PRODUCTION OF PHENOL-FORMALDEHYDE RESIN COMPOSITES

by

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SUMMARY

The main objective of this work was to examine the various stages of the production of industrial laminates based on phenol-formaldehyde resins, with a view of suggesting ways of improving the process economics and/or the physical properties of the final product. Aspects of impregnation, drying, and lamination were investigated. The resins used in all experiments were ammonia-catalysed.

Work was concentrated on the lamination stage since this is a labour intensive activity. Paper-phenolic lay-ups were characterised in terms of the temperatures experienced during cure, and a shorter cure-cycle is proposed, utilising the exothermic heat produced during pressing of 25.5 mm thick lay-ups. Significant savings in production costs and improvements in some of the physical properties have been achieved. In particular, water absorption has been reduced by 43-61%.

Work on the drying stage has shown that rapid heating of the wet impregnated substrate results in resin solids losses. Drying at lower temperatures by reducing the driving force leads to more resin (up to 6.5%) being retained by the prepregs and therefore more effective use of an expensive raw material.

The impregnation work has indicated that residence times above 6 seconds in the varnish bath enhance the insulation resistance of the final product, possibly due to improved resin distribution and reduction in water absorption.

In addition, a novel process which involves production of laminates by in situ polymerisation of the phenolic resin on the substrate has been examined. Such a process would eliminate the solvent recovery plant - a necessary stage in current industrial processes. In situ polymerisation has been shown to be chemically feasible.

KEY WORDS: Laminates, phenol-formaldehyde, industrial production.

Title: Production of phenol-formaldehyde resin composites

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1. INTRODUCTION

1.1 General

Laminated plastics consist of superimposed layers of resin-impregnated filler which have been bonded together to form a single piece. They are usually produced in the form of sheets, tubes, rods and bars, from which finished articles can readily be machined.

The development of 'modern' laminates may be traced back to the advent of thermosetting resins and to the demands of the electrical industry(1). For the insulation of transformers and other electrical apparatus paper-shellac resins boards were employed. However, with the development of high-voltage and high-power electrical plants, materials with better electrical insulation properties, and relatively more heat-resistant than the thermoplastic shellac-based boards were needed. The invention of phenol-formaldehyde resins enabled suitable laminates to be produced.

Following the first patent on phenolic composites(2), several additional patents were granted between 1918 and 1919 covering the use of impregnating baths and drying ovens to handle continuous webs(3), of alcoholic solutions to saturate the paper, and pressure to consolidate the sheets(4). Methods of manufacturing tubes and rods were also mentioned(5, 6).

Today, the high-pressure industrial phenolic laminates reinforced with either paper, cotton or glass, have good electrical and mechanical properties and they are employed widely in engineering and other applications.

1.2 Phenolic Laminates

Production of laminates involves several inter-related stages in which impregnation, drying (including solvent recovery) and pressing (laminating) are the main ones.

Even though the phenolic laminating industry has been in existence for more than 50 years, it has retained its basic characteristics. It is only in the past 15-20 years that 'substantial' changes have been made, particularly in the field of decorative laminates. These changes, however, have been more in the nature of refinement than that of innovation.

In order to increase capacity and production efficiency, longer dryers of modular construction, and closer control of the impregnation and drying stages with on-line measurements have been employed. Larger presses with an increased number of openings have also been used. Changes in the phenolic resin compositions include the use of styrene or other vinylidene compounds for improved electrical properties(7, 8); 'styrenated' phenolic resins are currently employed in the production of electrical grade laminates. Friedel-crafts and related polymers have also been developed for special applications(9).

Despite the major efforts undertaken, production of phenolic laminates remains largely an art rather than a science, and there is a lack of understanding of the basic principles involved and their relations to the physical properties of the final product.

This encompasses aspects of the lamination process such as resin-filler relationships and thermal and chemo-rheological behaviour during pressing.

Published work on these and other areas of the process has been scarce. A contributory factor to this is probably the fact that detailed process conditions still remain primarily of a confidential nature. It is true that a considerable amount of work has been directed towards the more important component, namely the resin matrix, and several instrumental techniques have been developed specifically for the study of the thermosetting process, with varying degrees of success. However, many of these methods have found limited application either as quality control tools or as means of providing a comprehensive analysis of the lamination process.

