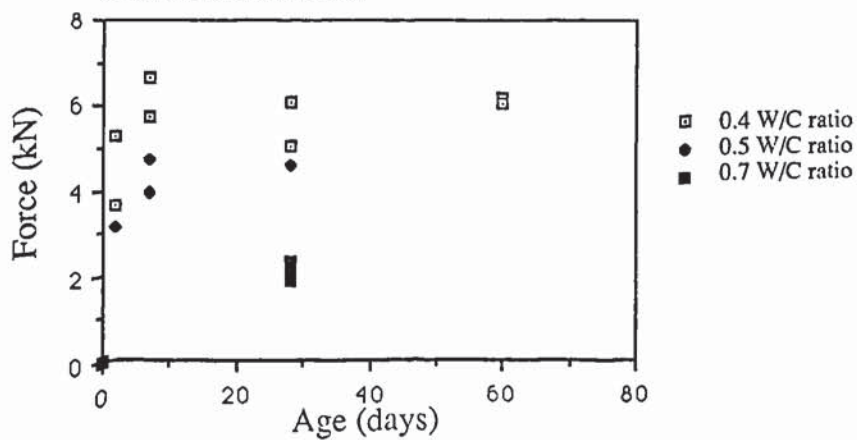
TABLE 4.3

STRENGTH DATA FOR SINGLE-INTERFACE SHEAR SPECIMENS

RESIN / POLYMER	TYPE	LOAD	LOCUS OF FAILURE
AY103 + HY931	Epoxy	6.83 kN	Mostly through cement
P38	Unsaturated polyester	3.48 kN	Half interfacial, half through cement
Fastglass	Unsaturated polyester	2.25 kN	Through cement
Glycerol / maleic acid	Unsaturated polyester	-----	Yielded constantly under load
Glycerol / phthalic anhydride	Saturated polyester	1.10 kN	Mostly interfacial, some through polymer
MMA prepolymer	Acrylic	0.97 kN	Mostly through cement
Styrene prepolymer	Acrylic	-----	Yielded above 0.75 kN

FIGURE 4.16
FAILURE LOADS IN SINGLE-INTERFACE
SHEAR SPECIMENS

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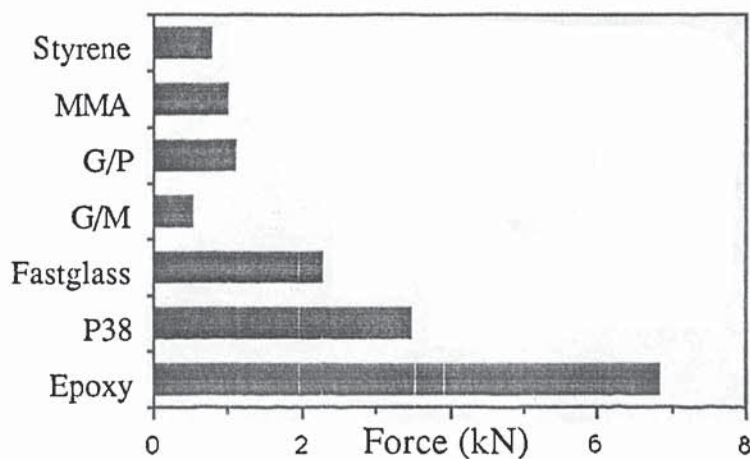
TABLE 4.4

STRENGTH DATA FOR ADHESIVE LAYER SHEAR SPECIMENS

RESIN / POLYMER	TYPE	LOAD	LOCUS OF FAILURE
AY103 + HY931	Epoxy	4.04 kN	Through cement
P38	Unsaturated polyester	3.58 kN	Mostly through cement, some interfacial
Fastglass	Unsaturated polyester	4.94 kN	Through cement
MMA prepolymer	Acrylic	2.03 kN	Half through cement, half interfacial
Styrene prepolymer	Acrylic	0.97 kN	Mostly interfacial, some through cement
Superglue	Acrylic	2.06 kN	Partially through cement, polymer flaking on cement surface
Eve-o-stick	Contact adhesive	0.70 kN	Initial failure through cement, then progressive yielding of polymer strands still attached to cement surface

FIGURE 4.17
FAILURE IN ADHESIVE LAYER SPECIMENS

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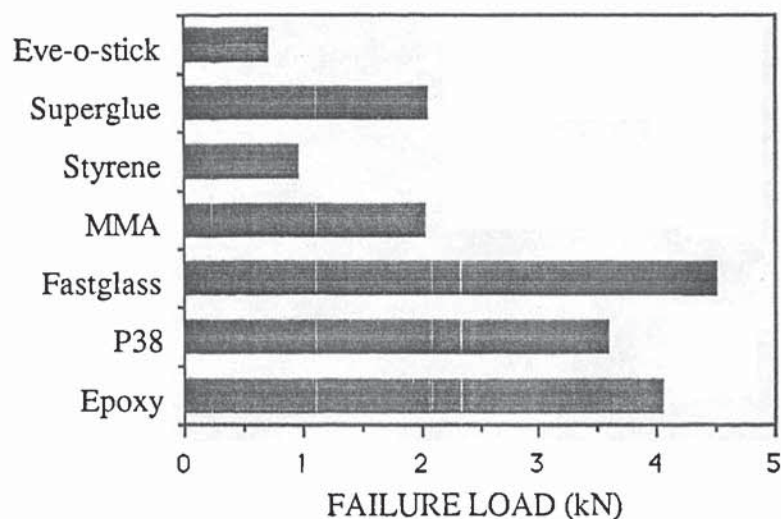
5 REACTIONS BETWEEN POLYMERS AND CEMENTS

5.1 INTRODUCTION

Many workers have suggested that interactions take place between the constituents of cements and polymers. These interactions may take the form of physical or chemical bonding across the interface, or the formation of reaction products *(fig 1.1)*. This chapter is concerned with the isolation and identification of any reaction products formed between hydrated OPC and MMA/PMMA.

In this type of investigation a major experimental problem is that the yields of reaction products are generally very small, since they are produced only at the polymer/cement interface. It was hoped that by using hydrated cement crushed to a fine powder, the interfacial area could be considerably increased compared to that of simple adhesion surfaces.

The individual cements and polymers were first characterized by the various techniques mentioned in *chapter 3*. This was followed by characterization of polymer/cement mixtures of 50:50 ratio prepared as follows : - a) polymerisation of monomer in contact with powdered hydrated cements (polymer cement), and b) simple mixing of hydrated cement and ground polymer (physical mix). In this way it was hoped that any chemical differences observed between the two would correspond to reaction products. Attempts were then made to synthesize possible reaction products, and to identify limiting conditions or reagents necessary for their formation.

The polymer used almost exclusively for this work was PMMA. This was chosen because MMA is well characterized, and its polymerisation chemistry simple.

A number of instrumental techniques were used in this work, including differential thermal analysis (DTA), infrared spectroscopy (IRS), X-ray diffraction (XRD) and ion chromatography.

5.2 PREVIOUS WORK

Several papers have been published concerning polymer/cement chemical reactions. The experimental technique used almost exclusively was that of thermal analysis, particularly differential thermal analysis. However, there are a number of references to polymer/ceramic interactions in chemically similar materials, particularly dental cements, where the technique most commonly employed was IRS.

5.2.1 DIFFERENTIAL THERMAL ANALYSIS

In the early seventies, two reports written by Dikeou(*ref 107*) and Depuy (*ref 108*) first discussed possible reactions between hydrated cement pastes and MMA. Depuy studied reaction products of MMA and calcium hydroxide, using DTA and XRD. The reactions were performed on mixtures of calcium hydroxide, water and MMA in different proportions, sealed in small cans and maintained at temperatures of 20 to 90°C for several weeks. Examination of the reaction products indicated that there were two possible solid reaction products depending on the amount of water present in the original mixtures. Above about 5% water a product thought to be calcium methacrylate formed, and below 5% a product not readily identifiable, but thought to be calcium hydroxymethacrylate was detected.

Gebauer *(ref 15)* published results from studies of the interactions of cement and polymer (and mortar and polymer) in polymer impregnated cement composites. The study was in terms of the preparation, strength, corrosion resistance and chemical interaction of the two substances. Several polymers were used, in particular polymethyl methacrylate and polystyrene (PS) from the monomer styrene (S). Two different processes were used to prepare specimens.

First, specimens were prepared from a prepolymer, unhydrated cement paste and water, prepolymer/cement ratio being 0.1 and W/C ratio being 0.3. Specimens were sealed in moulds and the cement allowed to cure for 28 days. At the end of this time the polymer was cured either by exposure to Co-60 γ-rays, or by heating to 70°C for several hours. In the latter case either 2% benzoyl peroxide or 3% azobisisobutyronitrile was used as the catalyst.

Secondly, cement pastes of 0.35 and 0.46 W/C ratio were cast into small cylinders, cured at 100% relative humidity for one day, then in tap water for a further 27 days. Following this, the cylinders were oven-dried at 105°C for 48 hours then vacuum dried

at 50°C for a further 48 hours. Impregnation was carried out by soaking in monomer (plus catalyst as appropriate) for three hours in a vacuum chamber. The polymer was cured by γ-radiation and promoted-catalytic means as before, wrapping the cylinders in foil to minimize monomer evaporation. With this procedure it was possible to achieve a polymer loading of 6 - 7%.

Samples were subjected to a number of physical, chemical and environmental tests. Those used for thermal analysis were first ground then mixed with calcined alumina in a ratio of 1:3. This procedure was repeated for samples of pure polymer and pure cement. DTA was carried out on approximately 0.6 g of sample in a nitrogen atmosphere.

Results from the prepolymer mixes showed a reduction in mechanical strength (compared to polymer-free samples) in MMA but not in PS. Amount of bound water was also lowered in the MMA cements and about constant with PS, indicating that MMA inhibited the hydration of cement particles. Of most relevance to this project was the DTA work which showed attenuation of the characteristic calcium hydroxide peak at 530°C seen in hydrated cements, where the cement had been mixed with MMA prepolymer. No attenuation was observed with PS, and it was concluded that a reaction had taken between MMA/PMMA and calcium hydroxide. Other features noted on the thermograms were an endothermal feature at 400-430°C attributed to the decomposition of PMMA, and a similar endotherm at 420-450°C attributed to the decomposition of PS. No significant differences were noted between samples cured by heating or irradiation.

Similar thermal effects were noted in the polymer impregnated samples, and the same MMA/PMMA reaction inferred. Again, no reaction with S/PS was noted. Endotherms due to polymer decomposition were shifted to the region 350-380°C for PMMA (410-430°C in PS), and endotherms in the 100-220°C region attributed to retained capillary water, C-S-H gel and sulfoaluminates.

Similar work by Auskern *(ref 76)* correlated reaction results between MMA and calcium hydroxide with those of MMA and hardened cement pastes. Distinctions were drawn between reactions having occurred between monomer and calcium hydroxide/cement as such, and those occurring between PMMA and calcium hydroxide/cement during the DTA run itself. It was suggested that MMA reacts with calcium hydroxide to form methacrylic acid in a similar manner to its reaction with alkalis. Reaction products would then be calcium salts of methacrylic acid. Endotherms at about 430°C observed in the thermograms of such mixtures were attributed to this compound. Unlike

Gebauer, evidence was not found for its presence in impregnated cements, however this was explained in terms of the limited contact between MMA and calcium hydroxide during polymerisation, the latter being as a lining to pore walls compared to a powder in the earlier experiments. Reactions of this kind were not thought to be detrimental to the mechanical performance of impregnated cements.

Investigation of high water/cement ratio impregnated cements was carried out by Ishizaki *(ref 78)*. The work was in terms of the polymer loading, thermal properties and reactions of the composites. He used 0.6 and 0.65 W/C ratio cements and mortars cast in small rectangular moulds, cured for 1 day at 95% relative humidity, then a further 2 or 6 days. These were dried at 120°C for 40 hours then soaked in MMA containing 2% azobisisobutyronitrile. Polymerisation was carried out at 80°C for 3 hours, using different wrapping techniques to minimize monomer losses. DTA was carried out on samples of the composites. It was found that a decrease in the size of calcium hydroxide peaks occurred with increasing polymer loading, and an increase in the size of a peak in the region 650-1000°C also noted. Powder XRD traces showed this to be calcium carbonate. It was concluded that there was no evidence for a reaction between calcium hydroxide and MMA/PMMA during impregnation or polymerisation - the decrease in calcium hydroxide peak being due to carbonation by the breakdown products of the polymer during the DTA run itself.

Ramachandran *(ref 77)* examined impregnated cements approaching complete hydration. These were of W/C ratios 0.37 and 0.7 cured for 260+ days. Specimens were dried at 110°C to constant weight, then soaked in MMA for four hours under vacuum. Polymerisation was accomplished by heating to 80°C for 48 hours, then a further 48 hours at 110°C under high pressure. 5% azobisisobutyronitrile was used for the catalyst.

Analysis of the specimens showed that the 0.37 W/C specimens were 83% hydrated with 19.9% porosity and 17.8% polymer loading; the 0.7 W/C specimens were 97.2% hydrated with 42.2% porosity and 41% polymer loading.

DTA runs were carried out in nitrogen and air, using 50 mg of sample passed through a 100 μm sieve and at a heating rate of 10°C per minute. The samples used were pure cements, pure polymers, impregnated cements and physical mixtures of pure cement and polymer in a ratio of 4:1. The results showed a number of peaks, of particular interest being those at 215-225°C (interpreted as loss of water from cement minerals), 525°C (interpreted as dehydration of calcium hydroxide) and 800-830°C (interpreted as

decomposition of calcium carbonate). On the 0.37 W/C ratio samples the calcium hydroxide peak became a doublet.

As with Auskern and Ishizaki, Ramachandran could find no evidence for a reaction occurring between the cement and MMA during impregnation or polymerisation to PMMA, but did not rule out the possibility. He too interpreted the attenuation of calcium hydroxide peaks first reported by Gebauer as due to carbonation by the decomposition products of the polymer - the doublet seen on 0.37 W/C ratio samples being seen as two reactions:- First, carbonation of the calcium hydroxide and second, dehydration of the residual hydroxide.

Polymer/cement reactions have also been detected where polymer is used as a pre-hydration additive. Cook *(ref 109)* concluded that some acrylic polymers react with calcium hydroxide in hydrating cements. Of those tested, polystyrene and polyisoprene showed no reaction, polyacrylamide and PMMA showed some reaction and polyvinyl acetate and polyester-styrene showed significant reaction. These conclusions were reached by following the diminution of calcium hydroxide peaks, and although reactions were inferred, they were not identified. Also, although reactions are described in terms of polymers, it was monomers that were added, to be polymerised after the cement had hydrated for seven days.

The assertion that reactions with polymers occur was questioned by Ramachandran *(ref 110)* simply on the grounds of DTA, further evidence in support of the reactions being supplied in response *(ref 111)*. This area has also been reviewed by Ghosh *(ref 112)*.

It is thus evident that the nature of the reaction occurring between such polymers and cements, and subsequent influence on properties is not fully understood.

5.2.2 CHARACTERIZATION OF POLYMERS AND CEMENTS USING IRS

Several sources quote spectra and absorbence tables for many hydrated and unhydrated minerals (for example Gadsen *(ref 113)*). In addition a number of papers have been published on the uses of IRS in the chemical analysis and hydration chemistry of cements *(ref 114)*. Most authors tend to avoid assigning all the peaks in an infrared spectrum to specific bond vibrations, as cements are complex inorganic mixtures with many peaks overlapping. A further reason for this is that IRS finds use in determining the proportions of different components in mixtures. Ghosh *(ref 115)* for example, quotes spectra for alite, belite, calcite, dolomite and quartz to enable their estimation in

mixtures. In this case the nature of peaks is unimportant, so long as peaks due to the different components can be identified. However, by studying data for the individual mineral phases it is possible to identify the main peaks in cement spectra.

Cements can be considered composed primarily of four main minerals C_2S, C_3S, C_3A and C_4AF_6. Hydration produces calcium hydroxide, and reaction with atmospheric carbon dioxide produces some calcium carbonate. Ghosh *(ref 116)* quotes a considerable amount of spectral information about these phases, a summary being given in *appendix 1*.

In the polymer field, both MMA and PMMA are well suited to investigation by IRS. Being organic molecules, there is a wealth of literature concerning the substances themselves, and the specific bonds present. A rigorous study of the bonding within the polymer itself is beyond the scope of this work - however, a typical account of bonding in MMA and PMMA may be found in Bellamy *(ref 117)*. This can be summarized as follows:-

C-H and C-CH$_3$ around 3000 cm^{-1}

C=O 1718 cm^{-1}

C=C 1640 cm^{-1}

C-O 1310-1250 and 1200-1100 cm^{-1}

The C=C bond is of particular interest when considering the polymerisation of MMA, since it is the opening of this bond that actually results in polymerisation.

5.2.3 USE OF IRS TO CHARACTERIZE POLYMER/CERAMIC REACTIONS

There is a growing interest in the chemistry taking place during the setting of certain dental materials, particularly glass ionomer cements and related materials. Bonding in these is very similar to that in MDF cements, and has been studied using IRS. Glass ionomer cements consist of powdered aluminosilicate glasses mixed with polymeric acids. In turn, these are related to polycarboxylate cements where a powdered metal oxide is mixed with a polymeric acid. In all three types, bonding takes place via acid-base reactions between polycarboxylic acids and inorganic bases, forming polymeric salts i.e. carboxylates. Thus formation of carboxylates in these systems is indicative of bonding reactions. In the infrared, this is characterized by the single carbonyl absorbence of the polymeric acid splitting into two carboxylate resonance bands of lower wave number.

Carboxylate groups are present in a number of substances for example carbonates, oxalates and soaps (alkali metal salts of fatty acids *(ref 118)*). Some of the most thorough attempts to characterize carboxylate was carried out by Douville *(ref 119)* and co-workers who studied a considerable variety of metal oxalates. The two carboxylate frequencies of such substances are in the regions 1200-1400 cm^{-1} and 1500-1600 cm^{-1}. Leyte *(ref 120)* quotes carboxylate frequencies in polycarboxylate cements made from polymethacrylic acid and a number of metal oxides in aqueous solution. Of particular interest to building cements are the salts with sodium (1561 and 1396 cm^{-1}), potassium (1554 and 1392 cm^{-1}) and calcium (1540 and 1400 cm^{-1}). Setting mechanisms were also described by Crisp *(ref 121)* who found that the rate of hardening of cements made using divalent metal oxides with polyacrylic acid decreased in the order $Mg^{2+}>Ca^{2+}>Zn^{2+}>Cu^{2+}$. With trivalent metal oxides such as Al^{3+} the rate was slower still. A number of possible structures for the polycarboxylates were proposed, some having partial covalent character. Comparisons were made between polycarboxylates and glass ionomer cements, the former having some plasticity under stress, the latter remaining brittle. It was suggested that divalent ions link adjacent polymer chains in such a way that slip can occur under stressing, whereas trivalent ions pin chains preventing movement under stress.

5.2.4 ION CHROMATOGRAPHY

A further technique used in this project to study polymer/cement reactions is that of ion chromatography. This is a relatively new application of the technique, being more commonly used for trace metal analysis, biological and medical determinations. There is a large amount of data published on elution orders and rates using different eluents and machine conditions. Some common ions found in cements have been widely studied - metal cation orders are well established, but there is little data on cement anions other than chloride and sulphate, eluting in that order in most eluents *(ref 122)*.

5.2.5 X-RAY DIFFRACTION

A considerable amount of XRD data for cement minerals and associated substances has been published. This project used the data tabulated by Taylor *(ref 123)*. Because of their amorphous nature, polymers generally do not give clear X-ray reflections, so are unsuited to examination by this method.

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Maleki-Toyserkani *(ref 124)* observed significant diminutions in XRD peak heights for cement minerals present in polymer impregnated cements. This was interpreted as evidence for polymer/cement reactions consuming phases present in the cement.

5.3 RESULTS AND DISCUSSION

5.3.1 EXPERIMENTAL TECHNIQUES

It was hoped that DTA (and XRD) would help resolve the discrepancies in results obtained by Depuy *(ref 108)*, Gebauer *(ref 15)*, Ramachandran *(ref 77)* and Maleki-Toyserkani *(ref 124)*, concerning possible interactions of MMA/PMMA and cement hydration products. In addition, it was hoped that the process technology of polymer impregnated cements could be simulated.

In industry, cured cement blocks are oven-dried at 100°C+, prior to impregnation. Samples used in this work were first dried at 105°C, and as a result, DTA shows no peaks due to the gel phase as these occur below 100°C. For all the mixtures a 50:50 ratio was chosen. This was somewhat arbitrary, but did allow peaks due to the cement and PMMA to be easily distinguished. A heating rate of 10°C per minute was used, as in Ramachandran's work.

Some problems were encountered in getting uniformity between samples; All were sieved to 300 μm this being the finest sieve, filings of polymer would pass in a significant volume. The cement and polymer cement samples would easily pass finer sieves. As a result the different mixes had different densities. It was decided that a roughly equal mass would be added to the crucible rather than an equal volume - the thermograms being quantitative with respect to mass. Loading of the crucibles was done with a small spatula holding the crucible with a pair of tweezers and tapping it on the bench occasionally to level the powder, none being forced in.

It was convenient to produce the thermograms on the same chart recorder settings so that the relative magnitude of the different peaks was easily determinable. This meant that some peaks went off-scale but did allow resolution of some of the finer features.

The majority of DTA runs were carried out in still air to allow resolution of oxidation effects, though nitrogen and nitrous oxide atmospheres were used to identify specific peaks.

As stated above the main aim of these experiments was to try to establish if there was any reaction between calcium hydroxide and PMMA/MMA in simulated impregnated cements. The calcium hydroxide peaks produced were too small to allow quantitative measurement, although their relative magnitudes were easily apparent.

The thermograms presented here, are those representative of several repeated experiments. Some thermograms proved to be unrepeatable, and were discounted.

Far fewer problems were encountered with the other techniques, though their limitations became apparent with use. IRS proved to be very fast as far as sample preparation and data acquisition was concerned. Less than half a gram of sample was required for each run, and the plotted spectrum of high quality. It was particularly useful having computer-aided analysis since this allowed for manipulation of data, helping to maximize peak heights and sharpness. This was particularly apparent with cements which substantially absorb infrared radiation. Using the computer, spectra can be enhanced to reveal peaks that were vague on the original rather featureless spectrum.

Ion chromatography also provided rapid and reproducible analyses. However, the technique has two weaknesses : - 1) it requires reaction products to be water-soluble, and 2) can only work well on molecules that are of small to moderate molecular mass. Thus large water-soluble polymer reaction products cannot be eluted, and may cause damage to the apparatus.

5.3.2 CHARACTERIZATION OF PURE CEMENTS

Using DTA all the cement samples showed only a strong calcium hydroxide peak at 530°C and an occasional very weak calcium carbonate peak starting at 700°C. These were identified by reference to thermograms for pure calcium hydroxide and pure calcium carbonate *(fig 5.1)*. No gel peaks were seen in the samples having undergone heating to 105°C thus decomposing the gel *(fig 5.2 a&b)*.

Using IRS, several additional absorbencies were noted on hydration of OPC when compared to unhydrated cement*(fig 5.3 a&b)*. IR spectra for hydrated cements were all very similar. There were however differences between the two W/C ratio samples and their four different cure times that were slight but noticeable *(fig 5.4 a&b)*. All the spectra showed the following absorbencies (cm^{-1}) : -

3640 sharp, 3440, 2910 shoulder, 1800 sharp, 1650, 1485 and 1430 twin, 1130 shoulder, 980 broad, 880 sharp, 725 sharp.

As cure time increased it was possible to see development of small sharp peaks at 1800 cm^{-1} and 880 cm^{-1}. These two peaks tend to suggest a slight increase in calcium

hydroxide with increasing cure time, as would be expected. Changes between the W/C ratios showed subtle differences in some of the larger peaks, particularly in the 3440 cm^{-1}, 3640 cm^{-1} and 1485-1430 cm^{-1} regions. The overall nature of these changes is uncertain, however the peak at 3640 cm^{-1} is attributable to -OH. It seems likely then, that more -OH is bound in cements of higher W/C ratio (see *Appendix 1*).

Ion chromatograms of water extracts from pure hydrated cements are discussed later in section *5.3.6.3*.

5.3.3 CHARACTERIZATION OF MMA AND PMMA

5.3.3.1 DIFFERENTIAL THERMAL ANALYSIS

Thermograms 1 and 2 in *figure 5.5a* represent the polymer used at the start of the series of experiments, and at the end. There would appear to be no significant differences between the two, thus it was assumed that the polymers used throughout were identical.

Traces 2 and 3 in *figure 5.5a* show the effect of grain size, the first being 300-600 μm and the second less than 300 μm. Again it would appear that there are no significant differences - the grain size of PMMA may not significantly affect the thermograms of polymer/cement mixtures.

PMMA thermograms are characterized by broad endotherms at 330°C and 400°C followed by a large sharp exotherm at 450°C (trace 4 *fig. 5.5a*).

As thermograms of cements and PMMA tended to be somewhat variable in character, experiment *5.3.3.2* was carried out in order to examine the physical state of PMMA during the DTA run itself, in the hope that it would account for any discrepancies between runs.

5.3.3.2 IDENTIFICATION OF POLYMER EFFECTS DURING DTA

Examination of the contents of the pans extracted from the DTA furnace at different points on the thermogram showed some of the different processes taking place during heating *(fig 5.5 b&c)*. These observations suggest that four chemical and physical processes are taking place on heating PMMA in a restricted supply of air: -

a) Between room temperature and about 260°C PMMA powder begins to swell.

b) From 260°C onwards the polymer undergos thermal disintegration yielding a yellow/brown residue.

c) At about 400°C MMA distils off from PMMA.

d) At around 450°C MMA vapour begins to oxidise, coating objects in contact with it with a dark brown residue.

Swelling of polymer grains may well be related to the glass transition temperature of the material, this being in the region 140-170°C. As for the other effects, it may be somewhat unrealistic to assign exact temperatures to these processes, as it may be difficult to distinguish decomposition effects from oxidation effects. Furthermore, since the decomposition of PMMA yields MMA and a dark residue, decomposition followed by oxidation may start at low temperatures, only becoming significant at higher temperatures. This would account for the gradual discolouring of the polymer. Similarly, the fusion of polymer grains could be explained as follows: - MMA distils off the molten surface of polymer grains that coalesce once cooled, on removal from the furnace.

The overall interpretation is that the exotherm at d *(fig 5.5b)* is a decomposition/oxidation effect seen on all samples containing polymer. Evidence for there being two processes comes from DTA runs in a nitrogen atmosphere, where a peak still occurs indicating an exothermal reaction taking place not related to oxidation. DTA runs in N_2O (i.e. an enriched oxidising atmosphere) show this peak to be a doublet. The peak at b is probably due to the polymer undergoing glass transition, an endotherm being expected. But since the swelling results in less material coming into contact with the thermocouple, an exotherm develops. The peak however, is often masked. The endotherm at c represents the major distillation of MMA from PMMA, fluctuations in this region being caused by bubble formation or slumping of grains other than those of the polymer. This peak is also often masked by decomposition/oxidation effects. However, in a nitrogen atmosphere where oxidation is suppressed, the endotherm is again resolved.

5.4.3.3 CHANGES IN THE IR SPECTRUM OF MMA BY ITS POLYMERISATION

A number of significant changes can be seen between the infrared spectra of MMA and PMMA (fig 5.6 a&b). As expected, PMMA shows a greatly diminished absorption at 1640 cm^{-1} due to opening of the C=C bond in MMA, resulting in polymerisation. There is however, a residual peak indicating either incomplete polymerisation of the

monomer, or the aromatic rings of the benzoyl perxoide polymerisation catalyst. It is also noticeable that most peaks due to the polymer are broader towards higher wavenumbers, possibly indicating a greater diversity of bond environments in the polymer compared to the monomer. Some peaks can be seen to have coalesced, particularly C-O peaks, these being shifted to slightly higher wave numbers.

MMA may be co-polymerised easily with other acrylic monomers, e.g. methacrylic acid *(figs 5.7 and 5.8)*. Note the shift in C-O and C=O frequencies to higher wavenumbers, and the abundance of -OH groups from the acid.

5.3.4 CHARACTERIZATION OF PHYSICAL MIXES AND POLYMER CEMENTS

5.3.4.1 PHYSICAL MIXES

Both DTA and IRS were used for this purpose. The IRS data was relatively easy to interpret, and is discussed later in terms of differences due to reaction products whereas the DTA data is somewhat complex in nature, and requires individual interpretation.

Theoretically, the thermograms produced from physical mixes should be a direct addition of their components. Thus the thermograms that might be expected would show a broad endotherm in the region 330-400°C from the decomposition of PMMA to MMA, followed by a sharp exotherm at 450°C from the oxidation/ignition of the residue. This in turn would be followed both by endotherms at 530 and 700°C due to calcium hydroxide and calcium carbonate respectively. In the 26 day, 0.6 W/C ratio sample this would appear to be the case, but with progressively younger ages of cement the endotherm at 330-350°C merges into the following exotherm *(fig 5.9a)*. The 0.37 W/C ratio sample shows a small endotherm feature at 370°C and a broad exotherm from 300-460°C. There is an additional minor endotherm at 440°C, the exotherm peaking at 460°C. With the 0.37 samples *(fig 5.10a)* there is a development of the general exothermal feature in the 300-460°C region with increasing age, contrary to the pattern in the 0.6 W/C ratio case. This would indicate some interaction between the polymer and the cement as it starts to give off MMA. Possibly there is some exothermal reaction overturning the effect of the MMA-producing endotherm. Having said that, the calcium hydroxide peaks at 530°C are still well defined and relatively large. There seems to be no difference in size between the different ages and W/C ratios. Similarly, all the traces show a small endotherm at 700°C from calcium carbonate. No other peaks from possible MMA/cement interactions were noted.

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5.3.4.2 POLYMER CEMENTS

Examination of the 0.37 W/C ratio polymer cements shows an initial broad exotherm at 300-400°C on the 5 day sample that becomes diminished until it is non-existent on the 26 day sample *(fig 5.10b)*. It is followed by a small endotherm peaking at about 310°C that diminishes until it too merges into one large exotherm in the 26 day sample. This endotherm was often seen with small fluctuations around its peak. Although not always present, this behaviour was attributed to either the movement of the powder as the monomer distils off or to bubble formation. In all cases the residue after the run could be seen to have contracted to form a tube around the thermocouple recess in the crucible.

The 0.6 W/C ratio samples again have broad exotherms peaking at 460°C *(fig 5.9b)*. All ages but the 5 day show another peak on this major exotherm at 380°C with a small endotherm feature at about 420°C. Like the 0.37 W/C ratio polymer cements this endotherm is often characterized by minor fluctuations, the residue again ending up around the thermocouple recess. It would seem that the fluctuations are again due to the movement of the powder or bubble formation.

All samples showed a small endotherm feature at 700°C due to calcium carbonate, possibly formed during the DTA run itself.

5.3.4.3 DIFFERENCES BETWEEN POLYMER CEMENTS AND PHYSICAL MIXES

All the thermograms of polymer cements showed well-defined calcium hydroxide peaks at 530°C, all of about the same height but significantly diminished from those in the physical mixes. This was true for both the 0.37 and 0.6 W/C ratios. This then can be seen as evidence to support the hypothesis that there is some reaction between calcium hydroxide and PMMA/MMA in polymer cements. The peaks were too small for quantitative measurement, but the diminution seems quite clear and reproducible. Again, no other peaks from reaction products of calcium hydroxide and PMMA/MMA were apparent.

In the IR work, with both physical mixes and polymer cements, it was easy to identify absorbencies due to cement and polymer, following their characterization. At first sight there are no vast differences between physical mixes and polymer cements, less than

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would be expected from the DTA work. However this could be expected since possible reactions would only be interfacial, the amount of product formed being small, and DTA being subject to masking effects. Nevertheless, there are some differences, primarily a peak at 1601 cm^{-1}. This is very small if not absent for the case of the physical mixes, but sharp on polymer cements. This was the case for all the eight different cements used, the difference being most noticeable by comparison with the adjacent band at 1645 cm^{-1} *(figs 5.11a&b and 5.12a&b)*. The peaks are marked with stars in the figures.

Clearly, the identification of the 1601 cm^{-1} band is of great importance in the study of reactions between polymer and cement; standard texts such as Bellamy *(ref 117)* give only a few possibilities for the band, carboxylate being the most likely.

5.3.4.4 XRD STUDIES

Specimens aged 5 days, 0.6 W/C ratio

Reflections due to the amorphous polymer were poorly defined, having maxima at around 32°. All the traces were relatively free from noise, in contrast to the 5 day, 0.37 W/C ratio samples. Comparison of the different physical mixes showed an enlargement rather than a diminution in some of the peaks with increasing cement content, particularly the 18.3° peak indexed as calcium hydroxide. This is definitely spurious as the amount of calcium hydroxide must be increasing with an increasing cement content. Therefore, it was not possible to use these traces as a calibration for the quantities of minerals remaining in the polymer cement *(fig 5.13a)*.

Contrary to what was expected, the peaks of the polymer cement are larger than those of all the physical mixes. This observation again must be spurious since the polymer cement can at maximum have only have half the mineral content of the 100% cement sample. There is however one obvious difference between the polymer cement and the physical mixes and that is the complete absence of the strong peak at 38.5° present on all the physical mixes. This, and the peak at 44.8°, do not index to common cement minerals and were thought to be the spurious peaks seen in the 5 day, 0.37 W/C ratio epoxy samples.

Calcium hydroxide was easily indexed, other possibilities being listed in *table 5.1*.

Specimens aged 5 days, 0.37 W/C ratio

Two broad peaks were present due to the amorphous polymer, these having maxima at around 14° and 16°. All the traces showed a considerable amount of noise compared to most of the others. Comparison of the physical mixes shows a gradation from the 100% polymer peaks to the 100% cement peaks. This was particularly noticeable for the peaks indexing as calcium hydroxide at 18.1° and 34.2°. The gradation is not sufficiently accurate to use as a calibration for the polymer cement, but the trend is as expected (n.b. this did not seem to be the case in the 0.6 W/C ratio 5 day cure sample). Examination of the polymer cement showed peaks about the same size as those of the corresponding 50:50 physical mix. It was not possible from these results to see a decrease in the quantity of calcium hydroxide due to possible reactions with the polymer (*fig 5.13b*).

As mentioned above, calcium hydroxide was easily indexed, other possibilities being listed in *table 5.2*.

General points

This work was intended to reinforce the DTA results that indicated that there was some sort of reaction between PMMA and cement hydration products, consuming calcium hydroxide. The technique seems useful for identifying the mineral composition, but would not appear to be sensitive enough for quantitative measurement of the small amounts of reaction product found here.

5.3.5 CONCENTRATION OF REACTION PRODUCTS BY SELECTIVE DISSOLUTION OF POLYMER

By stirring and soxhlet extraction in chloroform, all the polymer that it was possible to dissolve from polymer cements was removed. Chloroform is a particularly good solvent for MMA/PMMA, so any remaining polymer was assumed to be bonded in some way to the cement. Chloroform has the effect of solvating individual polymer chains held together by intermolecular forces. It does not however have the ability to interfere with covalent or ionic bonding. Thus any polymer bonded to the cement through chemical reactions should become insoluble in chloroform.

Examination of the infrared spectra produced showed a greatly diminished, but still noticeable carbonyl peak and well defined small peaks in the region of 1550-1630 cm^{-1},

superimposed on the normal cement peaks *(fig 5.14)*. This suggests two major possibilities: - It is conceivable that a certain amount of monomer and polymer becomes trapped in the cement's fine pore structure, inaccessible to the chloroform solvent, but there would appear to be far too much polymer left to account for it all by this process. So it seems reasonable to suggest that there is a significant amount of polymer adhering to the cement surface.

5.3.5.1 NATURE OF REACTION PRODUCTS

Removal of the extractable polymer had the effect of revealing peaks in the carboxylate region. This tends to suggest that there could be actual chemical bonding between cement and polymer. The insolubility of these products in chloroform, and the presence of carboxylate groups tends to suggest some ionic bonding, possibly between metal cations in the cement and carboxylate groups incorporated in the polymer. If so these could act as anchors for polymer chains (see below).

Polymer chain

$$
\begin{array}{ccccccc}
CH_3 & CH_3 & CH_3 & CH_3 & CH_3 & CH_3 & CH_3 \\
| & | & | & | & | & | & | \\
-C & -C & -C & -C & -C & -C & -C- \\
| & | & | & | & | & | & | \\
C & C & C & C & C & C & C \\
O\ \ O & O\ \ O & O\ \ O\text{-} & O\ \ O & O\text{-}\ \ O & O\ \ O & O \\
| & | & & | & & | & | \\
CH_3 & CH_3 & & CH_3 & & CH_3 & CH_3 \\
& + & & + & & & \\
\end{array}
$$

M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M-M

Cement surface with some ionised metal ions
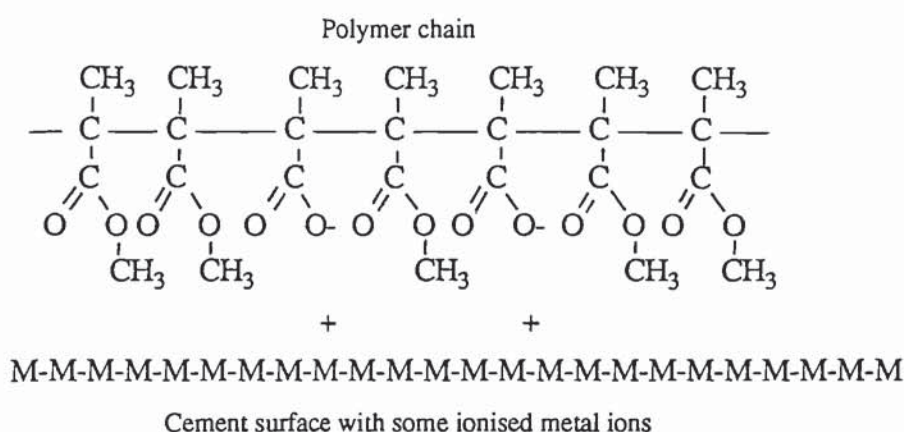
Some speculative work on possible reaction products formed on impregnating cements with MMA was published by Gebauer *(ref 15)*, Auskern *(ref 76)* and Dikeou *(ref 107)*. This has been discussed in some detail in section *5.2.1*, but would seem to limited to reactions between ester/acid monomer molecules with calcium hydroxide. Certainly calcium hydroxide is a particularly abundant phase in all the hydrated cements examined, however the other silicate, aluminate and ferrite phases produced on hydration are also basic. If metal methacrylates are formed with calcium, it also seems reasonable to expect that methacrylates of aluminium, iron, magnesium, potassium, sodium and possibly silicon would be formed. Also, since different parts of the monomer molecules undergo polymerisation and conversion to carboxylates, a monomer molecule can be part of a polymer chain and still possess a carboxylate group. Thus, to say that the methacrylates formed in cements are simple calcium salts of

methacrylic acid monomer is an oversimplification; it would therefore be expected that polymeric complexes of the metal cations would represent the bonding between polymer and cement.

5.3.5.2 THE NATURE OF CARBOXYLATES

Carboxylates are discussed in great detail by Bellamy *(ref 117)* and Leyte *(ref 120)*. They indicate that the infrared spectra of such compounds show very distinctive features: carboxylates are the salts of carboxylic acids formed by the action of the acids on cations. The process is ionic, H^+ being lost from the acid in the normal way, a resonance structure being set up in the resulting ion (see below).

$$R-C\overset{O}{\underset{OH}{\diagdown}} + M^+ \longrightarrow R-C\overset{O}{\underset{O}{\diagdown}}+M + H^+$$

Carboxylic acid   Cation   Carboxylate
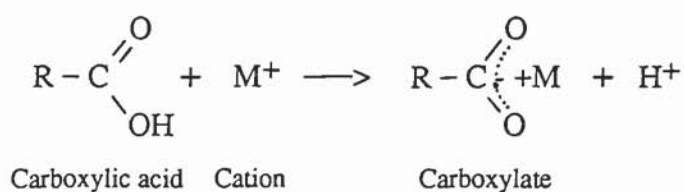
Infrared spectra of the above reaction would show several changes, most noticeably the elimination of the C=O absorbence of the acid being replaced by two new absorbencies due to the carboxylate resonance structure. Thus, if carboxylate is formed by polymer/cement reactions we would expect to see a reduction in the size of the carbonyl band and the development of two new bands in the 1615-1550 cm^{-1} region *(ref 117)*.

Re-examination of the polymer cements shows that there are no new peaks as such, other than the 1601 cm^{-1} band. But careful examination of the 1550 cm^{-1} region shows several small features, suggesting the other carboxylate peak. The carbonyl peaks do not show any noticeable diminution in size, but since the amount of carboxylate formed may be very small, and bearing in mind that polymer and cement may not have been mixed originally, or in the KBr disks in exactly 50:50 proportions, diminution in the carbonyl absorbence may be undetectable.

The following experiments were designed to examine these possibilities, in the hope of answering the following questions : -

a) is methacrylate formed by reaction of cement minerals with MMA?
b) do molecules of methacrylic acid (corresponding to methacrylates) become incorporated into growing MMA polymer chains?

5.3.6 IDENTIFICATION AND PREPARATION OF POSSIBLE INTERFACIAL REACTION PRODUCTS

As Dikeou *(ref 107)* discussed, MMA reacts with calcium hydroxide in the presence of water to form salts of methacrylic acid. As discussed in section *5.2.1*, a reaction scheme would involve the base-catalysed hydrolysis of the ester to the corresponding acid, this reacting with calcium hydroxide to form salts of the acid. It was possible to prepare calcium methacrylate in the lab, and as expected, its infrared spectra showed strong and broad bands around 1500 cm^{-1}, i.e. in the carboxylate region *(fig 5.15 a&b)*. Similar peaks were found in the reaction products of methacrylic acid and calcium hydroxide. Refluxed mixtures of MMA, water and calcium hydroxide also showed carboxylate.

5.3.6.1 CALCIUM METHACRYLATES

These substances were prepared to see if they could be possible reaction products of calcium hydroxide and PMMA/MMA. This was first postulated by Depuy from work on polymer impregnated cements. Calcium methacrylates were prepared, and found to have three waters of crystallization per molecule. Their thermograms showed many complex and sharp peaks, characterized by a very strong exotherm in the region 450-570°C *(fig 5.1)*. IR spectra of calcium methacrylates are given in *figs 5.15a&b and 5.16*.

5.3.6.2 POSSIBLE REACTIONS WITH BENZOYL PEROXIDE

Many experiments suggested that reactions take place between cement and benzoyl peroxide. In most cases these were observed as side reactions whilst studying other behaviour. For this reason, much of the evidence for such reactions is given in later chapters, but may be summarized here as follows : -

1) Ion chromatography of water extracts from polymer cements sometimes shows a late-eluting ion consistent with benzoate.

2) Cements immersed in a solution of benzoyl peroxide dissolved in toluene develop a white encrustation identified as calcium benzoate *(figs 5.17, 5.18a&b and chapter 8)*.

3) Polymer extracts from polymer cements often had a white, cloudy appearance *(chapter 8)*. This did not appear to be due to MMA/cement reactions since no such product was observed in refluxed cements.

4) Polymer impregnated cements showed zoning in the impregnated regions, suggesting the formation of some reaction product *(chapter 8)*.

Benzoyl peroxide was of course used as the polymerisation initiator for MMA because of its ability to produce free-radical species. There is little evidence to suggest that the reactions observed involve free-radicals, the likelihood being that benzoyl peroxide itself reacts. The exact nature of the reaction is uncertain, but could involve oxidation of surface water in cements to form benzoic acid, this reacting with basic phases (particularly calcium hydroxide) to form calcium benzoate.

$$C_6H_5OOOOH_5C_6 + H_2O \longrightarrow 2C_6H_5OOH + 1/2\,O_2$$
$$2C_6H_5OOH + Ca(OH)_2 \longrightarrow 2(C_6H_5OO)Ca + 2H_2O$$
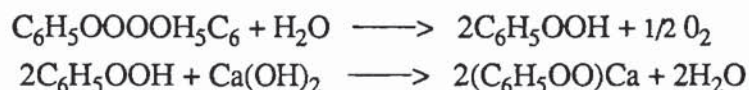
Whatever the reactions involved, they are potentially detrimental to polymer / cement materials, because they consume the initiator, producing water-soluble products.

Some confusion arises from the IR spectra of benzoyl peroxide and benzoates. Peaks attributed to carboxylate formation by reaction of MMA with cements may be confused with the ring vibration of benzoyl peroxide, and carboxylate absorbencies from benzoates *(fig 5.19)*. By comparing a polymer cement and physical mix made with 10% BP, the ring vibration is detectable in the physical mix at about 1599 cm-1. However, the polymer cement still shows larger peaks in this region due to carboxylate formation.

5.3.6.3 CHROMATOGRAMS OF POSSIBLE REACTION PRODUCTS

Bearing in mind the chemical nature of the cement and polymer used, there was only a limited number of ions that would ordinarily be expected to be present in their water extracts. In this study only anions were of interest, because reaction products of the polymer would most likely be negatively charged methacrylates. Mixed sodium standards of the most common of these were tested, the elution order being as follows *(fig 5.20 a&b)* : - carbonate/sulphate, methacrylate, chloride, silicate and benzoate. It was unexpected that sulphate eluted before chloride, with most other eluents the order is

reversed. Most importantly this shows that under these conditions, the peak due to methacrylate is easily resolved amongst other likely ions.

All the cements tested showed only three peaks in very similar ratios. It would appear that the ion concentrations of water extracts is not dependent on cure time or W/C ratio. Using spikes of standard ions, only the first peak was identifiable as carbonate or bicarbonate. The others were not conclusively identified, but solutions of aluminium metal in sodium hydroxide produced similar chromatograms. It therefore seems likely that the other peaks are due to aluminates, sulphoaluminates or aluminosilicates in a highly alkaline environment (pH 12-14),*(fig 5.21)*.

5.3.6.4 CHROMATOGRAMS OF REFLUXED AND POLYMER CEMENTS

As with the pure cement extracts, all the chromatograms showed the three peaks attributable to ions from cements, with an extra peak in the region attributable to methacrylate *(fig 5.22)*. This was checked by using methacrylate spikes *(fig 5.23)*. The same was also true of polymer cements, some having additional broad late-eluting peaks *(fig 5.24)*. The nature of these was not established, but could be benzoate from the decomposition of benzoyl peroxide, or oligomers of MMA. Nevertheless, it would seem that the presence of methacrylate in both refluxed and polymer cements is evidence for the reaction MMA -> methacrylic acid -> methacrylates. It would also seem that methacrylate forms by reaction with the monomer i.e. during impregnation or polymerisation, since the quantity of methacrylate formed was roughly the same in both. It is possible to envisage a situation where monomer molecules freshly converted to methacrylic acid molecules would either react with basic substances to form unpolymerisable salts, or become incorporated into the growing polymer chains. However, without firm identification of the late-eluting species in the polymer cement water extracts (or any other evidence), this is somewhat speculative.

5.3.6.5 QUANTITATIVE MEASUREMENT OF METHACRYLATE

The aims of this experiment were to find out if water is a limiting reactant in the formation of methacrylate, and to see if the amount of methacrylate formed is proportional to the amount of water present in the initial mixture. This appears to be the case in both refluxed and polymer cements *(fig 5.25 and table 5.3)*. In both cases the amount of methacrylate formed was very similar. It is possible that some of the newly-formed methacrylic acid becomes incorporated in the growing polymer - but again this is rather speculative.

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A further interesting feature was that even with prolonged oven-drying, and rapid transfer to reaction vessels, there is still some methacrylate formed when theoretically there is no water present. Two possible explanations are available for this : either MMA can react with bound or otherwise inaccessible water, or there is a methacrylic acid residue in the MMA. Since the reaction of methacrylic acid with bases liberates water anyway, a chain reaction could be envisaged where the liberated water produces more methacrylic acid, requiring only a minute quantity of methacrylic acid to start the process.

This behaviour also explains the lack of mechanical strength of specimens prepared by Gebauer *(ref 15)*, where a MMA prepolymer was added to the cement during hydration. This would almost certainly cause reaction of MMA with the cement and water, consuming a significant amount of the monomer and cement minerals. Indeed, the specimens prepared for testing the quantitative formation of methacrylate in this project became increasingly powdery with the more water that was used. At the original moisture content of the cement the specimens produced were crumbly solids.

Thermograms corresponding to the chromatograms described above are given in *fig 5.26*.

5.3.6.6 METHYL METHACRYLATE - METHACRYLIC ACID CO-POLYMERS

It should also be noted that the conversion of the ester to the acid is envisaged as a monomer rather than a polymer reaction. But if some of the acid becomes incorporated in the polymer before it reacts with bases, an ester-acid co-polymer could be formed. For this reason a 1:10 MMA : methacrylic acid co-polymer was used to make a polymer cement and physical mix. Methacrylic acid is itself highly polymerisable, doing so by an identical mechanism to that of MMA. Thus, co-polymers between the two monomers are readily made. Infrared spectra of such polymer cements show indications of carboxylate peaks. This is in agreement with what would be expected from the observations of pure MMA polymer cements. Certainly there would appear to be much less than a 1 in 10 conversion of ester molecules to acid molecules during contact with cements and subsequent monomer polymerisation, but it does demonstrate where carboxylate peaks occur if some conversion takes place.

5.3.6.7 POLYMERIC ACID SALTS

The reaction between calcium hydroxide and polymethacrylic acid was very rapid. Attempts to stir or crush the mixture immediately resulted in the formation of a ball of a sticky, putty-like substance. On oven drying at 105°C the ball remained intact, but became brittle and easily crushed. The ball appeared to be a coalescence of the calcium hydroxide. Similar observations were noted for hydrated cement powder, a large proportion of which being calcium hydroxide itself. However, on leaving the freshly-formed ball in the polymer solution for 1 hour, a white overgrowth was visible. This could be scraped off the surface of the dried ball for separate analysis.

Infrared spectra of the polymethacrylates are given in *Appendix 2* and *fig 5.7*. It can be seen that carboxylate peaks occur in slightly different positions depending upon the metal ion used. This would seem to be an explanation for why several, and not just two carboxylate peaks are seen in impregnated cements.

Evidence for MMA/methacrylic acid co-polymer formation, and hence bonding between cement and polymer still seems rather elusive. Clearly there is significant bonding between polymeric acids and soluble metal ions as the above experiments show. In addition, it is exactly these types of reaction that are proposed for the setting of glass ionomer cements. Nevertheless, since the exact position and shape of the carboxylate peak at $1601cm^{-1}$ in polymer cements could not be exactly reproduced in monomeric, polymeric or co-polymeric carboxylates, it is still possible that it represents bonding between unidentified metal ions and a MMA/methacrylic acid co-polymer of unknown proportions.

5.3.7 REACTIONS WITH OTHER ACRYLIC MONOMERS

Other evidence of possible reactions between MMA and calcium hydroxide was sought by the examination of physical mixes and polymer cements made with styrene rather than MMA. Styrene polymerises by the same mechanism as MMA, but having no functional groups (except the C=C that opens up during polymerisation) there should be no reaction with calcium hydroxide.

Polystyrene decomposes at slightly higher temperatures than PMMA, fortunately leaving the calcium hydroxide peak still easily resolved. Examination of the thermograms shows both the physical mix and partially polymerised samples have

similar sized hydroxide peaks, but the wholly polymerised sample has a greatly diminished peak.

This result is rather inconclusive as it suggests that no reaction has taken place after six hours heating, yet a significant decrease in the amount of calcium hydroxide has taken place after complete polymerisation was achieved.

Attempts were also made to identify possible reaction products between epoxy resin and cement minerals by comparison of physical mixes and polymer cements *(appendix 3)*. DTA thermograms were dominated by large exothermal effects from the polymer, but using IR there were no significant differences, suggesting a lack of reaction products.

5.3.8 CRITICISM OF THE DTA METHOD

It was noted that on all polymer cements and physical mixes there was a small peak at about 700°C attributable to the decomposition of calcium carbonate, being virtually non-existent on the thermograms of the cements themselves. Polymer cements and physical mixes of PMMA and pure calcium hydroxide demonstrated this point particularly well : on the physical mix a significant carbonate peak was seen, with a substantial calcium hydroxide peak. On the polymer cement however, the carbonate peak was even bigger and the hydroxide peak virtually absent. Since carbonate is present in the physical mix thermogram, this suggests some reaction having taken place between polymer and cement within the DTA apparatus itself. The reaction has been interpreted as follows: - In an atmosphere containing oxygen, organic compounds react to form carbon dioxide, water and other oxides. Thus, it is reasonable to expect that during the DTA run itself, calcium hydroxide becomes carbonated by the oxidation products of the polymer.

The fact that the hydroxide peak is absent on the polymer cement could be related to the intimacy of the mix between polymer and cement. It would therefore seem that DTA in still air is less reliable than expected in following the interactions between MMA and calcium hydroxide. The reactions (if they truly occur) could be masked by this carbonation effect.

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5.4 SUMMARY AND CONCLUSIONS

Experiments were carried out in order to examine the possibility that certain monomers (or their polymers) react with hydrated cements. Tests were carried out almost exclusively on MMA, this being a well-characterized monomer often used with cements, especially for impregnation. The following procedures were employed : -

1) Comparison of polymer : cement mixtures in a 50:50 ratio; in one polymerisation was carried out in contact with the cement (polymer cements) and in the other polymerisation was carried out in bulk before mechanically mixing with the cement (physical mixes). It was hoped that chemical differences between these would represent reaction products.

2) Water extracts were taken of polymer cements and cements refluxed with MMA. These were examined for water-soluble reaction products.

3) Reaction conditions were studied in order to investigate limiting reagents.

4) Possible reaction products were synthesized and characterized by instrumental techniques.

The following instrumental techniques were employed : -

1) Differential thermal analysis (DTA),
2) Fourier transform infrared spectroscopy (IRS),
3) X-ray diffraction (XRD), and
4) Ion chromatography.

It was concluded that : -

1) MMA reacts with cements to form methacrylates, primarily calcium methacrylates ; pure PMMA is inert.

2) The reaction has two stages a) hydrolysis of MMA to methacrylic acid, and b) subsequent reaction with basic substances. Thus water is a limiting reactant.

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3) The vast majority of methacrylic acid molecules formed react with basic cement minerals, particularly calcium hydroxide. Some however may become incorporated into the polymer chains. Evidence for this latter suggestion is inconclusive.

4) Polymethacrylic acid and its co-polymers with MMA bond very strongly to cement minerals when moistened. Thus if methacrylic acid molecules become incorporated into the growing polymer chains then actual chemical bonding can occur between cement and polymer.

5) Any interfacial bonding will tend to improve the mechanical properties of polymer/cement composites. However, the formation of water-soluble methacrylates and benzoates will tend to be detrimental to the mechanical and diffusional properties of such materials.

It should be stressed that these reactions occur because MMA is an ester, and not because it is an acrylic monomer. Thus MMA in a sense is a special case having a functional group - monomers with no functional groups e.g. styrene would not be expected to react in this way.

IRS and ion chromatography proved to be generally suited to the phases and reactions under investigation, however the usefulness of DTA is limited for the following three reasons: -

1) Only two minerals may be seen in the thermograms of the hydrated cements,

2) Physical changes in the polymer during heating may effect the heatflow to the thermopile in the instrument, thus masking peaks due to chemical effects, and

3) There would appear to be a reaction between calcium hydroxide and the oxidation products of MMA/PMMA, possibly masking peaks due to other calcium hydroxide reactions.

XRD was unable to supply evidence of reaction products, since their abundance in specimens was too low for detection by the technique.

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FIGURE 5.1

DTA TRACES OF CALCIUM SALTS
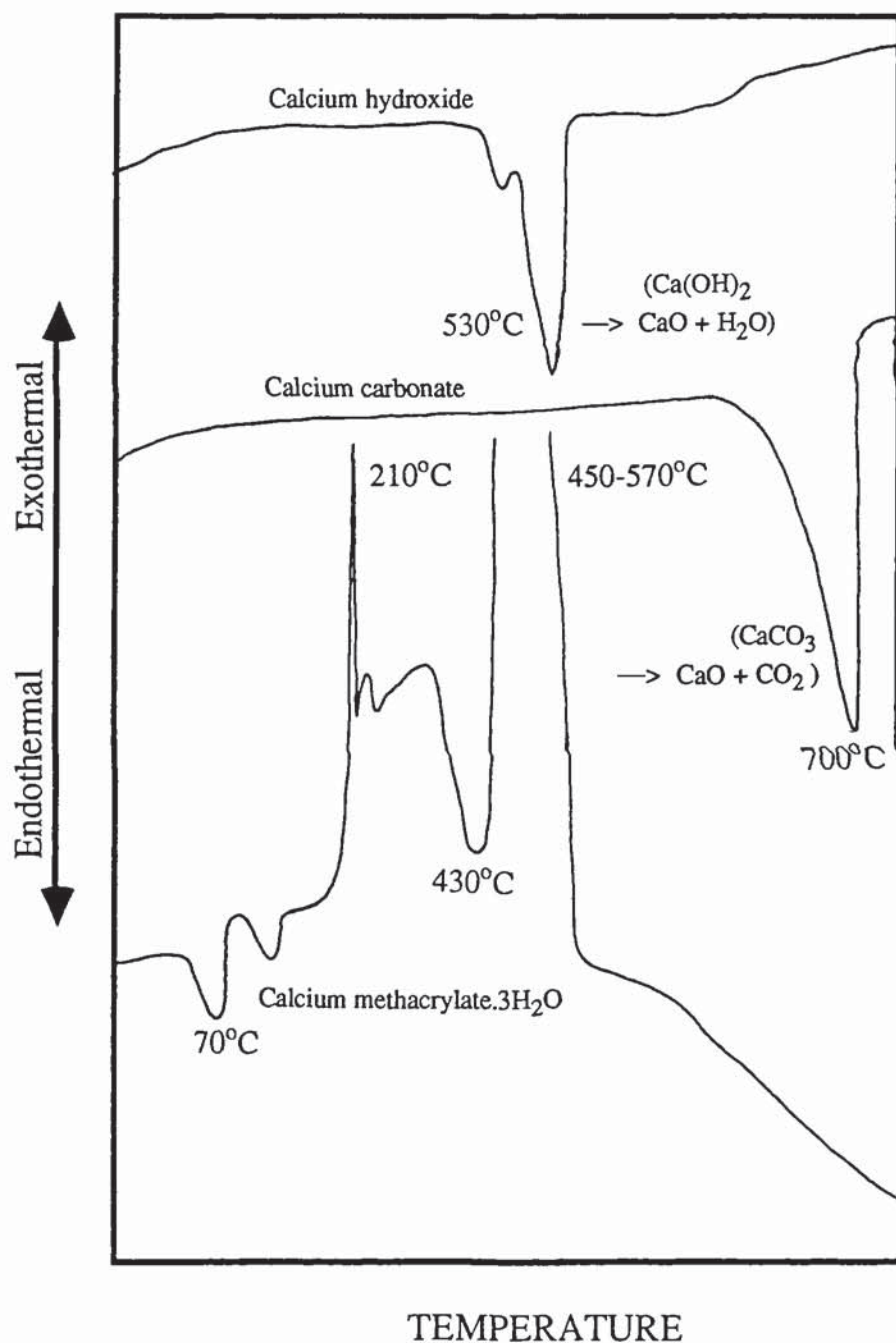
CHARACTERISATION OF PURE CEMENTS USING DTA

FIGURE 5.2b

O.6 W/C RATIO

Exothermal   Endothermal

5 day cure

$(Ca(OH)_2 \longrightarrow CaO + H_2O)$

530°C

12 day cure

19 day cure

26 day cure

TEMPERATURE

FIGURE 5.2a

0.37 W/C RATIO

Exothermal   Endothermal

5 day cure

700°C

$(Ca(OH)_2 \longrightarrow CaO + H_2O)$

530°C

12 day cure

19 day cure

26 day cure

TEMPERATURE
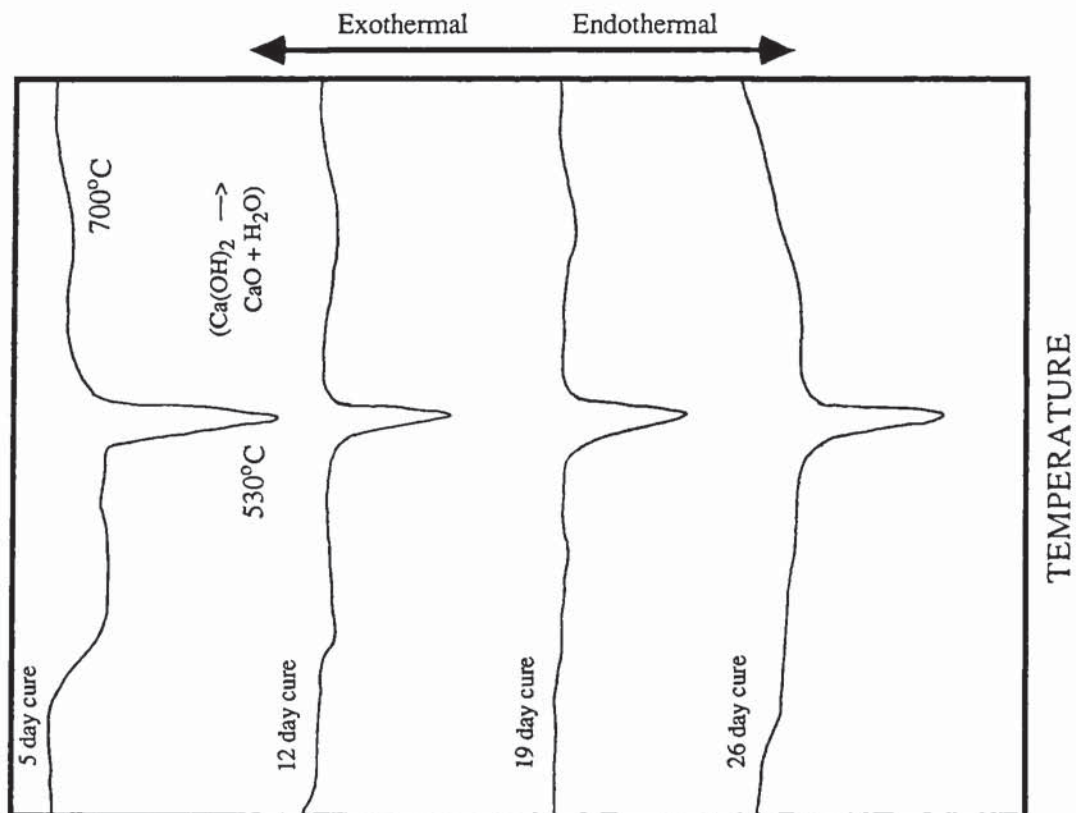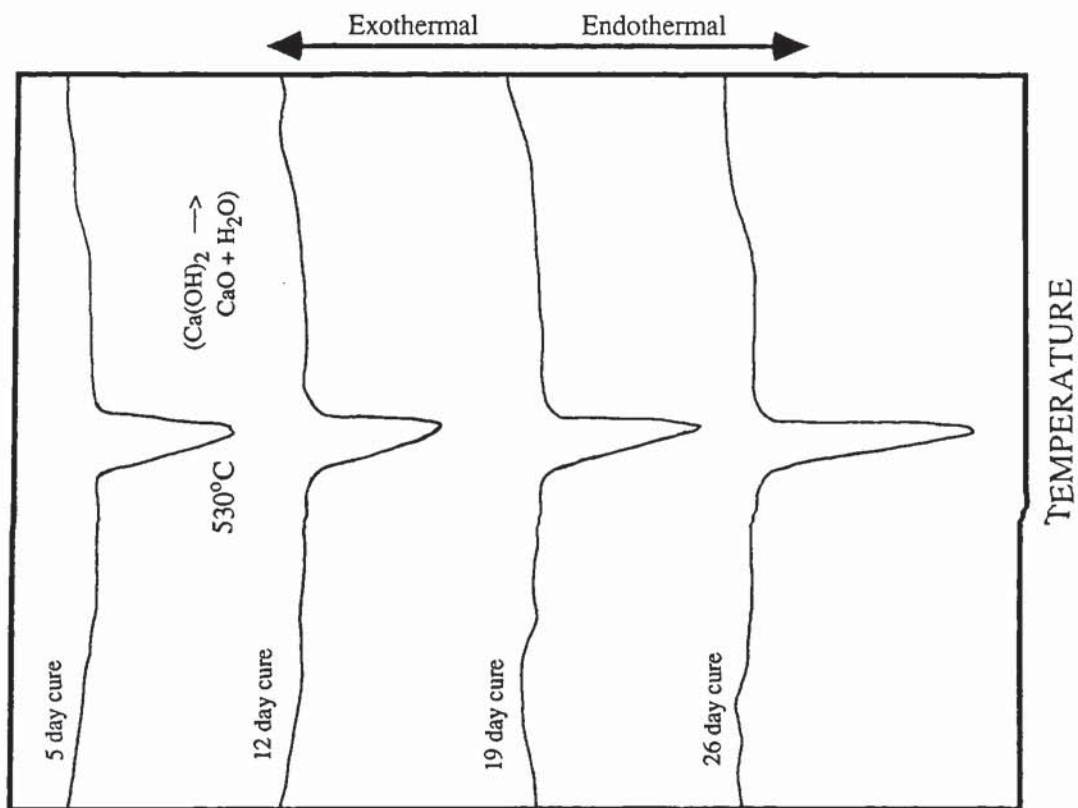
FIGURE 5.3a
INFRARED SPECTRUM OF UNHYDRATED OPC

FIGURE 5.3a — Infrared spectrum of unhydrated OPC. Percentage transmittance vs Wavenumbers (1/cm). Labelled features: -OH and H_2O, H_2O, C_2S, Silicates and aluminates.
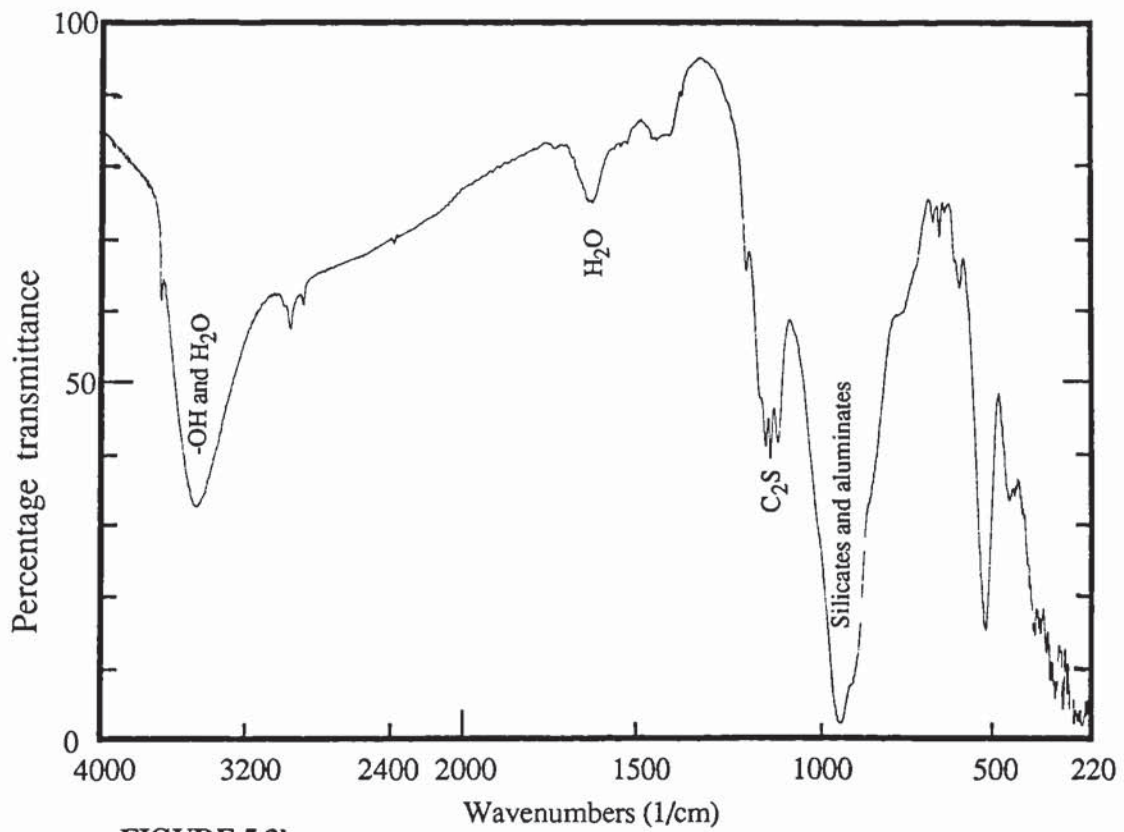
FIGURE 5.3b
INFRARED SPECTRUM OF HYDRATED OPC (0.6 W/C RATIO 19 DAY CURE)

FIGURE 5.3b — Infrared spectrum of hydrated OPC (0.6 W/C ratio 19 day cure). Percentage transmittance vs Wavenumbers (1/cm). Labelled features: -OH and H_2O, H_2O, $Ca(OH)_2$, Silicates and aluminates, $Ca(OH)_2$ or $CaCO_3$.

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FIGURE 5.4b
0.6 W/C RATIO PURE CEMENT
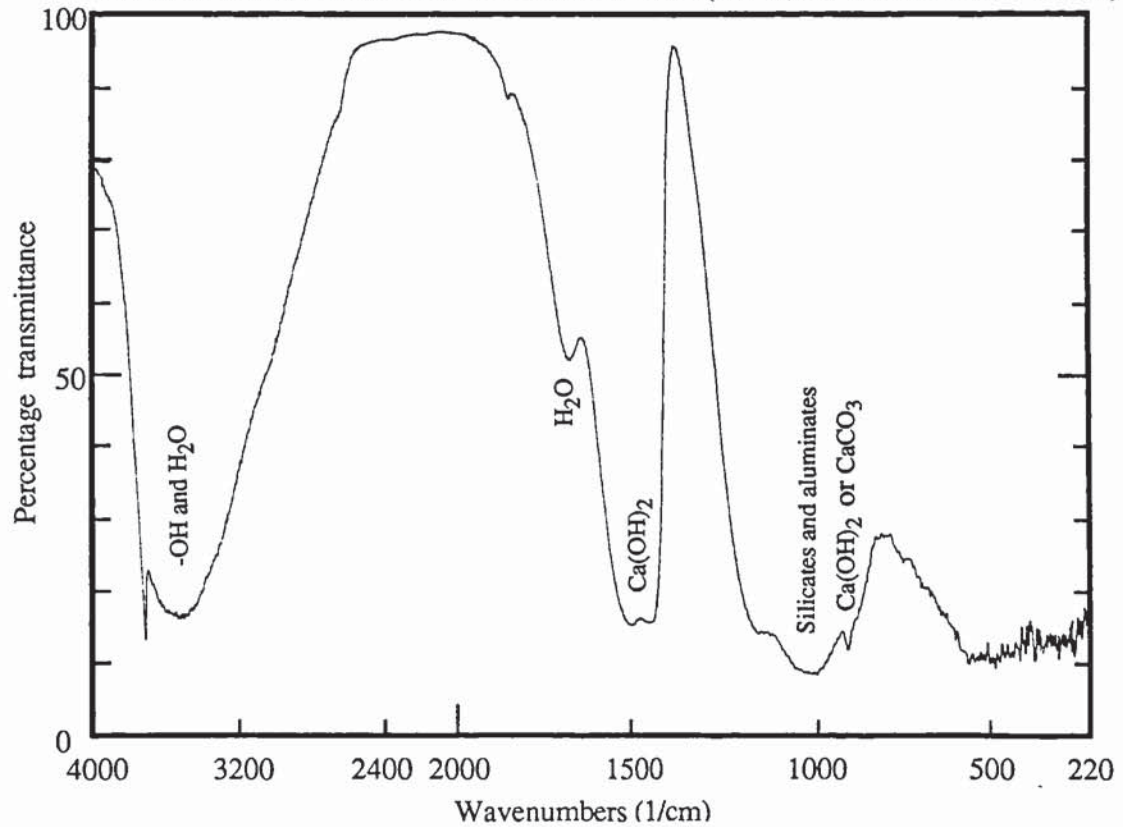
FIGURE 5.4a
0.37 W/C RATIO PURE CEMENT

INFRARED SPECTRA

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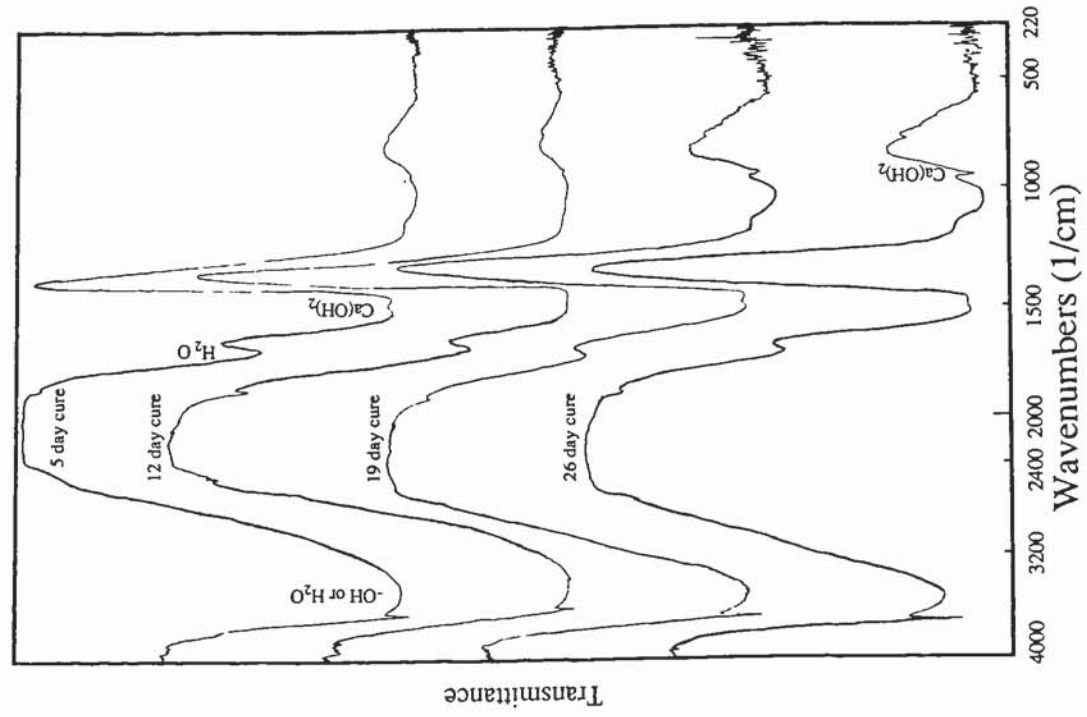
FIGURE 5.5a

CHARACTERISATION OF PMMA USING DTA

Used for 0.37 W/C ratio
5 day cure physical mixes
grainsize 300-600 μm

Used for 0.6 W/C ratio
26 day cure physical mixes
grainsize 300-600 μm

Used for 0.6 W/C ratio
26 day cure physical mixes
grainsize <300 μm

50:50 mixture of MMA/PMMA

450°C

330°C

400°C

70°C

60°C

340-430°C

Oxidation of PMMA/MMA

Distillation of free MMA from mixture

Distillation of MMA

Exothermal

Endothermal

1

2

3

4

TEMPERATURE

FIGURE 5.5b

IDENTIFICATION OF POLYMER PEAKS
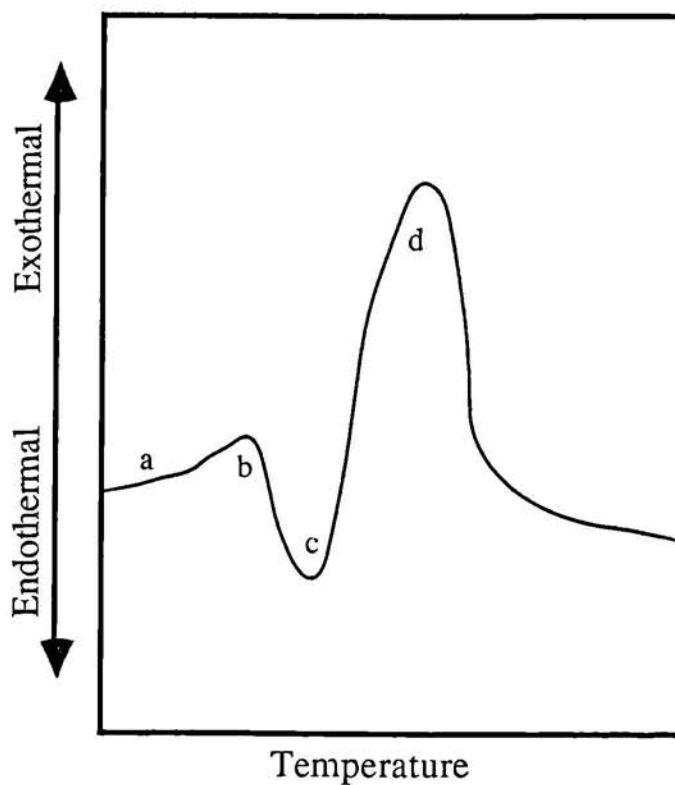
FIGURE 5.5c

IDENTIFICATION OF POLYMER PEAKS

The following notes refer both to figure 5.5b and 5.5c : -

Left : *PMMA begins to swell (peak a)*
Top : *PMMA begins to melt (peak b)*
Right : *MMA distills from PMMA (peak c)*
Bottom : *PMMA and MMA oxidise (peak d)*

FIGURE 5.6a

INFRARED SPECTRUM OF METHYL METHACRYLATE (MMA)
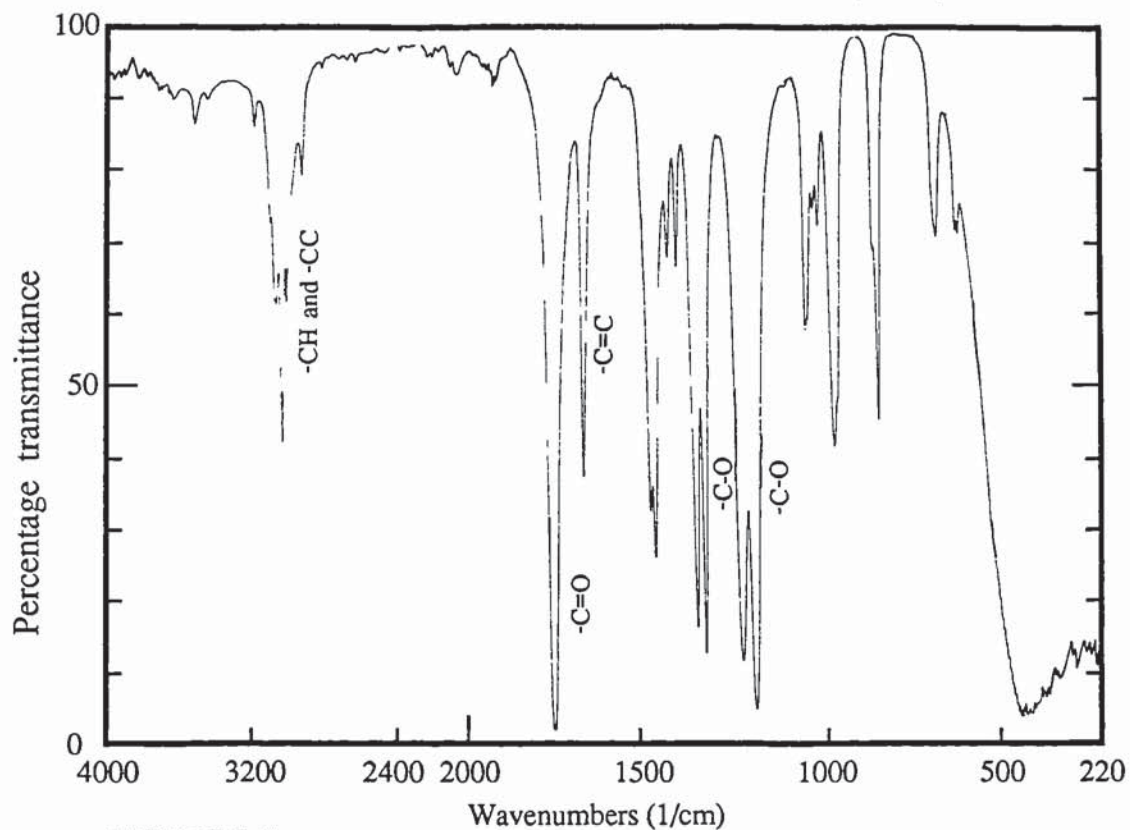
FIGURE 5.6b

INFRARED SPECTRUM OF POLYMETHYL METHACRYLATE (PMMA)
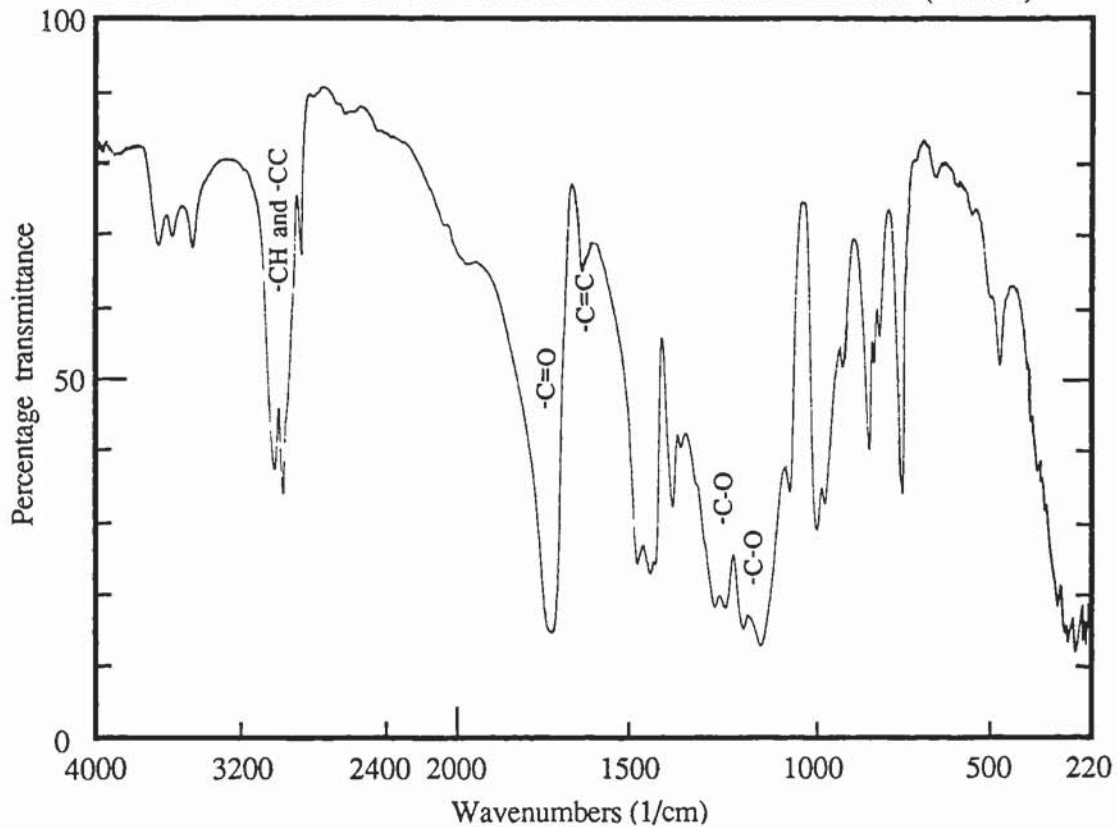
FIGURE 5.7
INFRARED SPECTRUM OF POLYMETHACRYLIC ACID (PHMA)
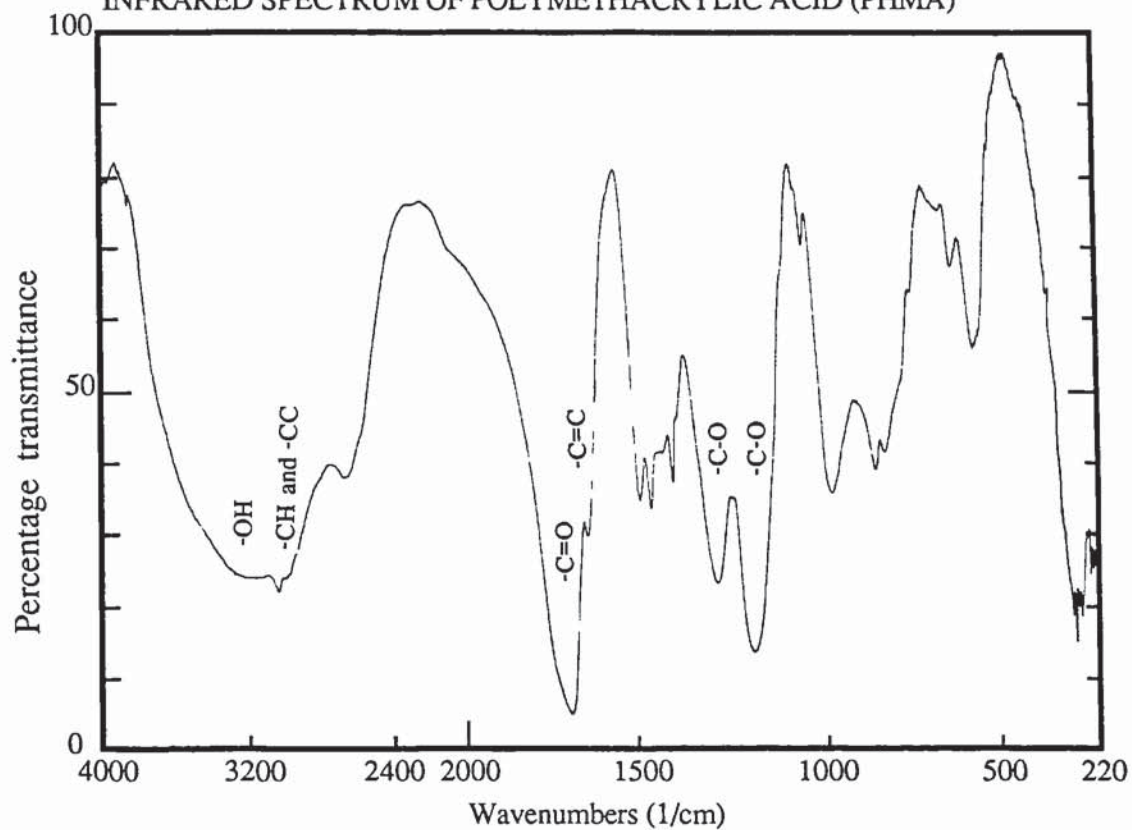
FIGURE 5.8
INFRARED SPECTRUM OF PMMA/PHMA CO-POLYMER

PHYSICAL MIXES AND POLYMER CEMENTS EXAMINED USING DTA   0.6 W/C RATIO

FIGURE 5.9a   PHYSICAL MIX

Exothermal   Endothermal

700°C
530°C
*
*
*
*
5 day cure
12 day cure
19 day cure
26 day cure
330-350°C

TEMPERATURE

* Note diminution of calcium hydroxide peaks in polymer cements, compared to physical mixes.
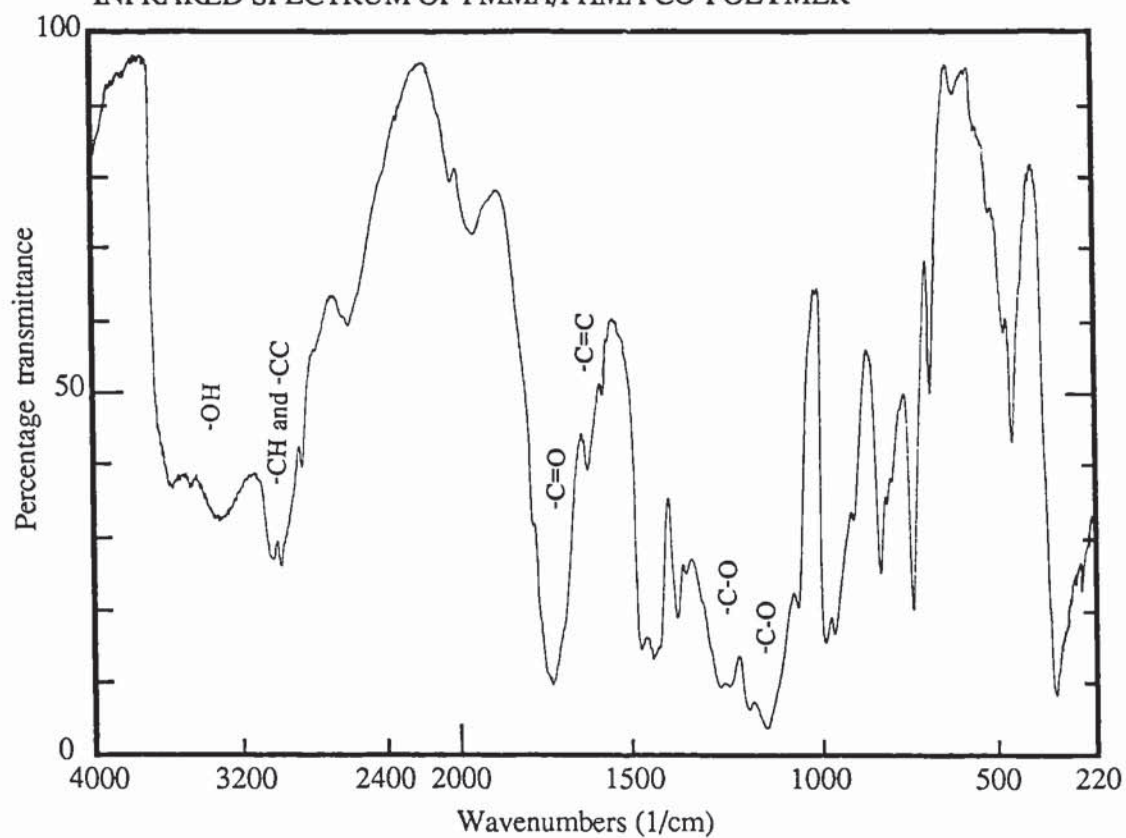
FIGURE 5.9b   POLYMER CEMENT

Exothermal   Endothermal

460°C
700°C
530°C
*
*
*
*
5 day cure
12 day cure
19 day cure
26 day cure
+ 420°C
380°C
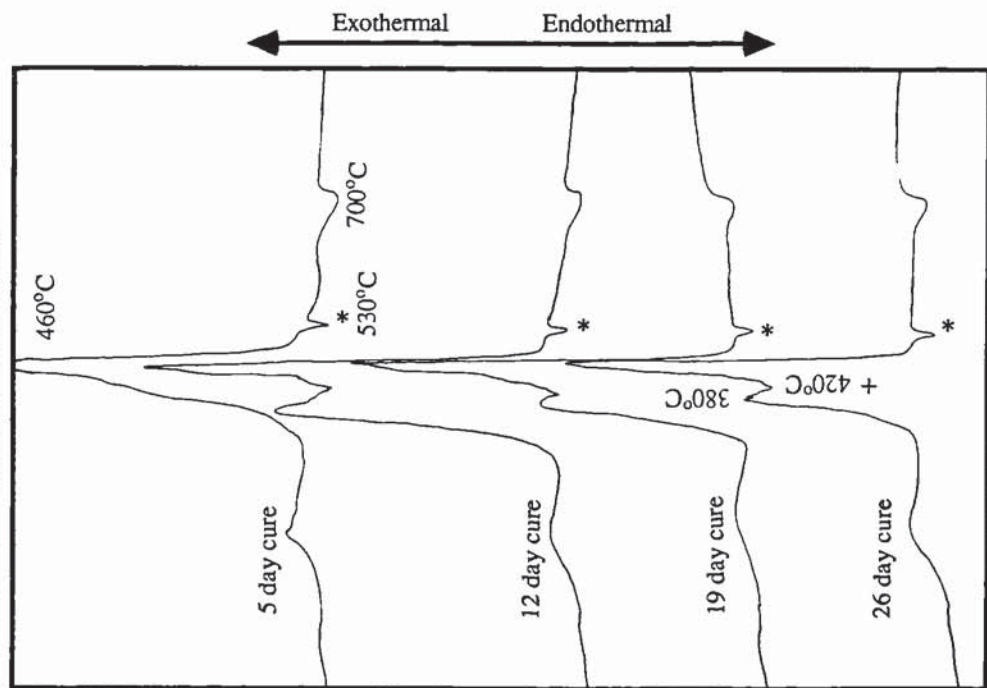
+ Possible decomposition of calcium methacrylate according to Auskern (ref 76).
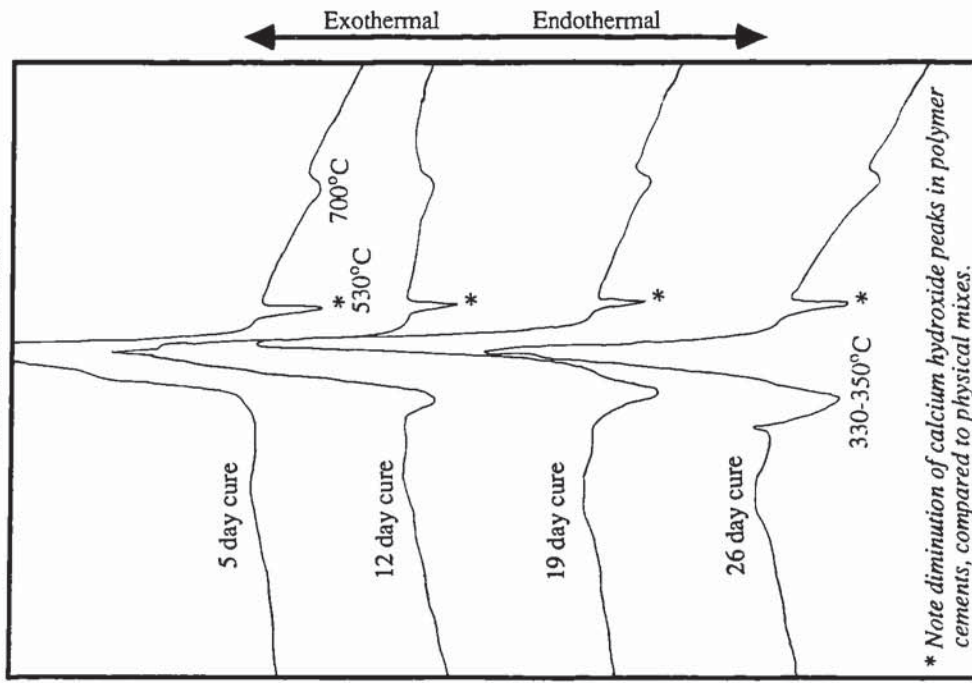
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PHYSICAL MIXES AND POLYMER CEMENTS EXAMINED USING DTA   0.37 W/C RATIO

FIGURE 5.10a   PHYSICAL MIX

FIGURE 5.10b   POLYMER CEMENT

* Note diminution of calcium hydroxide peaks in polymer cements, compared to physical mixes.

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FIGURE 5.11b
0.6 W/C RATIO PHYSICAL MIXES

INFRARED SPECTRA

FIGURE 5.11a
0.6 W/C RATIO POLYMER CEMENTS

FIGURE 5.12b
0.37 W/C RATIO POLYMER CEMENTS

FIGURE 5.12a
0.37 W/C RATIO PHYSICAL MIXES

INFRARED SPECTRA

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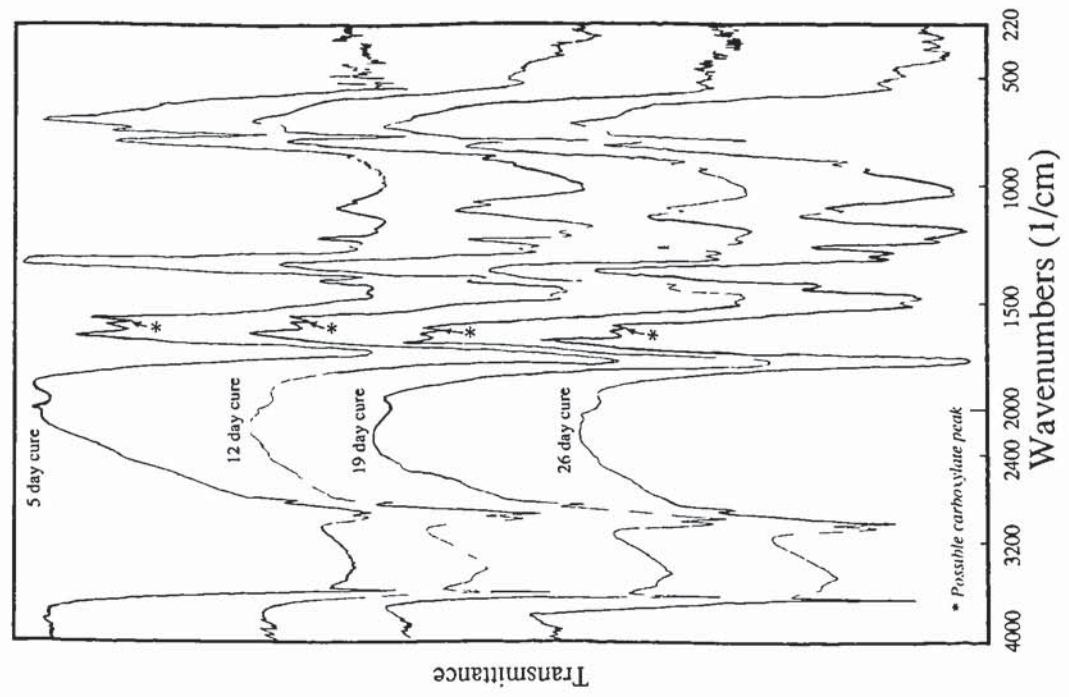
FIGURE 5.13a

XRD DATA FOR POLYMER CEMENT AND PHYSICAL MIXES USING
0.6 W/C RATIO 5 DAY CURED CEMENT
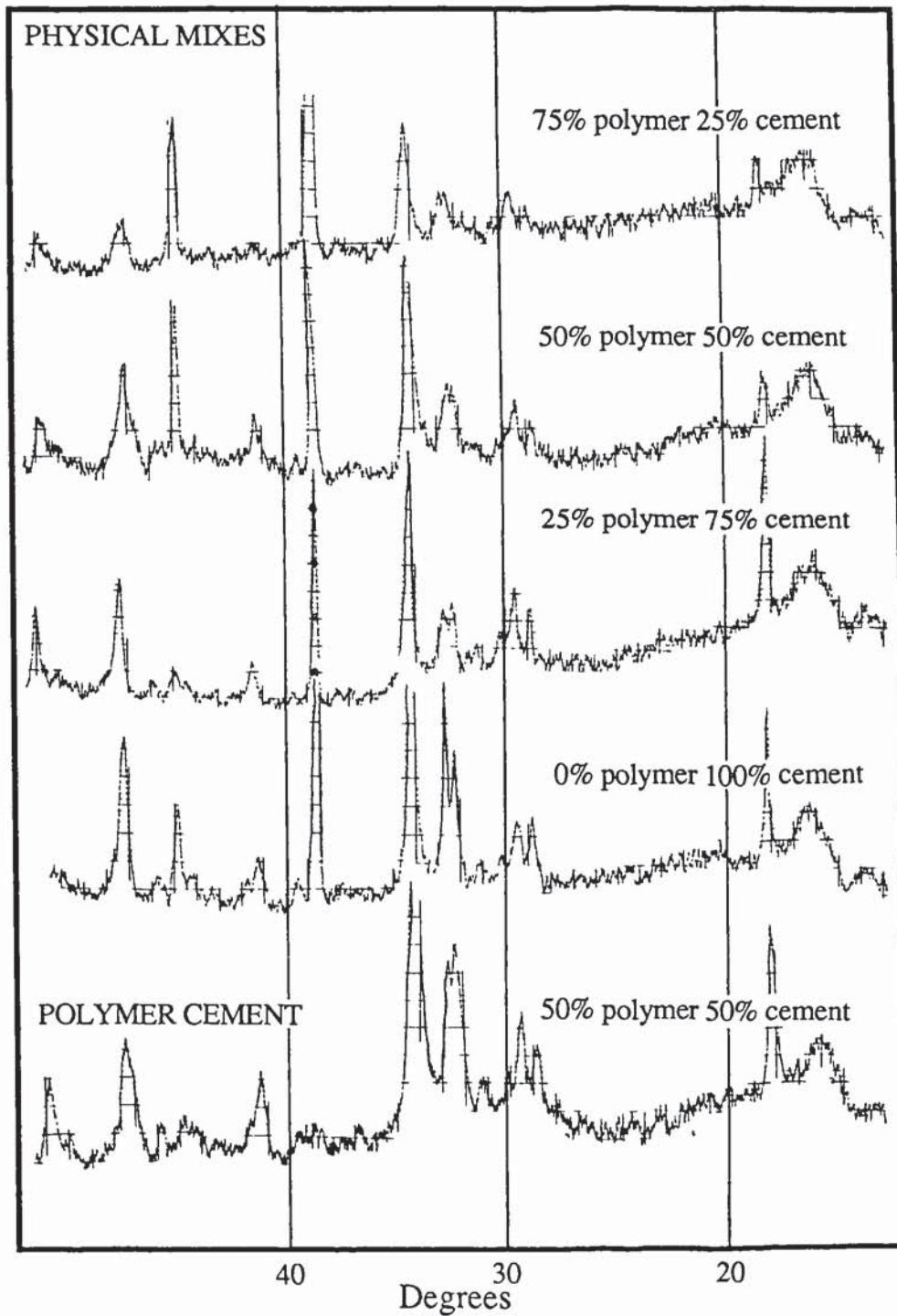
FIGURE 5.13b

XRD DATA FOR POLYMER CEMENT AND PHYSICAL MIXES USING
0.37 W/C RATIO 5 DAY CURED CEMENT
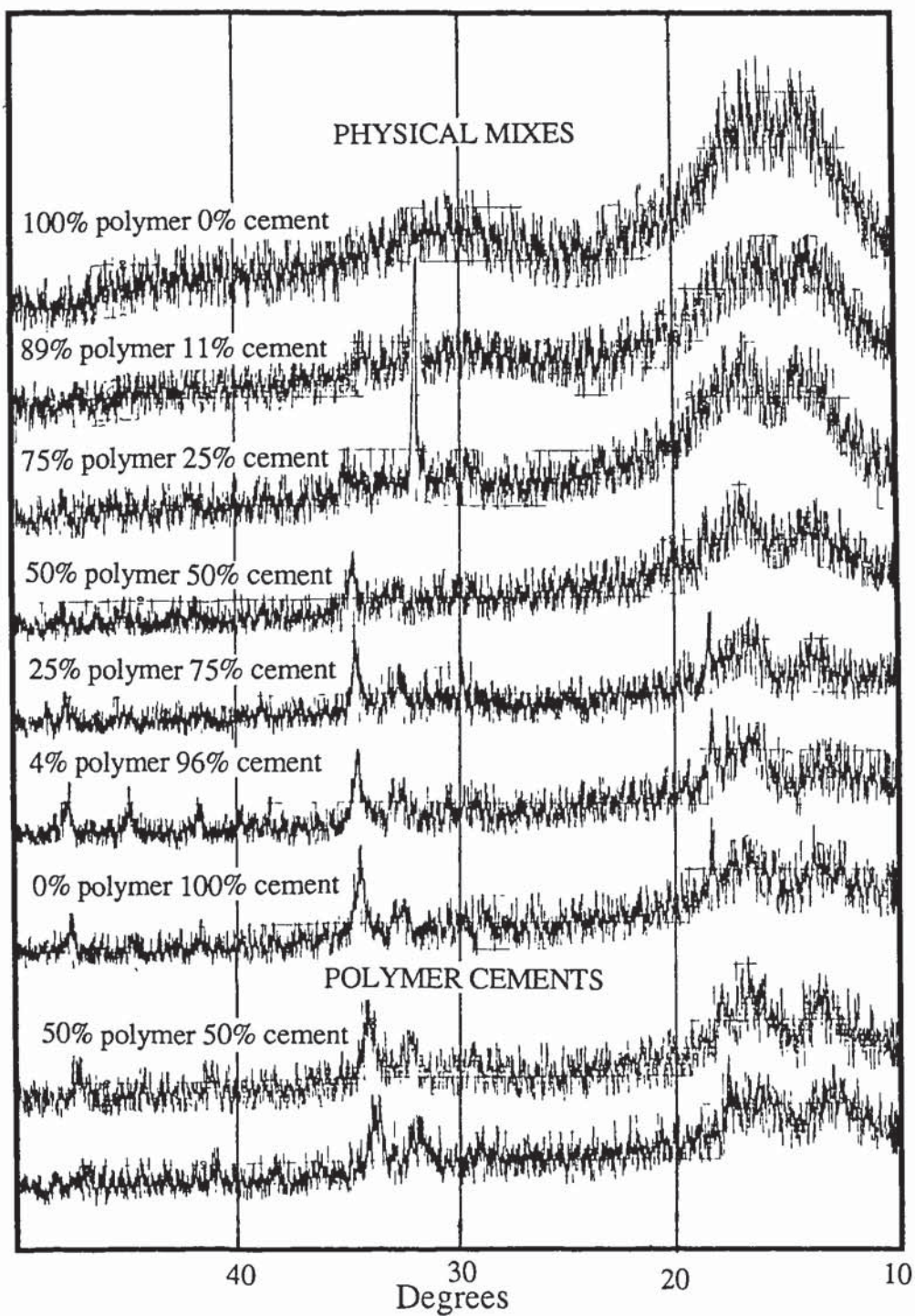
TABLE 5.1

IDENTIFICATION OF MINERALS BY COMPARISON OF
XRD REFLECTIONS TO TABULATED DATA (0.6 W / C RATIO 5 DAY CURE)

PEAKS ARE MEASURED ON A RELATIVE SCALE ; vvs > vs > s > m > w > vw

OBSERVED DATA (Given in figure 5.13a)		REFERENCE DATA (From Taylor (ref 123))	
Reflection angle in degrees	Plane spacing (nm)	Mineral	Plane spacing (nm)
18.3	0.4906	Calcium hydroxide	0.490vs, 0.3112 m, 0.2628 vvs, 0.1927 ms, 0.1796 ms
28.8	0.3198		
29.6	0.3120		
32.8	0.2882		
34.3	0.2844	Calcium carbonate	0.3035 vvs, 0.2285 s, 0.2095 s
38.5*	0.2734*		
41.5	0.2472		
44.8*	0.2326*	Dicalcium silicate	0.2794 vs, 0.2285 vs, 0.2748 s
47.2	0.2186		
50.8	0.2100		

*Peaks caused by instrumental effects

TABLE 5.2

IDENTIFICATION OF MINERALS BY COMPARISON OF
XRD REFLECTIONS TO TABULATED DATA (0.37 W / C RATIO 5 DAY CURE)

SIZE OF PEAKS IS MEASURED ON A RELATIVE SCALE ; vvs > vs > s > m > w > vw

OBSERVED DATA (Given in figure 5.13b)		REFERENCE DATA (From Taylor (ref 123))	
Reflection angle in degrees	Plane spacing (nm)	Mineral	Plane spacing (nm)
18.1	0.4960	Calcium hydroxide	0.490 vs, 0.3112 m, 0.2628 vvs
32.3*	0.2884*		
32.6	0.2860		
34.2	0.2740	Dicalcium silicate	0.2794 vs, 0.2285 vs, 0.2748 s
41.7	0.2314		
41.8	0.2312		
45.3	0.2168	Calcium carbonate	0.3035 vvs, 0.2285 s, 0.2095 s
47.8	0.2080		

*Peaks caused by instrumental effects

FIGURE 5.14

SELECTIVE DISSOLUTION OF MMA/PMMA USED WITH 0.4 W/C RATIO 28 DAY CURED CEMENT.
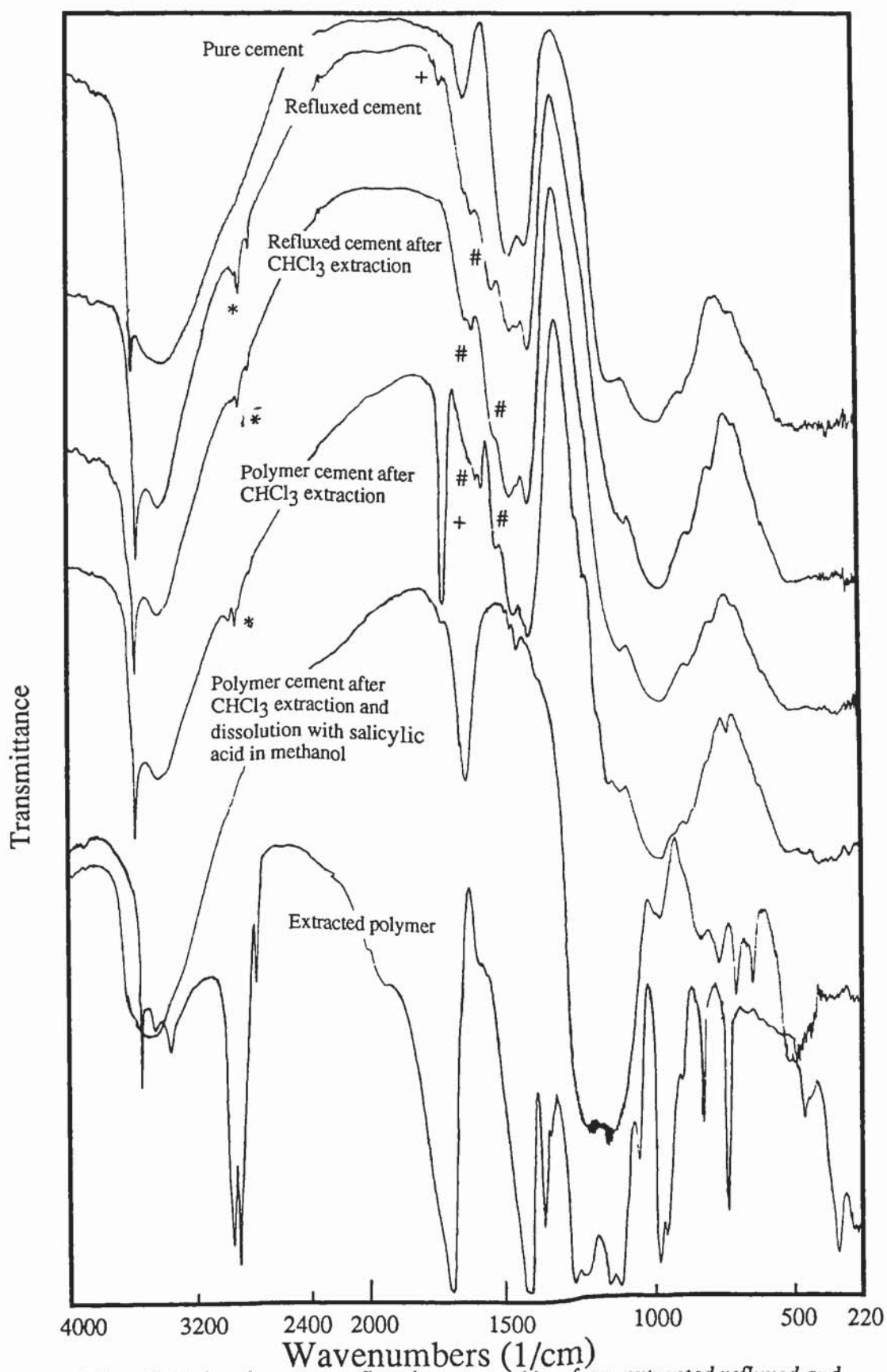
* Note C-H absorbance on refluxed cements, chloroform-extracted refluxed and polymer cements, indicating presence of organic compounds.
+ Note C=O of monomer/polymer on refluxed and polymer cements.
# Note carboxylate absorbances indicative of reaction products.