With increasing raw material costs, and the development of engineering thermoplastics with comparable or even better physical properties, it is clear that a close examination of the production of phenolic laminates, which would lead to improvement in both economics and physical properties, is warranted.

1.3 Aims of this work

The objectives of the project are three-fold:

(i) to examine each stage of a commercial process leading to a paper (or fabric) filled phenolic resin;

(ii) to identify areas where improvements in the economics and/or the physical properties of the product can be achieved;

(iii) to generate and evaluate alternative processes.

Objective (i) involved what it may be referred to as the 'familiarisation stage' during which a proportion of the research period was spent learning the process and related aspects.

1.4 The structure of the thesis

The contents of the thesis fall into four distinct but related parts.

Chapter 2 is a brief introduction to some of the traditional terms and their meaning used in the plastics industry.

The second part (Chapters 3 and 4) deals exclusively with phenolic resins and their cure characteristics. Following a short introduction on the historical development of the resins, work on the various chemical aspects involved in the initial reactions leading to prepolymer formation are discussed. Chapter 4 considers the heat curing of the resins and the relevant chemistry at the crosslinking stage. Some of the techniques used to characterise degree of cure are also examined.

The third part (Chapter 5) is a logical consequence to the above and discusses primarily the production of phenol-formaldehyde laminates and the various unit operations involved. The manufacture of resins is also included.

The remaining four chapters present the experimental work as related to a paper-phenolic laminate possessing good electrical and mechanical properties. The phenolic resins used throughout the work were styrenated, ammonia-catalysed.

Due to the broad and open-ended nature of this work, in-depth analysis of each area examined was not possible.

Work was mainly concentrated at the lamination stage (and to a lesser extent, the drying stage) since it affects significantly both the physical properties of the final product and the economics of the process. Any improvements at this stage could be realised in the immediate future. This stage is perhaps the most complex from thermal and chemo-rheological considerations (important characteristics); also, published work is almost non-existent. It is the least controlled stage of the process.

2. POLYMERS AND POLYMERISATION

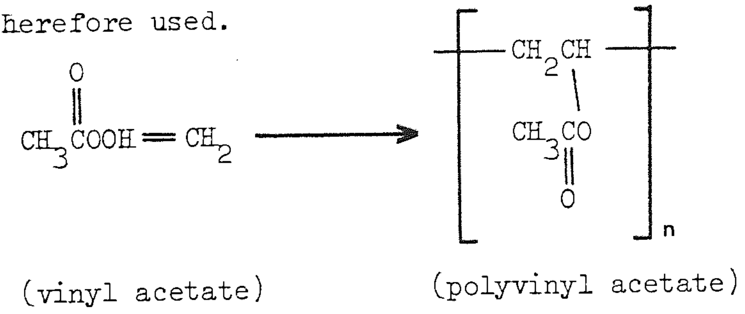
2.1 Definitions

A polymer may be defined as a large molecule made up of one or more structural units repeated any number of times(10), and are synthesised from 'monomers'. With vinyl monomers or certain monomers that undergo ring-opening reactions, the repeating unit contains the same atoms as the monomer, whereas with most difunctional or polyfunctional monomers the repeating unit contains fewer atoms because of by-product formation(11).

The degree of polymerisation (DP) refers to the number of repeating units in the polymer chain, and hence is related to the length of the chain. In the case of poly (vinyl acetate) shown in figure 2.1, if DP = 500 the molecular weight of a particular polymer chain is obtained as follows:

$$\begin{aligned} \text{Molecular weight} &= \text{molecular weight of repeating unit} \times \text{DP} \\ &= 86 \times 500 \\ &= 43{,}000 \end{aligned}$$

In practice the chain lengths in a polymer sample vary in magnitude and 'average degree of polymerisation' ($\overline{\text{DP}}$) is therefore used.



$$\overset{\displaystyle O}{\overset{\|}{CH_3COOH}}=CH_2 \longrightarrow \left[-CH_2CH(CH_3\underset{\underset{\displaystyle O}{\|}}{CO})-\right]_n$$

Figure 2.1 Polymerisation of vinyl acetate. (Molecular weight = 86; n = DP).