FIGURE 5.15a

INFRARED SPECTRUM OF HYDRATED CALCIUM METHACRYLATE
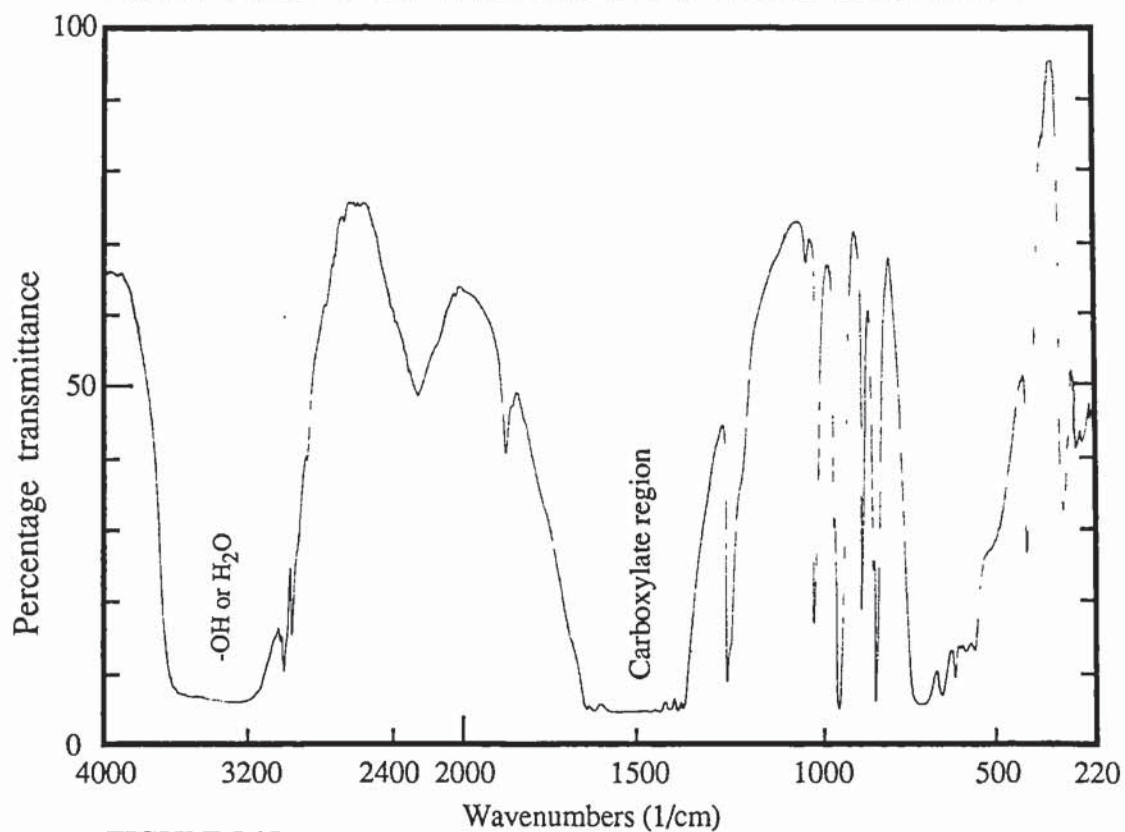
FIGURE 5.15b

INFRARED SPECTRUM OF ANHYDROUS CALCIUM METHACRYLATE
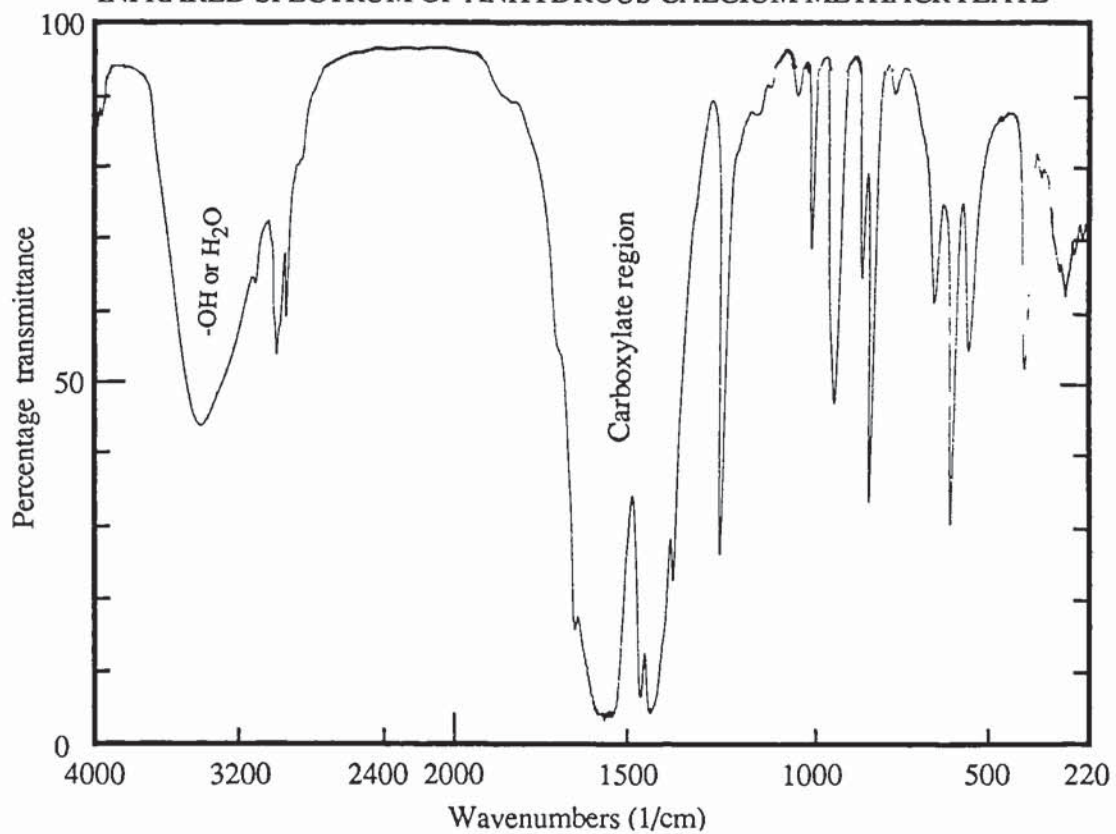
FIGURE 5.16

FIGURE 5.16
INFRARED SPECTRUM OF CALCIUM POLYMETHACRYLATE

FIGURE 5.17

INFRARED SPECTRUM OF CALCIUM BENZOATE

FIGURE 5.17
INFRARED SPECTRUM OF CALCIUM BENZOATE

n.b.Compare with figure 5.18a&b
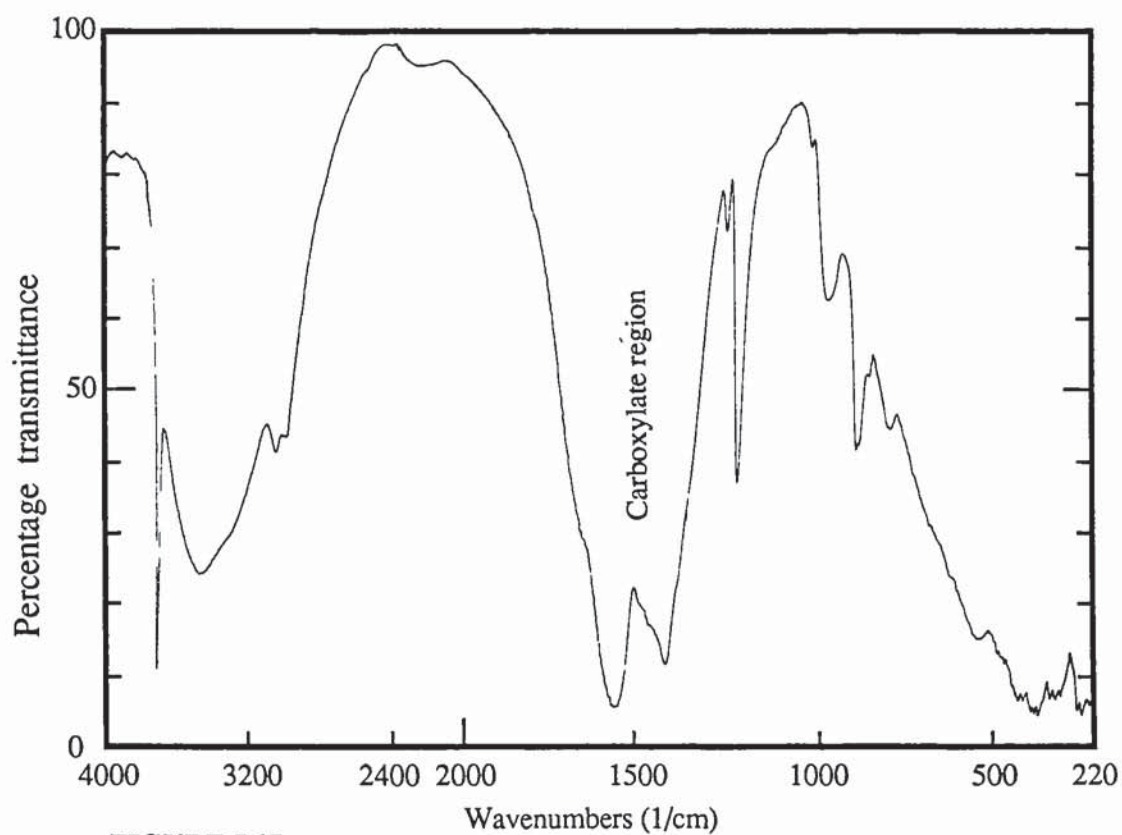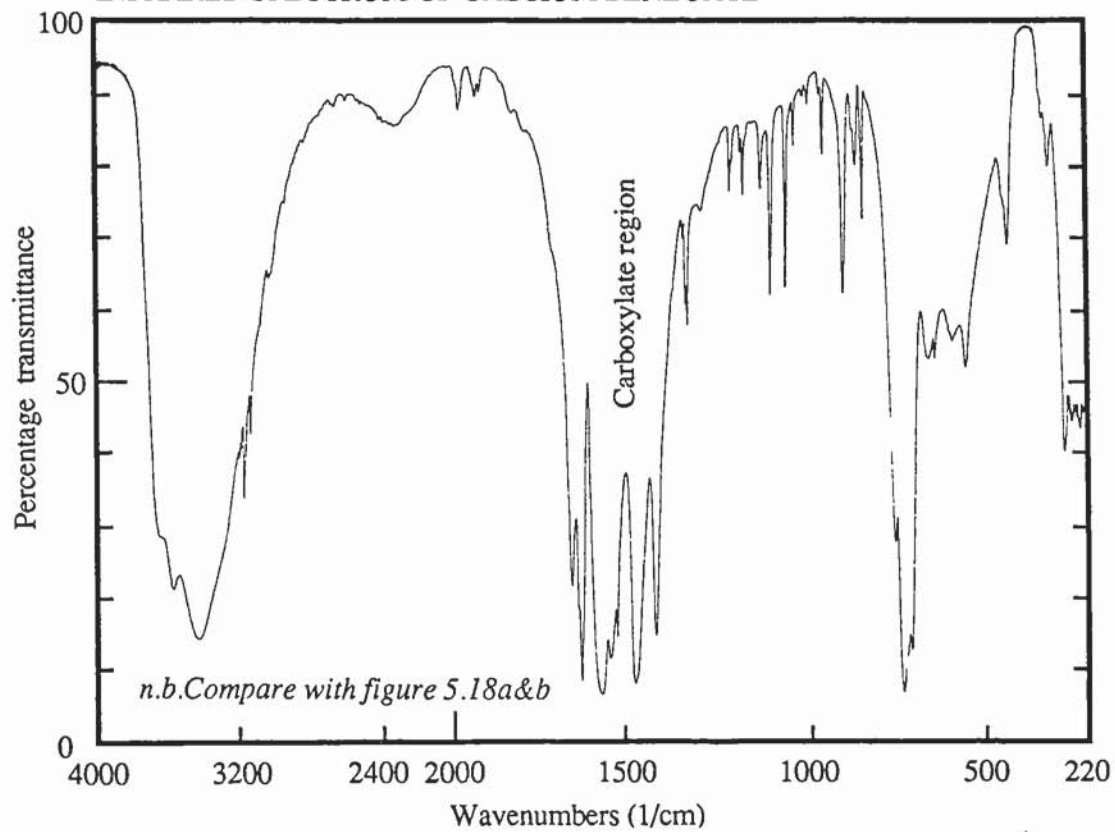
FIGURE 5.18a

INFRARED SPECTRUM OF REACTION PRODUCT BETWEEN 0.7 W/C
RATIO CEMENT CURED FOR 2 DAYS AND BENZOYL PREOXIDE.
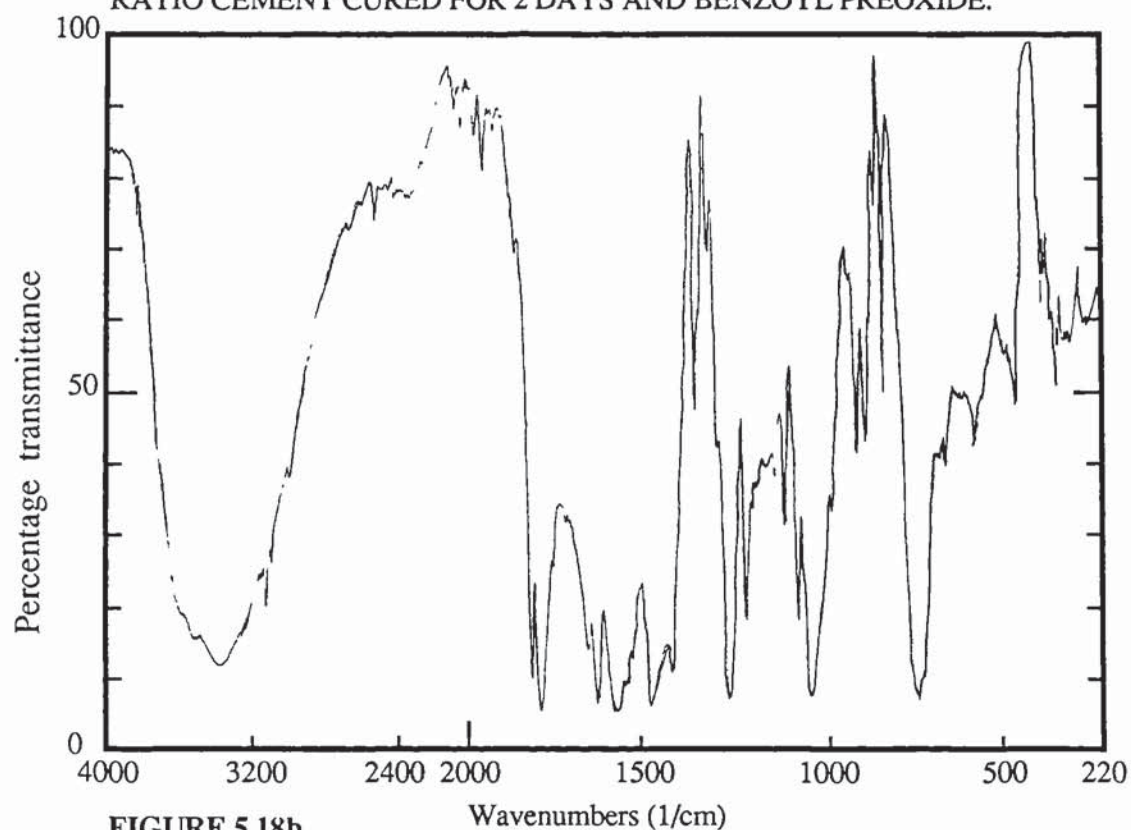
FIGURE 5.18b

INFRARED SPECTRUM OF REACTION PRODUCT FOLLOWING
EXTRACTION IN HOT WATER.

n.b.Compare with figure 5.17

173
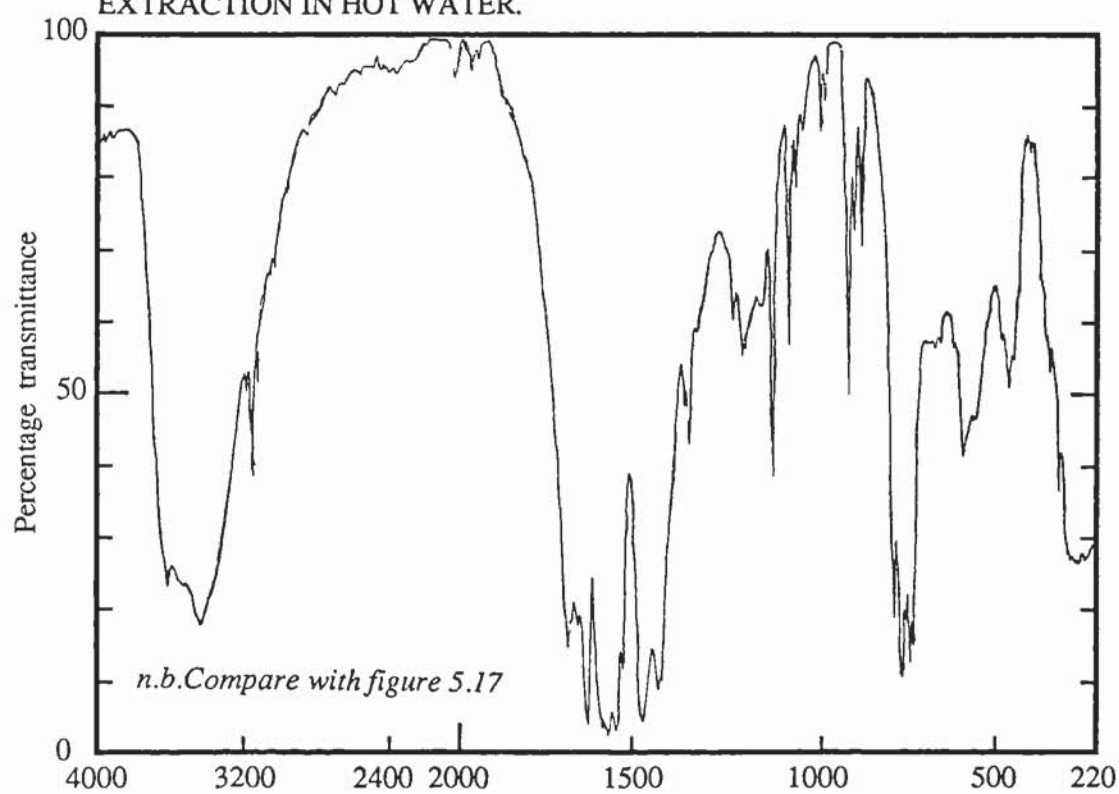
FIGURE 5.19

0.6 W/C RATIO 5 DAY CURED CEMENT USED WITH MMA CONTAINING 10% BENZOYL PEROXIDE
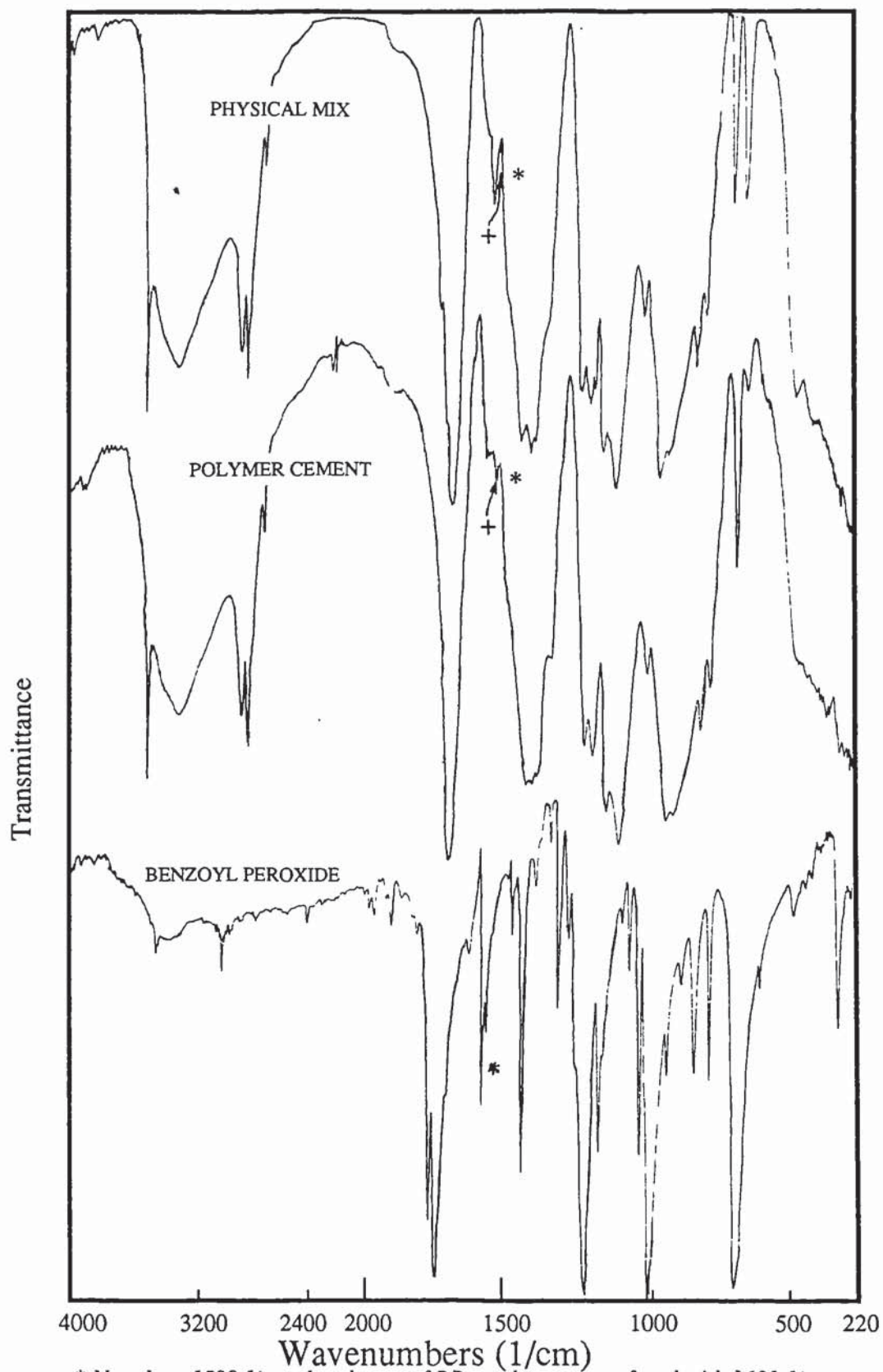
* Note how 1599 1/cm absorbance of BP can become confused with 1601 1/cm absorbance of carboxylate.
+ Note also larger carboxylate peak in polymer cement compared to physical mix, indicating reaction.

FIGURE 5.20a

CHROMATOGRAM OF FIVE MIXED SODIUM STANDARDS
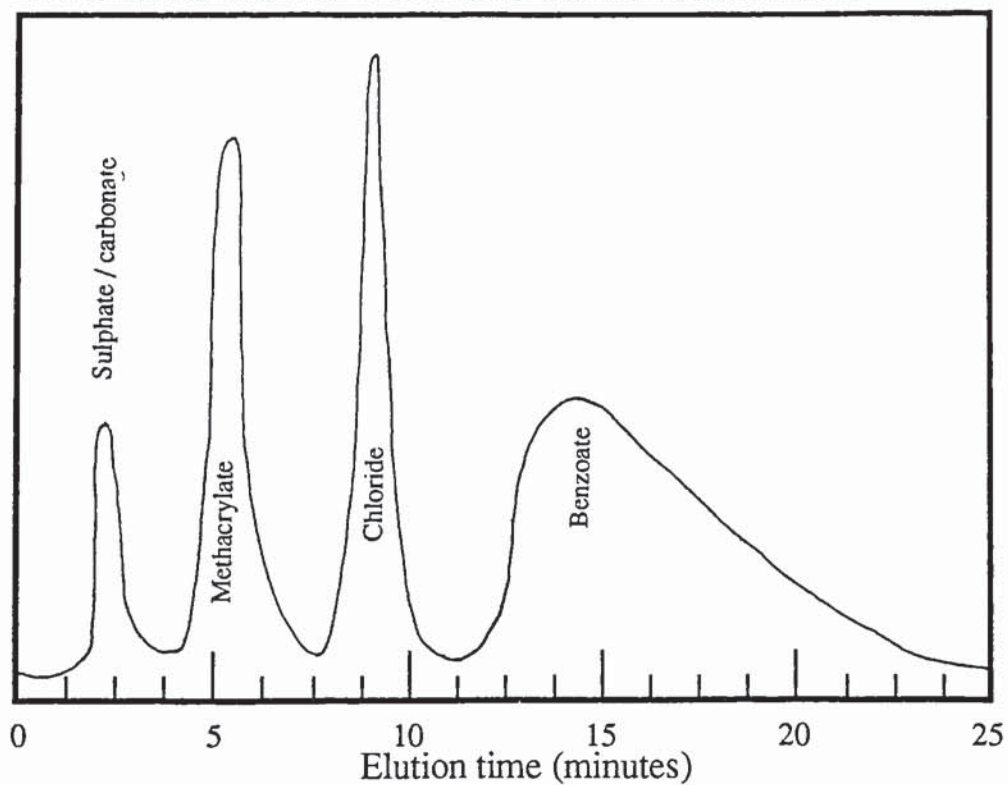
FIGURE 5.20b

CHROMATOGRAM OF SIX MIXED SODIUM STANDARDS
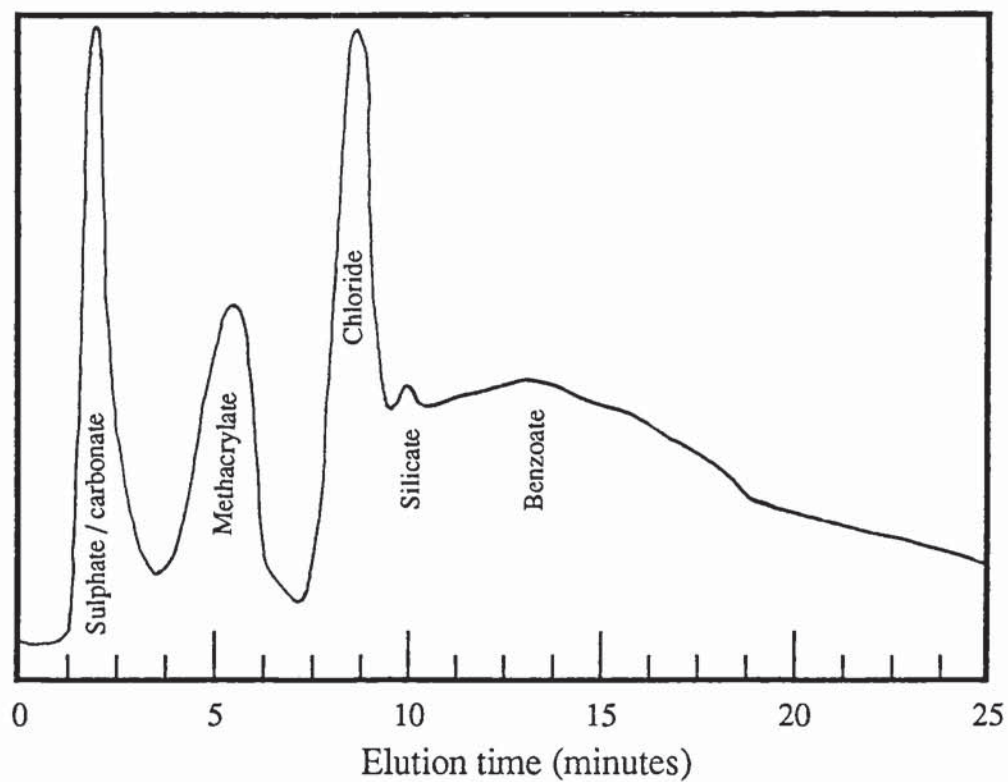
FIGURE 5.21

CHROMATOGRAM OF IONS EXTRACTED FROM 0.4 W/C RATIO 240 DAY CURED CEMENT

Elution time (minutes)
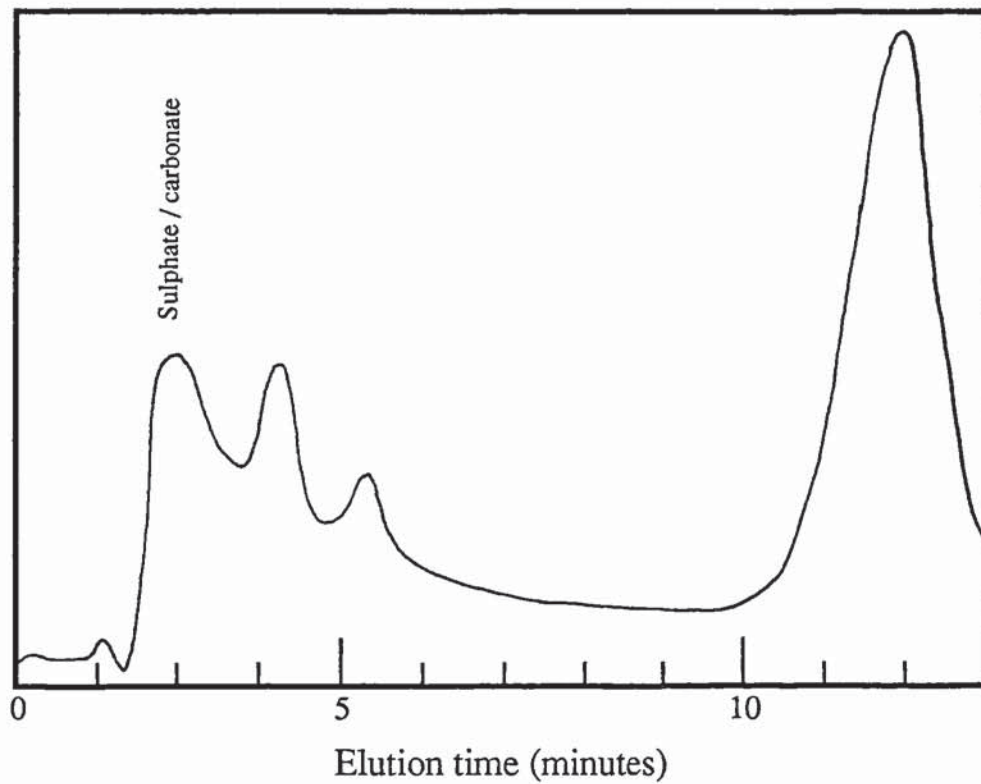
FIGURE 5.22

CHROMATOGRAM OF REFLUXED CEMENT (0.4 W/C RATIO 240 DAY)

Elution time (minutes)
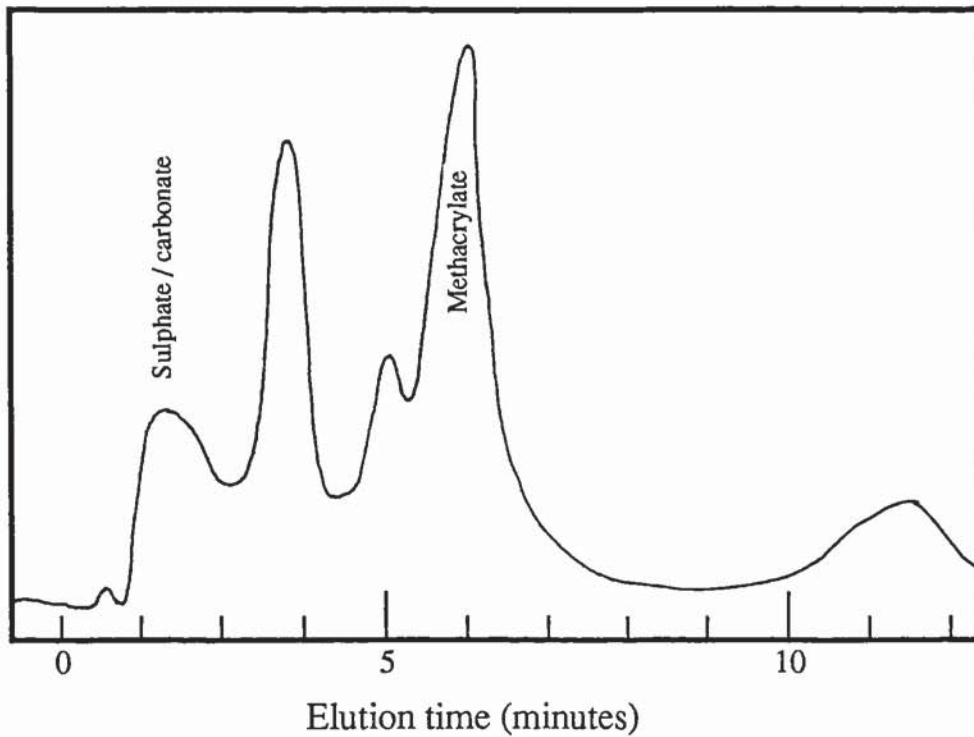
FIGURE 5.23

CHROMATOGRAM OF IONS EXTRACTED FROM 0.4 W/C RATIO 240
DAY CURED CEMENT WITH METHACRYLATE SPIKE

Elution time (minutes)
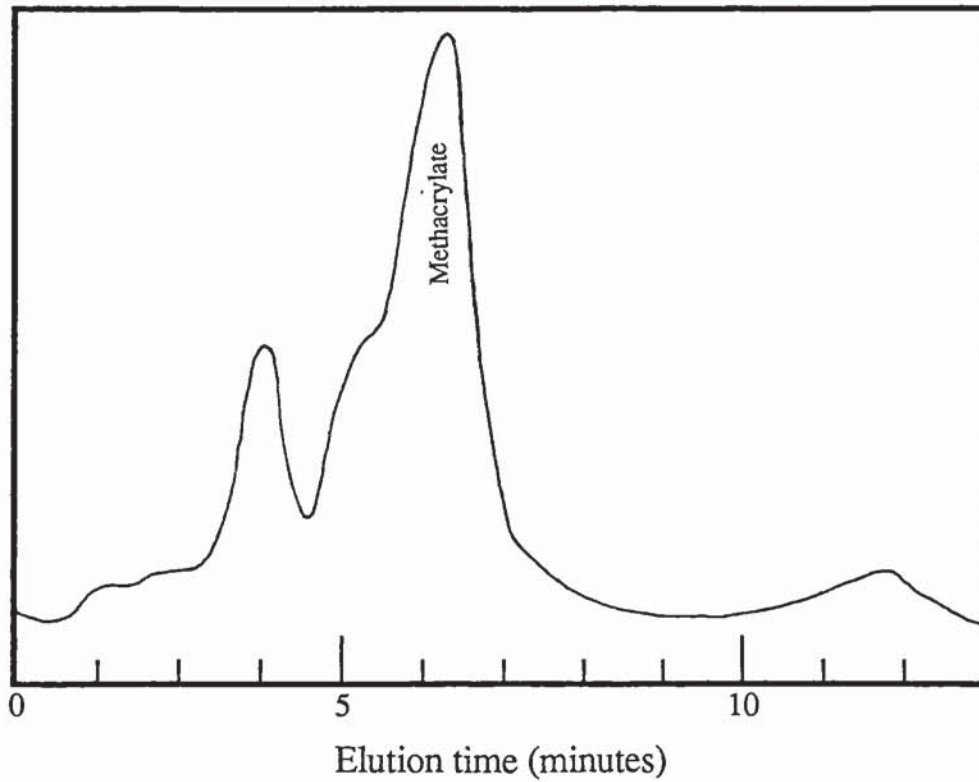
FIGURE 5.24

CHROMATOGRAM OF IONS EXTRACTED FROM POLYMER CEMENT
MADE WITH 0.4 W/C RATIO 240 DAY CURED CEMENT

Elution time (minutes)

177
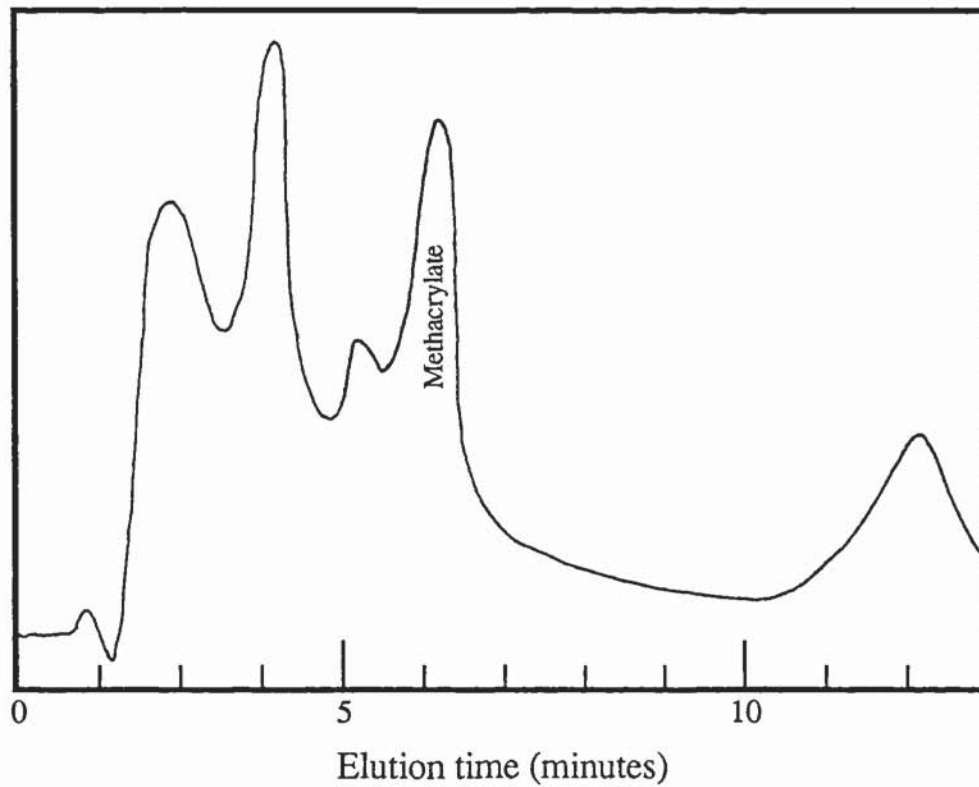
FIGURE 5.25

QUANTITATIVE MEASUREMENT OF METHACRYLATE
USING ION CHROMATOGRAPHY
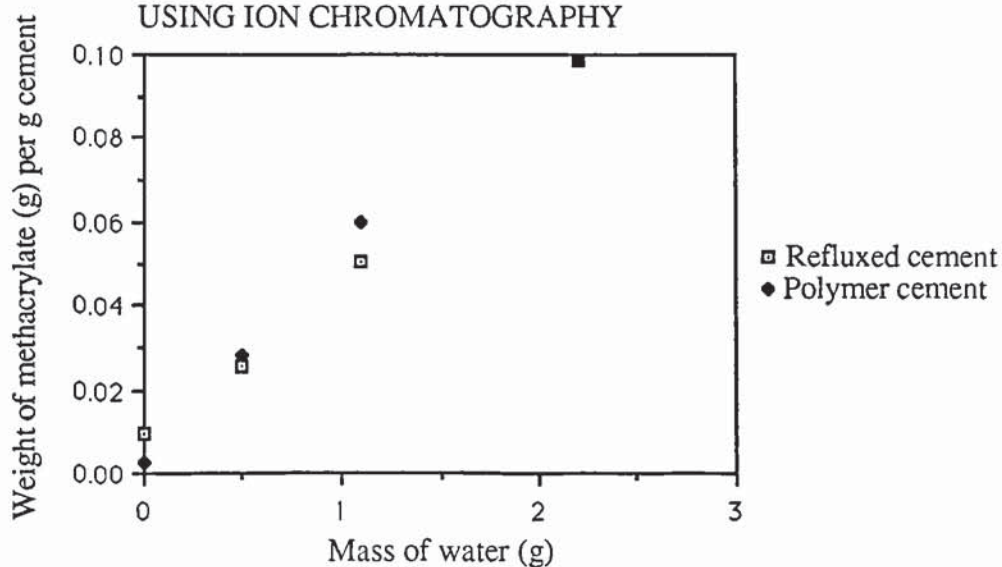
TABLE 5.3

METHACRYLATE PRODUCED VERSUS
ORIGINAL WATER CONTENT OF CEMENT
(5 g cement used in every case)

Mass of Water (g)	% of original moisture content	Mass of methacrylate per g cement (g/g)	
		Refluxed cement	Polymer cement
0	0	0.0095	0.0027
0*	0	0.0097	-----
0.5	25	0.0254	0.0278
1.1	50	0.0506	0.0599
2.2	100	0.0986	0.0990

** Transferred to polymerisation vessel immediately
after oven drying.*

FIGURE 5.26

DTA TRACES FOR POLYMER CEMENTS MADE WITH DIFFERENT
AMOUNTS OF WATER

Polymer cement using 5 g MMA,
5 g cement, 0 g water

530°C   700°C

Polymer cement using 5 g MMA,
5 g cement, 0.5 g water

Polymer cement using 5 g MMA,
5 g cement, 1.1 g water

460-570°C

210°C

Polymer cement using 5 g MMA,
5 g cement, 2.2 g water

Exothermal

Endothermal

TEMPERATURE

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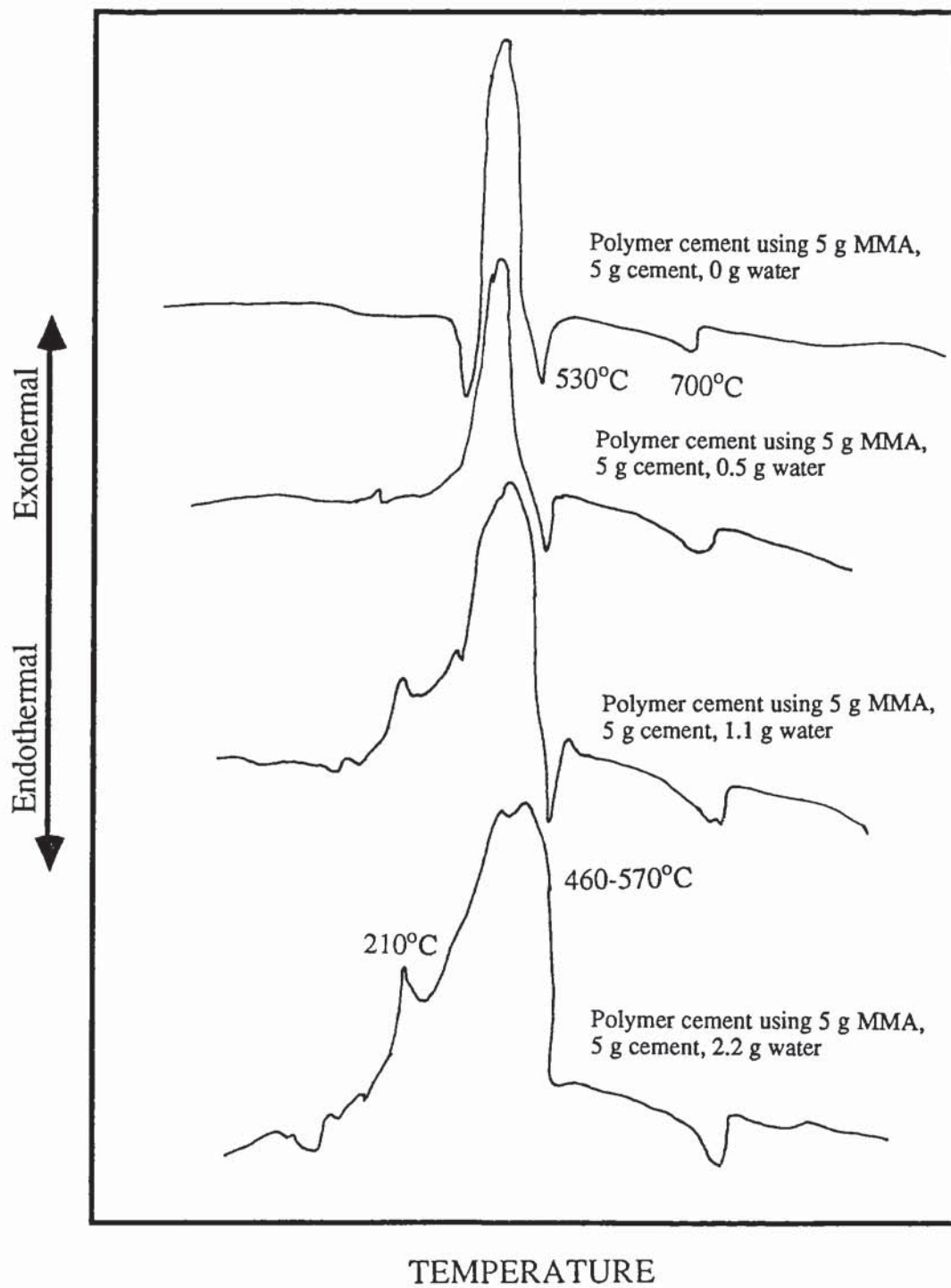
6 STUDIES OF THE INTERFACE BETWEEN CEMENTS AND POLYMERS

6.1 INTRODUCTION

When polymers are used in conjunction with cement systems, it is particularly important to establish the nature of the surface where they come into contact. Assessment of the cement surface presents a number of problems, not least that complete hydration of cement minerals is an extremely slow process, taking years to complete. The surface therefore changes in chemical composition and physical structure as hydration proceeds.

For the purposes of this project, the 'surface' is taken to mean both the surface of the solid mineral phases on fractured or machined surfaces, and those comprising the pore walls. A distinction may be made between interactions that directly affect the mineral composition and bonding of the cement as a whole and those that modify an existing mineral structure by surface interactions. Where polymer is added to hydrating cement, interactions take place not only with the hydrating minerals, but with ions in solution: on the other hand, resins and polymers used with cured cements interact primarily with hydrated phases and any remnants of the pore solution. This chapter deals with the latter of these.

Assessing the nature of the interface presents two major problems : - First, that it is hard to expose actual impregnated regions, and second that the amount of any interaction product is generally very low. These problems were tackled using several different specimen configurations, experimental and instrumental techniques.

6.2 PREVIOUS WORK

In studying adhesive interactions between phases it is of great importance to assess the nature of their interface. Hardened cement surfaces even at low W/C ratios are highly porous and permeable, allowing polymers to penetrate the adhesion surface to a greater or lesser extent. Mechanical interlocking therefore plays an important part in polymer adhesion. So long as the polymer has the ability to wet the cement surface and penetrate the outer parts of the cement structure, and can be polymerised there, strong bonding will occur between the two components.

The contribution that chemical bonding makes to the overall bond strength is hard to measure, since it is impossible to cause true interfacial failure, especially when the interface is not a uniform plane. In particular, the interface between an abraded cement and a polymer would be composed partially of the flat cement surface and partially of the area where the polymer touches the pore walls *(fig 1.1)*. However, in gathering evidence for chemical bonding the complications of mechanical testing may be avoided by searching for interfacial reaction products. It should be noted that evidence for compound formation at an interface is not necessarily proof of bonding; the compound must have the ability to join the two components, and not just be an elimination product between the two.

On the other hand, the addition of a very small proportion of appropriate functional groups to a polymer chain can promote adhesion, the amount of reaction product being too small to isolate *(ref 74)*.

6.2.1 SURFACE WATER

Sergi *(ref 125)* and Thomas *(ref 126)* showed that hydrated cements exposed to different humidity environments show differences in their equilibrium weights. This is attributable to the amount of water present in the structure of the cement.

Oven-dried cement surfaces are never completely free from water, and adsorb moisture quickly to reach equilibrium with the humidity to which they are exposed. Polymer therefore meets a highly alkaline surface with adsorbed water present. This feature is very important to chemical bonding between cements and polymers, since the cement surface will be reactive particularly to hydrophyllic acidic species, or species that react in the presence of water (or an alkaline environment) causing bonding or polymerisation. In addition, calcium, sodium, potassium and aluminate may be derived from cements as

water-soluble ions. Polymers that co-ordinate with these ions in an alkaline environment can have the potential to bind the ions and cause the mixture to gel *(refs 120 & 121)*.

6.2.2 SURFACE ANALYSIS TECHNIQUES

With the realization that surface interactions play an important part in many chemical processes, there has been an increasing interest in surface analysis. Current high-vacuum technology has allowed the development of a number of instrumental techniques for this purpose. The most well-established of these is SEM, producing a visual image of surface topography. Other techniques have been developed including the following *(ref 127)* : -

1) Attenuated total reflection infrared spectroscopy (ATR). This yields chemical information about the bulk surface by measuring absorption of infrared radiation over a range of wavelengths, and does not require vacuum apparatus.

2) Secondary ion mass spectrometry (SIMS). This involves destructively bombarding the surface with an ion beam and sorting the ions produced in a mass spectrometer. It is relatively expensive and the results are hard to interpret, yet allows depth profiling and the production of much chemical information.

3) Auger electron spectroscopy (AES). This technique can be used to map visually the distribution of a desired elements on a surface by bombardment with monoenergetic X-rays, yielding electrons by the auger process *(see 3.3.7)*. The process is destructive in the case of organics and gives little chemical information.

4) X-ray photoelectron spectroscopy (XPS). This is a technique highly sensitive to the chemical environment of atoms, yielding information from the first few nm of the surface *(see 3.3.7)*.

This last technique was used extensively in this work because of the nature of the information it produces. A considerable amount of information has been published concerning the detection of elements and their chemical environments using XPS. A good account is given by Wagner *(ref 128)*, indexing XPS peaks from a comprehensive range of organic and inorganic compounds. The text was used extensively in this work.

6.2.2.1 STUDY OF CEMENTS USING XPS

XPS has found only limited use in the study of cements, possibly because of the specimen preparation, rarity and cost of the apparatus, and nature of the data produced; i.e. in most studies of cements there is no need to determine the chemistry of the actual surface rather than the bulk surface. Nevertheless, XPS has been used in hydration studies. Regourd *(ref 129)* interpreted changes in XPS spectra of C_3S, β-C_2S and C_3A on hydration in terms of the physical and chemical nature of the hydrates. By plotting Ca/Si and Al/Si ratios against time, three stages of hydration were recognized in the silicates, and two in the aluminate.

6.2.2.2. STUDY OF POLYMERS USING XPS

Solid organic polymers are highly suited to examination by XPS, yielding chemical information without significant destruction of the polymer surface. Surface processes are detectable, for example oxidation of C-H and C-C bonds to C=O. Also, studies of contamination and cleaning ability of different solvents have been conducted with a view to bio-medical applications of polymers *(refs 127 and 130)*.

6.3 DISCUSSION

6.3.1 MICROSCOPIC EXAMINATION OF INTERFACIAL REGIONS

Thin sections of the interface between PMMA and cements presented problems in identifying the actual interface itself, since PMMA proved to be featureless in plane polarized light and crossed nicols. Specimens were prepared primarily for impregnation studies, making the interface particularly difficult to identify in thin section, being diffusional rather than planer. Polished specimens before sectioning show the area of impregnation as a darker zone around the outside of cement specimens *(fig 6.1)*. Evidence of bulk reactions may be seen within these zones, and are discussed later in *chapter 8*. No interfacial reaction products were detectable in thin section.

Epoxy resin/cement interfaces are partially diffusional, penetration being greater with increasing W/C ratio *(fig 6.2)*. Viewed in thin section, there was no indication of reaction products. Some striking features were visible under crossed nicols, characterized by light coloured bands radiating from points on the cement surface *(fig 6.3a)*. These were attributed to stress concentrations in the resin during curing. Careful examination also showed tiny bubbles in the resin, adjacent to the cement surface, lighter coloured bands also radiating from these *(fig 6.3b)*. Since both resin and hardener are viscous on mixing, it is likely that the bubbles represent entrapped air rather than evidence of some gaseous reaction product. A physical effect of these could be to provide interfacial defects promoting disbonding of the polymer.

6.3.2 CHARACTERIZATION OF POLYMER SURFACES BY XPS

Surfaces of PMMA were examined by survey spectra and high resolution spectra in the regions of their constituent elements. For PMMA this was only carbon and oxygen, hydrogen being undetectable by the technique *(fig 6.4a&b)*.

6.3.3 CHARACTERIZATION OF CEMENT SURFACES BY XPS

A number of cement surfaces were examined using XPS, the samples having been prepared with different W/C ratios, cure time and dried by different techniques. Survey spectra, together with high resolution spectra were taken in the regions of the major cement elements carbon, silicon, aluminium, oxygen and calcium. Data processing involved scaling each spectrum to have the major C_{1s} peak at 284.6 eV. In certain cases synthesizing individual closely-spaced peaks from larger composite peaks was done,

with the aid of computer methods. A typical survey XPS spectrum with the peaks indexed is shown in *figure 6.5*. The three wide-scan spectra *(fig 6.6a-c)* represent widely differing W/C ratios (0.4 and 0.7), and different surface preparation techniques (machined and fractured). High resolution peak shapes for the common elements in cements are displayed as follows : - O_{1s} *(fig 6.7a&b)*, $Ca_{2p3/2}$ *(fig 6.8a&b)*, C_{1s} *(fig 6.9a&b)*, $Si_{2p3/2,2p1/2}$ *(fig 6.10a&b)* and Al_{2p} *(fig 6.11a&b)*.

On all the cement samples there were no significant peak shifts or relative height variations for the element regions examined, suggesting identical chemical environments for the atoms on the surfaces examined. This was quite a surprising result considering the widely differing W/C ratios and cure times examined. Fracture and machined surfaces also proved indistinguishable. Thus over the areas irradiated (70-100 mm^2) chemical differences between minerals become averaged to produce surfaces homogeneous on this scale.

Figure 6.12 shows the C_{1s} region of a cement fracture surface, specimens having been examined immediately after fracture. Computer methods have been used to synthesize four peaks from which the experimental spectrum may be reproduced. Ion etching has been used to reveal the composition just beneath the surface. 40 and 100 minutes etch time were used to produce the middle and lower spectra, representing only a few nm etch in each case. It would seem from the relative peak areas that the environments corresponding to 281.7 and 284.6 eV are more abundant in the uppermost layers of the surface, corresponding in the literature to carbides and C-H environments respectively. Peak synthesis in the C_{1s} regions for evaporation surfaces and corresponding fracture surfaces show far less of these environments on evaporation surfaces *(fig 6.13, 6.14 and table 6.1)*. This suggests that the surface is partially contaminated with carbon-containing compounds from the atmosphere, a peak at this position being found in most spectra of any composition, prepared in air. This peak is gradually removed by ion etching (284.6 eV peak). However, the chemical environment associated with the 281.7 eV peak similarly diminished could only be identified from the literature as carbide, this seeming an unlikely compound to still be in hydrated cements.

6.3.4 EFFECT ON SURFACE CHEMISTRY OF DIFFERENT DRYING TECHNIQUES

Drying specimens by heating, vacuum or alcohol replacement resulted in only minor differences in the position and size of the C_{1s} peak. However, the K_{2p} peak was

enhanced on oven-dried specimens. This was not so for specimens dried in a vacuum or by alcohol replacement *(figs 6.15 & 6.16)*.

Potassium in the form of KOH is highly soluble in water, particularly at elevated temperatures. On oven drying it would seem that potassium is transported through the pore system from the centre of the specimen towards the evaporation surface where it is deposited on evaporation of the water *(table 6.1)*. Examination of peaks in the sodium region did not clearly show this effect; however there was about eight times as much potassium in the OPC used than sodium *(table 3.1)*. Alcohol replacement does not appear to show this effect. Since it is water replacement that causes drying this suggests that there is not the same water flow through the pore system as there is on oven-drying, KOH being insoluble in isopropanol. Vacuum drying too does not seem to produce this flow, either because a) drying times are slower and solubility of KOH in colder water lower, or b) transportation of water in the vapour phase occurs.

6.3.5 CHARACTERIZATION OF CEMENT ADHESION SURFACES

Cement adhesion surfaces were studied in two ways: - First, cements with PMMA bonded to them had the polymer removed by dissolution with chloroform. This should leave ionically bonded cement/polymer reaction products on the revealed cement surface *(see 5.3.5)*. Second, cement surfaces were refluxed with MMA, some subsequently being washed with chloroform. Spectra of all surfaces showed features attributable to reaction products, though this was seen in the carbon region alone. Two lines of evidence suggested this conclusion : -

1) If peak areas (related to elemental abundances) are determined for all the elements on the surfaces of interest, there is a slight rise in the amount of carbon on MMA-refluxed surfaces. PMMA adhesion surfaces revealed with chloroform show even larger amounts of carbon. The latter were washed for six hours with pure chloroform, an excellent solvent for PMMA. Thus it seems unlikely that the carbon residues are simply incompletely dissolved polymer. Also, the chlorine region of the spectrum was also investigated to see if there were any traces of chloroform left, the amount found being negligible. These observations alone suggest the presence of a chloroform-insoluble carbon-containing compound formed between cement and polymer, this being polymeric rather than monomeric, since only a slight increase in carbon was noted with MMA-refluxed cement surfaces. Two 0.4 W/C ratio cements were examined in this respect, 28 day cure *(fig 6.17a-d)* and 90 day cure *(fig 6.18a-d)*.

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2) Carbon regions of the spectra were examined in detail by simple comparison*(figs 6.19a-d)* and comparison following computer-synthesis of peaks*(6.20a-d)*. New peaks and different relative abundances (compared to pure cements) were noted on PMMA adhesion and MMA-refulxed surfaces. Peak identification by reference to tabulated data for different compounds *(ref 130)* proved inconclusive, since some of the compounds suggested by this approach seemed highly unlikely. The shapes of the actual spectra were convincingly synthesized by four major peaks. The major carbon peak at 284.7 eV was attributed to C-H and C-C from atmospheric contamination as well as from the actual surface. The 289.1 eV peak was consistent with carbonate, C-O appearing at 286.4 eV. However, as in *6.3.3* the only tabulated compounds emitting at 283.1 eV were carbides, the possibility of this being somewhat remote.

6.3.6 CHARACTERIZATION OF INTERFACIAL REACTION PRODUCTS

Adhesion surfaces and refluxed surfaces

A possible interfacial reaction product was characterized, this being calcium methacrylate *(fig 6.21a&b)*. Survey spectra, together with high resolution spectra, were taken in the O_{1s}, $Ca_{2p3/2}$ and C_{1s} regions. Peaks in the C_{1s} region at 284.7 and 283.4 eV attributable to C-H and the 'carbide' environment, are relatively large in calcium methacrylate compared to pure cements. Since these peaks are relatively enlarged on cement adhesion surfaces and MMA refluxed surfaces, this could suggest the presence of the substance. However, calcium methacrylate also shows several minor carbon environments not conclusively identified on adhesion and refluxed surfaces. Calcium methacrylate may not be the only possibility for reaction products on adhesion surfaces since benzoates from benzoyl peroxide may also be present *(see chapter 5)*. However, since refluxed cements contain the environments also seen on adhesion surfaces, benzoyl peroxide cannot alone be responsible. It is also possible that benzoyl peroxide and calcium methacrylate are indistinguishable, further work being required to find out.

Fracture surfaces of PIC

MMA-impregnated cement has an XPS spectrum dominated by the C-H and C-O environments of the polymer *(fig 6.22)*, with no clear indication of calcium methacrylate. From the work in *chapter 5*, it seems highly likely that calcium methacrylate is present in PIC. This however, would require some dissolution technique similar to that used with polymer cements to reveal it.

6.3.7 THE ROLE OF WATER AT THE POLYMER/CEMENT INTERFACE

Water is present unavoidably on all cement surfaces even after drying. Although little free water remains after drying, a significant amount of adsorbed water is left. Monomers and polymers therefore come into contact with this water when they meet the cement surface. In many circumstances this has no effect, but with some monomers or polymers could have either beneficial or detrimental effects.

Actual bonding in the sense of gelling was achieved when moistened polymethacrylic acid was mixed with common metal oxides found in cements. Those of calcium, sodium and potassium caused gelling, all others tried did not. The gels did not retain their properties on oven-drying, becoming weak and crumbly. Evidently, water was necessary to cause gelling, probably by mobilizing the ions allowing co-ordination, salt formation and hydrogen bonding to occur. As discussed earlier, gelling of this kind has given rise to the development of dental silicate cements, bone bonding agents and macrodefect-free cements.

Chapter 5 examined reactions taking place between cements and MMA. The possibility of alkaline hydrolysis of the ester to form methacrylic acid and subsequently calcium methacrylate was discussed. This is only a 'useful' reaction if the calcium methacrylate becomes incorporated into the growing polymer chains. But since water extracts of polymer cements*(see 5.3.6.4)* contains almost as much calcium methacrylate as refluxed cements, then we can presume that only a small percentage of the ester molecules converted to the acid become incorporated in the polymer. However, as Souheng *(ref 74)* discusses, the incorporation of 0.1 to 0.001% functional groups can noticeably assist the adhesive properties of a polymer. The process may also occur on pore walls, further work being required to ascertain this.

6.4 SUMMARY AND CONCLUSIONS

Experiments were conducted into the physical and chemical nature of the interface between polymers and cement. Both polymer and cement were characterised, together with possible reaction products. Evidence for interfacial reaction products was sought in a number of ways : -

1) Flat adhesion surfaces were prepared, and polymer bonded to them. Solvents were used to reveal regions at or near the interface. Spectroscopic and microscopic techniques were used to assess the surface.

2) Additional information was obtained by sectioning adhesive interfaces and polymer impregnated cements to assess the depth of penetration, thickness of any reaction layers and hence extent of the interface. Various forms of photomicroscopy were used to this end.

Techniques included optical microscopy, this yielding information on the physical nature of the polymer/cement interface. Of particular importance was the use of X-ray photoelectron spectroscopy, this allowing assessment of the chemical nature of surfaces.

It was concluded that : -

1) Epoxy resin develops internal stresses on curing.

2) There was no clear microscopic evidence of reaction products between polymer and cement in either MMA/PMMA or epoxy resin.

3) There seems little difference in the chemical nature of cement surfaces of differing W/C ratio and cure time so long as the same OPC and drying technique is used.

4) Oven drying cements causes the most water-soluble ions to migrate towards evaporation surfaces. This is particularly noticeable for potassium.

5) MMA-refluxed cements and polymer adhesion surfaces show carbon-containing compounds insoluble in a good monomer/polymer solvent. It was not possible to determine the nature of these compounds.

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FIGURE 6.1
POLISHED SURFACE OF CEMENT / PMMA
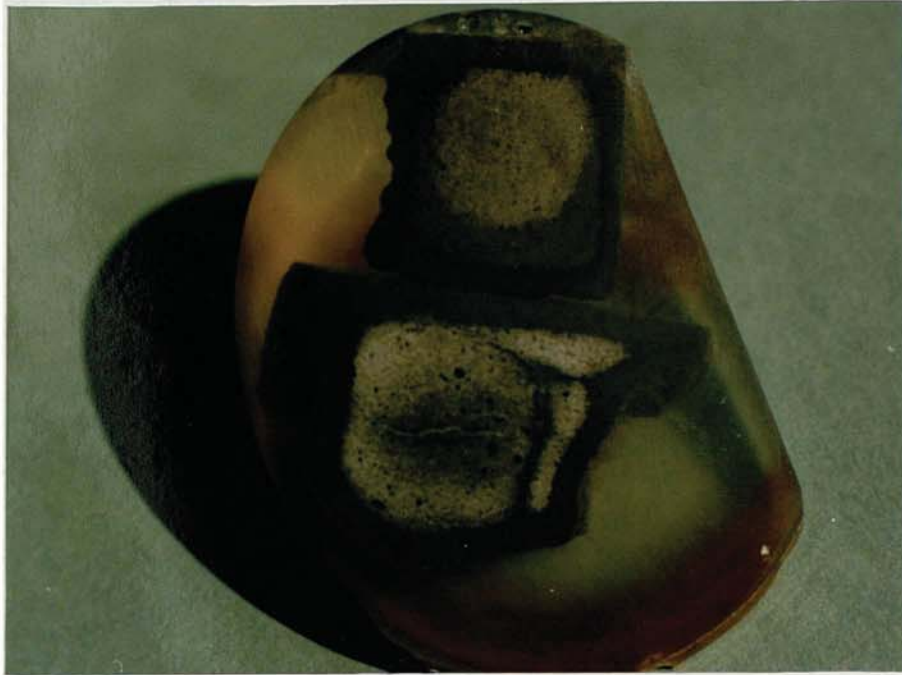
Note darker zone of polymer impregnation. Horizontal dimension = 50 mm.

FIGURE 6.2
POLISHED SURFACE OF CEMENT / EPOXY RESIN

Note darker zone of polymer impregnation. Horizontal dimension = 20 mm.

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FIGURE 6.3a
STRESS CONCENTRATIONS IN EPOXY RESIN (Thin section)
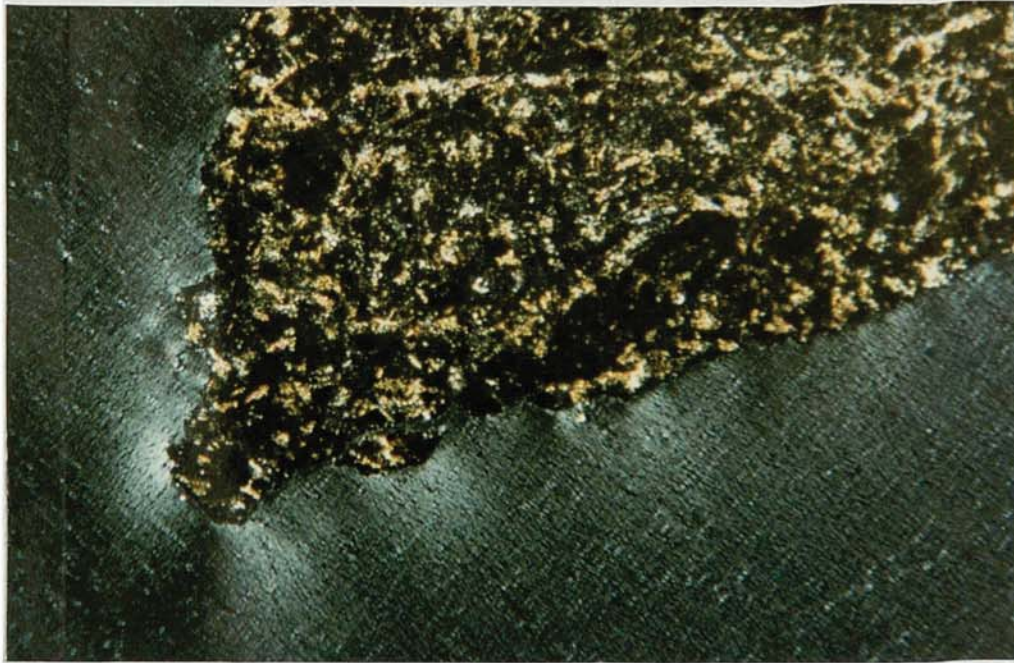
Note radiating lighter bands indicating stress concentration.
Horizontal dimension = 5 mm.

FIGURE 6.3b
BUBBLES IN EPOXY RESIN ON CEMENT ADHESION SURFACE (Thin section)
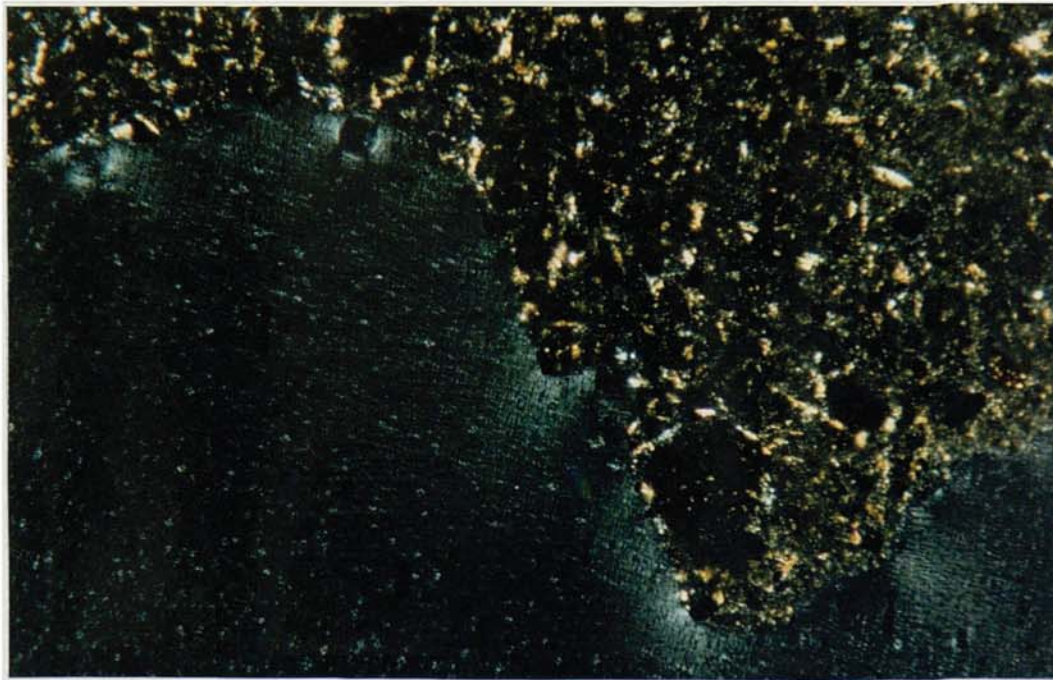
Note radiating lighter bands indicating stress concentration.
Horizontal dimension = 2 mm.

FIGURE 6.4a
SURVEY SPECTRUM OF PMMA
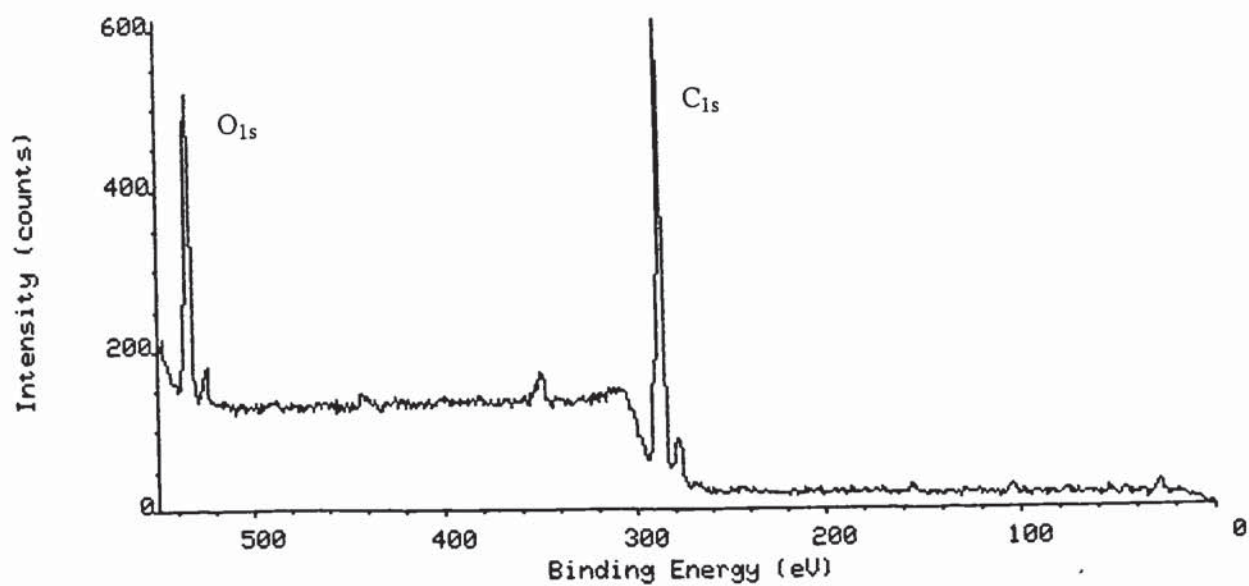
FIGURE 6.4b
HIGH RESOLUTION SPECTRUM OF PMMA (C$_{1s}$)
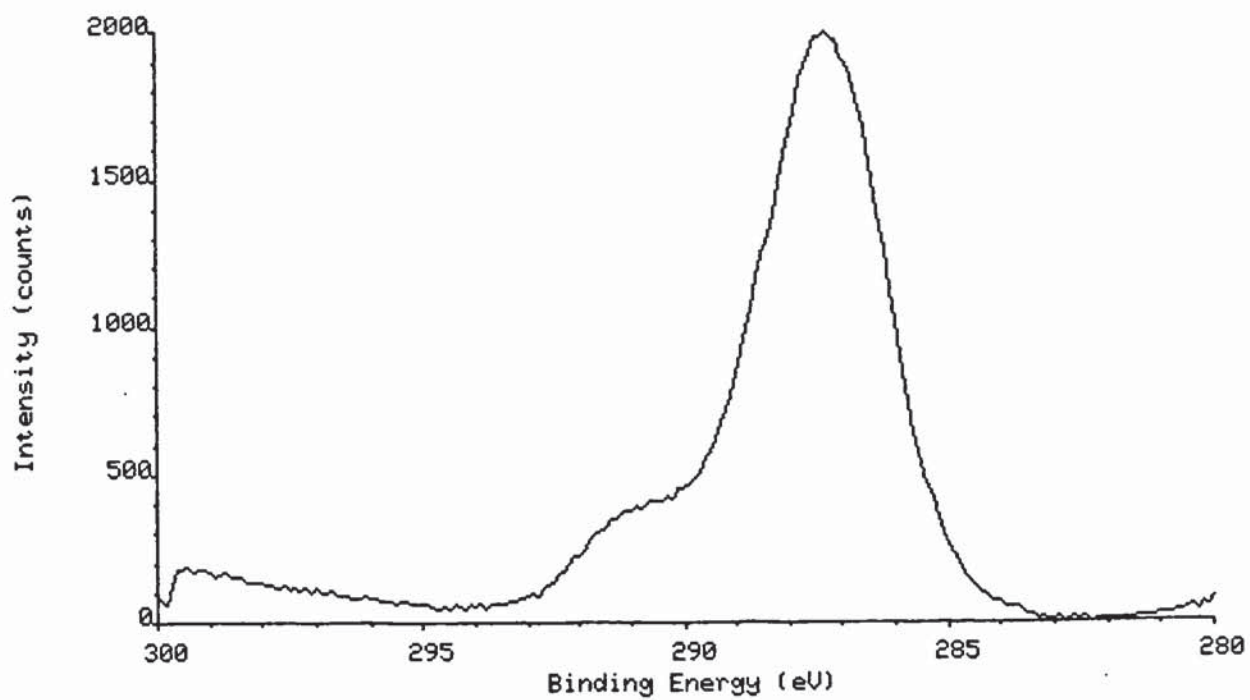
FIGURE 6.5

XPS SPECTRUM OF A TYPICAL CEMENT (0.4 W / C RATIO, 90 DAY CURE)
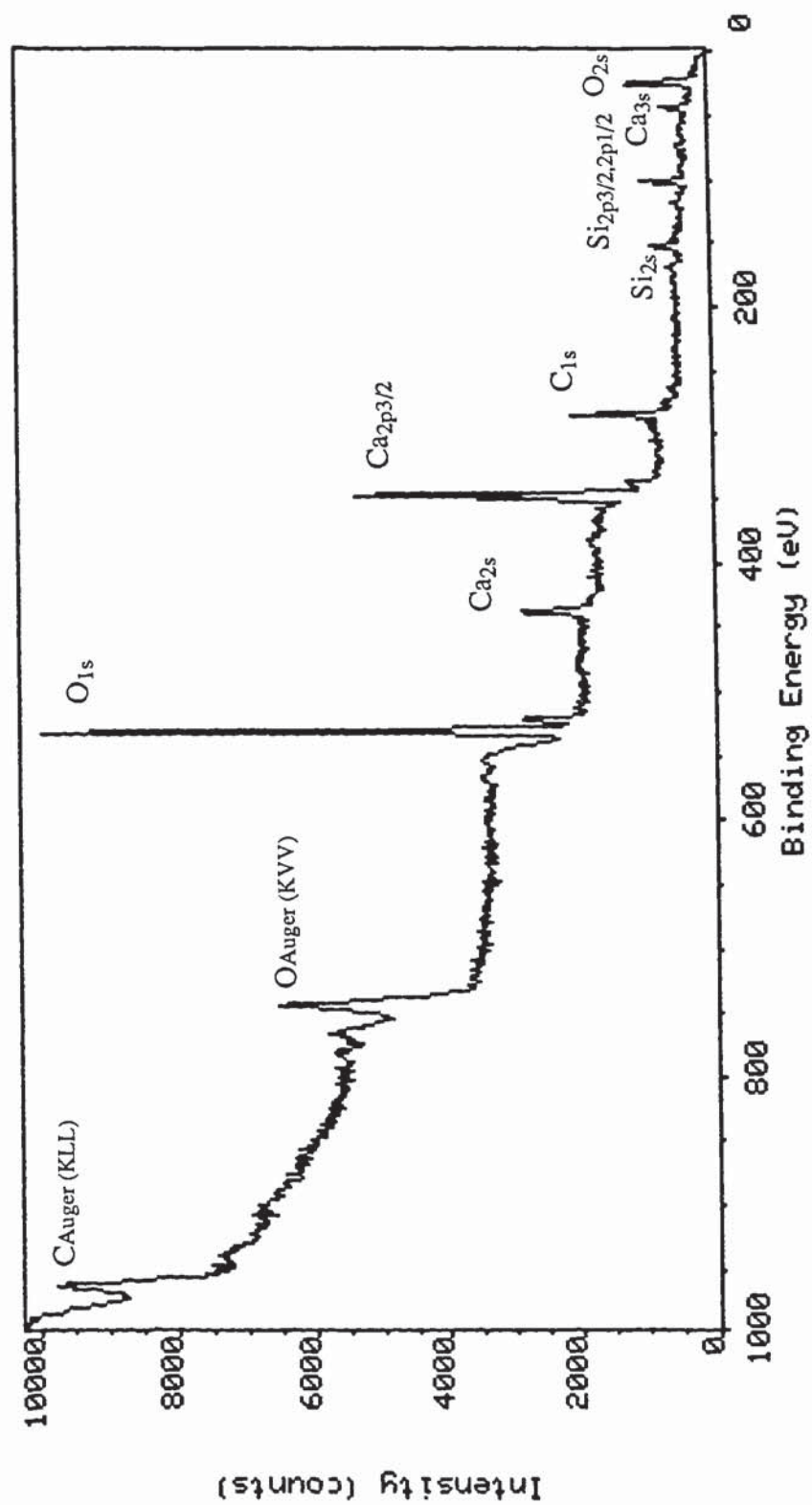
FIGURE 6.6

XPS SPECTRA OF MACHINED AND FRACTURED CEMENT SURFACES

a) 0.4 W / C RATIO, 28 DAY CURE, FRACTURED

b) 0.7 W / C RATIO, 28 DAY CURE, FRACTURED

c) 0.4 W / C RATIO, 90 DAY CURE, MACHINED
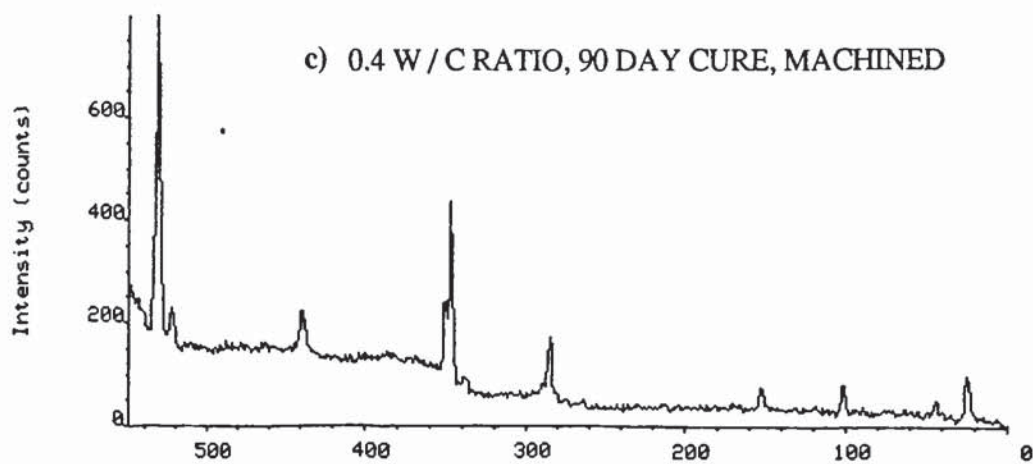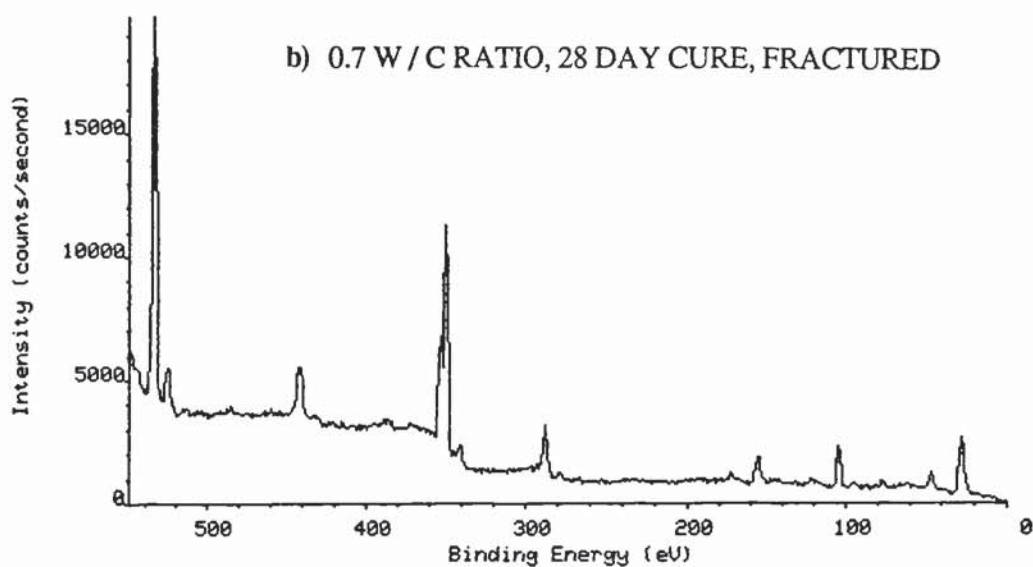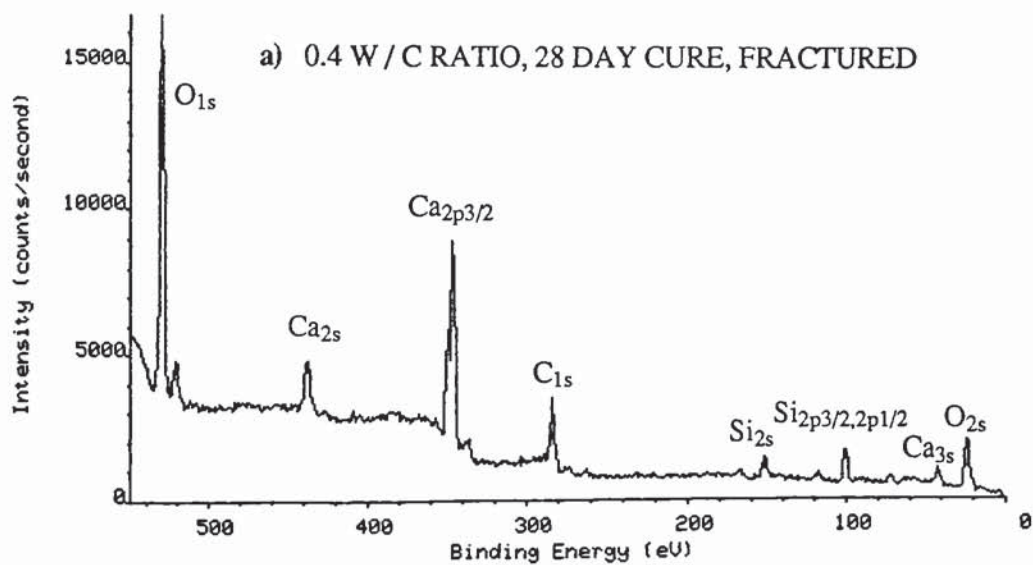
FIGURE 6.7a
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN O_{1s} REGION
W / C RATIO = 0.4, 28 DAY CURE
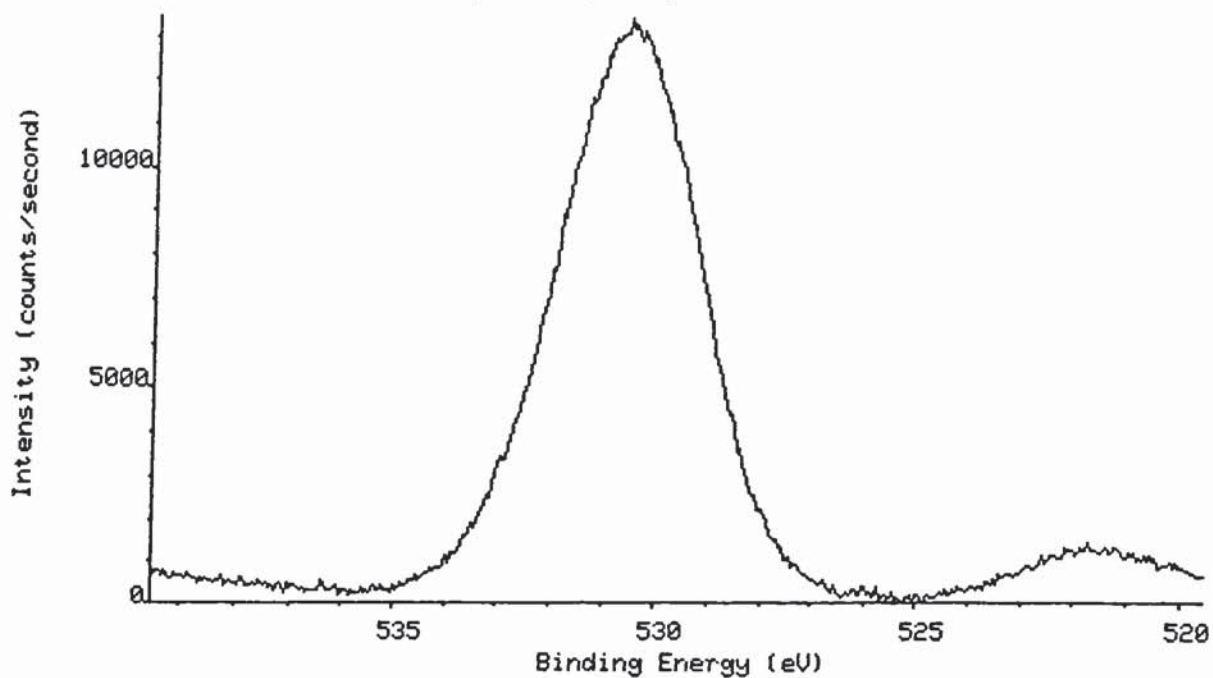
FIGURE 6.7b
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN O_{1s} REGION
W / C RATIO = 0.7, 28 DAY CURE

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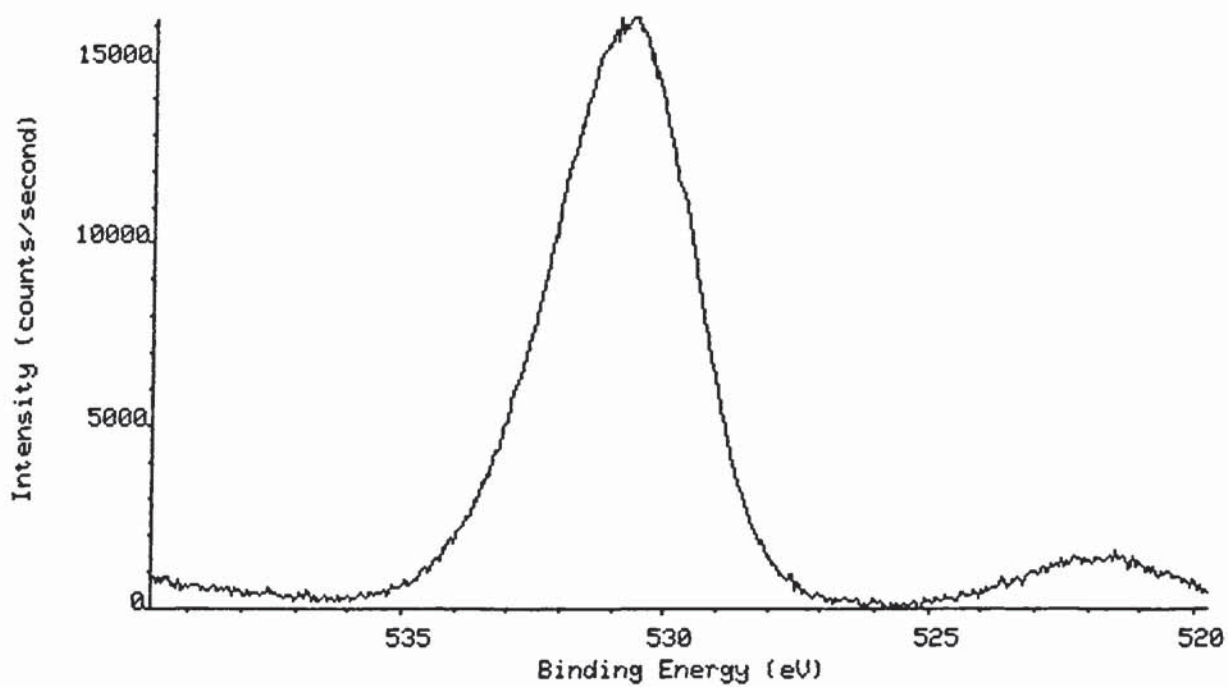
FIGURE 6.8a
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN $Ca_{2p3/2}$ REGION
W / C RATIO = 0.4, 28 DAY CURE
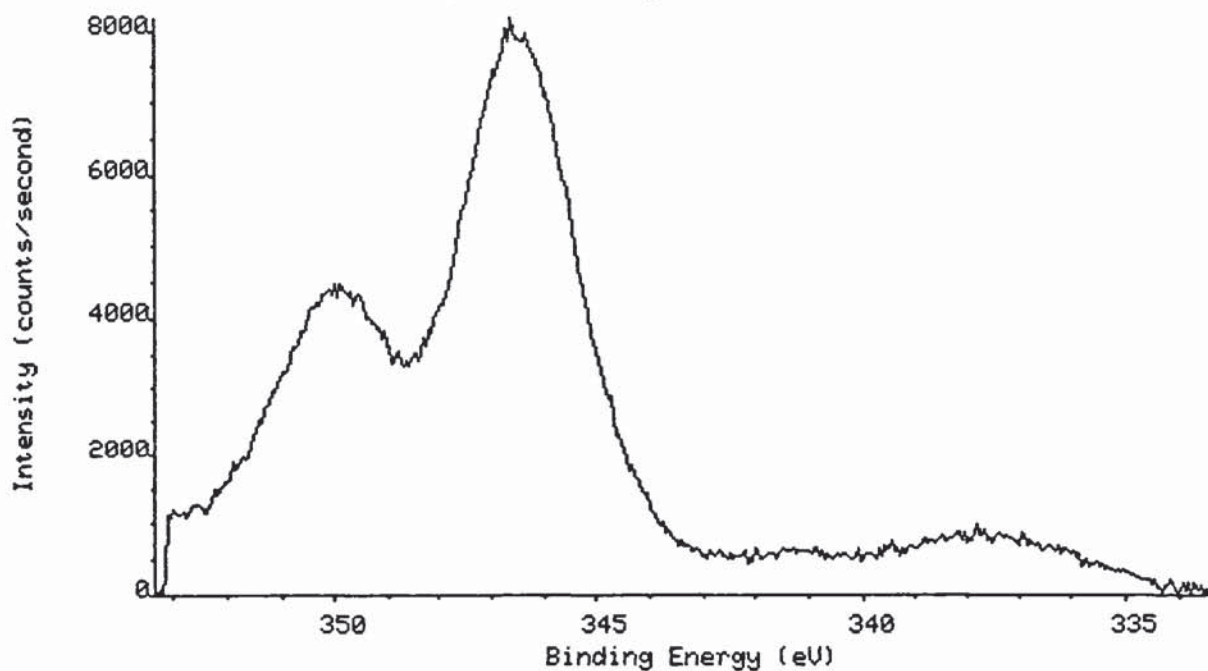
FIGURE 6.8b
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN $Ca_{2p3/2}$ REGION
W / C RATIO = 0.7, 28 DAY CURE
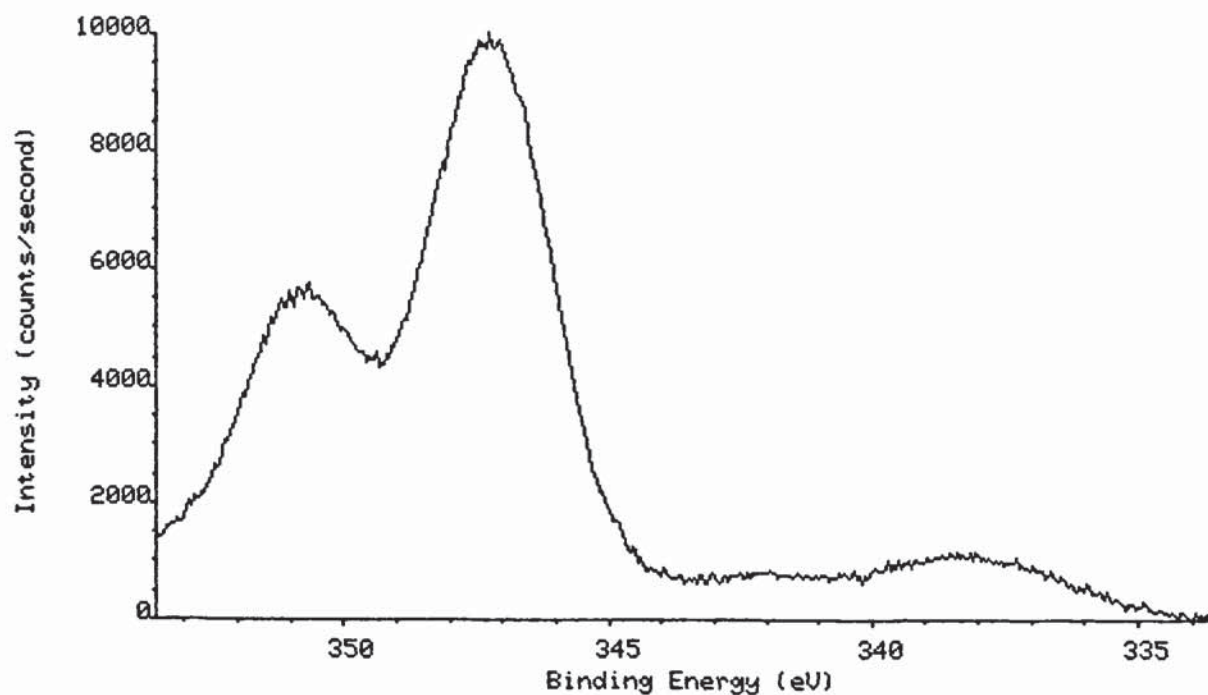
FIGURE 6.9a
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN C_{1s} REGION
W / C RATIO = 0.4, 28 DAY CURE
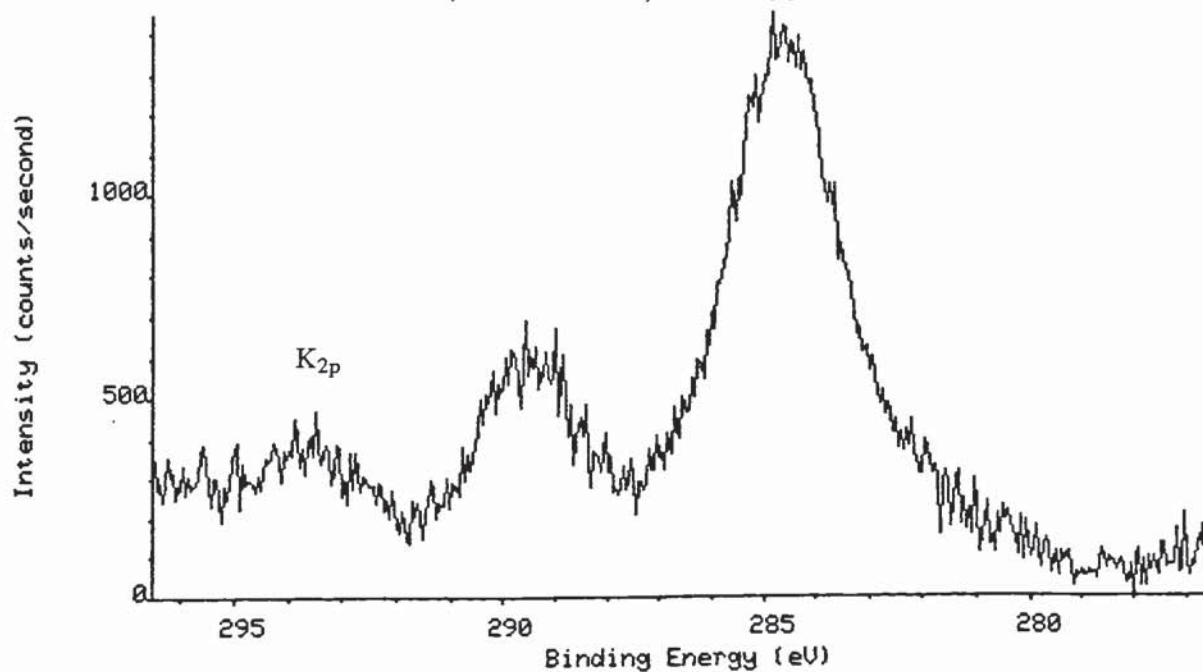
FIGURE 6.9b
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN C_{1s} REGION
W / C RATIO = 0.7, 28 DAY CURE

197
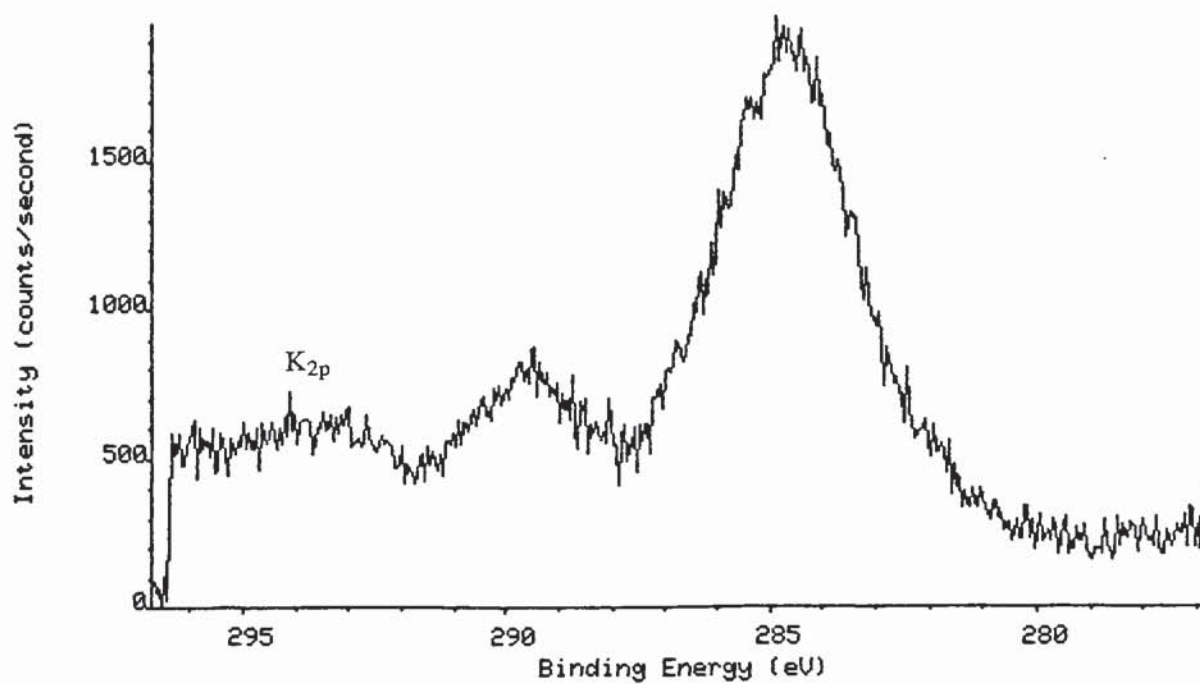
FIGURE 6.10a
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN $Si_{2p3/2,2p1/2}$ REGION
W / C RATIO = 0.4, 28 DAY CURE
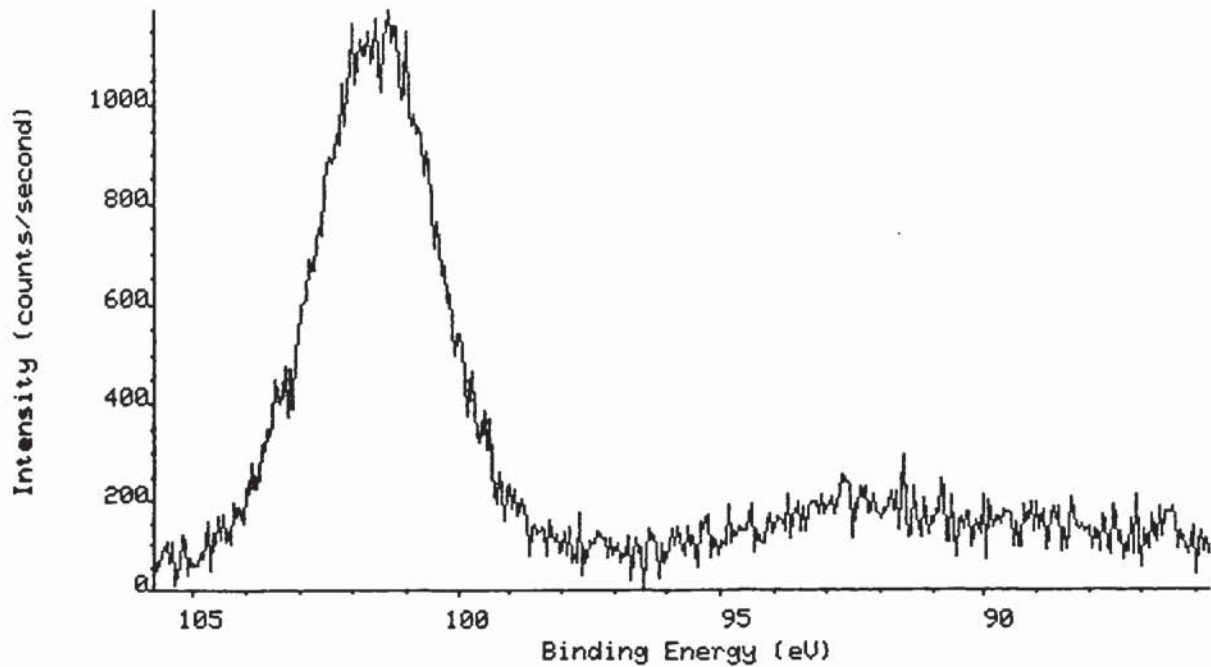
FIGURE 6.10b
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN $Si_{2p3/2,2p1/2}$ REGION
W / C RATIO = 0.7, 28 DAY CURE

198
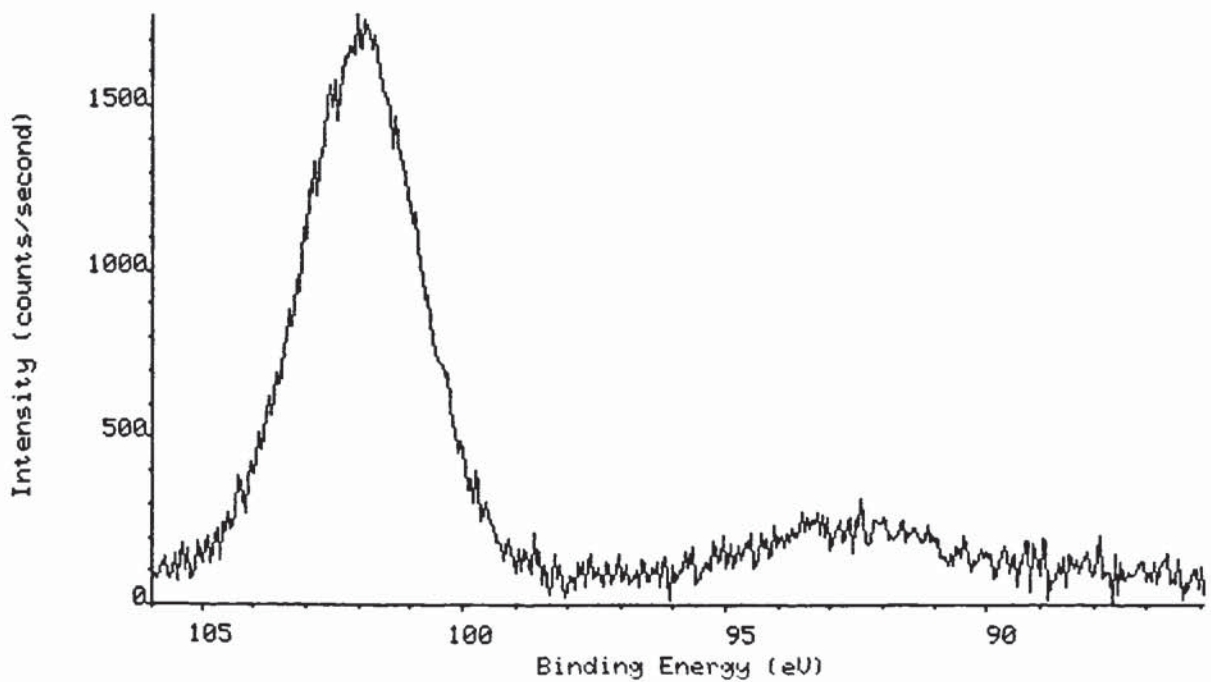
FIGURE 6.11a
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN Al_{2p} REGION
W / C RATIO = 0.4, 28 DAY CURE
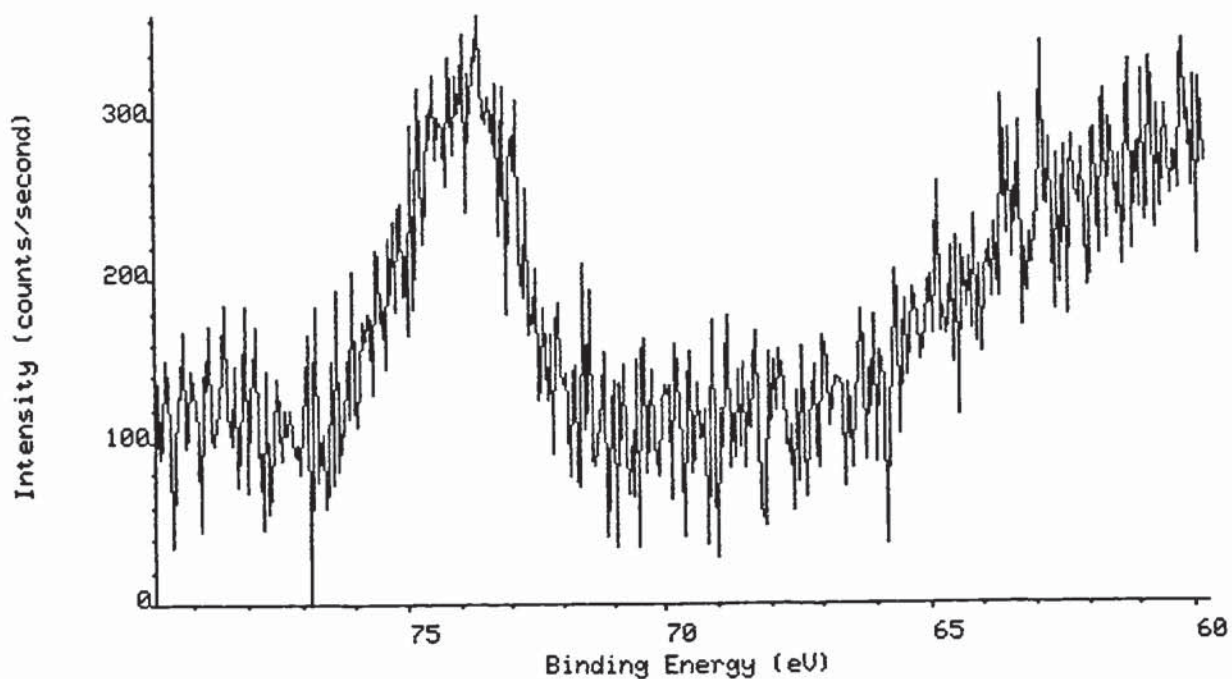
FIGURE 6.11b
XPS SPECTRUM OF MACHINED CEMENT SURFACE IN Al_{2p} REGION
W / C RATIO = 0.7, 28 DAY CURE

199
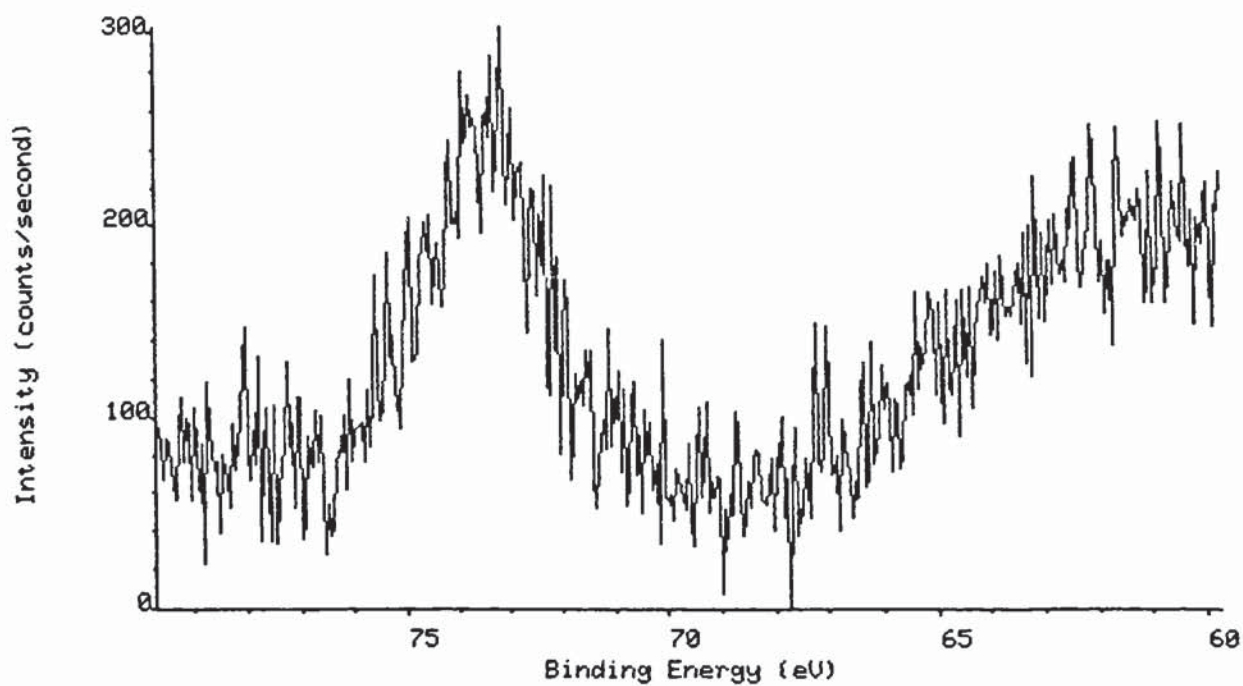
FIGURE 6.12
COMPOSITION OF THE UPPER LAYERS OF A CEMENT SURFACE
(C_{1s} REGION)

FRACTURE SURFACE UNETCHED

Fit: 1.3

100% Intensity:			973.		
100% Area			41020.		

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	C-CAR	281.7	76.6	2.0	38.2
GAUSS	C-H	284.6	98.3	2.0	49.1
GAUSS	C-O	286.0	11.3	1.2	3.4
GAUSS	CAR	283.3	27.8	1.3	9.0
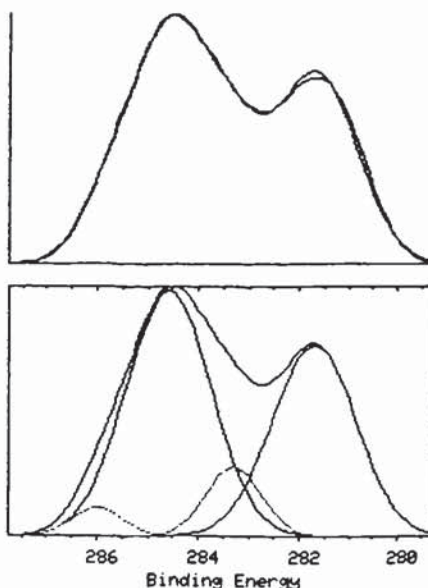
FRACTURE SURFACE AFTER
40 MINUTES ETCHING

Fit: 2.6

100% Intensity:			931.		
100% Area			40511.		

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	C-CAR	281.6	51.0	2.1	24.6
GAUSS	C-H	284.6	95.0	2.1	46.0
GAUSS	C-O	286.3	29.2	1.6	11.3
GAUSS	CAR	283.3	41.5	1.6	16.1
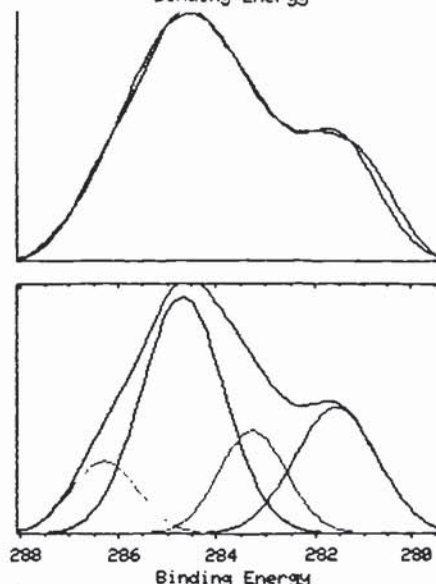
FRACTURE SURFACE AFTER
100 MINUTES ETCHING

Fit: 1.5

100% Intensity:			577.		
100% Area			24482.		