If a polymer is composed of one kind of repeated structural unit A, it is referred to as a homopolymer(10). If it contains more than one kind of structural unit the polymer is known as a copolymer and may be classified into four different forms (figure 2.2): alternating, random, block and graft copolymers. (In figure 2.2, A and B represent monomers which combine in the polymer structure).

On the basis of their molecular structure, polymers may also be described as linear, branched and network (figure 2.3).

2.2 Linear Polymers

These have the simplest structure and have no branching other than the pendant groups associated with the monomer (for example, the phenyl group of polystyrene). Linear polymers have only two end groups and exhibit reversible melting and solubility behaviour.

2.3 Branched Polymers

Slightly branched polymers show similar physical behaviour to that of linear polymers, but as the complexity of branching increases, their properties approach that of network polymers(12). In general, however, the majority of branched polymers are considered to behave in a similar manner to linear systems. Graft copolymers are examples of branched polymers.

2.4 Network Polymers

These arise when polymer chains are linked together or when

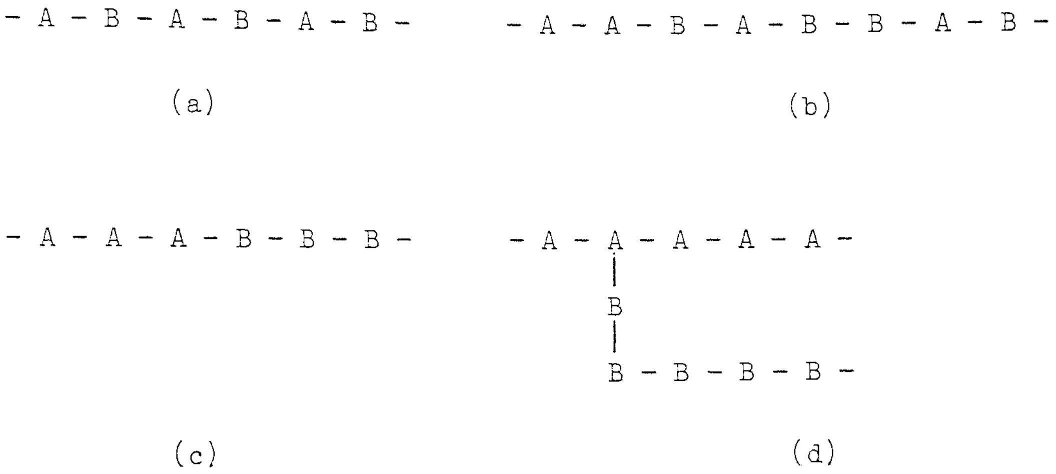


Figure 2.2 Classification of copolymers.
(a) Alternating; (b) random; (c) block; (d) graft.