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	C-CAR	281.9	31.5	1.9	14.8
GAUSS	C-H	284.6	86.6	1.9	40.9
GAUSS	C-O	286.3	37.7	2.0	18.7
GAUSS	CAR	283.2	54.1	1.9	25.5
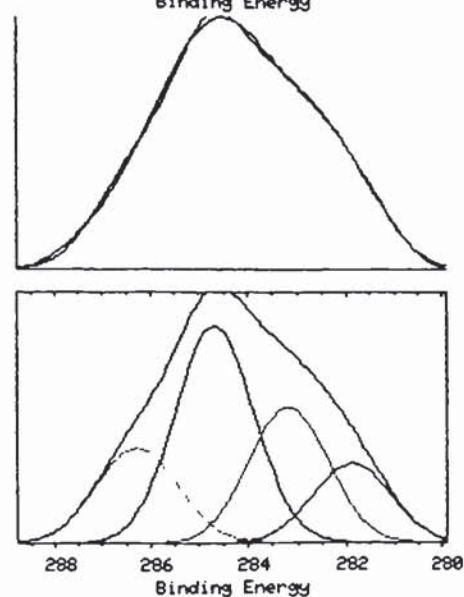
FIGURE 6.13
XPS SPECTRUM OF FRACTURED CEMENT EVAPORATION SURFACE
(C_{1s} region) W / C RATIO = 0.4, 90 DAY CURE

Fit: 1.4

100% Intensity: 1232.
100% Area   46531.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	C-CAR	281.7	37.9	1.6	16.9
GAUSS	C-H	284.6	78.7	1.6	35.1
GAUSS	C-O	285.8	29.9	1.8	15.0
GAUSS	CAR	283.2	58.7	2.0	32.7
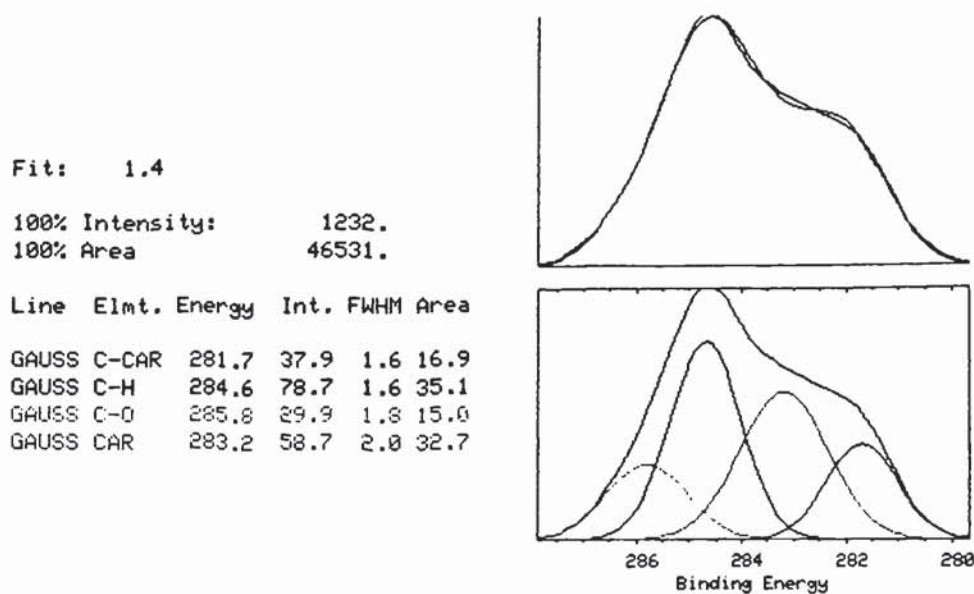
FIGURE 6.14
XPS SPECTRUM OF FRACTURED CEMENT INTERNAL SURFACE
(C_{1s} region) W / C RATIO = 0.4, 90 DAY CURE

Fit: 1.3

100% Intensity: 973.
100% Area   41020.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	C-CAR	281.7	76.6	2.0	38.2
GAUSS	C-H	284.6	98.3	2.0	49.1
GAUSS	C-O	286.0	11.3	1.2	3.4
GAUSS	CAR	283.3	27.8	1.3	9.0
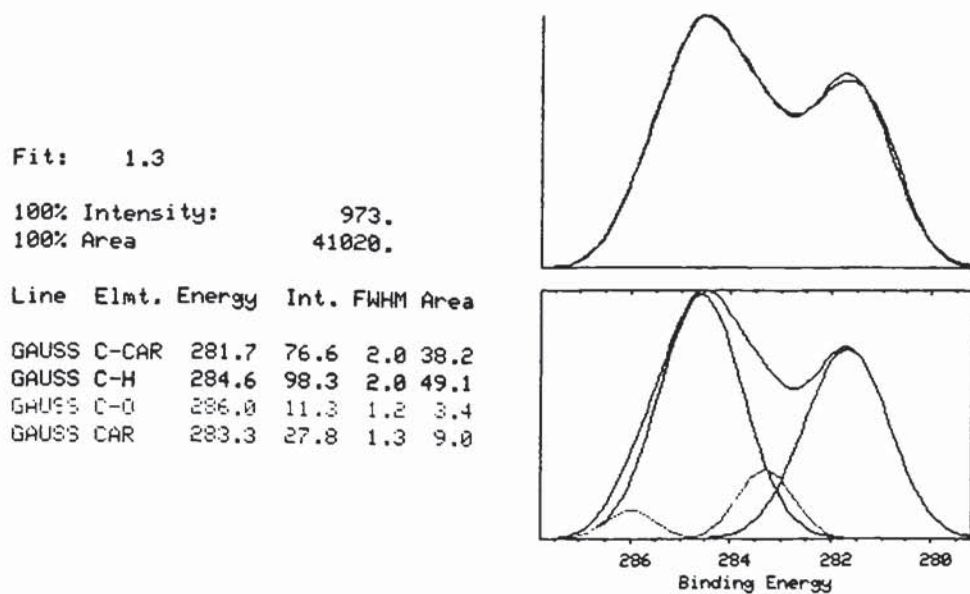
TABLE 6.1
ELEMENTAL CONCENTRATIONS ON EVAPORATION
AND INTERNAL SURFACES

ELEMENT	% MASS CONCENTRATION ON EVAPORATION SURFACE	% MASS CONCENTRATION ON INTERNAL SURFACE
C_{1s}	32.76	31.31
K_{2p}	0.92	0.38
O_{1s}	42.48	45.20
Ca_{2p}	23.84	23.11

FIGURE 6.15
EFFECT OF DRYING TECHNIQUE ON CHEMISTRY OF INTERNAL SURFACES 0.4 W / C RATIO CEMENT, 28 DAY CURE

OVEN DRYING

VACUUM DRYING

ALCOHOL REPLACEMENT
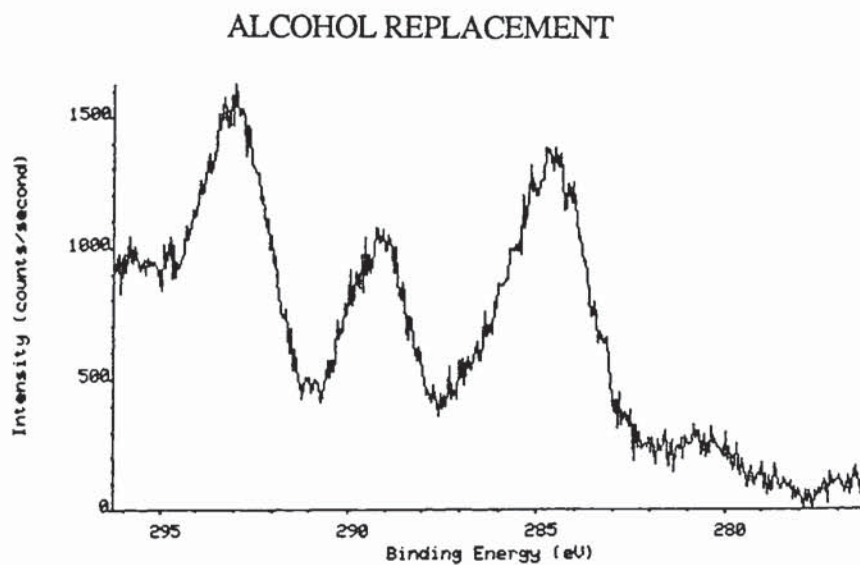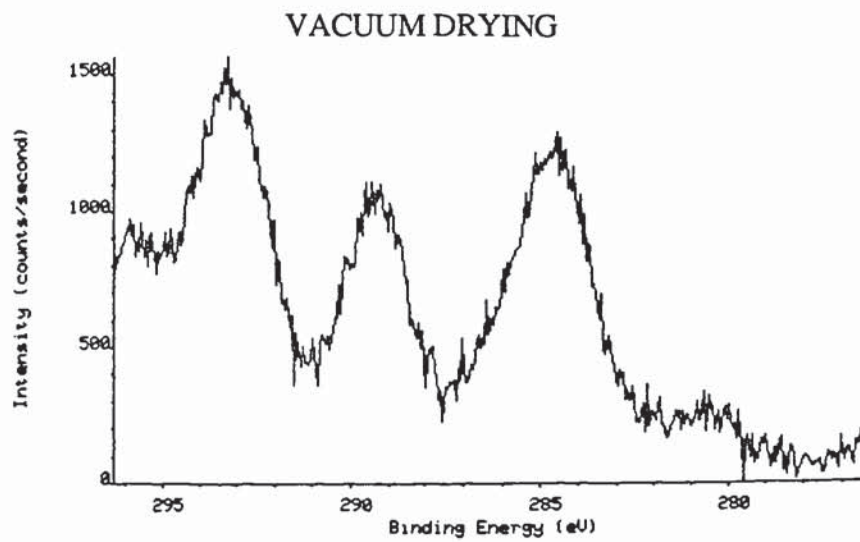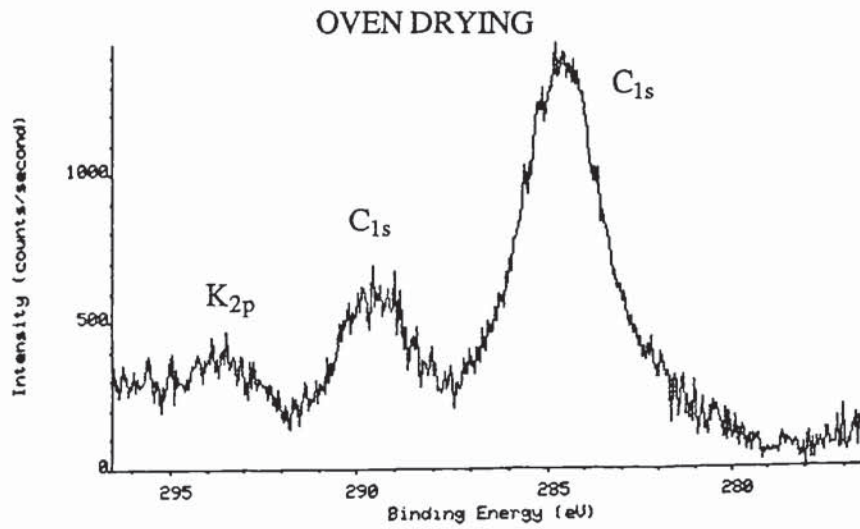
FIGURE 6.16
EFFECT OF DRYING TECHNIQUE ON CHEMISTRY OF INTERNAL
SURFACES 0.7 W / C RATIO CEMENT, 28 DAY CURE

203
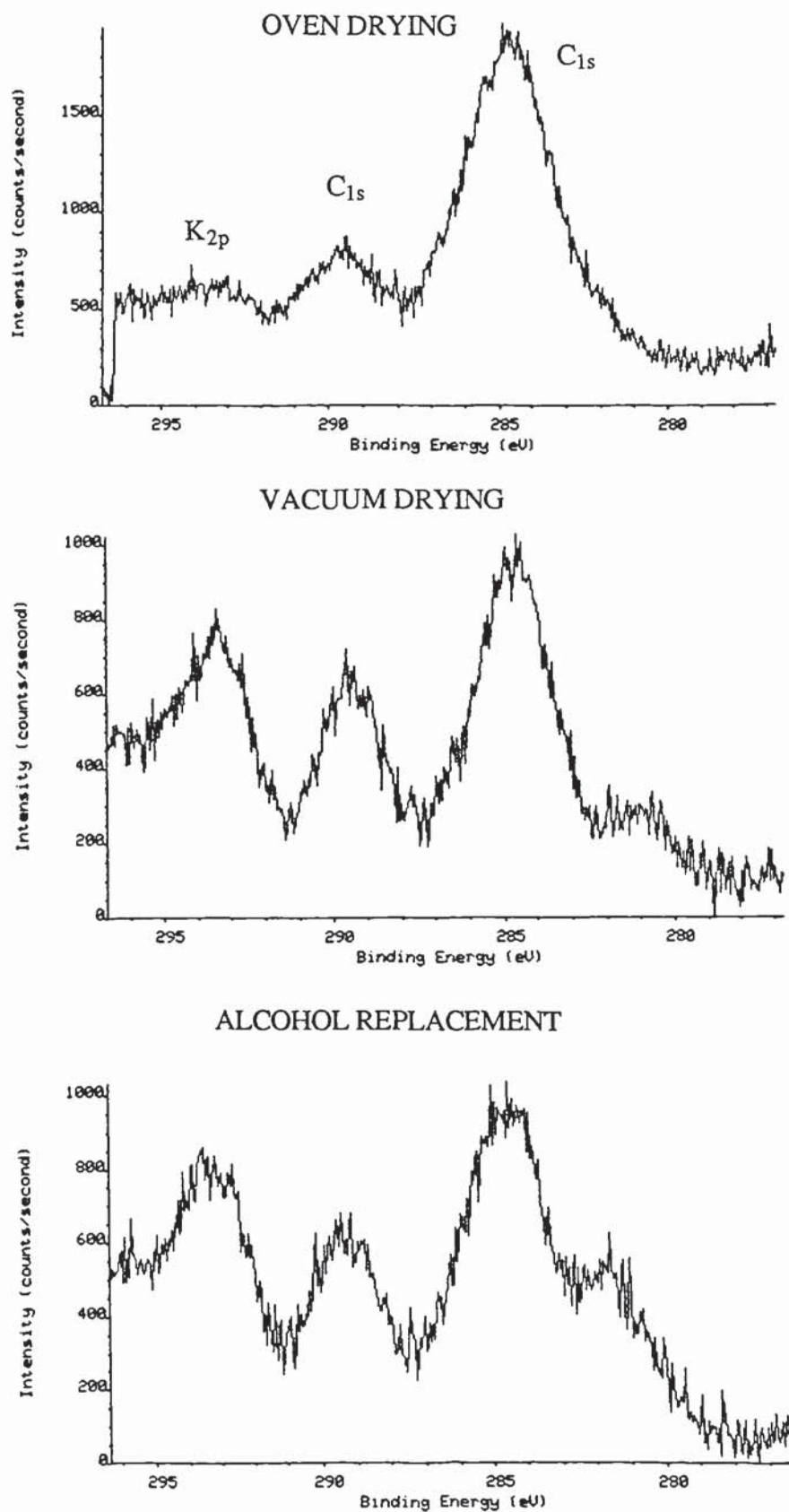
FIGURE 6.17

SURVEY SPECTRA OF POLYMER / CEMENT SAMPLES (0.4 W/C RATIO, 28 DAY CURE)

a) PURE CEMENT

b) PURE PMMA

c) REFLUXED CEMENT

d) CEMENT ADHESION SURFACE REVEALED BY DISSOLUTION OF PMMA WITH CHLOROFORM

204
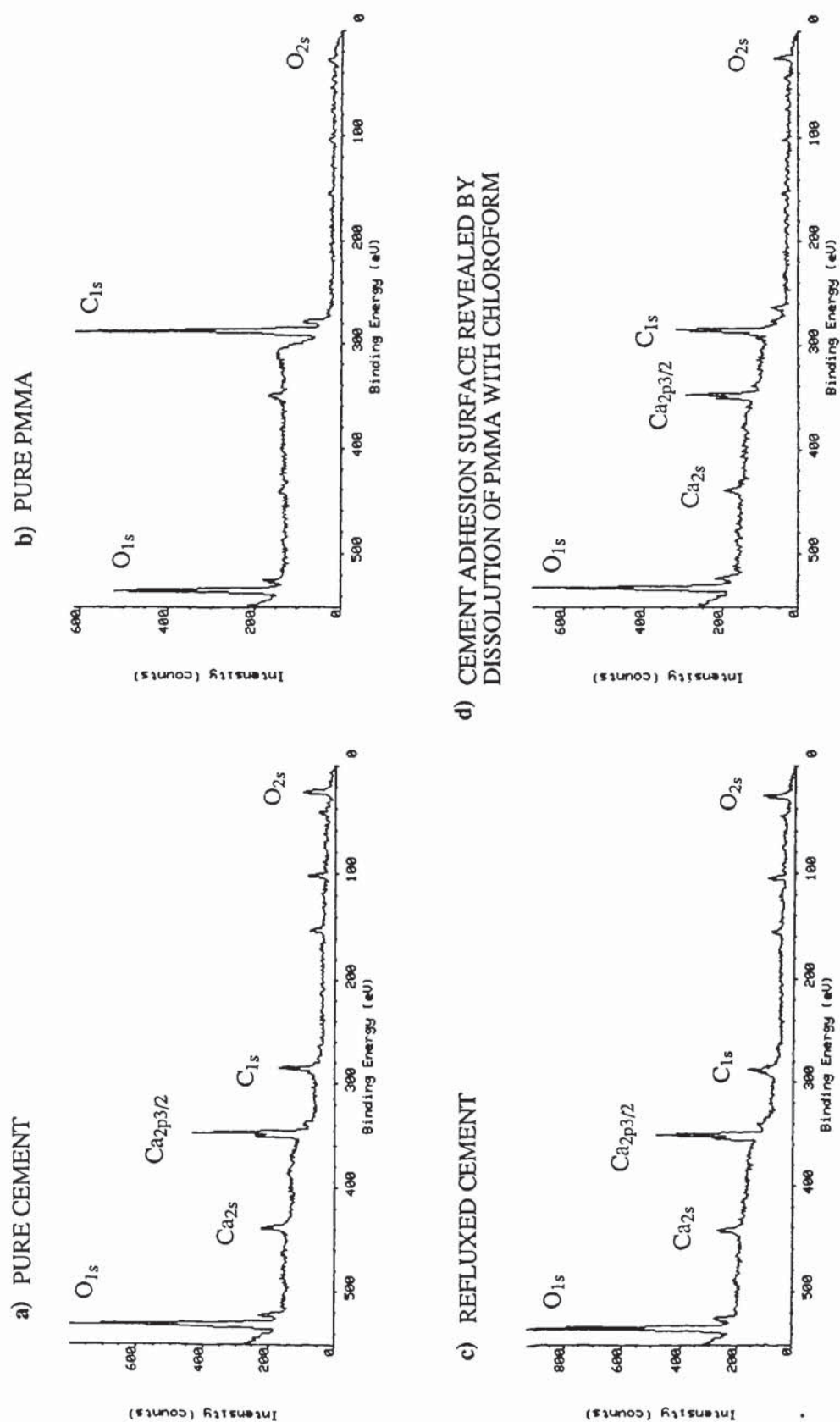
FIGURE 6.18

SURVEY SPECTRA OF POLYMER / CEMENT SAMPLES (0.4 W/C RATIO, 90 DAY CURE)

a) PURE CEMENT

b) REFLUXED CEMENT

c) REFLUXED CEMENT TREATED WITH CHLOROFORM

d) CEMENT ADHESION SURFACE REVEALED BY DISSOLUTION OF PMMA WITH CHLOROFORM

205
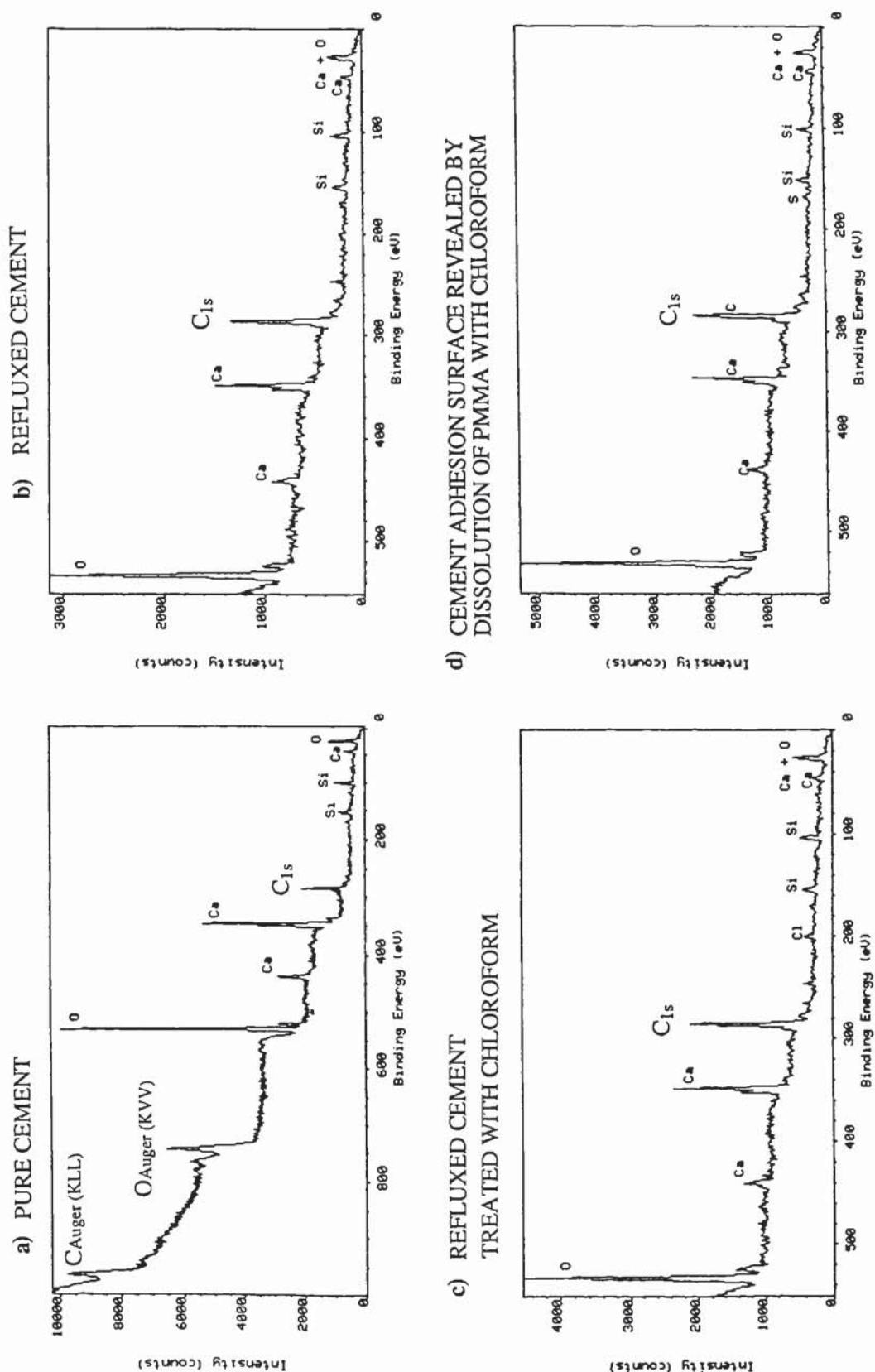
FIGURE 6.19

C_{1s} REGION SPECTRA OF POLYMER / CEMENT SAMPLES (0.4 W/C RATIO, 28 DAY CURE)
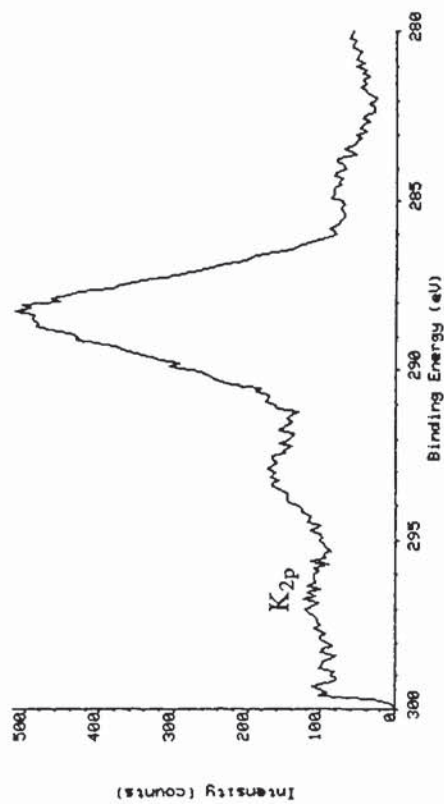
a) PURE CEMENT

b) PURE PMMA
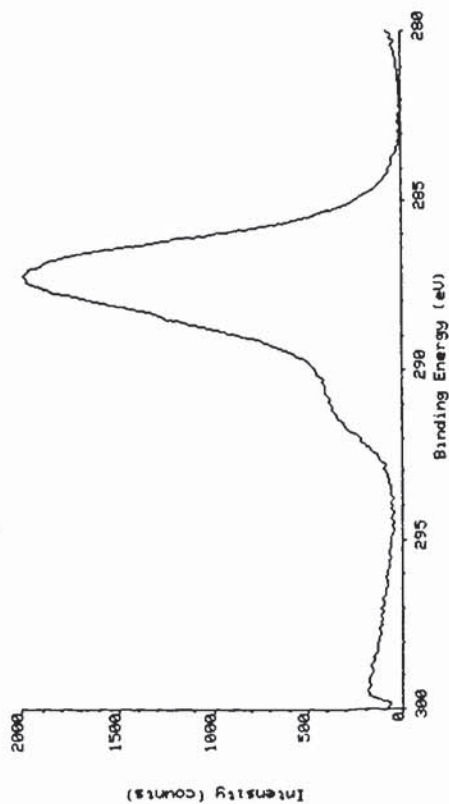
c) REFLUXED CEMENT
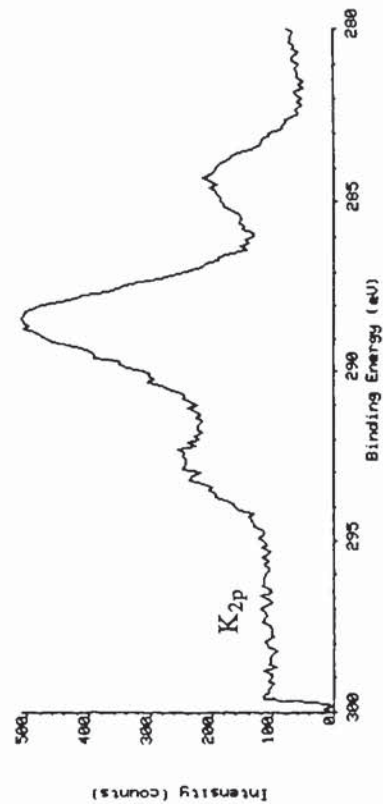
d) CEMENT ADHESION SURFACE REVEALED BY DISSOLUTION OF PMMA WITH CHLOROFORM
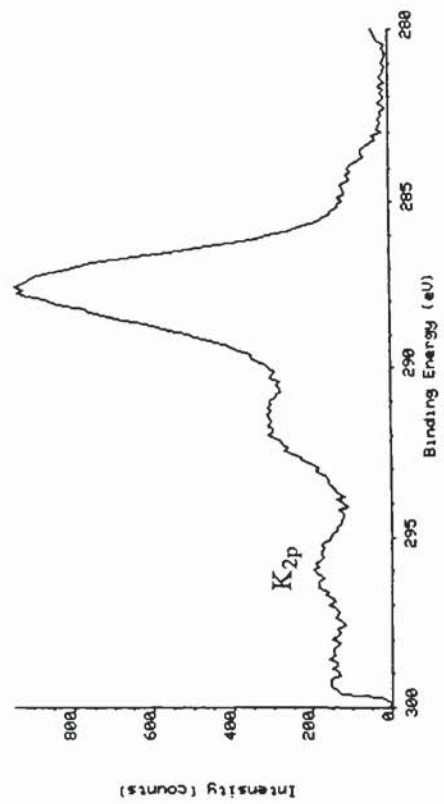
FIGURE 6.20

C_{1s} REGION SPECTRA OF POLYMER / CEMENT SAMPLES (0.4 W/C RATIO, 90 DAY CURE)

a) PURE CEMENT

Fit: 3.2

100% Intensity: 919.
100% Area: 65931.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	CAR	282.3	12.5	1.6	5.8
GAUSS	C-H	284.6	76.8	2.0	46.3
GAUSS	C-O	286.0	52.8	1.9	28.7
GAUSS	C=O	287.7	6.0	0.9	1.6
GAUSS	CO3	290.0	30.9	2.0	18.1

b) REFLUXED CEMENT

Fit: 1.9

100% Intensity: 3390.
100% Area: 138224.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	CAR	283.0	52.8	2.0	27.3
GAUSS	C-H	284.6	86.0	1.7	37.8
GAUSS	C-O	286.1	40.4	2.0	20.9
GAUSS	CO3	288.8	24.6	2.0	12.7

c) REFLUXED CEMENT TREATED WITH CHLOROFORM

Fit: 1.7

100% Intensity: 5452.
100% Area: 199750.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	CAR	282.8	42.7	2.0	24.5
GAUSS	C-H	284.5	90.8	1.7	44.4
GAUSS	C-O	286.0	30.0	2.0	17.2
GAUSS	CO3	288.8	22.3	2.0	12.8

d) CEMENT ADHESION SURFACE REVEALED BY DISSOLUTION OF PMMA WITH CHLOROFORM

Fit: 1.9

100% Intensity: 6500.
100% Area: 248126.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	CAR	283.1	33.8	1.7	15.9
GAUSS	C-H	284.7	94.2	2.0	52.0
GAUSS	C-O	286.4	33.7	2.0	18.6
GAUSS	CO3	289.1	23.4	2.0	12.9

FIGURE 6.21a
SURVEY SPECTRUM OF CALCIUM METHACRYLATE
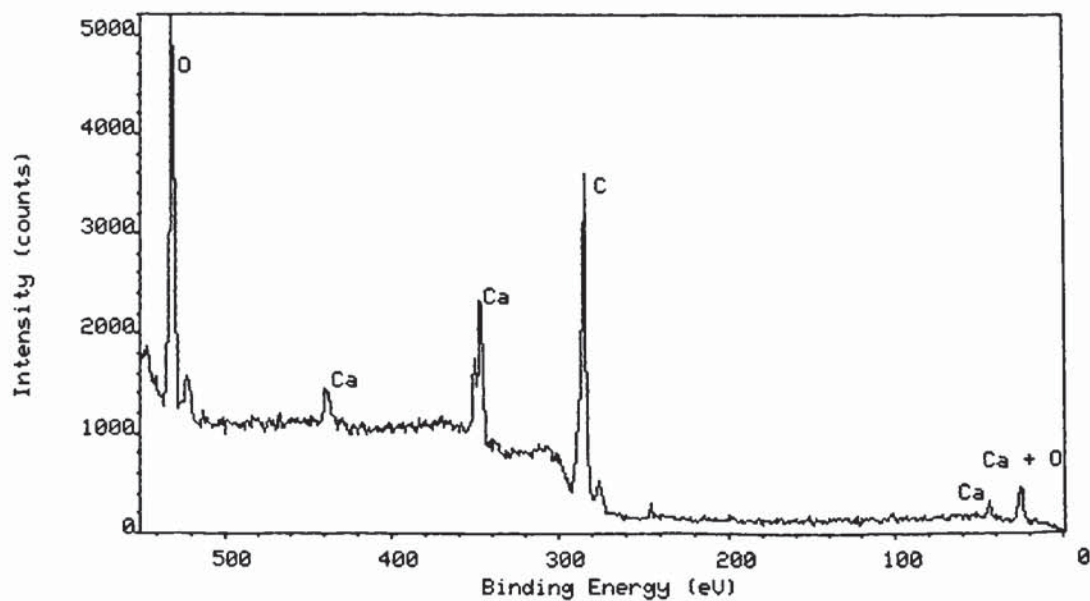
FIGURE 6.21b
XPS SPECTRUM OF CALCIUM MATHACRYLATE (C$_{1s}$ region)

Fit: 0.9

100% Intensity: 10744.
100% Area   375849.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	CAR	283.4	23.9	1.6	10.8
GAUSS	C-H	284.7	95.9	1.9	54.9
GAUSS	C-O	286.4	24.9	1.9	14.2
GAUSS	CO3	288.8	22.7	2.0	13.6
GAUSS	C=O	287.8	14.7	1.4	5.7

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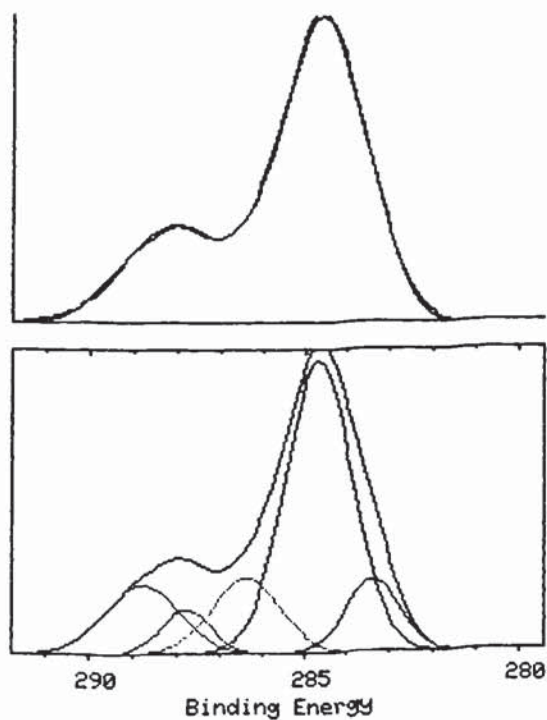
FIGURE 6.22
XPS SPECTRUM OF PMMA IMPREGNATED CEMENT (C_{1s} region)

Fit: 1.7

100% Intensity: 10920.
100% Area   327631.

Line	Elmt.	Energy	Int.	FWHM	Area
GAUSS	C-H	284.6	83.8	1.8	53.0
GAUSS	C-O	286.0	20.3	2.0	14.2
GAUSS	CAR	283.3	34.8	2.0	24.4
GAUSS	CAR	288.4	10.3	2.0	7.1

Binding Energy
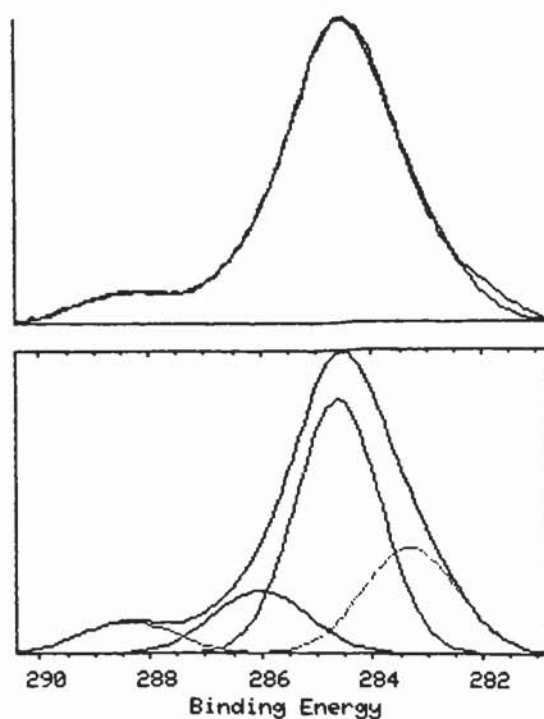
7 INTERACTIONS AFFECTING THE KINETICS OF POLYMERISATION

7.1 INTRODUCTION

Interactions take place between polymers and cements on a number of levels. These are expressed in various ways, particularly in their modification of mechanical properties, and in the formulation of reaction products - both of these areas have been discussed in earlier chapters. There is however a further class of interaction which is that affecting the polymerisation processes. Two major consequences result from such interactions : - 1) modification of the kinetics of polymerisation, and 2) alterations in polymer molecular weight. This chapter explored the former of these areas.

MMA monomer was used exclusively, being a commercially important, and well-studied monomer. It is a classic vinyl monomer, undergoing free-radical polymerisation by the opening of the double bond in its structure. Many workers have studied polymerisation of the substance using a variety of different initiators, benzoyl peroxide being the most important to this study. In consequence therefore, there is a considerable amount of data available concerning free-radical polymerisation generally, and also more specific data on MMA and BP.

Experiments were conducted into the effect of hydrated OPC on polymerisation rates, the monomer being mixed with powdered hydrated cements (polymer cements) and as an impregnant (polymer impregnated cement). In the case of polymer cements the monomer was in the form of a prepolymer to increase its viscosity thus limiting segregation of hydrated cement particles during polymerisation.

Polymerisation rates in the presence of cement were measured at a number of temperatures and compared to polymerisation rates in the absence of cement. The apparatus used exclusively for these experiments was an isothermal calorimeter, results being processed via computer techniques.

Attempts were also made to determine if there were any interactions between benzoyl peroxide and cements that could modify overall polymerisation rates in impregnated or polymer cements.

7.2 PREVIOUS WORK

7.2.1 KINETICS OF FREE-RADICAL POLYMERISATION

A clear account of the factors affecting free-radical polymerisation is given both by Lowry *(ref 131)* and Flory *(ref 132)*. Three major processes have been identified; those of initiation, propagation and termination of chains. Initiation involves the decomposition of initiator molecules to give pairs of radicals that add to single monomer molecules - the first units in the polymer chains. Propagation is the process whereby monomer molecules add to the free-radical at the end of growing chains, replicating a free-radical site at the new chain end. Termination is the name given to processes that end chain growth, these being combination or disproportionation between pairs of chains. The mathematical treatment of the rate of polymerisation involves certain simplifications, and can be summarized as follows:-

With initiator 'In' producing radicals 'R*' reacting with monomer molecules 'M', five rate constants may be defined:-

$$\text{INITIATION} \qquad \text{In} \xrightarrow{\ K_d\ } 2R^* \qquad\qquad (1)$$

$$R^* + M \xrightarrow{\ K_i\ } M_i^* \qquad\qquad (2)$$

$$\text{PROPAGATION} \qquad M_n^* + M \xrightarrow{\ K_p\ } M_{(n+1)}^* \qquad (3)$$

$$\text{TERMINATION} \qquad M_m^* + M_n^* \xrightarrow{\ K_c\ } M_m\text{-}M_n \qquad (4)$$

$$M_m^* + M_n^* \xrightarrow{\ K_{dis}\ } M_m(\text{-}H) + M_n(\text{+}H) \quad (5)$$
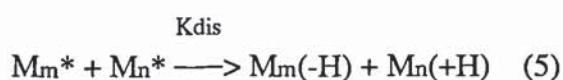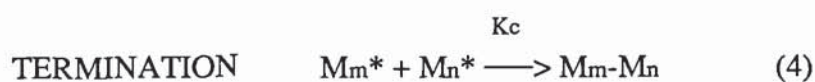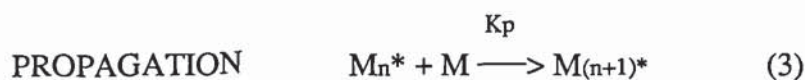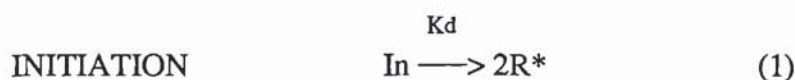
Kd is is only truly valid if all the radicals produced are available to start chains, some being lost by cage effects *(see 7.2.3)*. Thus we introduce a factor 'f' to account for the fraction lost. So, the decomposition of initiator molecules becomes expressed as:-

$$\text{In} \xrightarrow{\ K_d\ } 2fR^* \qquad\qquad (6)$$

Assuming that the rate of addition to the growing chains is independent of chain length, we can write an equation for the concentration of radicals directly from initiator molecules as follows:-

$$d[R*]/dt = 2fKd[In] - Ki[R*][M] \qquad (7)$$

Dissociation rate   Initiation rate

The overall rate constant for the two termination processes is given by:-

$$Kt = Kc + Kdis$$

Thus, since two radicals are destroyed in the termination step by both process, the rate of loss of growing chains is given by : -

$$-2d[Mn*]/dt = (Kc+Kdis)\ [Mn*][Mm*]$$

So:- $\qquad -d[Mn*]/dt = 1/2\ Kt[Mn*][Mm*]$

The above equations are written in terms of Mn*, but could equally have been written in terms of Mm*. However, if no distinction is made between growing chains of different lengths then [Mn*] = [Mm*].

Thus:- $\quad -d[Mn*]/dt = 1/2\ Kt[Mn*]^2 \qquad (8)$

Thus we can write an equation for the rate of change of the radical concentration, bearing in mind that propagation does not change the number of chains, only their lengths, so:-

$$d[Mn*]/dt = Ki[R*][M] - 2Kt[Mn*]^2 \qquad (9)$$

Initiation rate   Termination rate

Now we make the steady state assumption described by Barrow *(ref 133)*, that the initiator radicals react to produce polymer via an intermediate state of growing radical chains, the number of which being constant once initiation, propagation and termination have become established. Thus we can write the following : -

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$$d[R*]/dt = d[Mn*]/dt \approx 0$$

Thus:- $2fKd[In] = 2Kt[Mn*]^2$

So the rate of change of growing chain concentration is given by the following:-

$$[Mn*] = \{fKd[In] / Kt\}^{1/2} \qquad (10)$$

Thus we can write an expression for the rate of consumption of monomer as follows:-

$$-d[M]/dt = Ki[R*][M] + Kp[Mn*][M]$$
$$\text{Initiation rate} \qquad \text{Propagation rate}$$

Once a substantial number of monomer units have become added to the growing chain, $[Mn*]$ will be much greater than $[R*]$, so we can approximate the equation to:-

$$-d[M]/dt = Kp[Mn*] [M]$$

and substituting for $[Mn*]$ we obtain the expression:-

$$-d[M]/dt = Kp[M] \{fKd[In] / Kt\}^{1/2} \qquad (11)$$

and since $2fKd[In]$ is an expression of the initiation rate, it is often more convenient to express it as a single factor 'ri'. The equation for the rate of polymerisation of monomer is then:-

$$-d[M]/dt = Kp[M] \{ri /2Kt\}^{1/2} \qquad (12)$$

By examination of the above equation it is possible to see how the overall polymerisation rate is effected by changes in the individual rate constants for the different processes governing polymerisation. Thus in very basic terms, the polymerisation at a given temperature for given concentrations of monomer and initiator will be increased by an increase in Kp, Kd or f, and decreased by an increase in Kt.

7.2.2 MAJOR DEPARTURES FROM SIMPLE RATE EQUATION

Examination of equation (12) would lead to the conclusion that the polymerisation rate of a monomer would show a steady decrease proportional to the monomer

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concentration, so long as [In] remained roughly constant (i.e. [In]>>[R*]), throughout the life-time of the reaction. Work by Schulz *(ref 134)* showed that although this is true for methyl methacrylate and benzoyl peroxide in solutions up to 40% or so by weight, it is definitely not the case above this concentration. In bulk the effect is most noticeable, characterized by a roughly constant initial polymerisation rate followed by a very rapid increase, polymerisation of only 85% monomer being achieved. Flory *(ref 132)* and Norrish *(ref 135)* also noted the phenomenon, known as autoacceleration. It was explained in the following terms:- Disregarding the idea that new mechanisms come into effect as polymerisation progresses, and since an effect on Ki seems unlikely, it leaves only the possibilities that Kp increases or Kt decreases. The conclusion drawn by all three workers was that Kt decreases, the reason being related to the increase in viscosity of the mixture as polymerisation progresses.

Chain termination by radical combination is a very fast process; but if growing chain ends become embedded in a mass of polymer molecules, termination becomes dependent upon diffusion of radical chains. Thus the rate at which they can meet and eliminate greatly decreases. Kp on the other hand is relatively unaffected by viscosity, thus the overall polymerisation rate speeds up dramatically. Final proof of Kt decreasing was found by Matheson *(refs 136 &137)* who determined absolute values for the different constants during the autoacceleration phase of polymerisation.

7.2.3 MECHANISM OF DECOMPOSITION OF BENZOYL PEROXIDE

Davies *(ref 138)* gives a very full account of the decomposition and major reactions of benzoyl peroxide as an example of a typical diacyl peroxide. The first step involves homolytic scission of the O-O bond to produce two benzoyloxy radicals.

$$PhCOO\text{-}OOCPh \longrightarrow 2\ PhCOO*$$
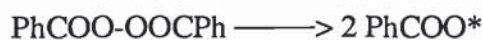
If radical scavengers are not present, then the benzoyloxy radicals further decompose to phenyl radicals and carbon dioxide.

$$PhCOO* \longrightarrow Ph* + CO_2$$

However, in the presence of radical scavengers, for example DPPH (see later) or polymerisable olefins (eg MMA), benzoyloxy radicals react immediately rather than undergoing decomposition to phenyl radicals and carbon dioxide.

Finally, if benzoyl peroxide molecules are decomposing in a solvent to form radical pairs, it is possible that they will fail to meet molecules they can react with before they collide with each other again. If this occurs then they will very likely recombine. On the other hand the radicals may be able to undergo reactions with the solvent as well as with their intended reactants. Either way, it can be seen that under certain conditions,not all radicals formed by thermal decomposition will be available to start chains. This process known as the cage effect is described by Barrow *(ref 133)*.

7.2.4 PROMOTION AND INHIBITION IN BENZOYL PEROXIDE

In simple terms, a promoter is a substance that can stimulate an initiator to dissociate faster at a given temperature than would ordinarily be expected. An inhibitor, on the other hand has the opposite effect, but does so by reacting with radicals to form non-radical products. Expressed in a kinetic sense, promoters increase Kd; inhibitors reduce it.

7.2.4.1 MECHANISM OF PROMOTION

Davies *(ref 138)* gives the reaction mechanism between benzoyl peroxide and dimethyl aniline (DMA), a known promoter. A very similar promoter dimethyl para-toluidine (DMT) was described by Swamy *(ref 5)* and employed by Lenton *(ref 13)* to stimulate the production of radicals from benzoyl peroxide within impregnated cements.

The reaction involves nucleophylic attack by the lone pair of electrons in nitrogen on the O-O bond. This produces intermediate species that decompose to form two radicals.

$$Ph\,N\begin{smallmatrix}Me\\ \\Me\end{smallmatrix} + \begin{smallmatrix}OCOPh\\OCOPh\end{smallmatrix} \longrightarrow [Ph - \overset{Me^+}{\underset{Me}{N}} - OCOPh] + [PhCOO^-]$$

intermediate species

$$Ph - \overset{Me}{\underset{Me}{N}}* + *OCOPh + PhCOO^-$$
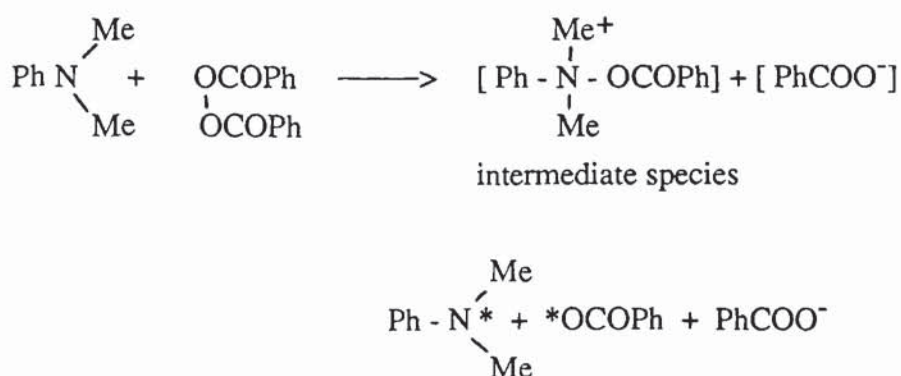
The mechanism is equally applicable to the formation of radicals from reaction with DMT as it is with DMA.

7.2.4.2 MECHANISM OF INHIBITION

The mechanism of inhibition reactions are complex, and a detailed consideration is beyond the scope of this project. However, shelf-life in general purpose reagent MMA is prolonged by using an inhibitor that has been widely studied, and is very commonly used - this being quinone. Flory *(ref 132)* discusses many aspects of inhibition with quinones. Foord *(ref 139)* was able to show that the incorporation of 0.02% benzoquinone resulted in a halving of the polymerisation rate of styrene with benzoyl peroxide.

It should be noted that the amounts of initiator added to monomers is very small. Such kinetic studies show that the rate of consumption of inhibitor is not dependent upon its concentration, only upon the rate of generation of radicals via decomposition of initiator. Since propagation is relatively slow there will be many collisions with molecules, including inhibitor molecules, before another monomer unit is added. Therefore, since it takes only one inhibitor molecule to end a chain, only a very small quantity of inhibitor is needed to limit or halt polymerisation completely.

$$\text{Mn}^* + \text{QUINONE} \longrightarrow \begin{array}{c}\text{Relatively stable} \\ \text{free-radical compounds}\end{array} \longrightarrow \begin{array}{c}\text{Non-radical} \\ \text{compounds from} \\ \text{unreactive radicals}\end{array}$$
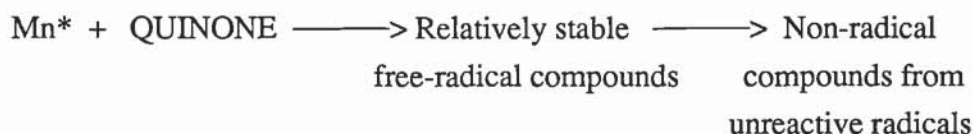
It should be pointed out however, that hydroquinone is the substance added to MMA commercially, this itself not being an inhibitor. But, reaction with dissolved oxygen results in the formation of quinone - a very good inhibitor.

$$\text{HO-C}_6\text{H}_4\text{-OH} \xrightarrow{\text{oxidation}} \text{O=C}_6\text{H}_4\text{=O}$$
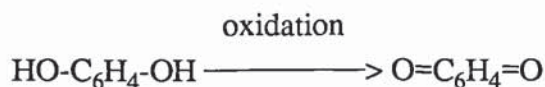
7.2.5 DETERMINATION OF PEROXIDES

Dissociation of peroxides to give radicals has been examined by a number of workers. Several methods have been developed to follow such reactions, some relying on determination of the remaining peroxide in a sample, and others following the resultant increase in radical concentration. Johnson *(ref 140)* summarizes the usefulness of available analytical techniques for different peroxides and environments. Five general techniques are available, these being titrimetric, polarographic, spectroscopic,

chromatographic and colourimetric methods. In this study the two most applicable methods were titrimetry and colourimetry, chosen for their suitability with aromatic peroxides and ease of measurement.

Titrimetric methods tend to rely upon determination of the remaining peroxide in a sample. Methods typically involve reduction of the peroxide group, followed by titration of the corresponding oxidized species. Typical are iodometric methods, where the peroxide oxidises iodide to iodine which is typically titrated against thiosulphate. The equations for the process are as follows:-

$$ROOR + 2I^- + 2H_2O \longrightarrow I_2 + 2ROH + 2OH^-$$

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

The initial oxidation of iodide is relatively slow. A number of experimental procedures have been developed making use of this chemistry, most requiring the peroxide solutions to be boiled for at least 2-3 minutes - some requiring hours. Deaeration of the mixture is also required, this being achieved by bubbling inert gas or addition of solid carbon dioxide. The latter produces gaseous carbon dioxide at room temperature and this bubbles through the mixture.

A more direct method was described by Bawn and Mellish *(ref 141)*, this relying on determination of the radicals produced by decomposition. They were able to follow the decomposition of benzoyl peroxide in a number of different solvents by a novel colourimetric procedure. The technique involved determination of the absorbence of the vivid purple free-radical substance diphenyl picryl hydrazyl (DPPH), with time. This substance was found to react with the initial free-radicals from the decomposition of benzoyl peroxide - benzoyloxy radicals. The resulting compounds were only faintly coloured, hence the progress of the reaction could be traced colourimetrically. Most importantly, the technique allowed for continuous monitoring of the reaction at different temperatures, after calibration of the colourimeter used.

The method relied on the fact that in the system : -

$$BP \longrightarrow 2R* \quad (slow)$$
$$R* + h* \longrightarrow Rh \quad (fast)$$

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Thus : - $-d[h*]/dt = 2k \, [BP]$

But : - $[BP] = 1/2 \, [h*]$

so : - $d[BP]/dt = -d[h*]/dt = k[h*]$

$$k = 1/t \; 2.303 \log [h*_t]/[h*_0]$$

Where : -

BP = benzoyl peroxide

R* = free-radicals formed from decomposition of benzoyl peroxide

$[h*_t]$ = hydrosyl concentration at time t, and

$[h*_0]$ = initial hydrosyl concentration.

Thus by plotting $\log [h*_t]/[h*_0]$ against time an initial linear relationship is observed for disappearance of the hydrosyl species, allowing calculation of k. The relationship departs from linearity as the concentration of DPPH becomes depleted, with the formation of an unidentified, pale straw coloured reaction product.

7.2.6 COMPUTATION OF RADICAL CONCENTRATIONS

Work on the rate of decomposition of benzoyl peroxide by Bawn and Mellish *(ref 141)* led to an expression for temperature dependence of the rate constant as follows:-

$$k = 3.0 \times 10^{13} \, e^{-29600/RT}$$

Where : - k = rate constant

R = universal gas constant

T = absolute temperature

As described in section 7.2.4, the decomposition was measured by following the decrease in concentration of a highly coloured hydrosyl species that reacted with newly formed radicals to form only slightly coloured products. The reaction was first order, i.e. the rate of reaction was proportional to the concentration of a single reactant, the stoichiometry of the reaction showing that the rate of loss of benzoyl peroxide (BP) was half the rate of loss of the hydrosyl species (h*). Thus, using the derivation given by Barrow *(ref 133)* it is possible to obtain an expression for the concentration of peroxide at a given time and temperature. The derivation is as follows: -

$$BP \longrightarrow 2R^* \text{ slow}$$

$$R^* + h^* \longrightarrow Rh \text{ fast}$$

Thus:- $-d[h^*]/dt = k[h^*]$

and:- $-1/[h^*]\, d[h^*] = kdt$

If the initial concentration of hydrosyl is $[h^*]_0$ at time t_0, then the quantity of hydrosyl lost over time t will be $[h^*]$. Thus:-

$$- \int_{[h^*]_0}^{[h^*]} 1/[h^*]\, d[h^*] = k \int_{t_0}^{t} dt$$

So:- $-\ln [h^*] - Ln[h^*]_0 = \ln [h^*]_0/[h^*] = kt$

$$\ln [h^*]/[h^*]_0 = -kt$$

$$[h^*]/[h^*]_0 = e^{-kt}$$

$$[h^*] = [h^*]_0\, e^{-kt}$$

Thus, using the above equation, it is possible to compute benzoyl peroxide concentrations at different temperatures after different times *(fig 7.1)*. Similarly, since the rate of production of radicals is twice that of the rate of loss of peroxide molecules, it is possible to compute radical concentrations at different temperatures after different reaction times *(fig 7.2)*.

Examination of *figure 7.2* shows that if x initiator molecules produce y radicals in 100 seconds at 40°C, at 70°C they will produce approximately 10000y radicals. This observation partially explains the increased rate of overall polymerisation in prepolymers over pure monomers. Prepolymers are partially polymerised monomers, having been heated to above 70°C before rapid cooling and storage *(see 3.1.2.3)*. Once their temperature is raised to the polymerisation temperature (40°C for instance) there will be 10000 times more initiating radicals present in prepolymers than corresponding pure monomers.

FIGURE 7.1

RATE OF DECOMPOSITION OF BENZOYL PEROXIDE
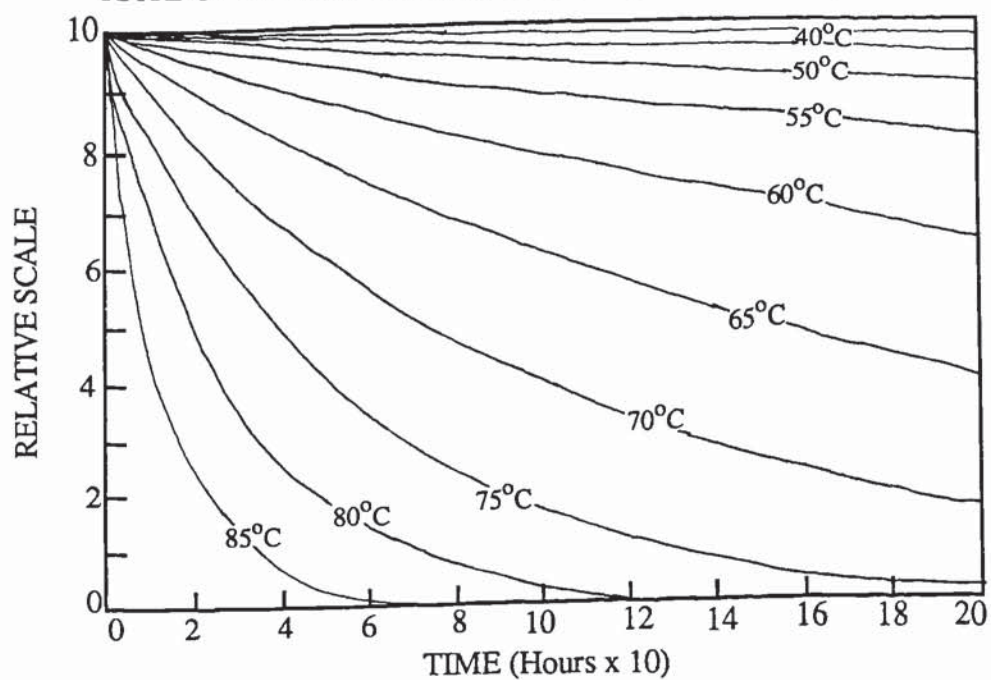
FIGURE 7.2

NUMBER OF FREE-RADICALS PRODUCED FROM 1 MOLE OF BENZOYL PEROXIDE
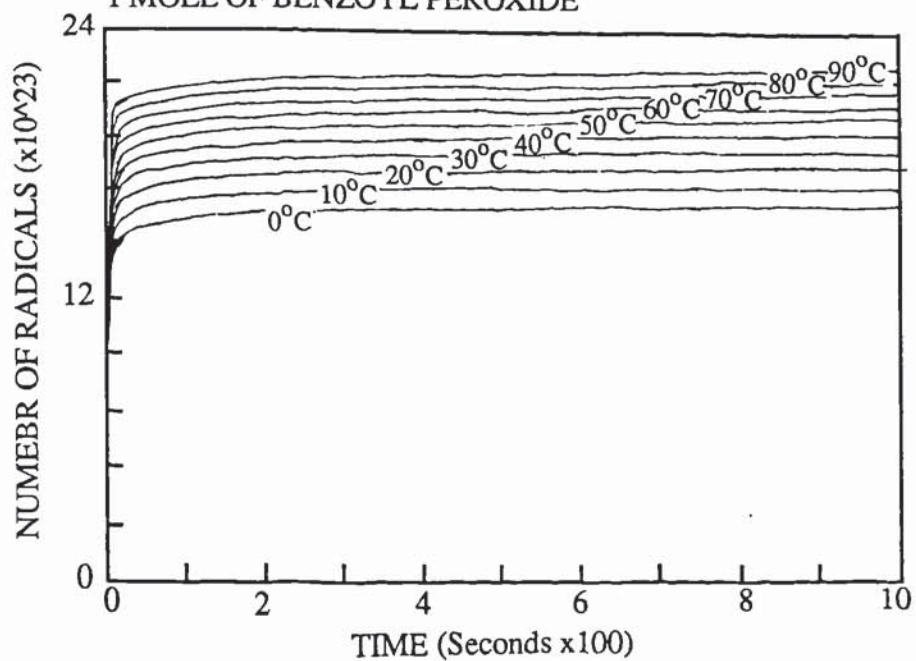
7.3 RESULTS AND DISCUSSION

7.3.1 EXPERIMENTAL AND INSTRUMENTAL DETAILS

It was hoped that examination of the rate and magnitude of heat output would indicate possible interactions or reactions taking place during polymerisation where cements are present. By comparison with the bulk polymer, a reduction in the overall amount of heat output would indicate either substantial termination by the cement itself, or that it has rendered some monomer unavailable for polymerisation. On the other hand, an increase in the overall amount of heat output would indicate some other major reaction occurring other than just polymerisation. Changes in the rate of heat output - for instance extra peaks not seen on thermograms - would also indicate other reactions taking place. Shifts in peaks attributable to polymerisation would indicate that cements interfere with the overall polymerisation rate.

Since measurement of heat output by the calorimeter used is only meaningful once isothermal conditions are established, there is a period over which measurement is not possible. The calorimeter was always run above room temperature, causing a 'dead-time' corresponding mainly to the heating up of the calorimeter cell to the temperature of its surroundings. Polymerisation reactions do occur in the dead-time, so efforts were made to minimise it. For this reason the calibration heaters were switched on until the output was more positive than -5.000 mV. Although this was very effective in minimising the dead-time, it did sometimes result in a slight overshoot above zero, showing up as a small peak at the start of the run. Fortunately this was negligible compared to the overall heat outputs.

As a consequence of the dead-time effect it was not possible to say exactly when the reactions started; thus the convention used was that measurements were taken from the time that the output first passed zero, i.e. there was no net heatflow through the thermopile.

Different sorts of sample preparation and containers were used throughout these experiments. Subsequent examination of the specimens yielded no evidence of polymer reactions behaving in a different way towards the centre or at the edges of samples - thus they were considered as behaving homogeneously. Heatflow properties were substantially different between sample types, thus it was very important to calibrate the apparatus after every run.

As predicted, the polymerisation rate is greatly increased by the use of a prepolymer. Most experiments using prepolymer could be carried out in roughly equal times by running the calorimeter at 40°C compared to 50°C for the monomer itself. This allowed the polymerisation reaction time to run near to completion within 20 hours, runs thus being possible on a daily basis. At these temperatures, the amount of heat lost whilst setting up the apparatus and allowing isothermal conditions to be established, was kept to a minimum. Certainly such errors were increased when operating at higher temperatures, but in all cases the the polymerisation rate was still relatively slow by the time the calorimeter output passed zero mV.

7.3.1.1 POLYMERISATION OF PURE MMA AND MMA PREPOLYMER

Thermograms of MMA and MMA prepolymer using 2% BP initiator show an initial rise in the rate of heat output, this steadily increasing to a sharp peak. Since heat output is directly related to polymerisation rate, the data may be re-plotted as percentage polymerisation against time, 100% being taken as 48.5 kJ mol^{-1} - the heat of polymerisation of MMA (see Vogel *(ref 46)*). The initial degree of polymerisation of the prepolymer was calculated by subtracting the total heat output of the pure prepolymer from that of the pure monomer itself, since Flory *(ref 132)*, Norrish *(ref 135)* and Schulz *(ref 134)* indicate that 100% polymerisation often does not take place in bulk polymerisation.

Prepolymers polymerise much faster than pure monomers, although the exact rate depends to a large degree upon the prepolymer's production history. Prepolymers are made by heating a monomer/initiator mixture to a temperature near the monomer's boiling point for a few minutes whilst rapidly stirring, until the mixture begins to thicken. The process rapidly decomposes the initiator, thus initiating a large number of chains. Subsequent rapid cooling prevents significant propagation of the chains, and held at 0°C, will not polymerise significantly further in weeks or months. The resulting product is a prepolymer. Clearly, the time and temperature range over which the prepolymer was produced are going to determine both the number of chains started, their molecular weights and the quantity of monomer still available for polymerisation. Thus, for comparative experiments using prepolymers, the same batch was used in each case.

7.3.1.2 MASS EFFECTS

Autoacceleration as described by Flory *(ref 132)*, Norrish *(ref 135)* and Schulz *(ref 134)* was observed in all thermograms. *Figures 7.3a&b* show thermograms and polymerisation rates of MMA with 2% BP of different sample weights. It can be seen that with increasing mass of monomer there is a slight increase in polymerisation rate. Autoacceleration under these conditions, although mostly related to thickening of the polymer leading to a decrease in termination rate, is also due partially to a rise in the temperature of the sample. This observation reflects the inability of the specimen to dissipate the energy released on the opening of the double bonds in the monomer. All the calorimetry experiments used about 1 to 5 g monomer, so the acceleration due to overheating should be no more than that shown in *figures 7.3a&b*. Certainly the temperature rise was nowhere near enough to boil the monomer - a problem experienced in other experiments using larger amounts of monomer.

7.3.2 EXPERIMENTS USING PREPOLYMER

7.3.2.1 POLYMER CEMENTS USING CEMENT OF DIFFERENT W/C RATIO AND CURE TIME

Overall heats of reaction were lower than the value obtained for the prepolymer itself. This suggests that the only major reaction taking place is polymerisation. It also seems possible that some of the monomer becomes absorbed by the finer pore structure of the cement, rendering it unpolymerisable. Comparison of peak positions between prepolymer and the polymer cements showed that the pure prepolymer always peaked first. There did not seem to be a relation between peak position, cure time or W/C ratio *(figs 7.4a&b and 7.5a&b)*. However, The 0.6 W/C peaks were all virtually symmetrical, but the 0.37 W/C ones showed indications of another feature after the peak. Examination of polymer cement samples after their runs were complete showed that segregation had occurred in spite of the high viscosity of the original prepolymer. Polymerisation had taken place at different rates in the lower cement-rich and upper polymer-rich layers. Cement and prepolymer were originally mixed in 50:50 proportions in the hope that the resulting polymer cements would be compatible with those used to examine other polymer/cement reactions. Segregation in these specimens was prevented by stirring the mixture until it thickened substantially. This was not possible in the calorimeter, hence the use of a viscous polymer cement.

7.3.2.2 KINETICS OF POLYMERISATION OF PREPOLYMER IN BULK AND IN POLYMER CEMENTS

Polymerisation of MMA prepolymer in bulk and mixed with 0.7 W/C ratio cement cured for 2 days was carried out at three different temperatures. *Figures 7.6a&b and 7.7a&b* show the thermograms obtained. Cement of 0.7 W/C ratio cured for 2 days was chosen for these experiments. There are a number of features of interest; First, both the prepolymer itself and the polymer cements have double-peaked thermograms. By examining specimens during polymerisation, the first peak was attributed to polymerisation within a lower segregated layer, and the second to polymerisation within an upper layer. As discussed in *7.2.2*, thickening of the polymer leads to autoacceleration; and as would be expected, between the peaks the polymer was characterized by an upper viscous layer and a lower rubbery layer. Segregation had therefore taken place within the prepolymer itself. This was not the case with the prepolymer used in *7.3.2.1 (figs 7.4a&b and 7.5a&b)*, and must be related to its formation history. It is possible that the original heating produced a significant number of long chains that settled out on heating within the calorimeter. Certainly at lower temperatures the second peak is large and broad, but almost indistinguishable from the first at higher temperatures. This suggests that at higher temperatures there is insufficient time for much segregation to occur before the mixture becomes rigid.

Examination of the thermograms of the polymer cements showed that the first peak is always larger, and due to polymerisation within the segregated layer. This also indicates that polymerisation is faster within the segregated polymer and cement layer. This was also noted for the specimens using 0.37 W/C ratio powders *(7.3.2.1)*, and could indicate that cements have some effect on K_t. Cement particles may restrict the diffusion of growing chains in a similar way to thickening, making it less likely that chains will meet and terminate, and more likely that they will propagate.

Comparison of prepolymer and polymer cement runs at identical temperatures shows that the cement powder's overall effect is to slow down polymerisation , in spite of possible effects on K_t. Examination of equation (12) *(7.2.1)* shows how rate constants for the different processes in polymerisation effect the overall polymerisation rate. Effects on K_i can be disregarded as the prepolymer already contains vastly more initiated chains than will be produced by subsequent initiation; a change in K_p seems possible as monomer must have to diffuse through the pore and grain structure of the cement powder. Also, as discussed above, the restraints on diffusion may well effect K_t. It is possible that cements themselves cause termination, the overall heat outputs

being lower than those in bulk polymerisation. The latter could also be explained by monomer lost in the pore structure unavailable for polymerisation, the overall retardation being quite pronounced. It was not however possible to identify interactions of this sort directly from these experiments. Overall heats of polymerisation for all prepolymer experiments are given in *tables 7.1 and 7.2.*

On a more practical level, examination of *figures 7.6a&b* shows that increasing the temperature by about 5°C results in a doubling of the polymerisation rate. This could be useful from an industrial standpoint. If impregnated articles are undergoing polymerisation in an oven, running the process with a 5°C rise in temperature for half the time could well be more economical, the nature of the articles being substantially unchanged.

7.3.3 EXPERIMENTS USING PURE MMA

7.3.3.1 MMA POLYMERISATION IN IMPREGNATED CEMENTS

The four cements tested all showed similar thermograms, *(figs 7.8a&b)*. There did not appear to be a relation between W/C ratio, cure time or polymer loading, although all peaked earlier than the bulk polymer. It thus seemed possible that the pore surface of the cement may have had some effect on BP causing an increase in K_i. The peaks themselves were all broader than those of the bulk monomer itself. Heat outputs were all similar and about 10% lower for those of bulk polymerisation. This effect was noted in all polymer cements and impregnated cements, and would appear to be due to some monomer loss in the pore structure .

7.3.3.2 KINETICS OF MMA POLYMERISATION IN BULK AND IN IMPREGNATED CEMENTS

Distilled MMA itself, rather than prepolymer, was polymerised at different temperatures, using 2% BP. MMA thermograms and polymerisation rates at the temperatures chosen are shown in *figures 7.9a&b and 7.10a&b.* All are characterized by a long period over which the polymerisation rate increases only slowly, followed by a sharp peak due to autoacceleration. Plotted on the same axes it would seem that more heat is evolved by polymerisation at higher temperatures - which seems highly unlikely. In addition, the calculated heat evolution at 55°C is 68.7 kJ/mol, i.e. in excess of that quoted by vogel *(ref 46)*, for the polymerisation of MMA. The discrepancy probably results from errors in the constants used for heat-flow calculation. No segregation

appeared to occur as in the prepolymer. Overall heat outputs of about 40 kJ mol^{-1} were achieved, these being about 20% lower than the heat of polymerisation of MMA. This was as expected from the mass experiment where 100% polymerisation was never achieved, and also in agreement with the findings of Flory *(ref 132)*, Norrish *(ref 135)* and Schulz *(ref 134)*.

Unlike the prepolymer experiments in *7.3.2.2*, the relationship between peak time and temperature was not apparent, and would require further work to determine the connection. Nevertheless, increasing temperature always led to an increase in rate.

Thermograms of impregnated cements were similar to those for MMA, showing a period where the polymerisation rate increases only slowly, followed by a large peak, somewhat broader than that for MMA. Overall heat outputs were lower than those of pure monomer suggesting loss of some monomer in the cement pore structure where it is rendered unavailable for polymerisation. This too was observed in the polymer cement experiments described in *section 7.3.2.2*.

The most striking feature about these experiments was that, at all temperatures used, the polymerisation rate was faster in impregnated cements than in bulk polymerisation. The rate was still much lower than that observed in the polymer cement experiments where a prepolymer was used, the high viscosity of prepolymer being unsuitable for impregnation. Equation (12) *(7.2.1)* relates the overall rate of polymerisation to the rates of the different processes occurring on polymerisation. As discussed in section *7.3.2.2*, cements could interfere with K_t and K_p to slow polymerisation down - if changes in K_i can be disregarded. Since this is not the case in these experiments, it would seem that cements may increase K_i or K_t significantly, leading to an increase in the overall polymerisation rate. A similar finding was made by Godard *(ref 92)* where polymerisation rates in MMA impregnated asbestos cement were observed to increase noticeably. The effect must occur in polymer cements, but it would seem that it is insufficient to make a significant difference to the rate of polymerisation of a prepolymer, where there is already a vast number of chains already initiated.

Overall heats of polymerisation for all experiments using pure MMA are displayed in *tables 7.4 and 7.5*.

7.3.4 MEASUREMENT OF INITIATION RATE OF BENZOYL PEROXIDE

Rates of decomposition of benzoyl peroxide were calculated following the basic procedure of Bawn and Mellish *(ref 141)*. For each run, decomposition rates were measured in two identical solutions under the same conditions, one containing cement powder. There appeared to be no detectable modification of the decomposition rate and resulting radical concentration measured by this technique, indicating that cement powders do not effect Ki or Kt. There was however a build up of some other reaction product after the initial linear phase. It seems likely that this product is a benzoate as discussed in *5.3.6.2.(figs 7.11 and 7.12)*.

7.3.5 INTERPRETATION OF RATE DATA

Reviewing all the polymerisation rate measurements, it seems difficult to draw definite conclusions as to the exact processes modifying the rates. There would appear to be three classes of interaction that could be responsible for the effects noted : -

1) Free-radical

Interactions could occur to directly change the concentration of free-radicals in the growing polymer. From the DPPH experiments, initiation and termination effects seem unlikely, yet modification of the propagation rate seems possible; the increase observed in impregnated cements could be associated with the alkalinity of the pore surface.

2) Chemical

Non-free-radical reactions could occur to consume the initiator, depleting the amount available to decompose, forming radicals. The presence of benzoates in BP/MMA/cement mixtures suggests that BP may be consumed by some reaction with the cement *(see 5.3.6.2)*.

3) Physical

The retardation noted in polymer cements could be associated with the physical restriction to diffusion the cement particles impart. In addition, the effects of polymerisation on the convex surface of cement grains may be different from that in the capillaries of the cement pore system.

This discussion is continued in *8.3.6.6*, where it is connected with polymer molecular weight data from the specimens used in this chapter.

7.4 SUMMARY AND CONCLUSIONS

Experiments were conducted into the effects of cements on the polymerisation kinetics of MMA, thermally catalysed by benzoyl peroxide. Both polymer cements and impregnated cements were studied at a number of temperatures, the data being compared with that for identical polymerisation in the absence of cement. A range of different W/C ratio cements at different cure times were used. All measurements were taken using an isothermal calorimeter, the data being processed by computer techniques.

The rate of decomposition of benzoyl peroxide in contact with powdered cement was studied, this being compared to the rate without cement.

It was concluded that : -

1) There are a considerable number of factors that affect overall polymerisation rates, thus sample preparation is vitally important if comparisons are to be made between different samples.

2) Overall polymerisation rates are decreased by contact with powdered cements, and increased in impregnated cements. Explanations for this effect are speculative as yet, further work being required for a fuller understanding.

3) Heat outputs on polymerisation were always lower in contact with cements than they were in bulk. This suggests either that other reactions consume monomer, or that the pore structure of cement renders some monomer unpolymerisable.

4) No effects on the rate of decomposition of benzoyl peroxide were noted, within the timescale of the experiments.

FIGURE 7.3a

EFFECT OF MASS ON POLYMERISATION RATE
(Heat evolution data)
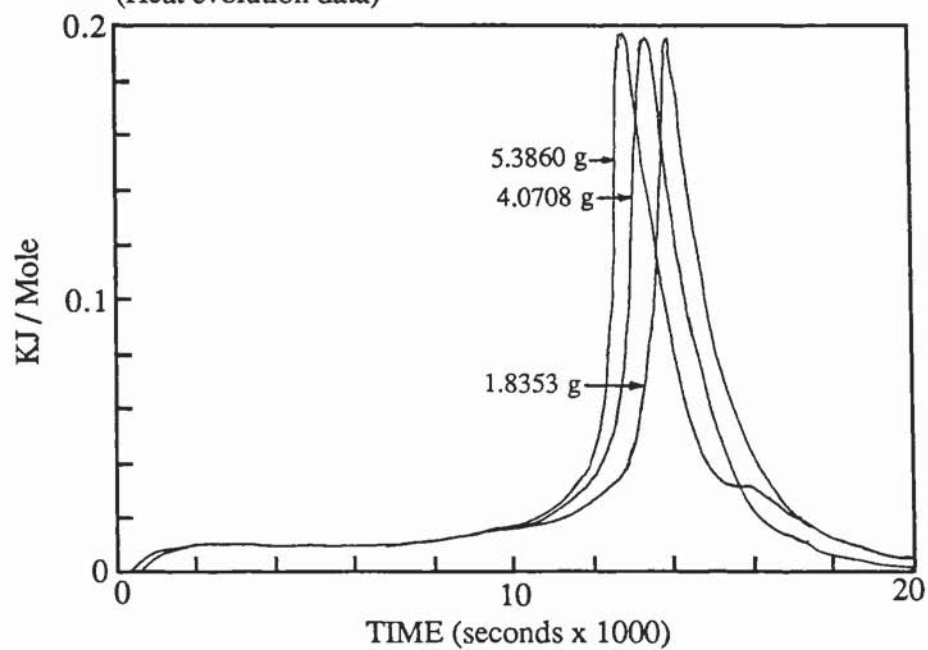
FIGURE 7.3b

EFFECT OF MASS ON POLYMERISATION RATE
(Degree of polymerisation data)
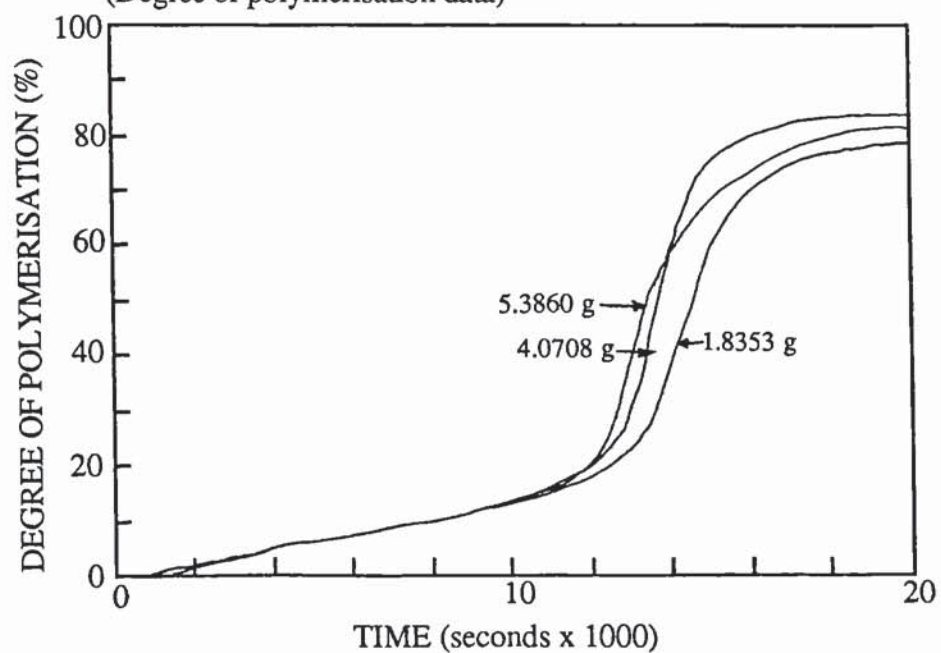
FIGURE 7.4a

POLYMERISATION RATES OF POLYMER CEMENTS, 0.37 W / C RATIO
(Heat evolution data)
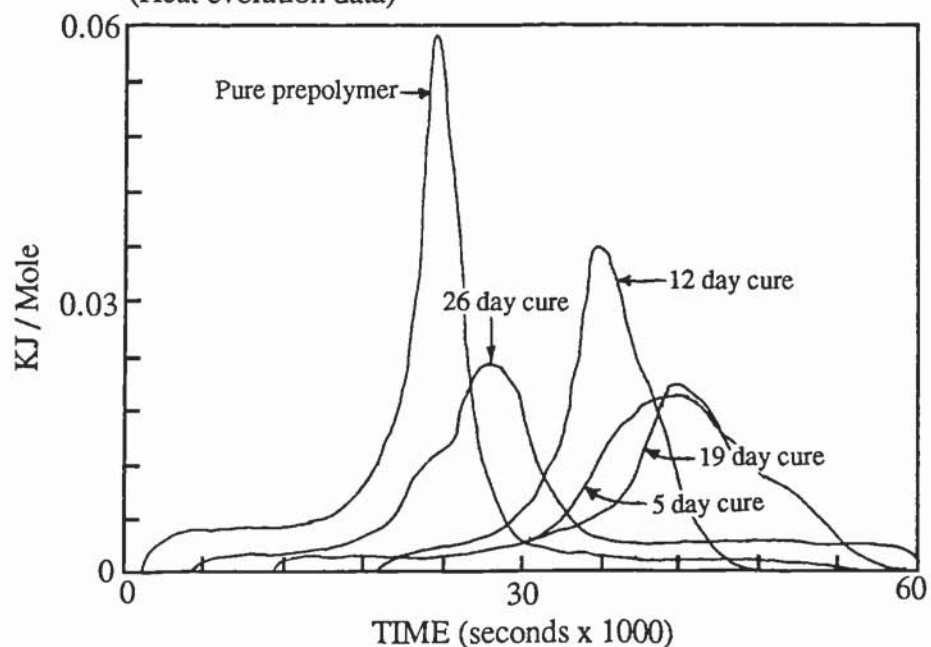
FIGURE 7.4b

POLYMERISATION RATES OF POLYMER CEMENTS, 0.37 W / C RATIO
(Degree of polymerisation data)

230
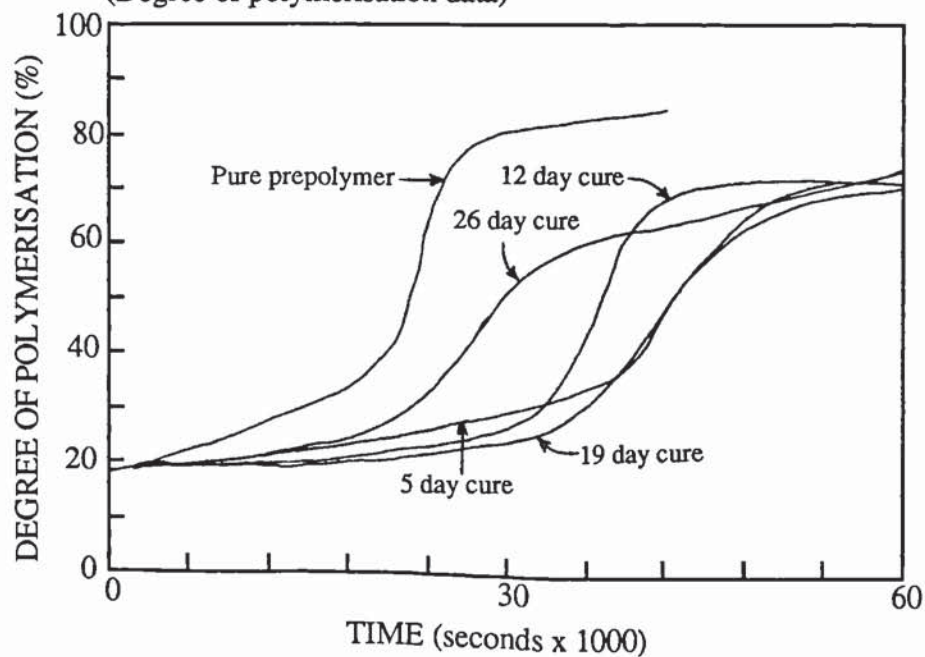
FIGURE 7.5a

POLYMERISATION RATES OF POLYMER CEMENTS, 0.6 W / C RATIO
(Heat evolution data)
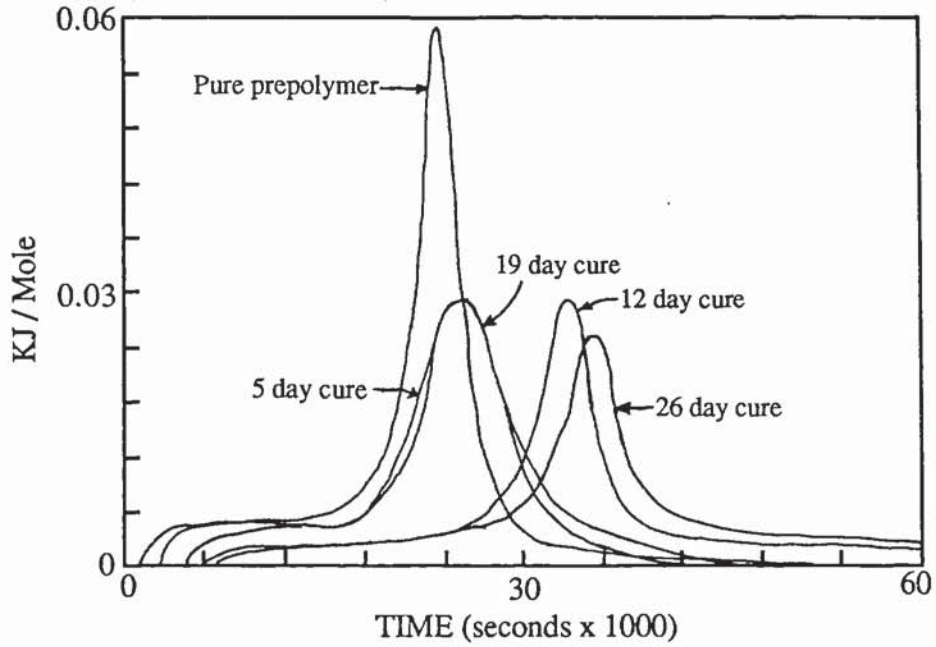
FIGURE 7.5b

POLYMERISATION RATES OF POLYMER CEMENTS, 0.6 W / C RATIO
(Degree of polymerisation data)

231
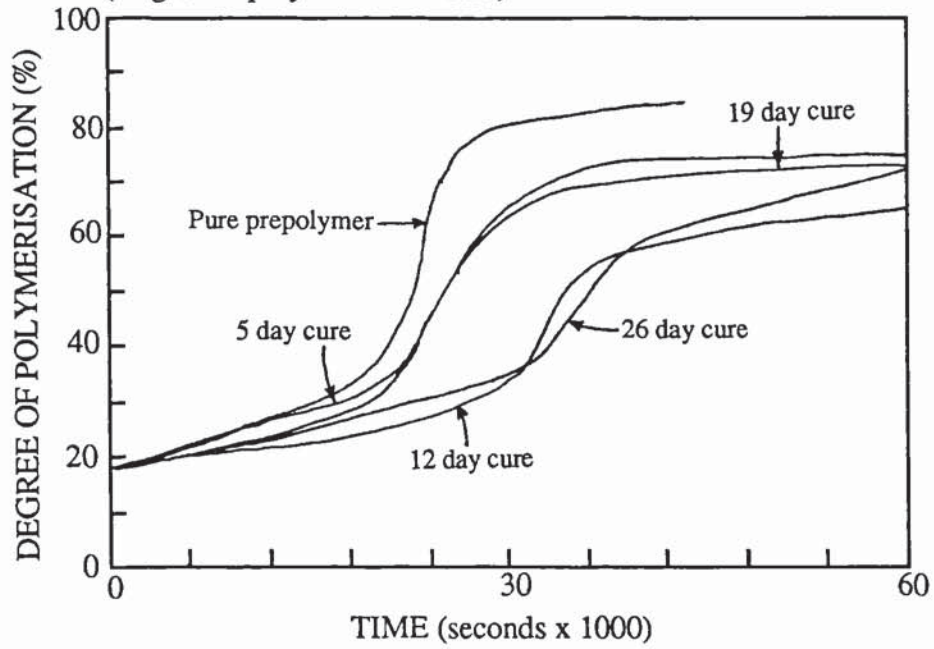
FIGURE 7.6a

POLYMERISATION RATES OF PREPOLYMERS
(Heat evolution data)
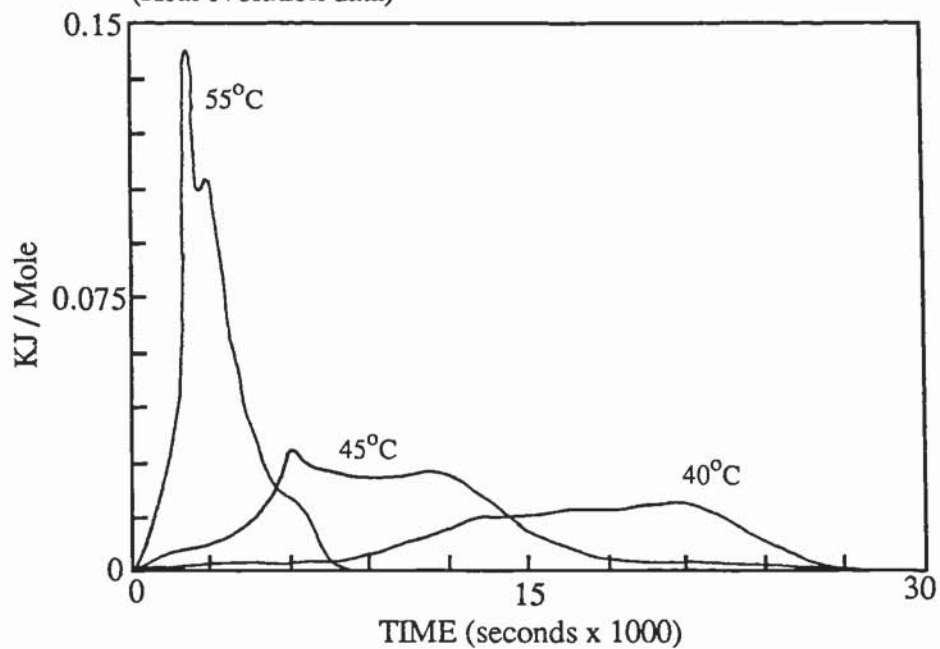
FIGURE 7.6b

POLYMERISATION RATES OF PREPOLYMERS
(Degree of polymerisation data)
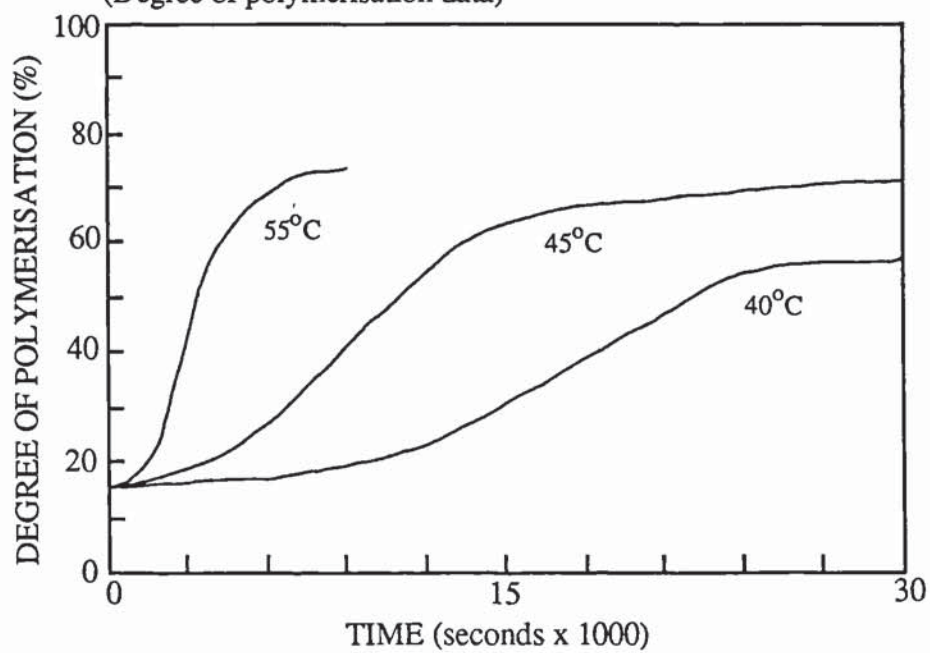
FIGURE 7.7a

POLYMERISATION RATES OF POLYMER CEMENTS
(Heat evolution data)
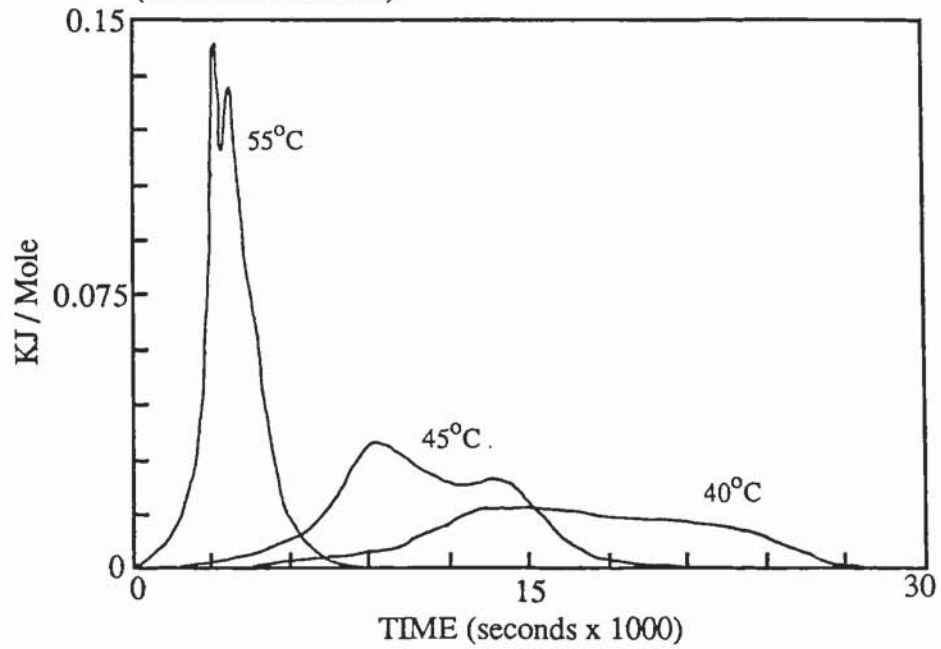
FIGURE 7.7b

POLYMERISATION RATES OF POLYMER CEMENTS
(Degree of polymerisation data)
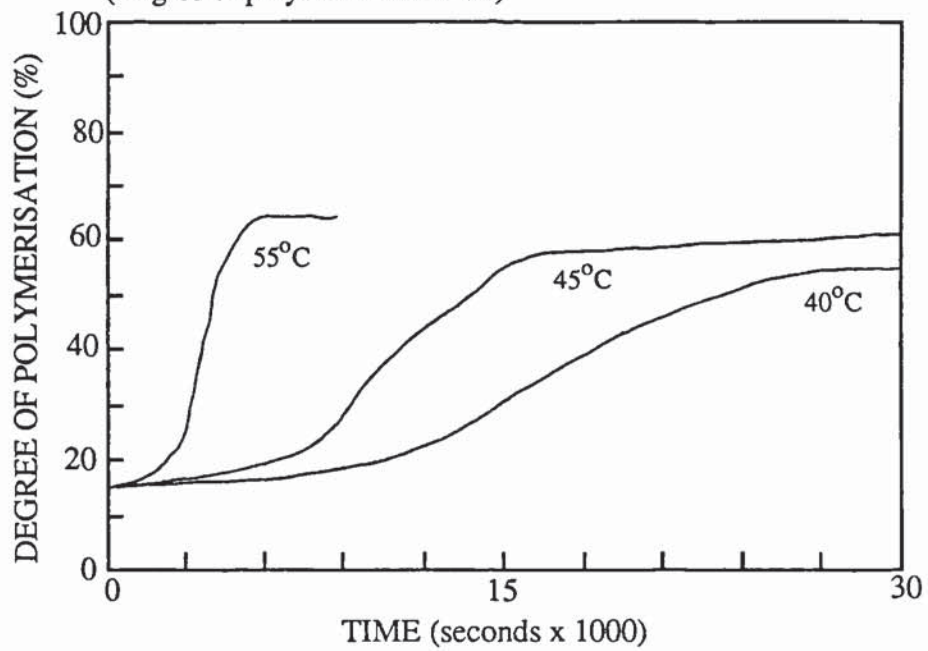
TABLE 7.1

OVERALL HEAT EVOLUTION DATA
FOR PURE PREPOLYMERS

Sample type	Temp. (°C)	Polymer weight (g)	Heat output (kJ/mol)
Pure pre-polymer (1)	40	2.3346	32.1
Pure Pre-polymer (2)	40	1.7106	20.9
Pure Pre-polymer (2)	45	1.7626	27.7
Pure Pre-polymer (2)	55	1.6248	28.0

TABLE 7.2

OVERALL HEAT OUTPUTS FOR 0.37 W/C
RATIO 26 DAY CURE POLYMER CEMENTS

Temp. (°C)	Polymer weight (g)	Cement weight (g)	Heat output (kJ/mol)
40	1.7939	1.7642	19.0
45	1.6347	1.6429	22.3
55	1.8395	1.8358	22.6

TABLE 7.3

OVERALL HEAT EVOLUTION DATA
FOR POLYMER CEMENTS AT 40°C

Sample type	Polymer weight (g)	Cement weight (g)	Heat output (kJ/mol)
0.37 W/C ratio 5 day cure	1.2294	1.2260	26.7
0.37 W/C ratio 12 day cure	1.2267	1.2211	25.2
0.37 W/C ratio 19 day cure	1.0416	1.0320	29.8
0.37 W/C ratio 26 day cure	0.9562	0.9387	26.3
0.6 W/C ratio 5 day cure	1.2037	1.2013	26.8
0.6 W/C ratio 12 day cure	1.1207	1.1137	23.1
0.6 W/C ratio 19 day cure	1.1300	1.1247	25.1
0.6 W/C ratio 26 day cure	1.1565	1.1507	26.8

FIGURE 7.8a

POLYMERISATION RATES OF POLYMER IMPREGNATED CEMENTS
(Heat evolution data)
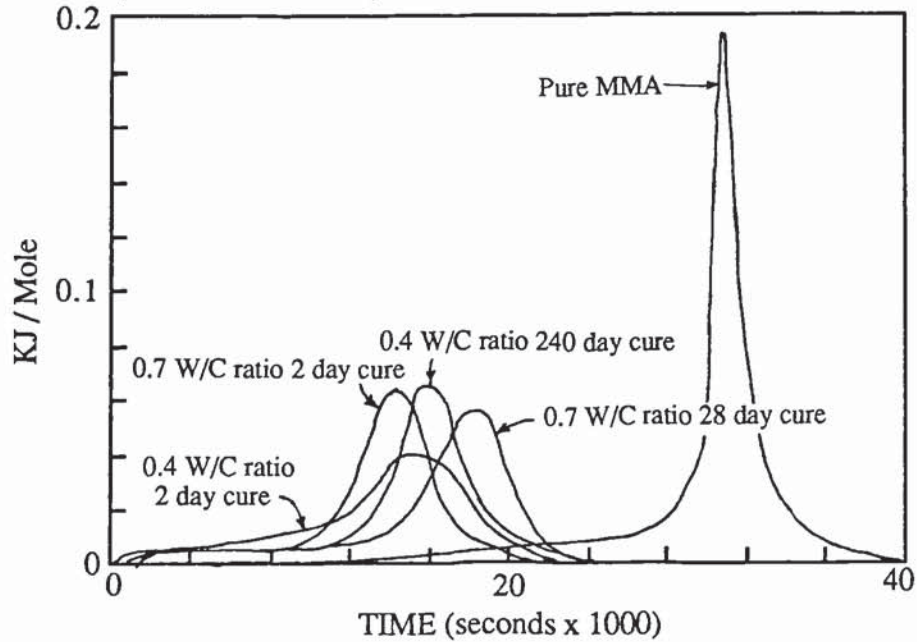
FIGURE 7.8b

POLYMERISATION RATES OF POLYMER IMPREGNATED CEMENTS
(Degree of polymerisation data)
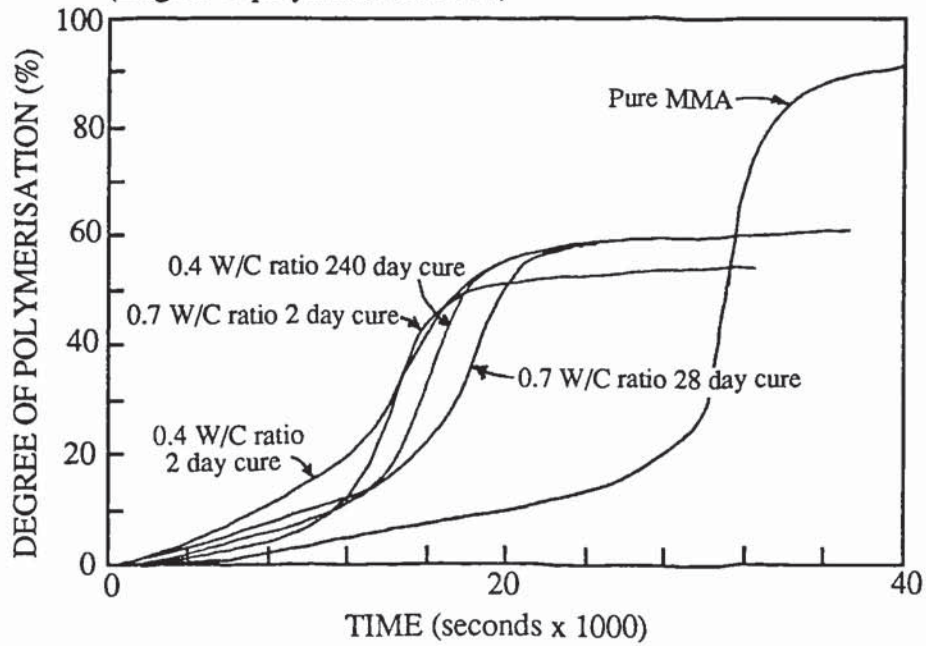
FIGURE 7.9a

POLYMERISATION RATES OF PURE MMA
(Heat evolution data)
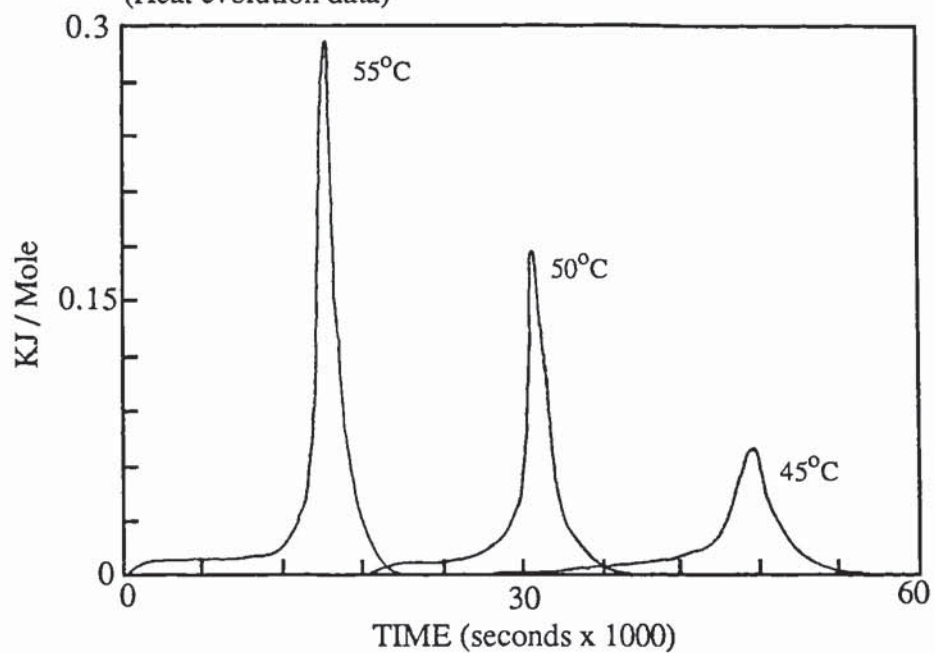
FIGURE 7.9b

POLYMERISATION RATES OF PURE MMA
(Degree of polymerisation data)
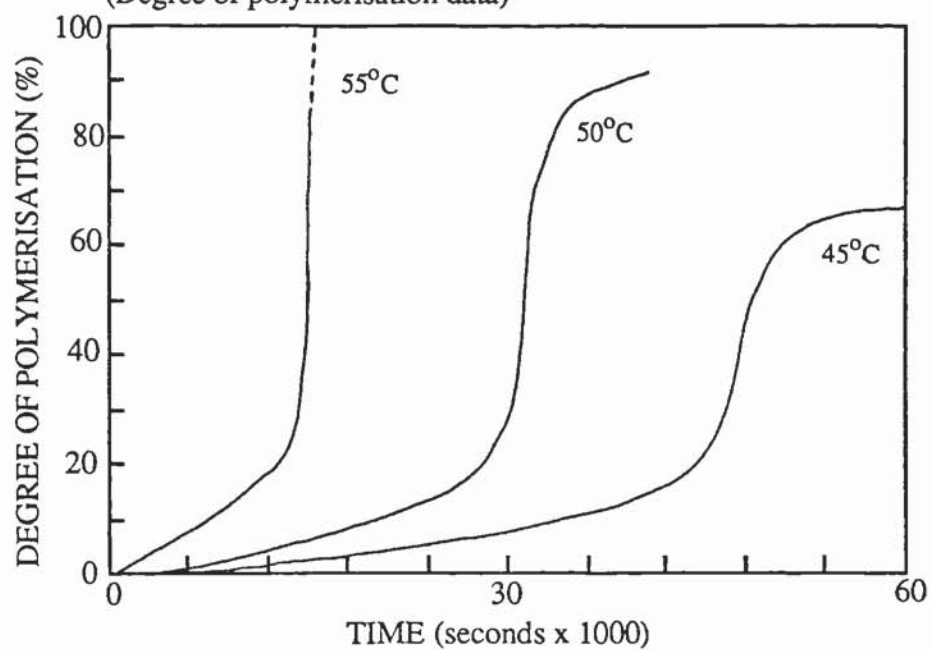
FIGURE 7.10a

POLYMERISATION RATES OF POLYMER IMPREGNATED CEMENTS
(Heat evolution data)
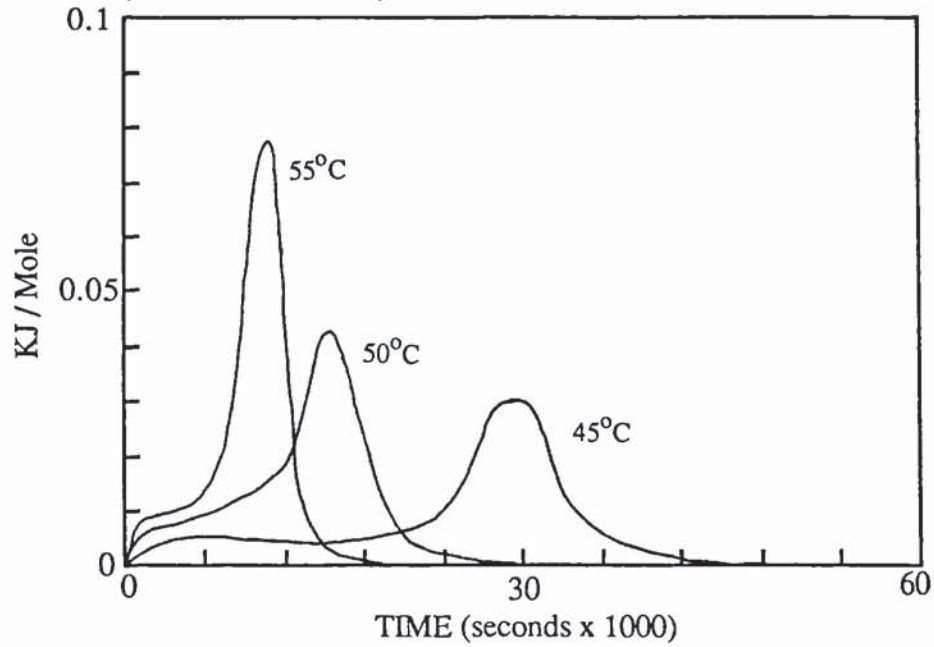
FIGURE 7.10b

POLYMERISATION RATES OF POLYMER IMPREGNATED CEMENT
(Degree of polymerisation data)
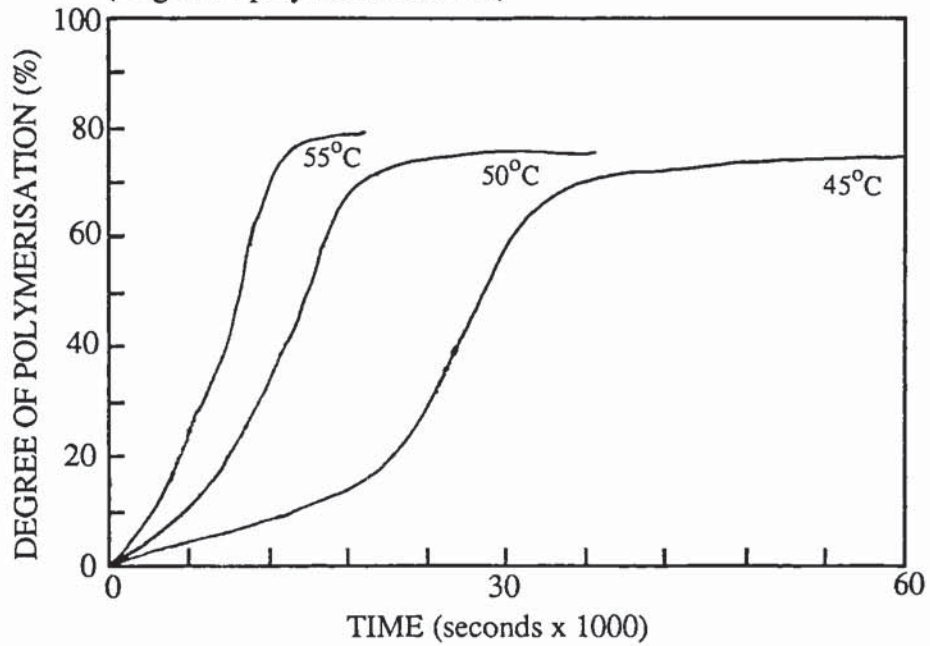
TABLE 7.4

OVERALL HEAT EVOLUTION DATA
FOR PURE POLYMERS

Temp ($^{\circ}$C)	Polymer weight (g)	Heat output (kJ/mol)
45	1.5883	33.3
50	1.6511	37.2
55	1.7162	68.7
50	1.8353	39.9
50	4.0708	41.8
50	5.3860	40.5

TABLE 7.5

OVERALL HEAT EVOLUTION DATA
FOR POLYMER IMPREGNATED CEMENTS

Sample type	Temp. ($^{\circ}$C)	Polymer weight (g)	Cement weight (g)	Heat output (kJ/mol)
0.7 W/C ratio 2 day cure	45	5.5883	12.0730	29.5
0.7 W/C ratio 2 day cure	50	5.5341	10.3875	29.4
0.7 W/C ratio 2 day cure	55	5.7780	10.7307	31.0
0.4 W/C ratio 2 day cure	50	3.9550	17.2940	30.1
0.4 W/C ratio 240 day cure	50	3.3376	18.1385	26.7
0.7 W/C ratio 2 day cure	50	5.5341	10.3875	29.4
0.7 W/C ratio 28 day cure	50	5.6117	13.4503	30.1

FIGURE 7.11
RATE OF DECOMPOSITION OF
BENZOYL PEROXIDE IN TOLUENE

Points in this region only used for calculation

With 2.0 g cement
Without cement
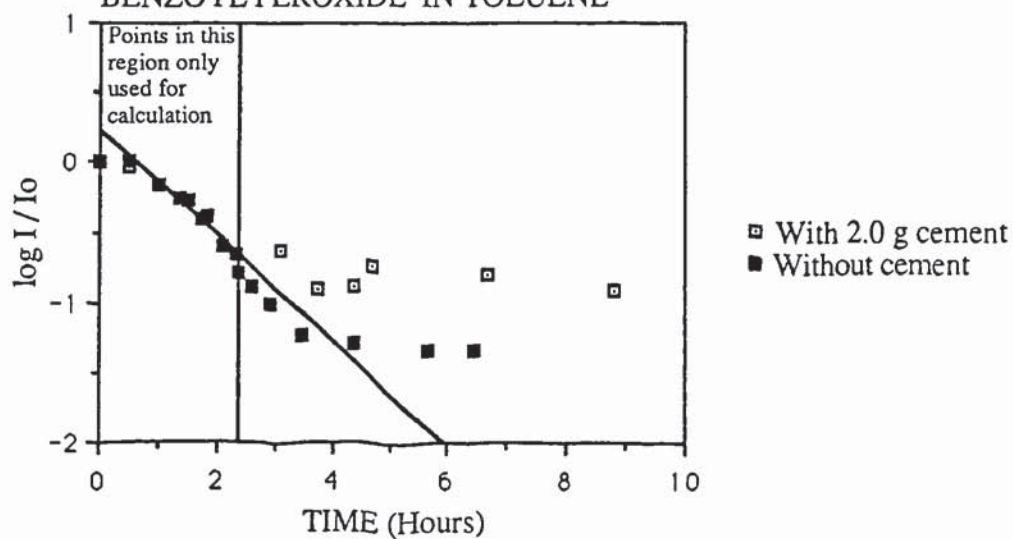
Temperature = 59.9 C
Initial concentration of BP = 1.0976 g/l
Initial concentration of DPPH = 0.0556 g/l
Rate of loss of DPPH without cement = -0.3783 1/h
Rate of loss of DPPH with cement = -0.4131 1/h

FIGURE 7.12
RATE OF DECOMPOSITION OF
BENZOYL PEROXIDE IN TOLUENE

Points in this region only used for calculation

With 30 g cement
Without cement
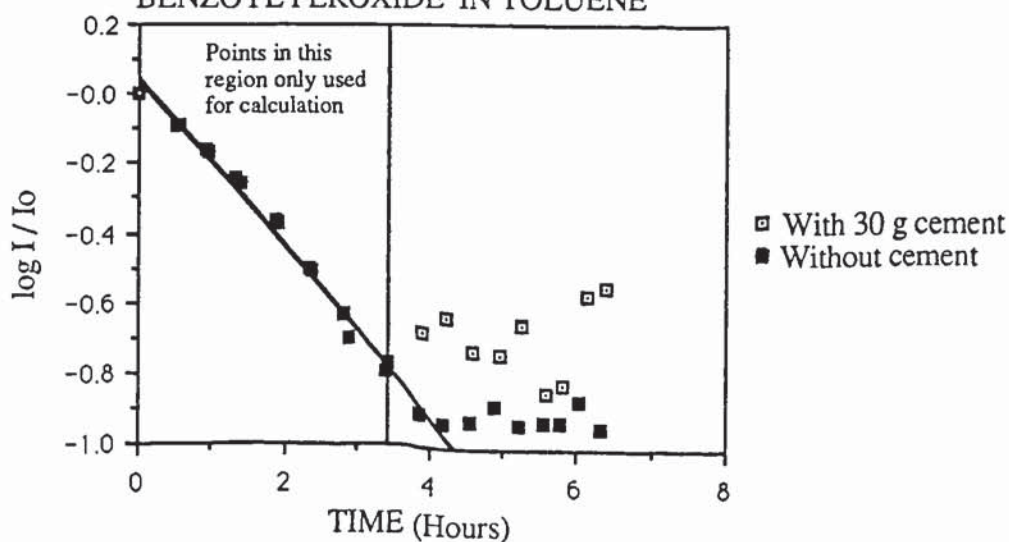
Temperature = 52.1 C
Initial concentration of BP = 3.0786 g/l
Initial concentration of DPPH = 0.0982 g/l
Rate of loss of DPPH without cement = -0.2384 1/h
Rate of loss of DPPH with cement = -0.2419 1/h

8 POLYMER IMPREGNATION STUDIES

8.1 INTRODUCTION

Polymer impregnation promises to be one of the most useful applications of polymer technology applied to the field of cements and concrete. Such materials are considered a class of composites in their own right, and have several advantages over ordinary cements and concretes: significant enhancement of mechanical properties are observed, and their polished surfaces show potential for decorative applications.

Polymer impregnated cement (PIC) is the term applied to composites where a significant depth of monomer penetration is achieved. But impregnation could also be said to take place from many adhesion surfaces where diffusion processes allow a small amount of penetration to take place. In terms of adhesion this is called 'mechanical' adhesion, the polymer forming a mechanical key with the cement pore structure *(see chapter 4.)*

Although a significant amount of information has been gathered about the mechanical properties of PIC, less is known about the interface and bonding between the two phases, and the state of the polymer itself. This project aimed to address some of these problems, especially : -

1) to examine the depth of penetration of different resins and monomers into adhesion surfaces,
2) to assess impregnation zones for evidence of polymer/cement reactions, and
3) to investigate the state of polymer from PIC in terms of their polymerisation histories and molecular weights.

Benzoyl peroxide-catalysed MMA was used for the majority of this work because of its low viscosity and widespread use as an impregnant. The techniques employed were those of optical and electron microscopy, and molecular weight determination via viscometric measurements. Molecular weights of polymer extracts from both the polymer cements described in *chapter 5* and PIC were compared to those for bulk polymer. Molecular weight data was also correlated with rate of polymerisation data, most specimens examined being those prepared in the calorimetry experiments described in *chapter 7*.

8.2 PREVIOUS WORK

Polymer impregnation of cements has been carried out for a number of reasons, particularly because it generally results in enhancement of mechanical properties of pre-cast cements. This derives from the lining or filling of pores in the cement structure, and is achieved generally by soaking. Monomers of low viscosity can penetrate the pore structure several centimetres from an impregnation surface, and can then undergo polymerisation in situ. The process of polymer impregnation of cements is somewhat complex, since it involves removal of pore water and its replacement with polymer. Steps are taken to maximise monomer inclusion and minimise its evaporation prior to polymerisation *(ref 5)*. A typical impregnation scheme would involve the following procedures : -

  1) casting of cement into the desired shape,
  2) curing as appropriate,
  3) removal of as much pore water as possible by drying,
  4) impregnation with monomer and initiator by soaking,
  5) wrapping to prevent monomer loss through evaporation,
  6) polymerisation by heating or irradiation, and
  7) finishing as desired.