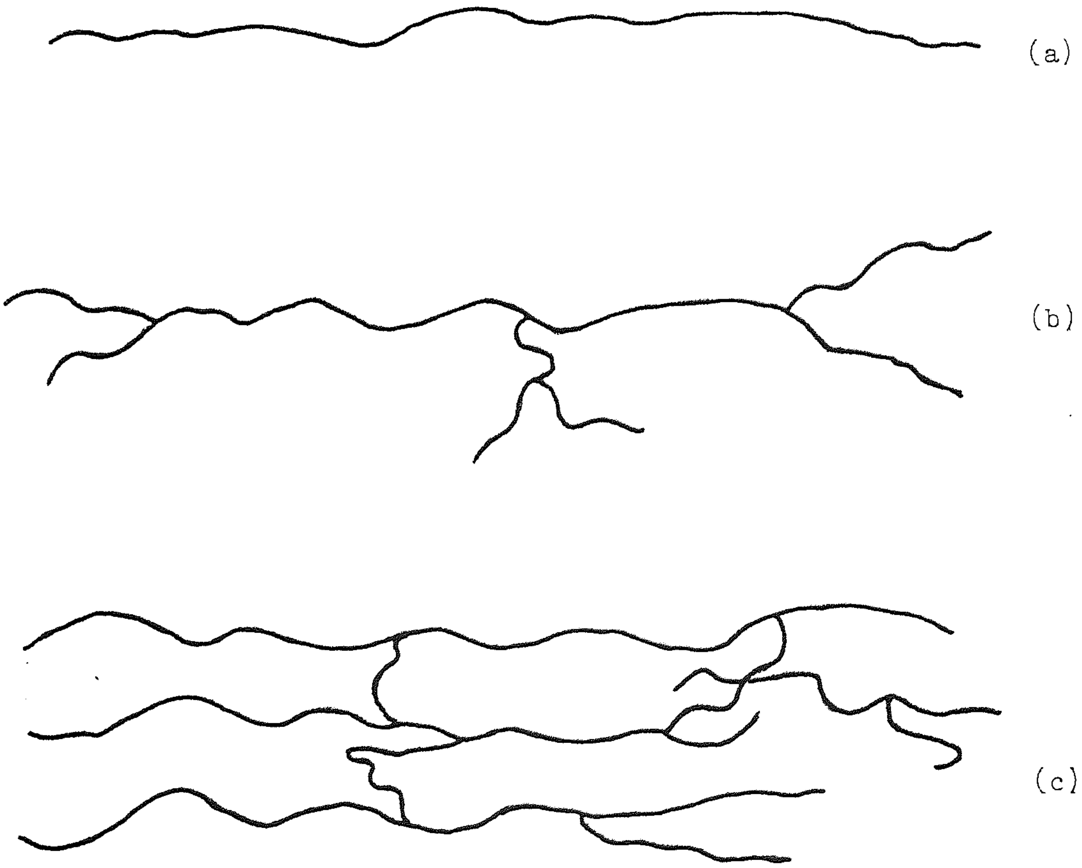


Figure 2.3 Schematic representation of polymer types.
(a) Linear; (b) branched; (c) network.

polyfunctional instead of difunctional monomers are used. (Functionality may be defined as the ability to form primary valency bonds or, as the number of positions in a molecule normally available for reaction under the specific conditions of the experiment(12).) The vulcanisation of rubber is an example of the crosslinking of linear rubber molecules through sulphur; whereas phenol with a functionality of three, reacts with formaldehyde which has a functionality of two, to form (under alkaline conditions) a three-dimensional network structure. Network polymers are also known as crosslinked polymers.

2.5 Crosslinking

Crosslinking is defined as the formation of chemical bonds between polymer chains resulting in a three-dimensional molecular structure(10). A low degree of crosslinking reduces the mobility of the polymer chains and prevents them from flowing over each other. With increasing degree of crosslinking, solubility in typical solvents decreases and ultimately complete insolubility and infusibility result, although even highly crosslinked polymer structures can exhibit swelling in the presence of solvents. The degree of swelling will depend partly on the crosslinking density, and partly on the affinity of solvent molecules for the polymer in question(11).

Examples of crosslinking techniques include vulcanisation, ionising radiation, and chemical reaction of appropriate functional groups on the polymer backbone.

2.6 Thermoplastic and Thermosetting Behaviour

It has been shown previously that polymers may be divided into linear, branched and network.

When linear and branched polymers are heated, the intermolecular forces are weakened and it is possible for the molecules to slide past each other(9). The result is softening of the polymer into a flowable state. Upon cooling below their softening point, these polymers harden. In theory, the process of softening by heating and hardening on cooling can be repeated indefinately. In practice, however, due to thermal aging brought about by repeated heating above the melting point, degradation occurs. Polymers that can undergo such cyclic process are called 'thermoplastic polymers', and materials based on these polymers are referred to as 'thermoplastics'.