8.2.1 EXAMINATION OF IMPREGNATED AND UNIMPREGNATED CEMENTS

Degree of impregnation may be assessed in a number of ways; visually, polymer impregnated regions appear as darker zones in cross-section, and in thin section are seldom observed filling or lining pores in the cement structure. A number of reviews are available for the microscopic identification of cement minerals using optical and electron techniques. Most ordinary portland cement clinkers contain the following approximate mineral composition : -

$$50\% \ C_3S$$
$$25\% \ C_2S$$
$$<10\% \ C_3A$$
$$<10\% \ C_4AF$$

Hydration of the silicates results in the formation of CSH gel, the aluminate and ferrite phases forming tetracalcium aluminate hydrate and calcium aluminoferrite hydrate respectively. The silicates produce calcium hydroxide in differing amounts. Since the

majority of clinker is composed of silicate phases, the hydration of OPC studied visually may be approximated to the hydration of grains of C_3S *(ref 142)*. Structures may be observed developing from the clinker, seen under the electron microscope as a collection of spheres of different sizes. These spheres hydrate both internally and externally from the grain surface, the latter being seen as a 'columnar' growth around grains. Calcium hydroxide also precipitates from the supersaturated solution, being seen as books of hexagonal plates. Once initial setting has occurred, the structure of hydrated OPC has few distinguishing features, since all the phases become interlocked. Surfaces may show the smooth well-defined ceramic character of clinker particles if the fracture surface passes through them, the CHS gel being generally massive and featureless. Books of calcium hydroxide crystals may also be included in the gel. Hydrates of the ferrite phase may be seen as needle-like crystals infilling voids. The pore structure may also be interpreted as the spaces between the interlocking solid phases.

8.2.2 ASSESSMENT OF THE AMOUNT OF POLYMER INCLUDED ON IMPREGNATION

Density measurements may be employed to assess the pore volume change on impregnation - however, such techniques involve varying degrees of complexity and are essentially destructive test procedures. For obvious reasons PIC articles used for structural applications cannot be investigated in this way, so the most common expression of polymer incorporation is as the percentage mass increase an object undergoes on impregnation *(refs 1, 5 and 143)*. The quantity is known as the 'polymer loading' calculated as follows:-

$$\text{Polymer load (\%)} = (W_i - W) / W \times 100\% \quad \text{where:-}$$

W = unimpregnated weight and
W_i = impregnated weight.

8.2.3 MINERALS AFFECTING THE PROCESSES OF FREE-RADICAL POLYMERISATION

Although many studies have shown how polymer impregnation enhances cement properties, less is known about the actual interactions taking place with the pore walls. Such effects are thought to be very significant, since PICs are stronger than predicted from the rule of mixtures *(ref 40)*. This finding advances the possibilities that a)

reactions take place between polymer and cement, b) crack propagation is modified, and c) in situ polymerisation changes the polymer state.

Several researchers have conducted studies into the third of these possibilities, in particular the molecular weight of polymer included in PIC. Other connected work has been conducted into polymerisation in porous media and the effects of aluminosilicate minerals on polymer molecular weights. In the light of this, PMMA is a particularly good polymer to investigate since it has been the subject of much research, and is hence well characterised.

8.2.3.1 EFFECT OF CEMENTS ON POLYMER MOLECULAR WEIGHTS

Mikhail *(ref 39)* conducted studies of the molecular weight of PMMA and polystyrene thermally catalysed by benzoyl peroxide, extracted from PICs, and found that average molecular weight is related to average pore size. It was concluded that there was no apparent relationship with cure time, but a tendency towards higher molecular weights for larger pore volumes. Ohama *(ref 143)* demonstrated that molecular weight reduces with increasing polymerisation temperature. This behaviour was also found by Madruga *(ref 41)* who also observed a decrease in molecular weight with increasing initiator concentration. Both observations are predictable from ordinary polymer kinetics in that increasing temperature and concentration of initiator results in the formation of more initiating radicals. Thus, more polymer chains are started, and from a finite supply of monomer, chain lengths will on average be smaller. Some anomalous behaviour was reported by Ohama *(ref 143)* who found the weight-average molecular weight of polymer extracts to decrease with increasing impregnation depth, the number-average molecular weight remaining roughly constant. According to standard polymer kinetics the reverse would be expected in that a thermal gradient would be established during the polymerisation process, the outside of the impregnated articles being hotter than the inside. Thus more initiating radicals would be formed in the outer layers leading to a lower molecular weight, the converse being true for the inner layers.

In a number of studies, yields of polymer from PICs were always found to be less than the polymer loading *(refs 41 and 143)*, good solvents having been used in their extraction. An interpretation of this behaviour is that interactions or reactions take place between monomer/polymer and cement rendering some polymer unrecoverable. Madruga *(ref 41)* was able to isolate two types of PMMA which he called 'free' and 'associated', the latter being interpreted as complexes, its molecular weight always being higher than that of free polymer.

8.2.3.2 EFFECT OF OTHER MINERALS ON POLYMER MOLECULAR WEIGHTS

Clay minerals have certain similarities to cement minerals in that they are both aluminosilicates, neutrality of charge being achieved by the inclusion of common metal cations in the crystal structure. Water is also present in both in a variety of different environments even after oven-drying. Clays are often used as fillers and pigments in acrylic paints and resins. These have been studied in terms of their effect on polymerisation processes. A survey of clay minerals by Solomon *(ref 90)* reported that all those studied inhibited the polymerisation of benzoyl peroxide-catalysed MMA. Lewis acid (i.e. electron-accepting) behaviour on the clay's part was proposed for this, two mechanisms being suggested : -1) preferential adsorption of initiating radicals at Lewis acid sites resulting in their termination by combination or disproportionation, 2) electron transfer from radicals to Lewis acid sites via carbonium ion formation. Aluminium in octohedral crystal edge sites was identified as the most likely position of the Lewis acid sites. In all cases initiation was achieved by thermal decomposition of benzoyl peroxide alone, and not in any way by the clays themselves. This was also found by Madruga *(ref 41)* in relation to cement minerals.

8.2.3.3 POLYMERISATION RATES EFFECTED BY CEMENTS

Cement minerals have been shown to affect polymerisation rates as discussed in *chapter 7*. Rates are related to the molecular weight of polymer formed. Although there are a number of competing factors to take into account it would generally be expected that a high polymerisation rate would produce low molecular weight polymer, and a low rate to produce a high molecular weight. If the processes of polymerisation are subject to interference from other substances then this will express itself as a change in molecular weight from that produced in their absence.

8.2.3.4 DETERMINATION OF POLYMER MOLECULAR WEIGHTS

Polymer molecular weights may be determined by a number of techniques including viscometry, osmometry, light scattering and gel permeation chromatography *(refs 51, 132 and 144)*. Although all of these techniques have high accuracies, only the viscometric technique requires simple apparatus, though somewhat time-consuming. Flory *(ref 132)* derives an expression for the relationship between polymer average molecular weight and viscosity based on the assumption that for a dilute polymer

solution its viscosity is determined by the amount of intermolecular 'friction', this being a function of concentration and chain length. The derivation is as follows : -

In dilute polymer solutions, the viscosity is determined by five major factors : -

> 1) The nature of the polymer,
> 2) the nature of the solvent and its behaviour in dissolving the polymer,
> 3) the amount of polymer present,
> 4) 'frictional' interactions between chains themselves, and
> 5) the physical conditions under which the viscosity was determined.

The fourth factor is of greatest importance here, since interactions take place between chains to different extents depending upon chain length. Longer chains have greater interactions, this leading to an increased resistance to shear of the solution and hence viscosity. Calculation of chain length involves equations accommodating the five factors listed above. The theory of this is discussed in elaborate detail by Flory *(ref 132)*, the following simplified version being given by Cowd *(ref 144)*.

If the viscosity of a polymer solution and its pure solvent are determined by some means, the 'specific' viscosity of the solution may be calculated as follows : -

$$\eta_{sp} = (\eta - \eta_o) / n_o$$ Where : - η_{sp} = specific viscosity,

$$\eta = \text{viscosity of polymer solution,}$$

and, η_o = viscosity of pure solvent.

Specific viscosity is thus an expression of the contribution the polymer makes to the viscosity of the solution as a whole. For a range of dilute polymer solutions of concentration C, plotting η_{sp}/C against C gives a linear relationship. Extrapolation to zero concentration yields a value of η_{sp}/C known as the 'intrinsic' viscosity of the polymer $[\eta]$. This is related to molecular weight by the following expression : -

$$[\eta] = kM^{\alpha}$$

Where : - M = number molecular weight (chain length),

k and α = constants dependent on factors 1,2,3 and 5 given above.

In determinations of viscosity using U-tube viscometers, it is possible to make the assumption that the viscosity of the polymer solutions are proportional to their flow

times through the viscometer. This is valid when the solutions are dilute, their densities being almost identical. Thus η_{sp} may be calculated simply by the expression : -

$$\eta_{sp} = (t_2-t_1) / t_1 \quad \text{where : -} \quad t_1 = \text{flow time of pure solvent, and}$$
$$t_2 = \text{flow time of polymer solution.}$$

Thus by determining viscosity over a range of concentrations, specific viscosity/concentration may be plotted against concentration, giving a linear relationship. The intercept is the intrinsic viscosity from which the average molecular weight may be calculated using the expression *(ref 50)* : -

$$[\eta] = kM^{\alpha}$$
Where : - $k = 1.81 \times 10^3$ and $\alpha = 1.22$, for PMMA in $CHCl_3$ at $25^{\circ}C$.

This is sometimes re-arranged as follows, the constants being different in both cases *(ref 51)* : -

$$M = k[\eta]^{\alpha}$$
Where : - $k = 4.3 \times 10^{-5}$ and $\alpha = 0.8$, for PMMA in $CHCl_3$ at $25^{\circ}C$.

Either form is applicable so long as the appropriate constants for a particular solvent are known. Constants for many solvents have been determined, the most commonly used of these being toluene, chloroform, benzene, acetone and methyl ethyl ketone *(refs 41, 143, 50 and 51)*.

8.3 RESULTS AND DISCUSSION

8.3.1 SPECIMEN PREPARATION

Specimens with a range of pore size distributions were prepared using OPC. These had W/C ratios of 0.4 and 0.7 and curing times of 2 to 240 days. Pore size distributions were characterised by MIP, and as expected there were more larger pores with higher W/C ratios and shorter cure times *(fig 8.1)*. It was hoped that by using extremes of pore size distribution, differences in the impregnant state could be detected on extraction, the differences being attributable to the pore size restrictions. Polymer loadings for cements as cast and using stacks of thin impregnated discs are given in *table 8.1*.

8.3.2 MACROSCOPIC EXAMINATION OF SPECIMENS

8.3.2.1 CEMENTS IMPREGNATED WITH MMA

Examination of sections through impregnated cylinders showed that high W/C ratio cylinders cured for up to 240 days are easily impregnated with MMA simply by soaking. Regions impregnated can sometimes be seen easily, and sometimes not. PMMA tends to darken the cement, and gives a cut, polished surface a shiny appearance; however some polymer was also found in the lighter regions*(fig 8.2a)*. A possible explanation is that the darker areas are regions of pore filling, and the lighter ones are areas of pore lining.

Other useful features may be seen, for example where significant monomer evaporation has occurred, polished sections show dendritic patterns close to the impregnation surface *(fig 8.2b)*. Also, since hairline cracks introduced during setting and drying of the cement provide a major route for the monomer to penetrate, monomer fills the cracks and shows their position. Cements of a low W/C ratio show tangential cracks, and those of a high W/C ratio show radial cracks. Darker zones are often seen closest to the impregnation surface, but it was also common to see an additional darker zone in the centre of the specimens. It would therefore seem that impregnation patterns are affected significantly by the cracking pattern, this varying with the W/C ratio. Polymer load will in turn be affected by cracking, and should only be regarded as a measure of the amount of the polymer included in that geometry of specimen, and not necessarily as the maximum amount of polymer the cement can hold based on its porosity.

8.3.2.2 PENETRATION OF ADHESION SURFACES BY OTHER POLYMERS

Sectioning specimens where polymer had been bonded to cement surfaces again showed some darkening due to impregnation from the adhesion surface. All the polymer and resin systems tested showed limited penetration of the adhesion surface with the exception of epoxy resin. Depth of penetration was of the order 0.2 mm, indicating that there is significant mechanical keying between cement and polymer. This fact was borne out by the strength tests described in *4.3.4 and 4.3.5,* where near interfacial failure was rare in epoxy, the general strength of polymer/cement bonds on a macroscopic level being attributed to mechanical keying, rather than chemical adhesion. Penetration along hair-line cracks was again visible, particularly where epoxy resin was bonded to one side of cement discs. This showed penetration along cracks to give a radial or tangential pattern on the non-polymer side of the disc.

8.3.3 OPTICAL MICROSCOPY

8.3.3.1 THIN SECTIONS OF CEMENT IMPREGNATED WITH MMA

In the body of the cement samples three features of mineralogical interest were noted : - a) hydrated calcium silicates with little or no birefringance, b) calcium hydroxide (Portlandite) with fine first order crystals and c) unhydrated cement clinker particles (i.e. C_4AF, C_3A, C_3S and C_2A) with light greys and pale yellows *(fig 8.3a&b)*.

Contrary to expectations, the polymer proved to be almost featureless in both plane polarised light and crossed nicols. All the common cement phases could be seen in thin section, the texture becoming larger-grained and more porous with increasing W/C ratio*(fig 8.3a&b)*. Impregnated regions were very difficult to see, even at low magnifications due to the general lack of features displayed by the polymer. This contrasted markedly to the macroscopic observations. However, some specimens did show zones darker than the body colour of the cements, these appearing as concentric bands a few mm inside the impregnation surface. Careful examination of these areas at high magnifications did not show any clear evidence of these being reaction rims since the appearance of the minerals was not substantially different to those in the body of the cements. The probable explanation is that the zones represent 'tide marks' of the benzoate phases formed by reaction of benzoyl peroxide with cement, that have become concentrated by the passage of MMA through the pore structure from the impregnation surface.

8.3.3.2 SECTIONS THROUGH MMA POLYMER CEMENTS

The polymer cements prepared in the calorimetry experiments described in *7.3.2* were sectioned to produce specimens polymerised at five different temperatures. The corresponding pure prepolymer was also sectioned, but proved to be almost completely featureless, even though the average chain lengths must be very different. The sections themselves showed sedimentation of the cement sieved to 300 μm. As expected, the amount of sedimentation was greatest at the lowest temperature, this taking the longest time to polymerise *(fig 8.4a&b)*. It was not clear if this effect was offset by the reduction in viscosity that must occur with higher temperatures. Nevertheless, even using prepolymers there was still significant sedimentation taking place in spite of their viscosities being high compared to the monomer itself.

Careful examination of the outsides of the cement particles did not yield any clear indications of reactions producing new minerals or consuming the existing mineral assemblage.

8.3.3.3 SECTIONS THROUGH CEMENTS EMBEDDED IN EPOXY RESIN

As with MMA-impregnated cements, the region where the polymer had penetrated was very hard to see in thin section, but obvious on macroscopic examination. There was no clear indication of reactions having taken place between polymer and cement, and the appearance of the individual cement grains and the overall texture remained unchanged in the impregnated region.

The polymer itself did show features in crossed nicols; First, extinction bands radiating from sharper parts of the cement surface and secondly, small bubbles on the cement surface *(fig 6.3a&b)*.

8.3.4 SEM OF IMPREGNATED AND UNIMPREGNATED CEMENTS

A number of mineral phases were observed on fracture surfaces, though their general character was rather featureless. These included : - a) Large hexagonal plates, b) small needle-like radiating crystals, and c) bundles of small spheres, these being most noticeable on cements of a high W/C ratio. Williamson *(ref 142)* indicates that these are calcium hydroxide, columnar hydration products or hydrates of the ferrite phase, and unhydrated cement respectively *(fig 8.5a&b)*. The random orientation of these minerals and the general loose texture gives some indication of the nature of the pore structure

between these minerals. This ranges in scale from actual voids, through the gaps between individual mineral growths to the spaces within the growths themselves.

Polymer impregnation was often hard to identify conclusively, the general texture of many cements examined being massive and rather featureless. However, the main result of impregnation was to make the textures even more massive *(fig 8.6a&b)*. Certain polymer features were apparent; voids could be seen partially filled with polymer, and fissures could be seen filled with polymer *(fig 8.7)*, particularly on high W/C ratio specimens of low cure times *(fig 8.8)*. In certain cases voids had indications of polymer lining, though it was uncertain if the features noted were only hydration products *(fig 8.9a&b)*.

8.3.5 LONG IMMERSION STUDIES

These experiments were conducted in order to investigate certain anomalies noted by Maleki-Toyserkani*(ref 124)*, where certain cement cylinders cracked on impregnation with MMA. Reactions were presumed to occur between polymer and cement resulting in the cracking. This possibility was investigated by immersion in both MMA and a solution of benzoyl peroxide (the polymerisation catalyst) in toluene, an inert solvent. This procedure was intended to simulate the soaking phase in the production of PIC.

After four months immersion in MMA, none of the cements appeared visibly changed, though there were slight increases in mass. It would appear that no reaction substantial enough to cause cracking occurs with the monomer alone. However, with the benzoyl peroxide in toluene solution, deposits began to appear after six weeks or so. These were apparent on the surface of all cements particularly those of lower W/C ratio and cure time. After three months fragments of cement could be seen to have spalled from the cement surfaces. A reaction thus appears to occur between benzoyl peroxide and cements under these conditions, benzoate formation being presumed *(table 8.2)*.

8.3.6 EFFECTS OF CEMENT ON POLYMER MOLECULAR WEIGHT

All molecular weights were calculated from viscosity measurements using the following relationships : -

Average molecular weight = 1.81×10^3 [Intrinsic viscosity]$^{1.22}$ *(ref 50)*

[Intrinsic viscosity] = 4.3×10^{-5} (Average molecular weight$_t$)$^{0.8}$ *(ref 51)*

Although it is possible that these coefficients may not strictly be applicable to extracted polymers (for reasons discussed later), the molecular weights thus calculated are relative, if not absolute. Comparison of the values obtained for molecular weights via the two equations shows about two orders of magnitude difference, also bringing the absolute values into doubt. However, the latter values of 10^5-10^6 seem more reasonable than the former (10^3-10^4), bearing in mind the small relative number of free-radicals formed from the decomposition of benzoyl peroxide available to initiate chains *(see figs 7.1 and 7.2)*.

8.3.6.1 SPECIMEN DESIGN AND POLYMER LOADING

Limitations are placed upon the depth of penetration of even low viscosity monomers by the nature of the cement pore structure and cracking pattern upon drying. Thomas *(ref 126)* demonstrated that polymer loading is variable between otherwise identical samples as well as with W/C ratio and cure time. For rate and molecular weight studies it was hoped that complete impregnation could be achieved to allow comparison between different cements. As this appeared an impossibility on the standard cement cylinders, it was decided that stacks of thin discs individually impregnated would be used. This produced thin specimens and minimised temperature gradients through the specimens during their polymerisation in the calorimeter *(see chapter 7)*. Heat transfer properties vary for different cements, this having some potential effect on molecular weight. By using thin specimens of low mass this problem was minimised.

Several papers have indicated that pore size effects molecular weight by limiting the supply of monomer within individual pores. To make valid comparisons between pore size and molecular weight it was necessary to examine polymer from completely filled pores, since a partially filled pore would itself place steric limitations on polymer growth.*Table 8.1* illustrates the enhancement in polymer loading by the disc technique.

8.3.6.2 CHAIN LENGTH DETERMINATIONS AT DIFFERENT TEMPERATURES

Results given in *figures 8.10 and table 8.4* demonstrate that for pure polymers, viscosity and hence chain length reduces with increasing polymerisation temperature. This was to be expected since at higher temperatures more chains are initiated, and in a finite supply of monomer the average chain length will be smaller. The 45°C polymerisation seems somewhat anomalous, not appearing to belong to the same family of lines denoting the other polymerisation temperatures. The lowest molecular weights

were shown by the polymers equivalent to polymer cements, these being polymerised at 65°C.

8.3.6.3 STATE OF POLYMER EXTRACTS

The general appearance of the bulk polymer was different from that extracted from both polymer cements and PICs. Bulk polymer was transparent or slightly yellow in colour, the extracts being translucent white or pale brown in solution. This did not appear to be due to major contamination by incomplete separation of polymer and cement for the following reasons: - 1) that the appearance was the same even after filtering via the soxhlet technique and centrifuging dilute solutions; 2) since major contamination affects viscosity significantly then it would be expected that all extracts would have viscosities either higher or lower than bulk. In every case the viscosity was higher in polymer cement extracts and lower in PICs, suggesting that this was not the case. Contamination may of course be different in each case - however this seems unlikely. Nevertheless, should contamination have occurred, viscometry is tolerant of this to some extent *(ref 50)*.

In *Chapter 5* evidence was presented for reactions between MMA and cements, thus it seems likely that extracts would contain some of the interaction products, namely calcium methacrylate and benzoates. It should be noted that if the actual nature of the polymer may no longer be 100% polymerised MMA, the viscosity coefficients are not strictly applicable.

8.3.6.4 CHAIN LENGTHS IN POLYMER IMPREGNATED CEMENTS

Each polymer impregnated cement was compared to a pure polymer of identical composition, polymerised at the same temperature. In every case the PIC extract had a lower molecular weight than the corresponding pure polymer *(table 8.3)*.

Between the extracts themselves the relationship between molecular weight and polymerisation temperature was uncertain *(fig 8.11 and table 8.3)* ; if the mechanisms and kinetics are the same for polymer inside cements as they are in bulk then the trend should be the same as for pure cements i.e. lower molecular weights for higher polymerisation temperatures. Unlike other studies there did not appear to be a clear correlation between molecular weight and pore size distribution; with both W/C ratios specimen molecular weights were higher at longer cure time and corresponding lower porosity. All specimens had largely similar molecular weights, whereas it would be

expected that with lower W/C ratios and longer cure times, average pore size is lower, hence molecular weights should be lower.

A possible explanation of the apparent anomalies in the work could be that the viscosity coefficients may not be strictly applicable to the extracts, because the polymers contain interaction products and groups other than those of MMA alone. In addition the viscosity lines do not appear to belong to the same families *(fig 8.12 and table 8.4)*.

8.3.6.5 CHAIN LENGTHS IN POLYMER CEMENTS

Each polymer cement was polymerised under the same conditions as a corresponding pure prepolymer, using the same batch of monomer and initiator mixture. By this procedure comparisons could be made between each pair, but not necessarily between pairs themselves, since there may have been minor variations batches, and the polymerisation histories may have been slightly different *(figs 8.13a-d and table 8.5)*.

In all cases the polymer cement extracts had a higher molecular weight than the bulk monomer, this being the reverse of that observed in PIC extracts. There was also a tendency to higher molecular weights at longer cure times.

8.3.6.6 CORRELATION AND INTERPRETATION OF MOLECULAR WEIGHT AND RATE DATA

Reference to the rate of polymerisation data in *chapter 7* indicated the following : - First, faster polymerisation rates are associated with lower molecular weights, both being caused by a rise in polymerisation temperature; secondly, polymerisation is accelerated in impregnated cements, the polymer produced having a lower molecular weight than bulk; and thirdly, polymerisation is retarded in polymer cements, the polymer produced having a higher molecular weight than bulk. Clearly interactions take place interfering with polymerisation processes. Care must be taken in the identification of those processes affected, since the overall rate and average molecular weight are subject to competing factors.

With reference to *chapter 7*, three types of interaction may affect polymerisation rate and chain length. Evidence for each is as follows: -

1) Free-radical

There is no evidence here or in the literature that cements themselves produce free radicals, thus they cannot be considered initiators.

Godard *(ref 92)* observed enhancement of the decomposition rate of benzoyl peroxide in asbestos cements due to the alkalinity of the pore surface. This seems possible in ordinary cements, although no effect was noted in the DPPH experiment described in *chapter 7*. The experiment used powdered cement, this being a mixture of alkalis, hydrated and unhydrated cement minerals rather than the alkali-rich pore surface of a solid cement. It is possible that the interaction is masked by other effects in powdered cements.

Clay minerals have the ability to modify termination rates *(ref 90)* by Lewis acid-base interactions with the C=C of acrylic monomers. Cements may perform similar reactions, this presumably being more noticeable in polymer cements where hydrated and unhydrated aluminosilicates come into contact directly with the monomer. This behaviour was not noted with the DPPH experiments *(7.3.4)*. However, a possible explanation could be that the rate of reaction between radicals and DPPH is orders of magnitude higher than that for radicals and cement minerals.

2) Chemical

Reactions were noted between benzoyl peroxide and cements *(chapter 5)*. These could have the effect of consuming benzoyl peroxide, rendering that consumed unavailable to provide initiator radicals. It is uncertain if the reaction producing calcium methacrylate modifies polymerisation rates.

3) Physical

Propagation rates in the polymer / monomer mixture are relatively unaffected by viscosity since this is mostly controlled by diffusion of the monomer to free-radical sites on growing polymer chains. However, if interactions occur with cement powder particles or pore walls, interfering with monomer diffusion, then the overall polymerisation rate would be modified. Adsorption phenomena could thus be invoked to explain differences of this kind between powders and pore systems.

A full explanation of the effects noted is still open to debate, but the following is suggested : -

1) The alkalinity of the cement pore surface accelerates polymerisation in PICs, either by enhancing decomposition of benzoyl peroxide to produce radicals, or by modifying diffusion of monomer molecules. These effects may offset any reduction in initiator concentration by non-radical reactions with cement. Thus in a finite supply of monomer more chains are started, the average molecular weight being reduced.

2) Polymerisation of polymer cements is retarded by two mechanisms; first, by physically restricting diffusion of monomer and secondly, by decomposition of benzoyl peroxide by reaction with cements, reducing the number of initiator radicals that can be formed. Thus in a finite supply of monomer fewer chains are started, the average molecular weight being increased.

8.4 SUMMARY AND CONCLUSIONS

Experiments were conducted into the penetration of resins and monomers into cement pore structures, such that they could be cured in situ. Macroscopic observations of PIC were made, and optical microscopy used to examine sections through polymer/cement interfaces. Polymer was also extracted from both polymer cements and impregnated cements prepared over a range of temperatures, this allowing determination of their average molecular weights. This data was correlated with the polymerisation rates of their formation, and the physical restrictions imposed by polymerisation in powders and pore systems.

It was concluded that : -

1) Viscous resins can easily penetrate cement surfaces, access to the deep pore structure being aided by micro-cracking. Cracking patterns of cements depend upon W/C ratio.

2) Higher polymerisation temperatures produced polymers of lower molecular weight in bulk and in association with cements.

3) There is a correlation between rate and molecular weight in the polymerisation of MMA catalysed thermally by benzoyl peroxide, in contact with cements. Molecular weights are higher than bulk in polymer cements, this corresponding to a decrease in rate. In impregnated cements the molecular weight is lower than bulk, this corresponding to an increase in rate. Further work is needed for a fuller understanding of the mechanisms by which these processes occur.

4) There was no apparent relationship between pore size distribution and molecular weight of polymer extracted from PIC, complete impregnation of all pores being presumed.

FIGURE 8.1
MIP DATA FOR DIFFERENT CEMENTS
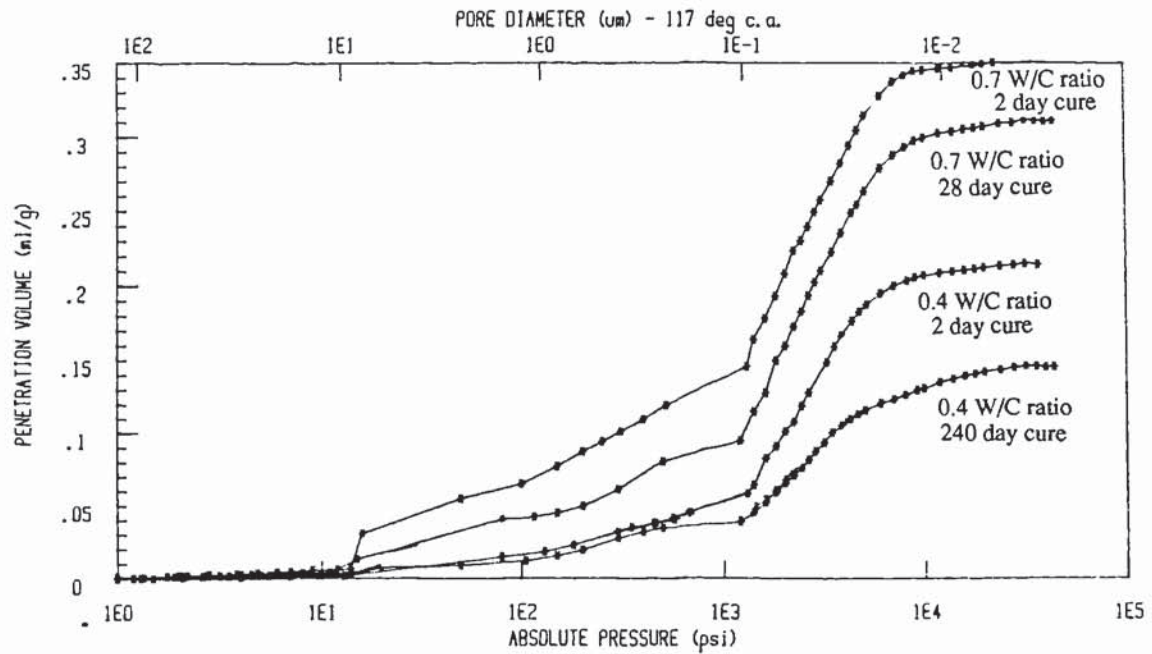
TABLE 8.1
POLYMER LOADINGS ON SOAKING

SPECIMEN	POL. LOAD AS CAST(%)	POL. LOAD AS DISCS(%)
0.4 W/C ratio 240 day cure	16.5	18.4
0.4 W/C ratio 2 day cure	20.1	22.9
0.7 W/C ratio 28 day cure	40.7	41.7
0.7 W/C ratio 2 day cure	46.3	51.1 53.3 53.8

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FIGURE 8.2a
CEMENT CYLINDERS IMPREGNATED WITH PMMA

*Top left , 0.4 W / C ratio 2 day cure; top right, 0.4 W / C ratio 240 day cure;
bottom left, 0.7 W / C ratio 28 day cure; bottom right, 0.7 W / C ratio 2 day cure.
Cylinder diameter = 49 mm.*

FIGURE 8.2b
CEMENT CYLINDERS IMPREGNATED WITH PMMA

*0.7 W / C ratio 28 day cure : - Note dendritic impregnation pattern caused by some
evaporation of monomer from surface. Cylinder diameter = 49 mm.*

Note darker rim parallel to impregnation surface. Horizontal dimension = 2 mm.

FIGURE 8.3b
ZONES INSIDE PMMA-IMPREGNATED CEMENT (Thin section)
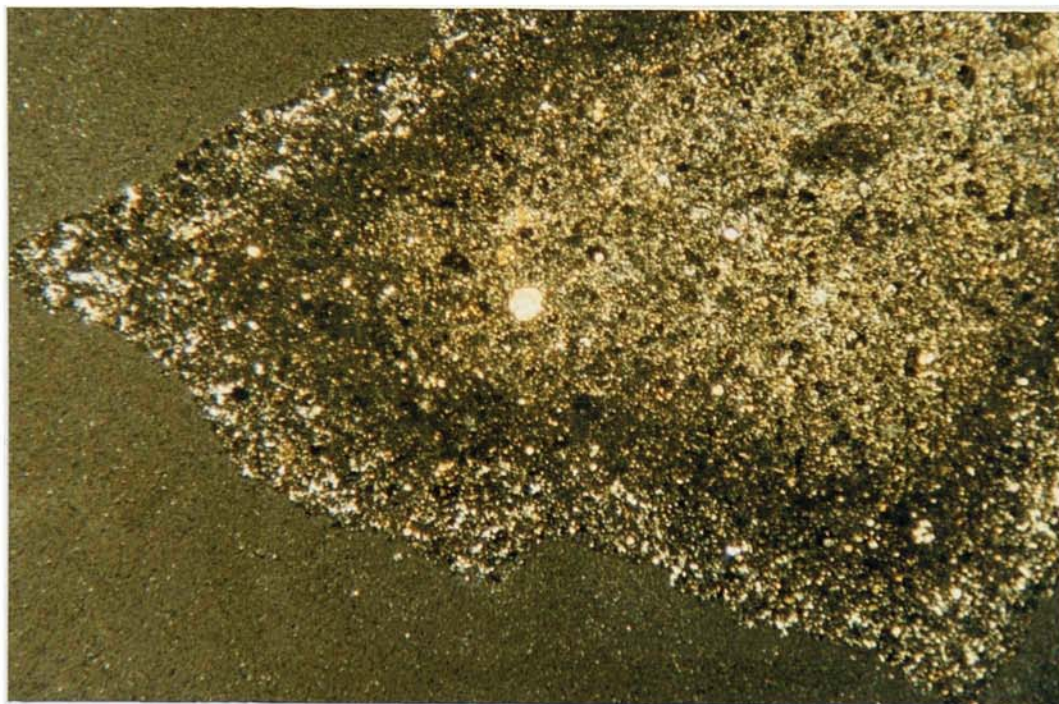
Note darker rim parallel to impregnation surface. Horizontal dimension = 5 mm.

FIGURE 8.4a
POLYMER CEMENT CURED AT 30°C (Thin section)
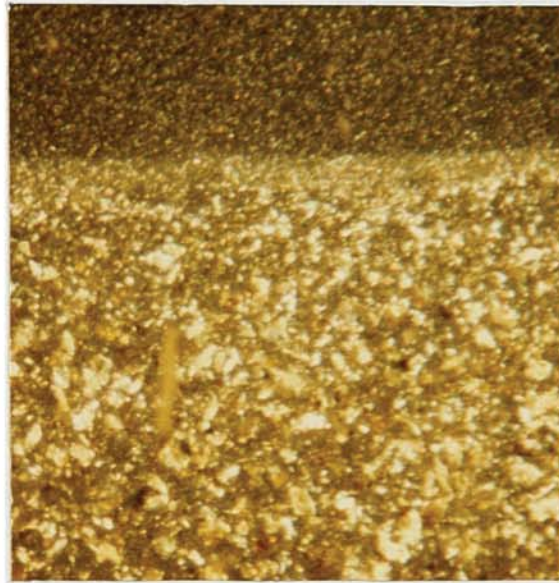
Note segregation of minerals due to slow curing. Horizontal dimension = 5 mm.

FIGURE 8.4b
POLYMER CEMENT CURED AT 55°C (Thin section)
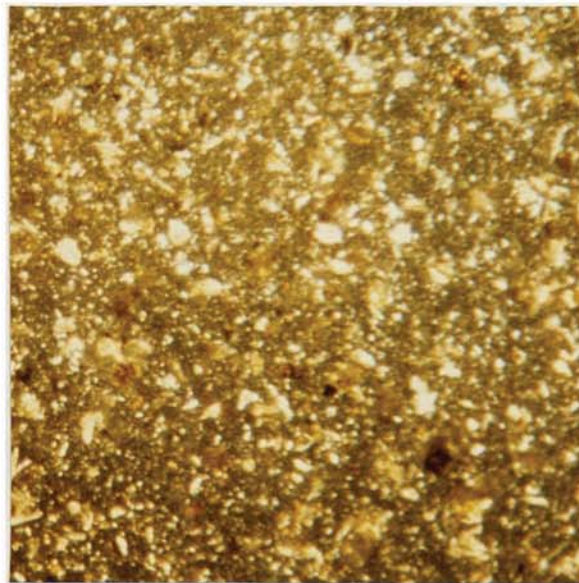
Note lack of segregation due to fast curing. Horizontal dimension = 5 mm.

FIGURE 8.5a
SEM OF UNIMPREGNATED CEMENT
(0.7 W / C RATIO 2 DAY CURE)
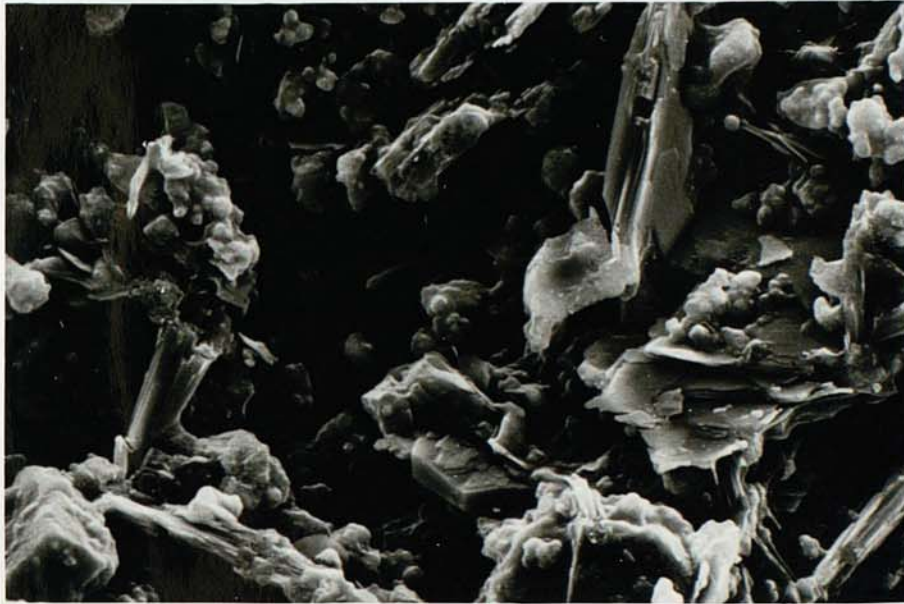
Note hexagonal crystals of calcium hydroxide, massive CSH gel, needle-like or columnar hydration products, and small spheres of unhydrated cement. (x 320)

FIGURE 8.5b
SEM OF UNIMPREGNATED CEMENT
(0.7 W / C RATIO 28 DAY CURE)
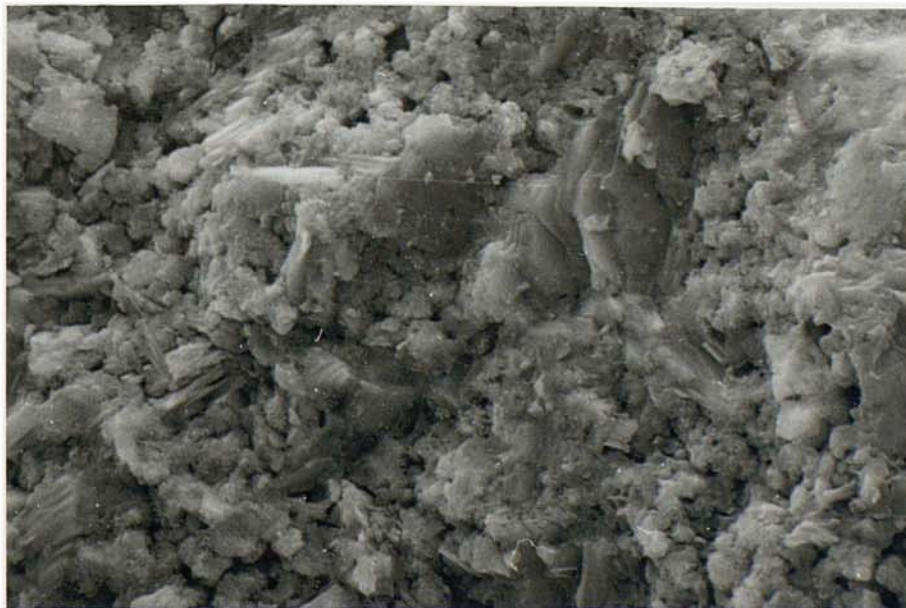
Note hexagonal crystals of calcium hydroxide, massive CSH gel, needle-like or columnar hydration products, and small spheres of unhydrated cement. (x 320)

FIGURE 8.6a
SEM OF IMPREGNATED CEMENT
(0.4 W / C RATIO 240 DAY CURE)

Note general featureless texture, polymer being hard to identify. (x 320)

FIGURE 8.6b
SEM OF IMPREGNATED CEMENT
(0.4 W / C RATIO 2 DAY CURE)
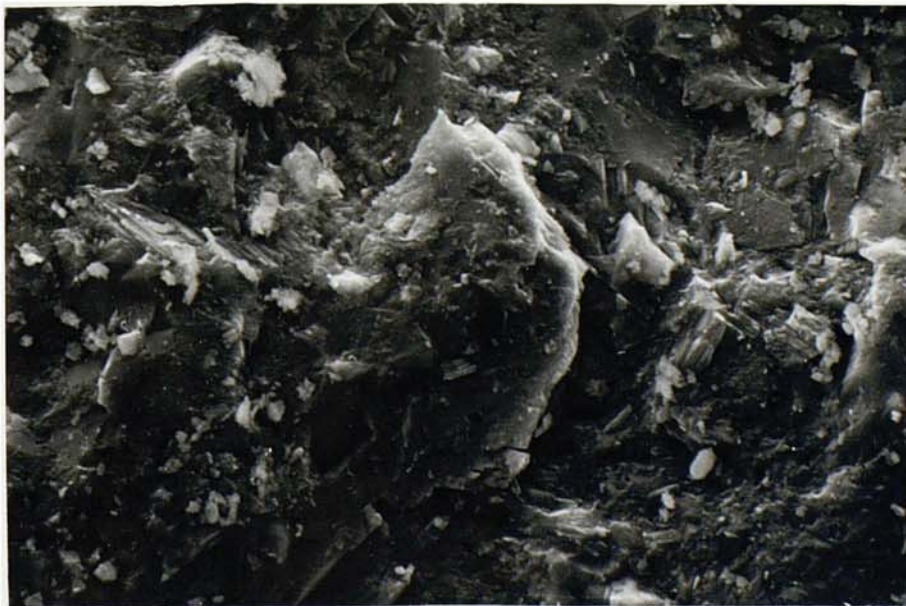
Note general featureless texture, polymer being hard to identify. (x 320)

FIGURE 8.7
SEM OF VOID LINED WITH POLYMER IN IMPREGNATED CEMENT
(0.4 W / C RATIO 240 DAY CURE)
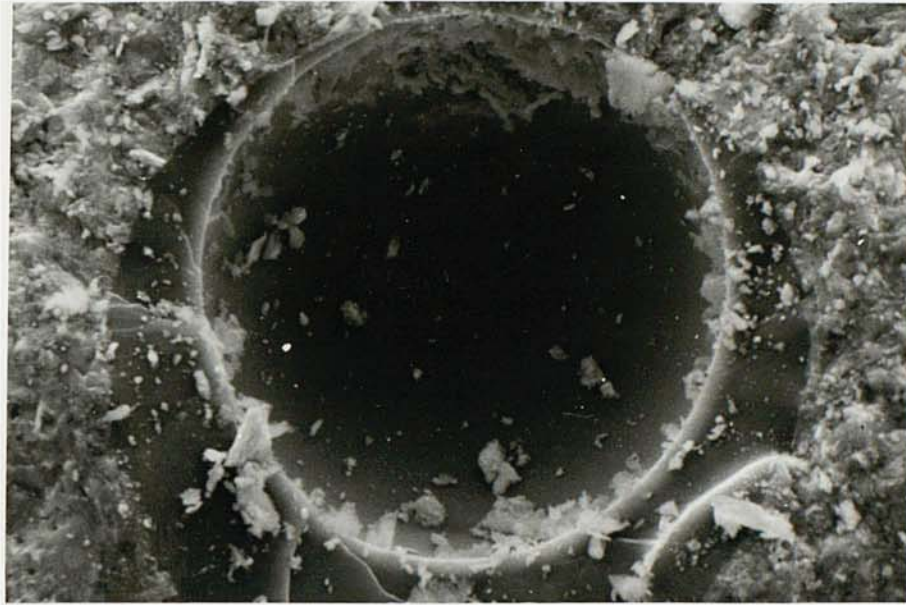
Note how air in the void has risen as a bubble producing asymmetrical lining. (x 160)

FIGURE 8.8
SEM SHOWING POLYMER FILLING LARGER CRACKS IN
IMPREGNATED CEMENT (0.7 W / C RATIO 2 DAY CURE)
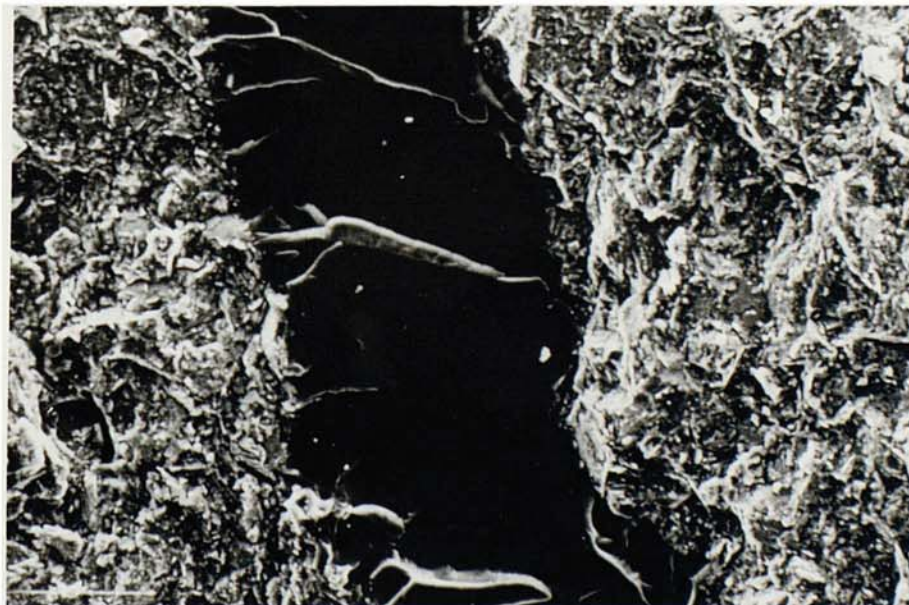
Note polymer as central dark band. (x 80)

FIGURE 8.9a
SEM OF VOID PRESUMED LINED WITH POLYMER IN
IMPREGNATED CEMENT (0.7 W / C RATIO 2 DAY CURE)
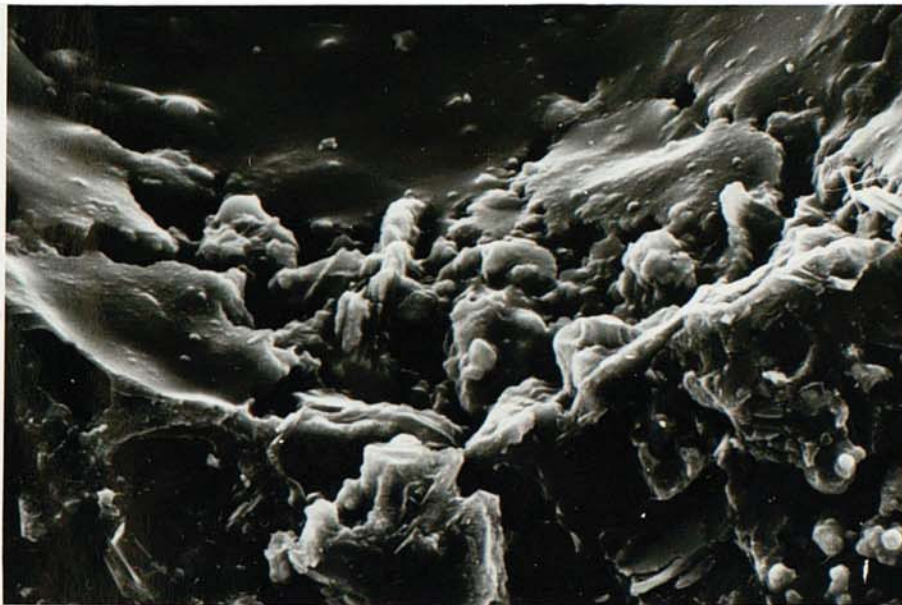
Note similarity between polymer and ordinary hydration products. (x 320)

FIGURE 8.9b
SEM OF VOID PRESUMED LINED WITH POLYMER IN
IMPREGNATED CEMENT (0.7 W / C RATIO 28 DAY CURE)

Note similarity between polymer and ordinary hydration products. (x 320)

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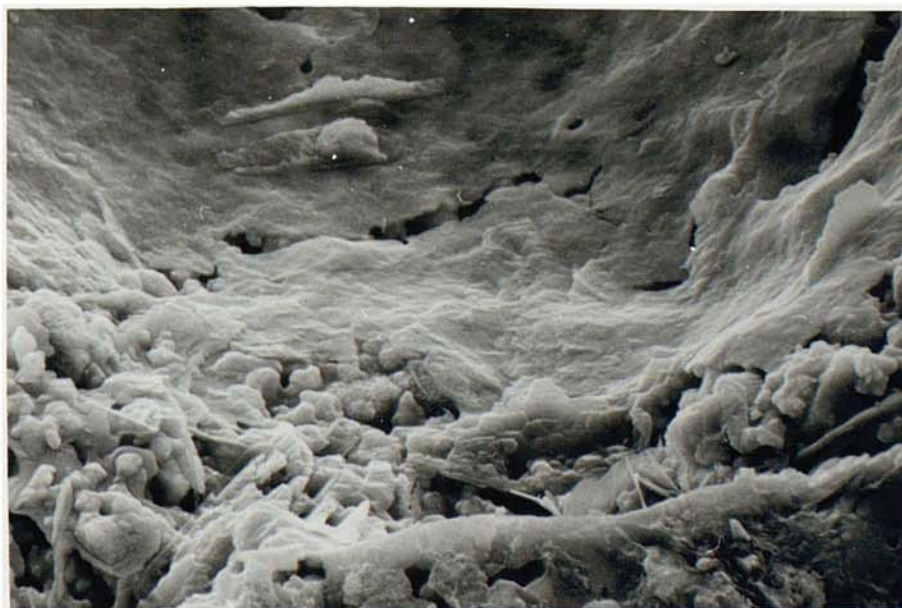
TABLE 8.2
CHANGES IN MASS OF CEMENT
SPECIMENS ON IMMERSION FOR 3 MONTHS

W/C ratio	Cure time (days)	Immersed in MMA		BP dissolved in toluene	
		Original weight (g)	Final weight (g)	Original weight (g)	Final weight (g)
0.4	2	64.8	66.0	57.0	61.2
0.4	60	49.7	50.8	55.5	59.4
0.5	2	48.2	49.5		
0.5	240	43.5	44.9		
0.6	2	35.6	36.9		
0.6	240	45.1	46.8		
0.7	2	35.8	36.6	36.8	39.9
0.7	7	32.2	33.5		
0.7	240	38.0	39.7	47.2	53.6

FIGURE 8.10

INTRINSIC VISCOSITIES FOR PURE PMMA
POLYMERISED AT DIFFERENT TEMPERATURES

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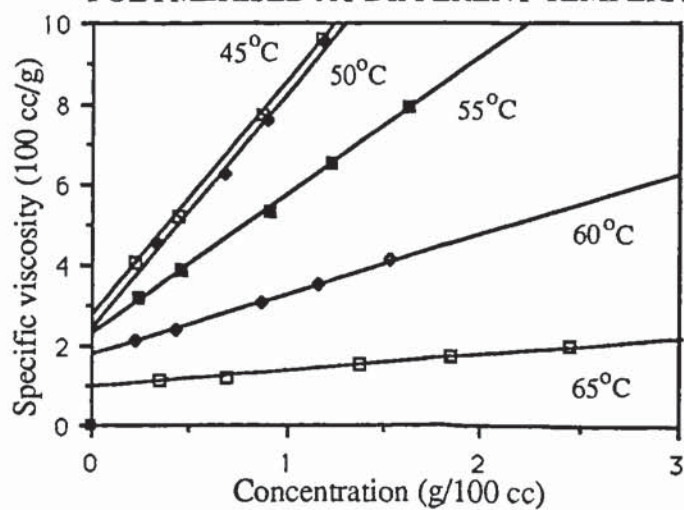
FIGURE 8.11
INTRINSIC VISCOSITIES OF POLYMER IMPREGNATED CEMENT EXTRACTS
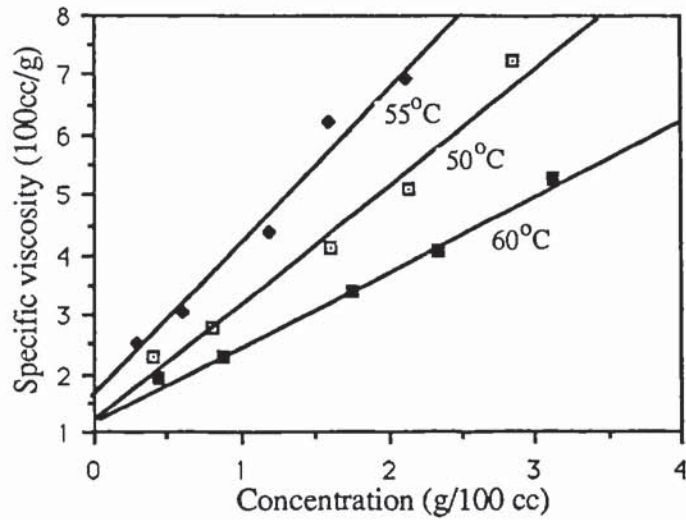
FIGURE 8.12
INTRINSIC VISCOSTIES FOR DIFFERENT PORE SIZE DISTRIBUTIONS

□ 0.4 W/C ratio 240 day cure
◆ 0.4 W/C ratio 2 day cure
■ 0.7 W/C ratio 28 day cure
◇ 0.7 W/C ratio 2 day cure

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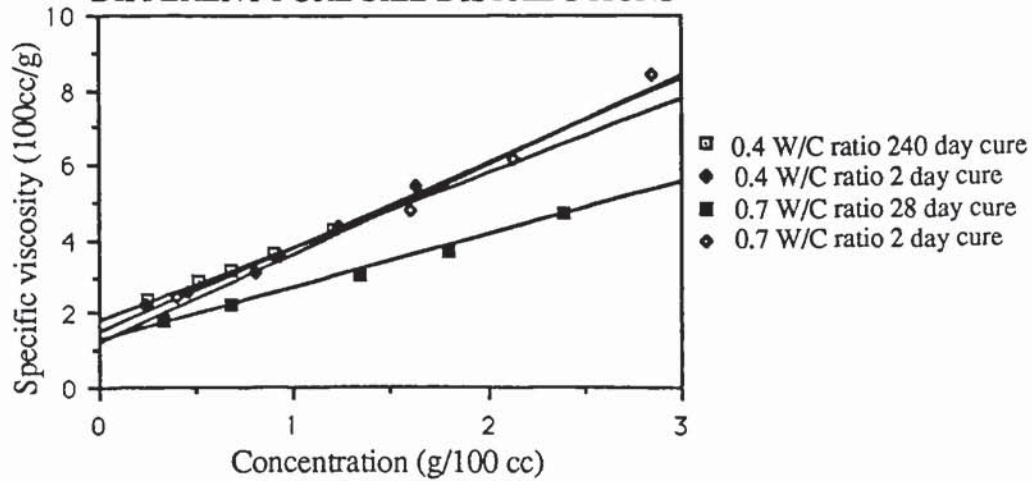
TABLE 8.3

MOLECULAR WEIGHT DATA FOR 0.7 W/C RATIO 2 DAY CURE
POLYMER IMPREGNATED CEMENT

Specimen	Temp.($^\circ$C)	Intrinsic viscosity (100cc/g)	Mol. wt. based on equation 1	Mol. wt. based on equation 2
PIC	60	1.2657	2.4×10^3	3.9×10^5
pure polymer	60	1.7951	3.7×10^3	6.0×10^5
PIC	55	1.6578	3.4×10^3	5.4×10^5
pure polymer	55	2.3343	5.1×10^3	8.3×10^5
PIC	50	1.2304	2.3×10^3	3.7×10^5
pure polymer	50	2.4622	5.4×10^3	8.9×10^5
pure polymer	45	2.7310	6.2×10^3	10.1×10^5

TABLE 8.4

MOLECULAR WEIGHT DATA FOR IMPREGNATED
CEMENTS AT 50°C

Specimen	Intrinsic viscosity (100cc/g)	Mol. wt. based on equation 1	Mol. wt. based on equation 2
PIC with 0.4 W/C ratio 2 day cure	1.6160	3.3×10^3	5.2×10^5
PIC with 0.4 W/C ratio 240 day cure	1.8514	3.8×10^3	6.2×10^5
PIC with 0.7 W/C ratio 2 day cure	1.2413 (1.2304)*	2.4×10^3 (2.3×10^3)*	3.8×10^5 (3.7×10^5)*
PIC with 0.7 W/C ratio 28 day cure	1.2840	2.5×10^3	3.9×10^5
pure polymer	2.4622*	5.4×10^3*	8.9×10^5

* From previous table

EQUATION 1 : - Ave. mol. wt. = $1.81 \times 10^3 \times$ [Intrinsic viscosity]$^{1.22}$(*ref 50*)
EQUATION 2 : - [Intrinsic viscostiy] = $4.3 \times 10^{-5} \times$ (Ave. mol. Wt.)$^{0.8}$(*ref 51*)

FIGURE 8.13

INTRINSIC VISCOSITY DATA FOR PREPOLYMERS AND POLYMER CEMENTS
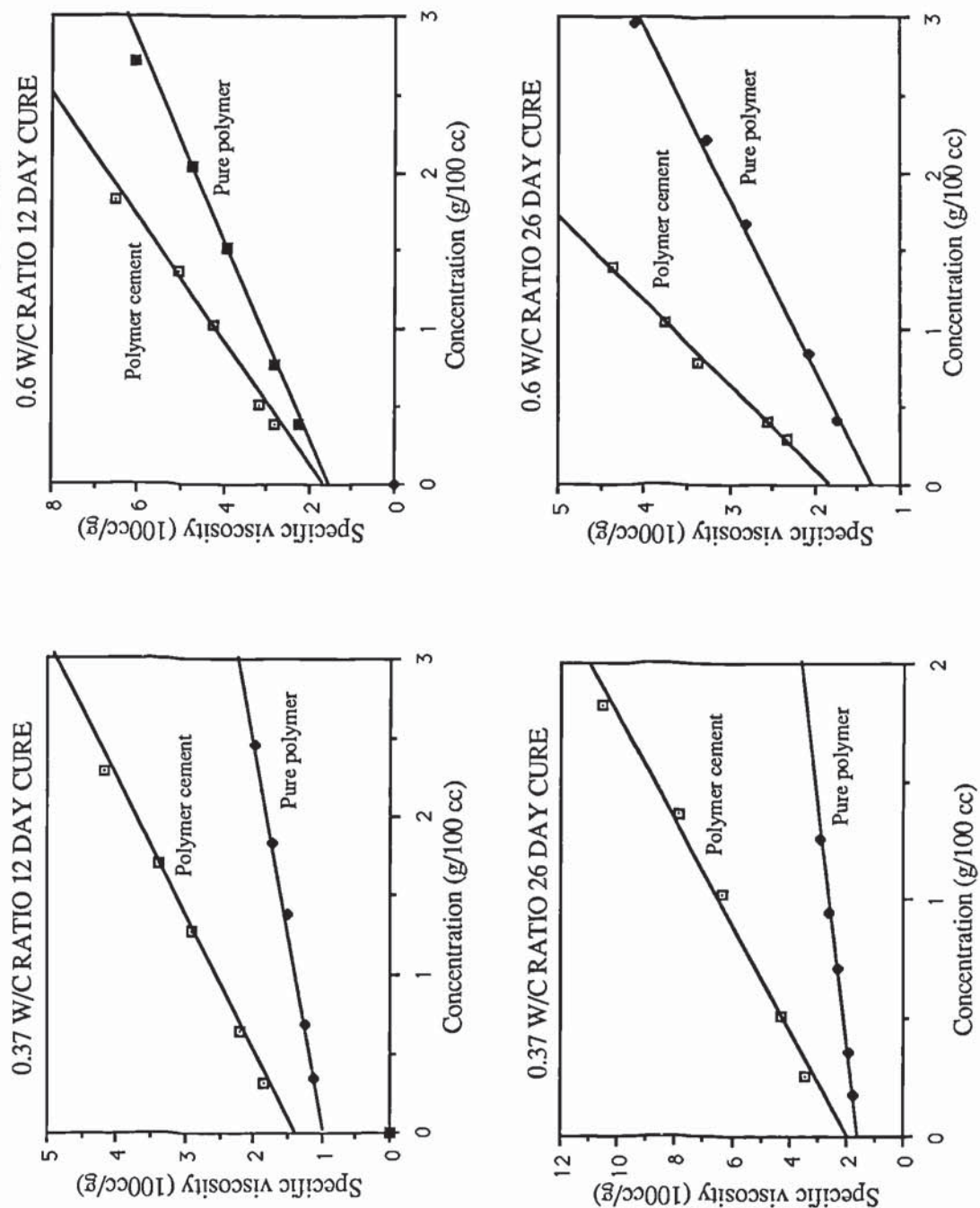
TABLE 8.5

MOLECULAR WEIGHT DATA FOR POLYMER CEMENTS

Specimen	Intrinsic viscosity (100cc/g)	Mol. wt. based on equation 1	Mol. wt. based on equation 2
Polymer cement with 0.37 W/C ratio 12 day cure	1.4378	2.8×10^3	4.5×10^5
Corresponding pure polymer	0.9491	1.7×10^3	2.7×10^5
Polymer cement with 0.6 W/C ratio 12 day cure	1.7983	3.7×10^3	6.0×10^5
Corresponding pure polymer	1.5628	3.1×10^3	5.0×10^5
Polymer cement with 0.37 W/C ratio 26 day cure	2.0236	4.3×10^3	6.9×10^5
Corresponding pure polymer	1.5220	3.1×10^3	4.9×10^5
Polymer cement with 0.6 W/C ratio 26 day cure	1.8368	3.8×10^3	6.1×10^5
Corresponding pure polymer	1.3214	2.5×10^3	4.1×10^5

EQUATION 1 : - Ave. mol. wt. $= 1.81 \times 10^3 \times [\text{Intrinsic viscosity}]^{1.22}$ *(ref 50)*
EQUATION 2 : - [Intrinsic viscostiy] $= 4.3 \times 10^{-5} \times (\text{Ave. mol. Wt.})^{0.8}$ *(ref 51)*

9 GENERAL DISCUSSION AND CONCLUSIONS

9.1 DISCUSSION

In recent years there has been increasing interest in the use of organic substances, particularly polymers to modify the properties of cement and concrete. Interactions taking place between the two phases may be considered of two types : - First, where polymer comes into contact with hydrated cements and is subsequently cured, and second, where polymer is mixed with the cement during the hydration process.