With network polymers, because of crosslinking the chains lose their mobility and the material has dimensional stability. It will not soften significantly on heating to temperatures below its decomposition temperature, and therefore it does not melt or flow and cannot be moulded. Such polymers are referred to as 'thermoset polymers' and materials based on them are called 'thermosets'. (The term 'thermosetting' is defined as 'having the property of becoming a thermoset by heat, catalysis or other chemical means'(10, 13)). Many thermoplastic materials may become thermoset by induced crosslinking, for example by the addition of a chemical crosslinking agent or by irradiation(10). The terms thermoplastics and thermosets are usually applied to plastics materials which exhibit those properties described above. It should be noted that polymers and plastics are not synonymous. Plastics are based on synthetic (or modified natural) polymers but contain, in addition to the polymer, impurities arising from their production processes and frequently also other materials deliberately added to achieve specific effects(14).

2.7 Polymerisation Processes

There are many processes by which small molecules can be bonded together to form large ones. Classification of these processes is usually based either on the reaction mechanisms by which the monomeric units are joined together, or on the experimental conditions that exist during the reaction.

(i) Basis : Reaction Mechanism

Traditionally, polymers have been classified into two main groups: addition and condensation polymers. (There is also a third group called 'rearrangement' or 'polyaddition' polymers; this group is, in many respects, intermediate between addition and condensation polymers). This classification was first proposed by Carothers(15) and it is based on whether or not the repeating unit of the polymer contains the same atoms as the monomer.

An addition polymer has the same atoms as the monomer in its repeating unit, while condensation polymers contain fewer because of the formation of by-products during the polymerisation process. The corresponding polymerisation would then be called addition and condensation polymerisation.

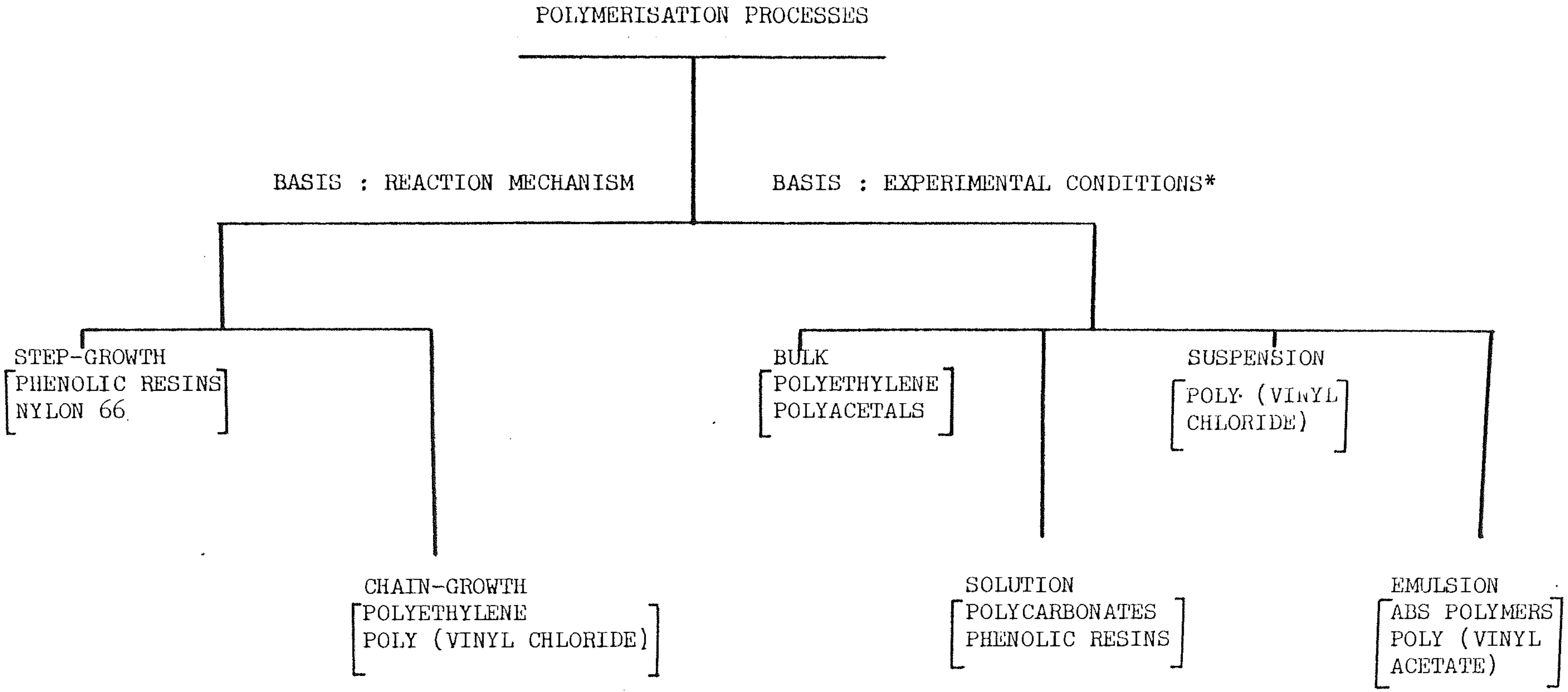
This classification however, can lead to confusion since it has been shown in recent years that many important polymers can be prepared by both addition and condensation reactions. Polyesters, polyamides and polyurethanes are such examples. More recently, the classification of polymers has been based on whether the polymerisation occurs in a stepwise fashion (step-growth), or by propagating from a growing chain (chain-growth)(16).

The two systems of classification have common features; most cases of step-growth reactions involve condensation polymerisation, and most cases of chain-growth reactions are addition polymerisation.

(ii) Basis : Experimental Conditions

On the basis of experimental conditions polymerisation processes are classified according to whether they are carried out in bulk (or mass), in solution in a suitable solvent, in suspension or an emulsion(17, 18). Gas and solid-phase polymerisation reactions have also been studied. The term gas phase really means bulk polymerisation in which monomer vapours are diffusing to the polymerisation site. Polymerisation in the solid-phase has not been employed on a large scale and it is therefore of no commercial importance as yet.

The classification of polymerisation processes is summarised in figure 2.4.



* The examples of polymers shown are cited under the process most commonly used in commercial production.

Figure 2.4 Polymerisation processes

This research project was concerned with the investigation of a process utilising a thermosetting resin of the phenol-formaldehyde type.

3. PHENOLIC RESINS

3.1 Introduction

The term 'phenolic resin'(10) describes a family of products which result from the reaction of phenols with aldehydes. Phenol and, to a lesser extent cresol, xylenol and resorcinol are the most widely used phenols. Formaldehyde and, to a lesser degree furfural, are almost exclusively used as the aldehydes.

Phenolic resins known as resols are thermosetting whereas novolaks show thermoplastic behaviour. Crosslinking of novolaks to thermoset structures is achieved by the addition of hexamethylenetetramine (section 3.3.4), usually abbreviated HMTA, which acts as a hardener. Therefore, since novolaks become thermosets by chemical means, they should be termed 'thermosetting' according to the definition given in section 2.6, but their initial form is thermoplastic and the distinction should be made.

In this chapter it is proposed to review the literature on phenol-formaldehyde (PF) resins since their early development. It will encompass the chemistry as related to the synthesis of resols (used exclusively throughout this project), as it is important in understanding the physical behaviour exhibited by phenolic resins at their final (cured) state.

3.2 Historical Development

3.2.1 History

In 1872 while studying phenolic dyes, Bayer(19) found that phenol reacting with acetaldehyde was converted to a resinous mass. However, little interest was shown and nothing was done with this resinous material. The industrial production of formaldehyde around 1890 and the consequent reduction in price caused some renewed interest and, in 1891 Kleeberg(20) was the first to work with formaldehyde. Using excess formaldehyde and hydrochloric acid as catalyst he obtained an infusible and insoluble resinous mass after a vigorous reaction.

In 1894 working independently both Lederer(21) and Manasse(22) obtained o- and p- hydroxybenzyl alcohols under alkaline conditions.

The first patent for a phenolic resin product was granted to Smith(23) when in 1899 he described a method for a cast cured resin which could be used as substitute for hard rubber. The resin could be made from phenol and formaldehyde (or acetaldehyde), with hydrochloric acid as catalyst and with a solvent diluent such as methyl alcohol to moderate the reaction. Luft(24) proposed a similar process but with aldehyde in excess of phenol.