The aim of this project was to investigate the first of such interactions, and thereby provide data to help interpret the macroscopic properties of polymer-cement systems by understanding the way in which the two phases interact on a molecular level.

In this work two polymers were chosen for detailed study. One was an amine-cured epoxy resin typical of those commonly used in industry for repair and adhesive applications. The other chosen was polymethyl methacrylate, being a simple and well-characterized polymer, finding some use as an impregnant for cements. Limitations were also placed on the cement used, a single composition of OPC being selected.

Studying the interactions between cements and polymers involves certain practical problems in that such interactions are generally interfacial, the amount of interfacial reaction product being small, and the interfacial region hard to reveal. Various configurations were used in the investigation, the hope being that a methodology could be developed for the study of other polymer/cement reactions.

Attempts were made to obtain information about the locus of failure between the two phases *(Chapter 4)*. A number of specimen geometries were tested with the primary aim of achieving some interfacial failure, this permitting surface examination of the interfacial region. Progressive stressing of polymer/cement joints resulted in failure, often through the cement, but some near-interfacial regions were sometimes exposed. It was expected that if the interfacial bond is stronger than one of the phases, the locus of failure would tend to pass through the weaker material.

Comparisons were made between the adhesion characteristics of different resins and polymers based on their locus of failure and adhesion strength. Commercial polyesters and epoxy were found to form bonds stronger than the cement. The ability to wet the cement surface was also found to be important in promoting adhesion. Surface

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penetration and hence mechanical keying was limited, some chemical bonding being inferred. The nature of this was uncertain, possibly acid-base.

It is highly likely that there is a relationship between adhesion strength, W/C ratio and cure time. However, the configurations used here were unable to produce such data.

Reactions taking place between MMA and cements were extensively studied *(Chapter 5)*. DTA, XRD, IRS and ion chromatography were used for this purpose. The use of polymer cements and physical mixes led to the detection of calcium methacrylate as a reaction product in the case of the former. Ion chromatography proved to be the most conclusive technique in this respect. Problems were encountered particularly with DTA because the reactions of interest were partially masked by reactions taking place during the DTA runs themselves. DTA, IR and XRD work was hampered by the small quantities of reaction product present in polymer cements. This could to some extent be alleviated by increasing the amount of cement present, the arbitrary 50:50 proportions chosen for the mixes being dominated by polymer effects. XRD in particular proved to be very inconclusive in this respect, calcium methacrylate having only poorly resolved reflections.

Nevertheless, there would appear to be a reaction between MMA and cements, proceeding as follows : -

$$\text{methyl methacrylate} + \text{water} \xrightarrow{[OH^-]} \text{methacrylic acid} + \text{methanol}$$

$$\text{methacrylic acid} + \text{basic phases} \longrightarrow \text{methacrylates}$$

$$\text{methanol} + \text{calcium hydroxide} \longrightarrow \text{uncharacterized compounds}$$
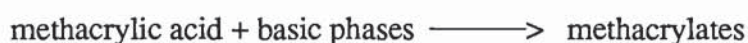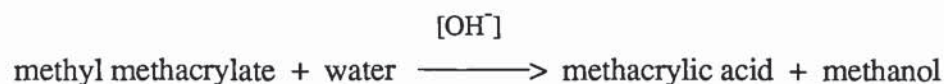
Ion chromatography clearly showed that the initial reaction requires water as a reactant. Methacrylates (particularly calcium methacrylate) are highly water soluble, hence their formation is generally detrimental to cements. Efforts should thus be made to dry cements as thoroughly as possible if MMA is to be used in conjunction with them. It was also shown that the the vast majority of methacrylate formed was derived from monomeric methacrylic acid. However, some acid groups could become incorporated into the polymer, this promoting bonding by acid-base attractions.

Attempts to characterize cement adhesion surfaces by XPS indicated that there were no significant differences in the surface chemistries of cement pastes of different W/C ratio and cure time; fracture and machined surfaces also being indistinguishable *(Chapter 6)*. Some slight variations in chemistry were noted for different drying techniques; the major feature was the amount of potassium present, this being about ten times greater in vacuum and solvent dried specimens compared to those oven-dried at 105°C. Examination of fracture surfaces from deep inside an oven-dried cement compared to its evaporation surface showed twice the amount of potassium on the evaporation surface. These results were interpreted as showing transport of highly water-soluble ions from deep in the pore structure, potassium being the most abundant of these in the cement studied. It was also hoped that the reaction products of MMA could also be detected on surfaces by dissolution of polymer on adhesion surfaces. Differences in surface chemistry were noted, in particular the abundance of carbon on surfaces exposed to MMA. Although several carbon environments could be resolved, the nature of some was uncertain. Nevertheless, a significant amount of carbon compounds were still adhering to the cement surface after treatment of monomer/polymer with a good solvent. These were interpreted as being reaction products.

Studies of the kinetics of polymerisation of MMA initiated with benzoyl peroxide indicated that interactions take place which affect the overall polymerisation rate *(Chapter 7)*. With polymer cements the rate was shown to decrease compared to bulk, the converse being true for impregnated cements. Though the former used prepolymers rather than pure MMA to minimise segregation of cement minerals, the results were reinforced by observing that all polymer cements solidified slower than the bulk monomer. Explanation of this phenomenon was complicated by the large number of variables that effect polymerisation of this kind. Most significant are monomer type, temperature, concentration and type of initiators, inhibitors and promoters. Cements did not appear to catalyse the decomposition of benzoyl peroxide, or themselves cause initiation of MMA; nor did they appear to cause measurable termination. Whatever the interaction, it would appear to be different between monomer exposed to the mineral assemblages in powders compared to those on pore walls.

The use of calorimetry in this study was only partially successful, in that all the data was recorded as chart recorder output, digitised and computed. Digitising did not prove to be accurate in calibrating the apparatus, thus overall heat outputs were subject to some error. However, rates of heat evolution were largely unaffected.

Polymer impregnation with MMA brings together a number of features discussed earlier. Of particular importance were attempts to correlate rate data with the molecular weight of polymer produced *(Chapter 8)*. In all specimens tested this was found to be greater in polymer cements compared to bulk, the converse being true for impregnated cements. Kinetic measurements showed that polymer cements polymerise slower than bulk, the converse being true for impregnated cements. Interpretation of these results is still somewhat speculative, since there are a number of competing factors to be taken into consideration. A reduction in molecular weight could be caused by a limiting of diffusion by cement pore structures; an increase in molecular weight could result from some inhibition of the growing polymer.

9.1.1 DEVELOPMENT OF A METHODOLOGY TO FOLLOW POLYMER/CEMENT INTERACTIONS

One of the aims of the project was to develop a methodology for the examination of polymer/cement interactions. These could be looked at in a number of ways ranging from trivial bulk strength modifications to the microchemistry of surfaces. Polymer/cement interfaces remain somewhat elusive since they are often diffusional, and it is hard to reveal interfacial regions by mechanical means. The following scheme could be adopted (although not all the techniques have been tried in the present work).

1) Examination of adhesion characteristics i.e. which phase is the stronger and how this relates to the strength of the interface. It is most important to assess the capacity of the polymer to wet the adhesion surface.

2) Comparison of polymer cements and physical mixes is useful in assessing whether or not there is a reaction between polymer and cement. Powdering cements considerably increases the surface area over simple plane adhesion surfaces, though their mineral composition may not be that on such a surface or the pore walls within a bulk cement.

3) Characterization of reaction products may be accomplished by a number of techniques, not all of which are applicable to some polymers. Reaction products of MMA were best identified by ion chromatography, this being suitable since calcium methacrylate is highly water-soluble. The polymer however is insoluble, and those soluble ions from the cement easily identified. Thus if reaction products have the appropriate solubility in water then ion chromatography would probably detect them.

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DTA suffers from the problems that reaction products are sometimes masked by other instrumental effects, their quantity being small in any case. The latter is also true of IRS, though it remains one of the few techniques for identifying bonding. Actual compound identification is often difficult due to the complexity of IR spectra, though changes in bonding between mixtures are often apparent.

Modern analytical chemistry often uses IRS in conjunction with nuclear magnetic resonance spectroscopy (NMR). The technique was not explored in this project, though also yields a large amount of information on bonding.

4) Surface analysis may be used to characterize adhesion surfaces if the problems in revealing them are overcome. This was possible in the case of PMMA since good solvents were available for the polymer that did not dissolve either the cement or reaction products. Solvent selection would be of prime importance for other systems.

Several techniques are available for surface analysis, XPS being the most applicable to this sort of work, since it has low surface penetration. Thus the microchemistry of the actual surface rather than the outer layers may be studied. A drawback with XPS is interpretation of spectra; peaks are resolved for each element, shifts being noted for the different chemical environments they encounter. Information on bonding rather than compound formation is thus obtained, the nature of some of the environments being uncertain or ambiguous.

5) The processes of cement hydration and organic polymerisation are time-dependent, often taking hours to approach completion. Thus interactions interfering with these processes are readily detected. Calorimetry has been shown applicable to this aim, for both cement solidification and organic polymerisation. Highly accurate calorimetry should also be able to detect reactions by measurement of overall heat evolution, all reactions being either exothermic or endothermic.

9.1.2 NATURE OF THE POLYMER / CEMENT INTERFACE

9.1.2.1 THE CEMENT / MMA INTERFACE

In the case of MMA the monomer is of low viscosity and can penetrate deep into the cement pore structure, and hence its use as an impregnant. Thus in a macroscopic sense the interface is diffusional: MMA coming into contact with a flat planar cement surface following drying will penetrate deep into the cement pore structure. On a microscopic

level the interface is between polymer and the cement pore walls. This surface is highly alkaline, composed predominantly of calcium hydroxide and lesser quantities of other alkalis, particularly potassium hydroxide. Traces of water are also present in a number of environments, even after prolonged drying. MMA easily hydrolyses to methacrylic acid in the presence of strong alkalis; Methacrylic acid reacts immediately with basic minerals, particularly calcium hydroxide to form calcium methacrylate. This itself is unpolymerisable, yet methacrylic acid can itself be co-polymerised with MMA. Thus small quantities of some polymeric methacrylates could be formed. The formation of (mono)methacrylates is detrimental to cements, due to their high solubility in water. Leaching could thus take place under certain circumstances, leading to increased permeability. The converse is true of polymethacrylates, in that they promote bonding by acid-base interactions.

The question could be posed "can these observations about the interface explain any of the macroscopic properties of cement / MMA systems?" MMA has a somewhat restricted use with cements, but remains one of the most commonly used impregnants for cements. The properties imparted by the polymer may be summarized by the following : -

1) Compressive strength and mechanical properties are improved.
2) Resistance to chloride diffusion is generally greatly improved, but in some cases it is actually made worse.
3) MMA used with hydrating cements is unsuitable for making composite materials.
4) Cement cylinders have been observed to split in impregnation with MMA.

Certainly the first two points are related to the polymer blocking or lining the cement pore structure, acting both as mechanical reinforcement to the structure and as a physical barrier to diffusion. There is however no direct evidence to suggest that there is any chemical bonding between cement and polymer. Reactions do take place, but these are essentially detrimental to the overall properties, being non-polymeric and highly water-soluble. This solubility provides a possible explanation for the increase in diffusion sometimes encountered, and since the reaction requires water as a limiting reagent, this also seems an explanation for the poor performance when water is present in the cement.

In the system studied, it is also important to consider the role of benzoyl peroxide as a reactant with cements. It has been shown that benzoyl peroxide exposed to cements decomposes to benzoic acid or benzoates, and although this may not actually be

detrimental to cements, the reaction does consume peroxides thus affecting the rate of reaction and chain length of polymer produced. On prolonged exposure to benzoyl peroxide in toluene, some of the hydrated cements used in this project began to develop cracks, some pieces eventually spalling off. This provides a possible explanation for the cracking sometimes observed on impregnation with MMA containing benzoyl peroxide, although the relative time-scales may be different. This problem at least may be completely avoided by initiating polymerisation by irradiation rather than thermo-catalytically.

The shortcomings of MMA used with cements indicate two possible approaches to impregnation (discussed also in the future work section). MMA molecules react with the water in cements by virtue of the fact that they are ester molecules, and not because they are acrylic monomer molecules. Potentially detrimental reactions of the type discussed above could thus be totally avoided by using monomers with no appropriate functional groups, for example styrene. On the other hand, if monomer molecules could be selected intentionally to react with the cement and remain polymerisable (unlike MMA), then significant interfacial chemical bonding could be achieved. This approach is similar to both the use of chemical coupling agents, each monomer molecule being its own coupling agent, and bonding in glass-ionomer and MDF cements where actual functionalised polymers are reacted with inorganic components.

9.1.2.2 THE CEMENT / EPOXY RESIN INTERFACE

The epoxy system chosen was not studied in as great detail as MMA, partly through the constraints of time, and partly because of certain inherent complications. Unlike MMA, the epoxy chosen was a commercially manufactured product. Consequently its exact formula and production history were unknown; thus it was not characterized as well as MMA.

Interfacial regions between polymer and cement proved hard to reveal mechanically, and no suitable solvent was available for dissolution of the cured resin, being extensively cross-linked. In section, the cement/epoxy interface showed little resin penetration into adhesion surfaces, yet microcracks fed from the adhesion surface were commonly filled, their bordering regions showing some resin impregnation. Substantial mechanical bonding thus occurs between cement and resin, cracks being healed by resin drawn by capillary action.

Reaction products between cement and the epoxy resin were not identified using DTA because large exotherms from oxidation/degradation of the resin dominate the thermograms *(Appendix 3)*. Ion chromatography was not attempted, although condensation products such as NaCl would be detected easily.

Similarly, XRD and IRS were unable to identify reaction products either because they do not react or because the amount formed is too little for detection. Whatever the reason, no obvious detrimental reactions of the kind noted for MMA were observed. Nevertheless, highly exothermal reactions were noticed occasionally, and their nature never established. A possible explanation could be attack by OH^- on the epoxide rings initiating ionic chain reactions which auto-accelerate, this process being observed in the polymerisation of propylene oxide.

$$\underset{\text{Epoxide}}{RCH\,CH_2} + OH- \longrightarrow RCH-CH_2 + RCH\,CH_2 \longrightarrow RCH-CH_2 \quad \text{etc.}$$
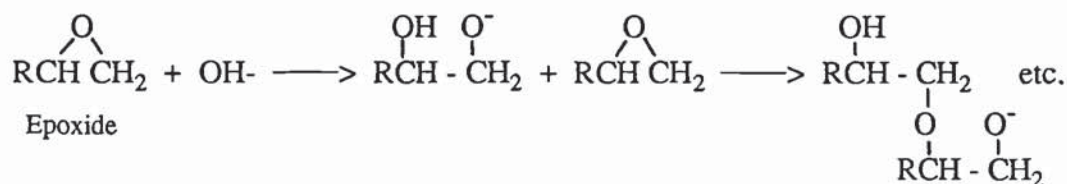
With the relatively low concentration of epoxide groups per resin molecule, it would be expected that reactions between epoxide rings and cements would be hard to detect. A way around this problem would have been the use of short-chain epoxide compounds, for example propylene oxide (as discussed in the future work section). Epoxy compounds show great potential for use with cements not just as resin mortars, but as part of composite systems themselves. They have the advantages of potential bonding to cements as well as to cross-linking agents.

9.2 CONCLUSIONS

1) It is important to study interactions between organic polymers and cements in order to aid selection of polymers, confer desired properties on cements and identify detrimental reactions.

2) Polymer/cement interfaces are difficult to reveal mechanically, but can be exposed if suitable solvents for the polymer are available. In this state reaction products may be studied by techniques of surface analysis.

3) Chemical reactions between polymers and cements may give misleading information when studied using DTA and XRD. However, IRS is useful in this respect, as is ion

chromatography, so long as the reaction products are water-soluble. The comparison of polymer cements and physical mixes is suited to all the above techniques, so long as the reaction product is abundant.

4) The use of MMA as an impregnant for cements is limited by detrimental reactions with water. Similarly, organic peroxides may be decomposed by reactions with cement surfaces.

5) The chemistry of the pore surface of cements is different from that of powdered hydrated cement, affecting the polymerisation of MMA and possibly other acrylic monomers.

6) Chemical bonding between cements and polymers can be aided by functionalising the polymer and promoting surface wetting. Appropriate monomer/polymer selection could give rise to substantial polymer-cement bonding similar to coupling agents.

7) Polymers that best exploit the nature of cements are those that cure in an aqueous or alkaline environment, for example base-catalysed epoxy resins and polymeric acids.

10 FUTURE WORK

This project has pursued a number of aspects of the interactions between cements and polymers, some having been studied experimentally in some detail, and others reviewed from published literature. Considering this project in the context of what is known and what is being researched at present, there are many areas that could be extended by further work, and several new ones that could be started.

For practical reasons, this project had to be limited in its scope. The main consequence of this was that interactions between polymers and hydrating cements were not studied, although this constitutes a significant proportion of the world-wide interest in the subject.

A second limitation of this project is the way it has had to concentrate on small-scale experiments rather than engineering materials themselves. This was of course not unexpected, since the nature of the project was fundamental research on specific systems, although the methodology could be extended to other systems. It is preferable to understand interactions on a molecular level before large-scale testing, so that it is possible to predict macroscopic behaviour and test the theories developed on the molecular level.

In a sense, this project has examined only those interactions that take place in 'ideal' cements. This is obviously a reasonable starting point, and leaves scope for further investigation of real building materials. Only cement pastes were used in this project although a diversity of materials would be used on site including concrete, mortar, PFAs and slags. Specimens were also oven-dried, a procedure that would rarely be carried out on site. A further dimension is added by considering that the majority of polymer/cement applications are as repair materials. These are used with unsound or carbonated cements. There is therefore scope for following bulk or interfacial reactions between polymers and actual building materials.

Bearing this in mind, the aims of further work diverge. Either it could be targeted at the understanding of existing materials and processes, or be used in the design of new ones.

10.1 METHODOLOGY FOR EXAMINATION OF POLYMER / CEMENT INTERACTIONS

Having assessed the usefulness of a variety of experimental techniques and specimens, these could be applied directly to existing polymer/cement materials. Many chemical companies have produced an increasing variety of polymeric substances for use with cements including waterproofers, paints, sealants, surface hardeners, flooring materials, resin mortars, injection resins and adhesives. It is perhaps surprising that few actual polymer/cement composites are marketed as yet, possibly because of technical limitations or the reluctance of industry to accept them as actual new materials.

In this project it became clear that the chemistry of MMA was far more accessible than that of the epoxy system chosen because of its relative simplicity. There is still a considerable amount of research that could be conducted into interactions with other simple molecules. The search for reaction products would appear to be complicated by polymerisation reactions, and it would be useful to examine bonding in their absence. What is required for polymer/cement composites are molecules that both bond to the cement minerals and remain polymerisable. MMA would not appear to fulfil these requirements, though did indicate compound formation by the production of carboxylic acid groups. Taking this approach, it would be useful to establish if there is compound formation with other functional groups, for example sulphonic acid, epoxide and isocyanate groups.

Once this was established, the problems of polymerising molecules containing appropriate functional groups could be addressed. Functional groups could be included in monomer molecules prior to polymerisation in situ, polymerised beforehand or grafted onto the polymer for addition before hydration of the cement. An example of this approach improved bonding between polypropylene and glass fibres by grafting maleic anhydride molecules onto polypropylene, these being reactive to the amine ends of silane/amine coupling agents, the silane bonding to the glass *(ref 145)*.

10.2 PROSPECTS FOR NEW MATERIALS

Developments to date have shown the potential polymer modified cements have for new engineering materials. However, so far some of the most interesting polymer/cement composites have been regarded rather as laboratory curiosities than as useful materials. If decisions were made as to the properties required from such composites, research could be directed towards realising such aims; polymers are used with the general aim

of improving strength and durability, yet specific targets could be envisaged, for example flexible cements, cements for pressing or injection moulding, and acid-resistant cements.

As yet, selection of polymers for this area of work has been somewhat elementary, considering the vast number of polymer systems and the wealth of knowledge available concerning their chemistry and production. Prospects for different polymer/cement composites are suggested as follows : -

Polymer concrete

In some ways polymer concretes could be regarded as somewhat less promising materials, the inorganic material being used primarily as a filler for a resin system. They are nevertheless very useful materials for repairs, and developments to improve adhesion, setting characteristics and corrosion protection imparted by the filler may be made. However, since the properties of such materials mostly rely on the properties of the resin, filler/resin interactions are of lesser importance than the chemistry and properties of the resin itself.

Polymer impregnated cement

Research into impregnation of cements could proceed down two paths : - First, by improving impregnation technology of existing structures, and secondly by improving that of pre-formed articles. In-situ polymerisation of volatile monomers remains a promising technique for pore blocking and hence physically inhibiting diffusion into cements, thus improving corrosion protection of steel in cements. MMA has been shown to have some inadequacies in this respect, the substance having been selected probably because it is relatively cheap and commonplace; the same may be said of benzoyl peroxide. As discussed above, it would be most useful to identify functional groups that perform bonding with cement minerals, then to construct molecules containing such groups whilst remaining polymerisable within cement pore structures. In addition, impregnants used to date (MMA, styrene and hot epoxy resin) harden to a tough rigid state within the pore structure, thus mechanically reinforcing the cement. It would be interesting to determine what properties a rubber-like polymer would impart to cements when polymerised in the pore structure.

A major limitation is placed on PIC by the necessity to remove water from the pore system before impregnation. This has generally restricted PIC to pre-formed articles.

The general hydrophobic nature of impregnants used to date necessitates this procedure, in fact this work demonstrated that MMA also reacts unfavourably with cements when water is present. If impregnants could be selected that are compatible with water i.e. solutions or emulsions then the dehydration stage of PIC production may be avoided. Many polymers are produced in an aqueous environment (e.g. urea/formaldehyde and phenolic resins), and with the appropriate design could be potential aqueous impregnants.

Pre-hydration polymer/cement composites

Possibly the most useful polymer/cement composites are those where polymer is incorporated into cements as a pre-hydration additive. Since the cement is the continuous phase, the materials are essentially ceramics rather than plastics, and have already been shown to have properties far in advance of ordinary cements and other polymer/cement composites. For example, the properties of PIC are limited by the amount of polymer that is incorporated in the cement, this being somewhat variable. However, by adding polymer before hydration a uniform distribution of polymer is achieved.

MDF cements in particular have mechanical properties far in excess of ordinary cements, approaching those of metals in some cases. They are also cheap to produce in energy terms, and can have a rubber-like consistency on production. This makes them suitable for cold forming by techniques normally applicable to plastics and metals. Setting mechanisms are not understood fully, and further work in elucidating the reactions taking place could lead to better processing and polymer selection.

Major limitations so far encountered with MDF are dimensional stability and water leaching of certain components from the final material. If thermosetting polymers or emulsified resin/cross-linking agent systems can be used in place of the water-soluble polymers normally used, these problems may be avoided.

10.3 MECHANICAL TESTING

Attempts to reveal polymer/cement interfacial areas by mechanical means proved to be largely unsuccessful, because the cohesive strength of the cement was less than both the cohesive strength of the polymer and the adhesive strength of the bond between the two phases. It could however be possible to measure adhesion strength of polymers by using sections of aluminosilicate minerals chemically similar to cement minerals. For

instance, feldspars are aluminosilicates containing sodium, potassium or calcium counter ions and water in lattice sites. Such minerals are very strong and hard, thus single interface specimens made with feldspar members could produce interfacial failure on loading.

A further un-related observation resulting from the mechanical testing work indicated that double interface specimens usually fail through the cement layer. This could be seen as the directing of the locus of failure through the cement in a predictable way, and could thus be the basis of a strength test for cements themselves.

10.4 OTHER RESEARCH

Several un-connected problems remain to be solved from this project, the most significant ones being as follows : -

1) What is the exact nature of the interactions affecting rate of polymerisation of MMA using benzoyl peroxide in polymer cements and polymer impregnated cements?
2) Is it possible to develop some experimental technique to confirm that the pore surface of cements has a different surface chemistry from that of hydrated cement powders?
3) What part does surface carbonation play in the interactions studied?
4) What are the unidentified species present in water extracts of cements detected using ion chromatography?
5) What is the nature of the interaction with cements that leads to acceleration of curing in the epoxy system studied?

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APPENDIX 1

TABULATED IRS DATA FOR CEMENT MINERALS AND ASSOCIATED SUBSTANCES

C_3S

855 cm^{-1}, 843 cm^{-1} strong and broad, 846 cm^{-1} sharp, 795 cm^{-1} shoulder, 692 cm^{-1} weak, 320 cm^{-1} strong

$\beta - C_2S$

995 cm^{-1}, 972 cm-1,940 cm^{-1}, 845 cm^{-1} strong, 815 cm^{-1} shoulder, 690 cm^{-1} weak, 668 cm^{-1} weak, 565 cm^{-1} strong shoulder, 520 cm^{-1} strong, 500 cm^{-1} strong, 440 cm^{-1} moderate, 360 cm^{-1} moderate.

γ-C_2S

950 cm^{-1} moderate, 850 cm^{-1} strong, 820 cm^{-1} shoulder, 690 cm^{-1} weak, 668 cm^{-1} weak, 565 cm^{-1} moderate, 520 cm^{-1} strong, 495 cm^{-1} strong, 440 cm^{-1} moderate, 360 cm^{-1} strong.

C_3A

894 cm^{-1} strong, 865 cm^{-1} strong, 845 cm^{-1} shoulder, 820 cm^{-1} strong, 787 cm^{-1} weak, 765 cm^{-1} weak, 741 cm^{-1} strong, 707 cm^{-1} strong, 610 cm^{-1} weak and broad, 580 cm^{-1} moderate, 540 cm^{-1} shoulder, 522 cm^{-1} moderate, 510 cm^{-1}, 465 cm^{-1} moderate, 411 cm^{-1} moderate, 385 cm^{-1} weak.

C_6AF_2

693 cm^{-1} strong and broad, 605 cm^{-1} strong 554 cm^{-1} strong and broad.

The composition can be further simplified by considering the minerals as mixtures of alumina, silica, calcium hydroxide, calcium hydroxide and water. Infrared spectra are published of these, from which bond vibrations in cements may be deduced *(refs 113 and 116)*.

ALUMINA

3450 cm^{-1} broad, 2000 cm^{-1} broad shoulder, 1630 cm^{-1} moderate, 1390 cm^{-1} weak shoulder, 950 cm^{-1} (and below) broad.

SILICA GEL

3460 cm^{-1} broad, 2000 cm^{-1} shoulder, 1870 cm^{-1} weak, (1730 cm^{-1} present on microsilica), 1630 cm^{-1} strong, 1200-1020 cm^{-1} very broad, 960 cm^{-1} moderate, 800 cm^{-1} strong, 600-350 cm^{-1} very broad.

CALCIUM HYDROXIDE

3520 cm^{-1} sharp, 3380 and 3310 cm^{-1} twin, 2520 cm^{-1} small, 1800 cm^{-1} small and sharp, 1650 cm^{-1} shoulder, 1520-1400 cm^{-1} broad, 1200 cm^{-1} small 1080 cm^{-1} broad, 880 cm^{-1} very sharp 750 cm^{-1} (and below) very broad.

CALCIUM CARBONATE

3480 cm^{-1} broad, 2990 cm^{-1} shoulder, 2890 cm^{-1} shoulder, 2600 cm^{-1} shoulder, 2530 cm^{-1} shoulder, 2140 cm^{-1} shoulder, 2000 cm^{-1} shoulder, 1800 cm^{-1} sharp, 1800-1000 cm^{-1} very broad, 880 cm^{-1} strong, 720 cm^{-1} very sharp, 590 cm^{-1} weak, 380 cm^{-1} (and below) broad.
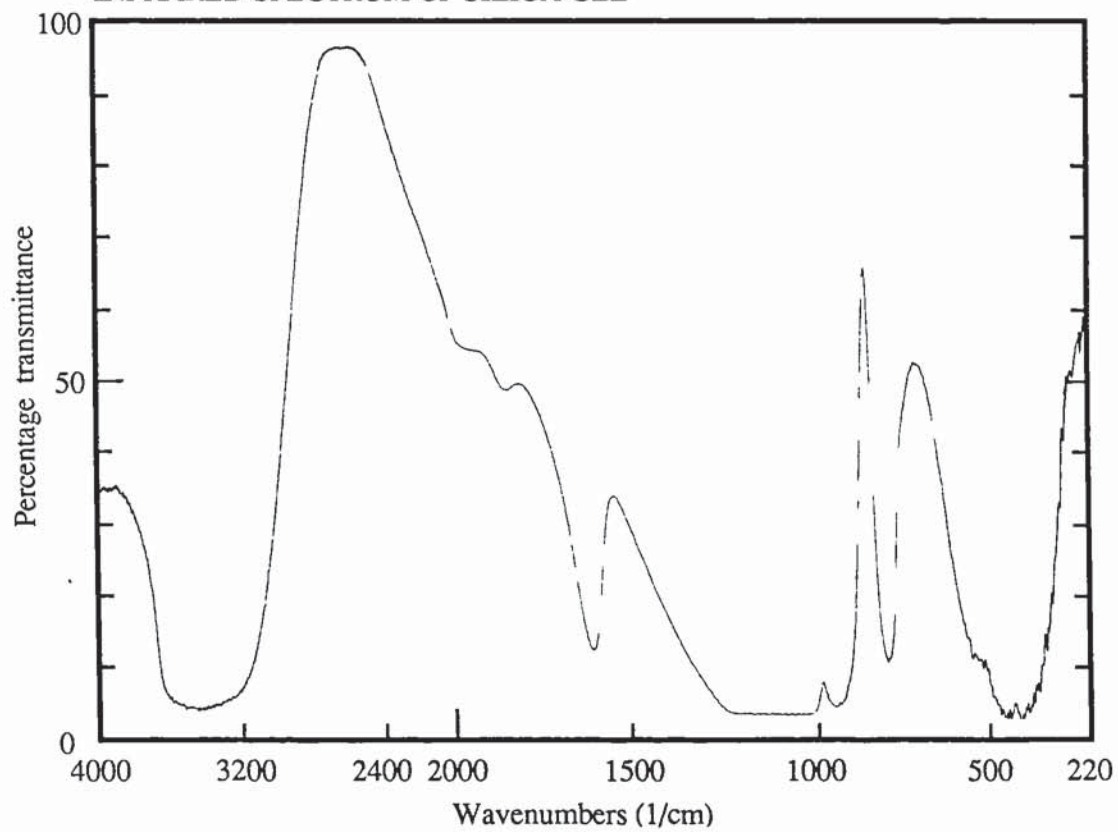
WATER

3630 cm^{-1} sharp (free water), 3600-2400 cm^{-1} very broad (-OH), 1640 cm^{-1}.
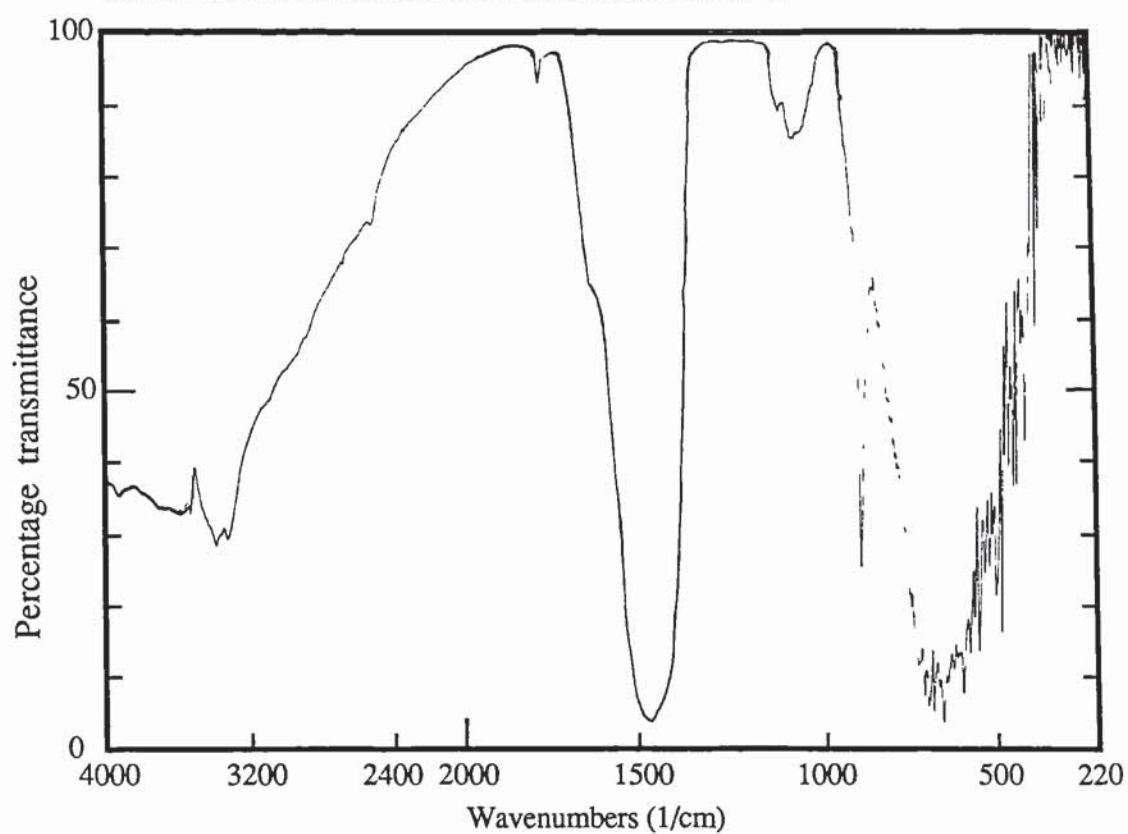
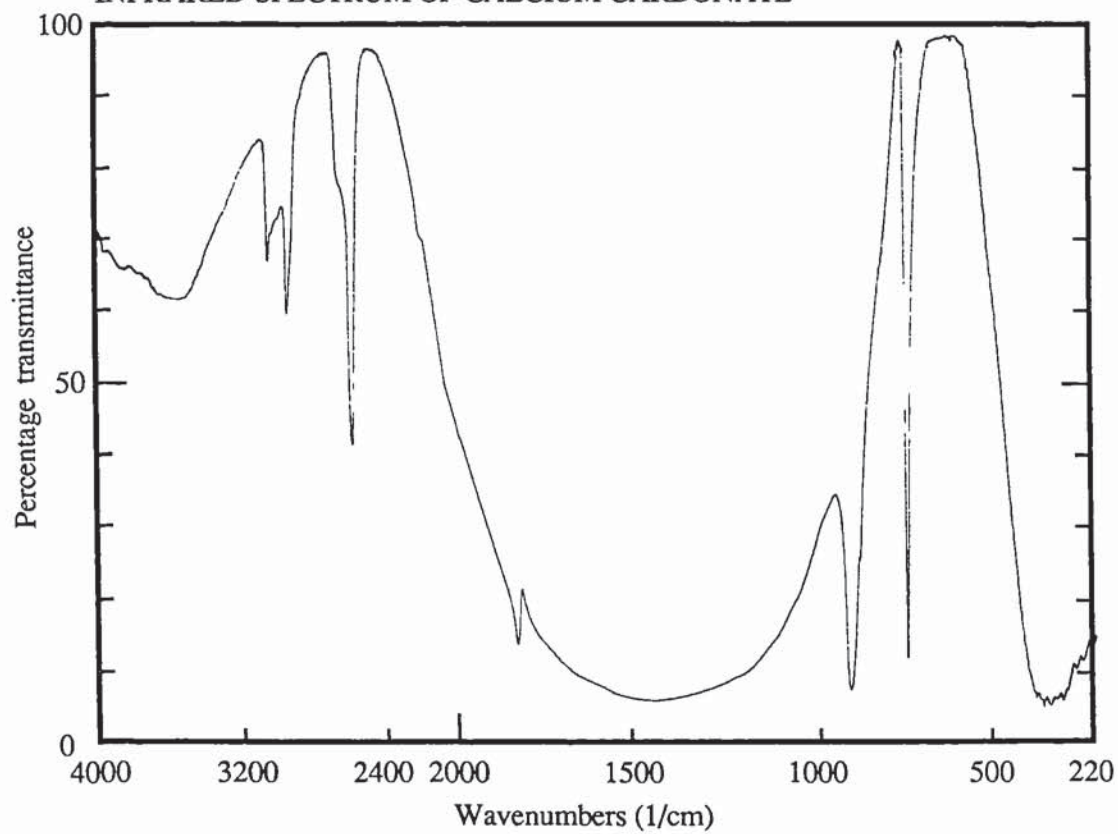# APPENDIX 2; INFRARED SPECTRA

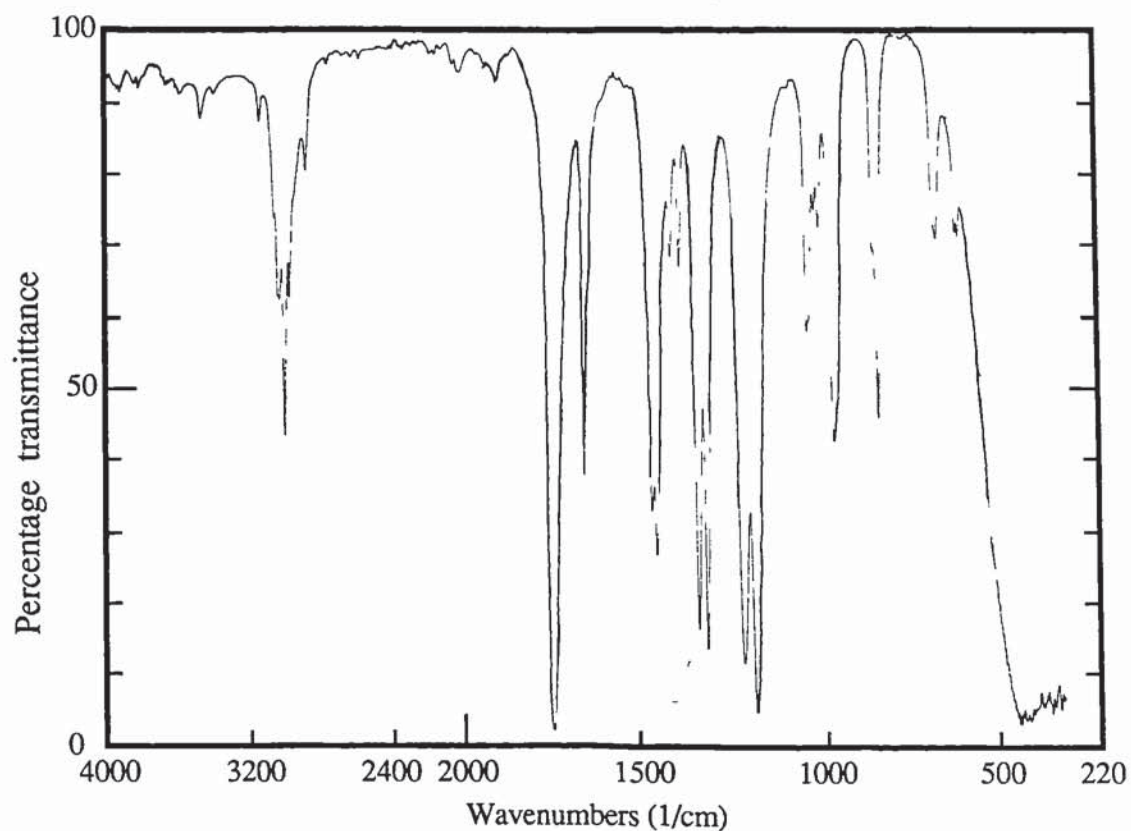INFRARED SPECTRUM OF ALUMINA
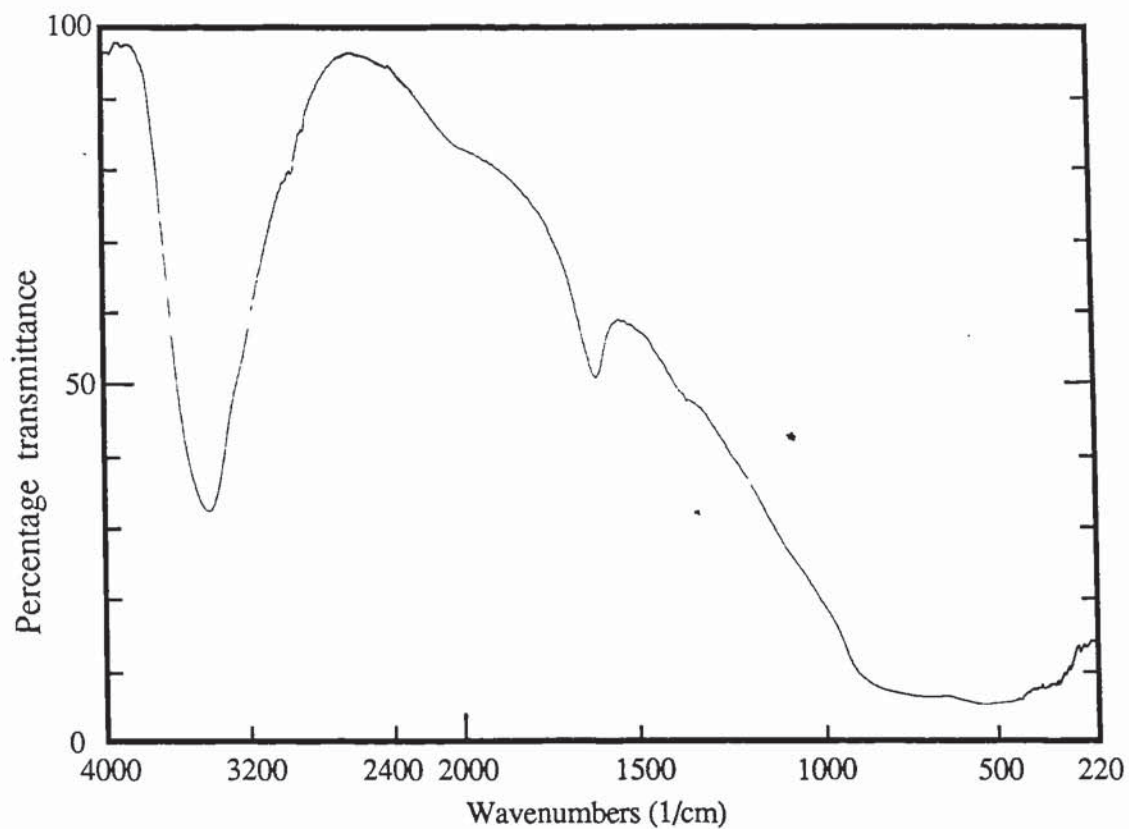
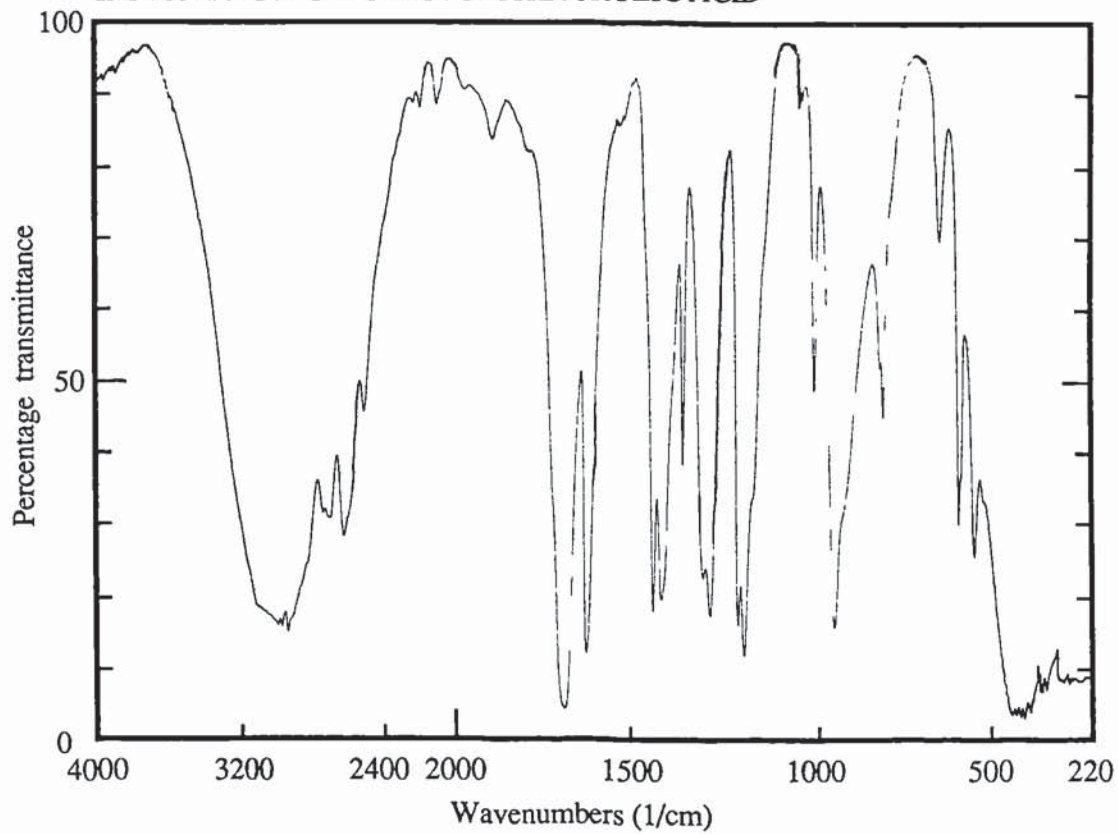INFRARED SPECTRUM OF SILICA GEL

INFRARED SPECTRUM OF CALCIUM HYDROXIDE

INFRARED SPECTRUM OF CALCIUM CARBONATE
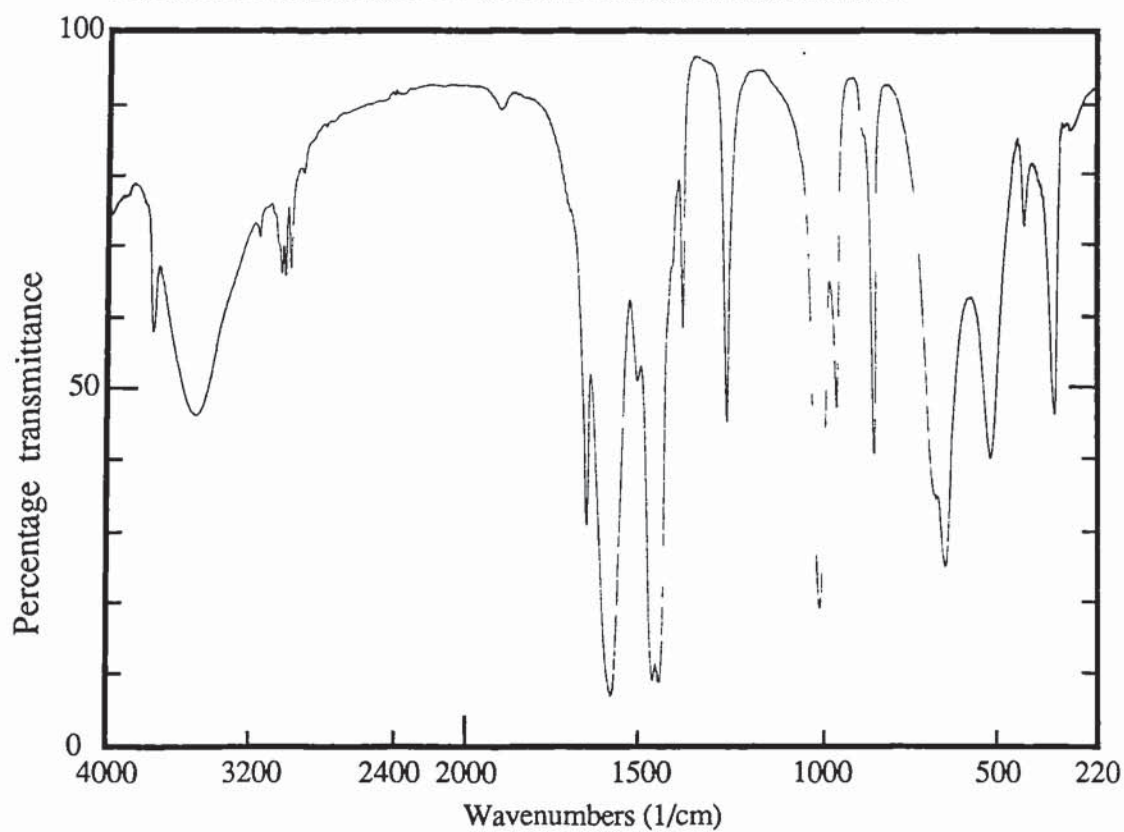
298

INFRARED SPECTRUM OF METHYL METHACRYLATE
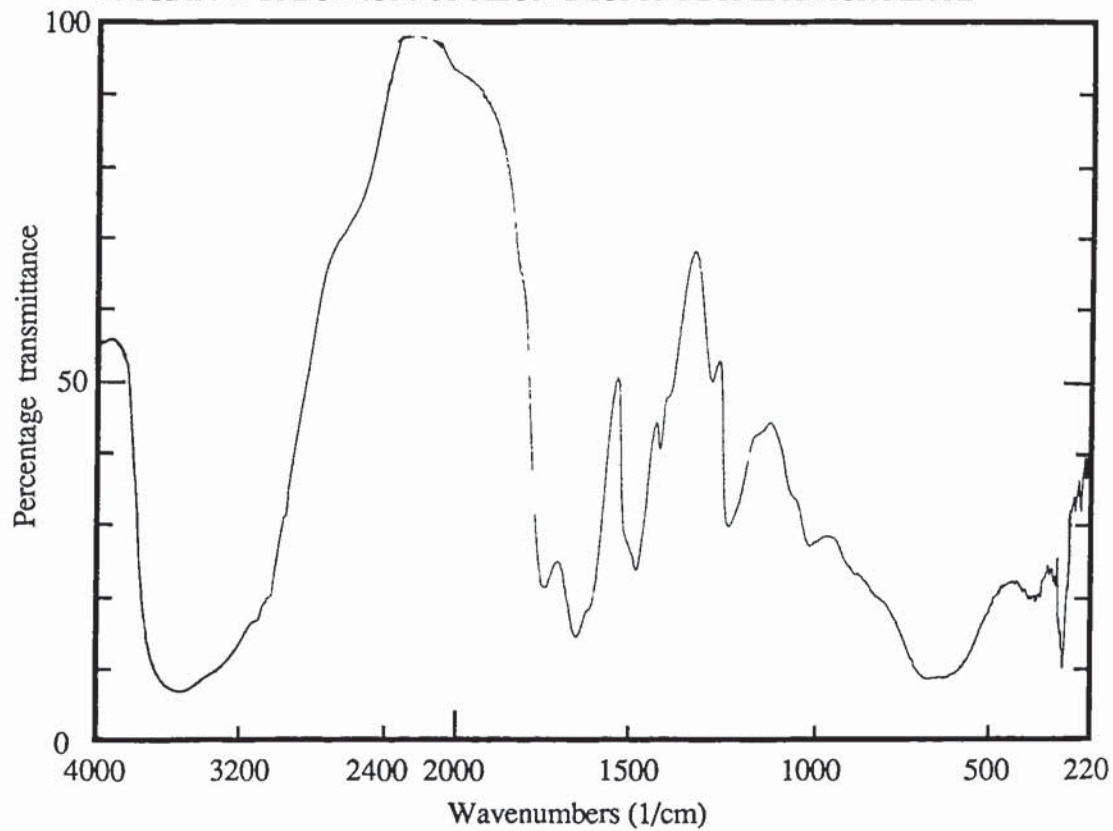

INFRARED SPECTRUM OF METHACRYLIC ACID

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INFRARED SPECTRUM OF ALUMINIUM METHACRYLATE

INFRARED SPECTRUM OF ALUMINIUM POLYMETHACRYLATE

APPENDIX 3

CHARACTERISATION OF EPOXY RESIN USING DTA

TEMPERATURE