One of the main difficulties which the early workers attempted to overcome was the rapidity of the reaction making control very difficult. The solution was provided by L.H. Baekeland with his classical work on phenol-formaldehyde reactions.

Baekeland's investigation of phenolic resins began in 1905.

By 1907 he had clearly defined the differences between the reaction of phenol with formaldehyde when using molar ratios of greater or less than one in acidic or alkaline media. In 1907 Baekeland applied for his famous 'heat and pressure' patent(25). Even from his first patent application Baekeland more than any of his predecessors had a clear appreciation of the commercial value of phenolic resins(26). The 'heat and pressure' patent became the turning point, indicating the importance of economic processing techniques for market acceptance.

At a meeting of the American Chemical Society in 1909, Baekeland disclosed the results of his studies for the first time(27). In this and a subsequent paper(28) he described the alkaline-catalysed resins, which he called 'Bakelite', and the acid-catalysed fusible resins which he termed 'Novolaks'.

He stated that the reactions of phenols with formaldehyde in the presence of alkaline catalysts occur in three stages:

A-stage: The initial condensation product in either the liquid or solid form, soluble in organic solvents.

B-stage: An intermediate solid product which could not melt but it became rubbery upon heating and it could swell in some organic solvents.

C-stage: An infusible and insoluble product not softened by heat.

(The terms A-, B-, and C- stages are also used to describe analogies in other thermosetting resins).

Lebach(29) introduced the nomenclature for the alkali-catalysed phenol-formaldehyde products. He called the resins in the A-stage 'resol', the B-stage product 'resitol' and the hardened C-stage product 'resite'.

A significant contribution to the development of resins and the production of moulding compounds was made by Aylesworth, who found that(30) novolaks could be cured favourably by the addition of hexamethylenetetramine (HMTA)

After 1910 other workers contributed to the development of phenol-formaldehyde resins but many of the proposals put forward were only minor modifications of the essential groundwork which had already been covered(31).

3.3 Raw Materials

Phenol and formaldehyde are the main ingredients in the synthesis of phenolic resins. Paraformaldehyde (a low molecular weight solid polymer of formaldehyde) is used in some cases as a source of formaldehyde. Hexamethylenetetramine (HMTA) is mainly used as a crosslinking agent for novolaks; but is also used as a catalyst instead of ammonia.

3.3.1 Phenol

Pure phenol melts at 40.9°C. It crystallises in long colourless needles and, when air-free it is translucent in appearance. Traces of water lower its melting point by approximately 0.4°C per 0.1% of water$^{(32)}$.

Phenol is highly soluble in polar organic solvents (e.g. methanol, ethanol), but not very soluble in aliphatic hydrocarbons (e.g. alkanes, alkenes). When exposed in air phenol rapidly develops a reddish colour especially if it contains traces of copper and iron. This happens if phenol is reacted in copper clad or steel reactors, or if phenolic resins are stored in steel drums.

Phenol is toxic, both solid and liquid phenol are quickly absorbed by the skin and can cause very severe damage. Some of its physical properties are presented in table 3.1.

3.3.2 Formaldehyde

Pure, dry formaldehyde is a colourless gas which condenses on cooling to a liquid that boils at - 19°C at atmospheric pressure and freezes to a crystalline solid at -118°C$^{(33)}$.

Formaldehyde in the pure form is, however, not readily available. As a gas monomeric formaldehyde is characterised by a pungent odour and is extremely irritating even when present in very low concentrations$^{(34)}$. It polymerises slowly at room temperature (20°C) but is stable at temperatures between 80° and 100°C.

The most important commercial sources of formaldehyde are aqueous solutions usually containing small amounts of formic acid and in some cases up to 15% methanol, and solid polymeric hydrates (paraformaldehyde). The presence of methanol is

PROPERTY	PHENOL	FORMALDEHYDE
Formula	C_6H_5OH	HCHO
Molecular weight	94.1	30.0
Melting point (°C)	40.9	-118
Boiling point (°C)	181.4	-19.2
Specific gravity ($25^\circ/4^\circ$)	1.071	0.815 (-20°C)
($40^\circ/4^\circ$)	1.132[a]	1.088[b]
Solubility (g/100g)		
water	8.2	very soluble
alcohol	∞	very soluble
ether	∞	very soluble
Flash point (°C)	79	64
Explosion limits (vol. %)	2 - 10	7 - 72
MAK value (mgm^{-3})	19	12

(a) Reference 35.

(b) Commercial aqueous solution.

MAK = Maximum workplace exposure.

(Data taken from references 32, 36 and 37)

Table 3.1 Properties of phenol and formaldehyde to stabilize the solution and retard the formation of polymers (see also section 3.4.2). Formalin is the most commonly used commercial source of formaldehyde, containing about 37% (W/W) of formaldehyde.

3.3.3 Paraformaldehyde

Paraformaldehyde is a white solid with melting range of $120^\circ - 170^\circ C$. Its odour is the characteristic pungent odour of the monomeric formaldehyde.

It is a mixture of low molecular weight polyoxymethylene glycols analysing at 91-98% CH_2O.

Paraformaldehyde is formed according to equation (3.1):

$$nHOCH_2OH \rightleftharpoons HO(CH_2O)_nH + (n-1)H_2O \qquad (3.1)$$

(methylene glycol) (Polyoxymethylene glycol)

Although it has been proposed that $n_{av.} = 8$, it has also been concluded that the largest number of molecules have $n > 12$(36).

Paraformaldehyde depolymerises in the presence of water to form lower molecular weight polyoxymethylene glycols; under identical conditions it will assume the same equilibria as formaldehyde (section 3.4.2).

It is only seldom used in resin production because it is more expensive than aqueous formaldehyde solutions, and because of problems associated with the exothermic heat evolution(38).

In certain cases where water is not desired in the reaction medium, paraformaldehyde offers some advantage in comparison to aqueous formaldehyde. This is because the reaction of paraformaldehyde with an active hydrogen (e.g. phenol) to form a methylol group (hydroxy methyl - CH_2OH) is anhydrous. No water results other than that in the raw materials. However, formaldehyde is not active in the form of polymers and so paraformaldehyde must be depolymerised with some water or alcohol, using a catalyst if necessary. In the case of alcohols hemiformals are formed. If used in resin production, paraformaldehyde gives rise to a better yield from a reaction vessel(38).

3.3.4 Hexamethylenetetramine (HMTA)

Hexamethylenetetramine, also known as 'hexa', is a colourless, odourless crystalline solid in pure form(36). Anhydrous HMTA sublimes on heating in air with slight decomposition but does not melt. It dissolves readily in water with evolution of heat; the heat of solution is 20.1 KJ/mole at infinite dilution(39). In water, hydrolysis to ammonia and formaldehyde is slight (equation 3.2) with a dissociation constant (K) of 1.4×10^{-9}. A mildly basic character is also shown in aqueous solutions (pH is 8 - 8.5). In methanol or ethanol, HMTA

$$\underset{\text{(HMTA)}}{(CH_2)_6N_4} + 10\ H_2O \rightleftharpoons 6CH_2O + 4NH_4^+ + 4OH^- \qquad (3.2)$$

is less soluble with a solubility of 8.5g and 3g per 100g of solvent respectively.

HMTA is used almost exclusively for crosslinking of novolak resins and is usually prepared from formaldehyde and ammonia according to equation (3.3).

$$6CH_2O + 4NH_3 \rightleftharpoons (CH_2)_6N_4 + 6H_2O \qquad (3.3)$$

Since HMTA contains no oxygen, no water is liberated when it is employed as a source of methylene groups. This is of importance in the final hardening of phenolic resins where liberation of water would lead to bubble formation(36) in the finished product. It is sometimes used as a catalyst in the synthesis of resols instead of ammonia yielding equivalent results.

Properties for paraformaldehyde and HMTA are shown in tables 3.2 and 3.3.

3.4 Chemical Aspects

Although phenolic resins have been known and widely used for nearly 70 years, their detailed chemical structure remains to be established. Their complexity is now well recognised and the various structures present will mainly depend on the following:

(i) mole ratio of formaldehyde to phenol;

(ii) pH of the reaction mixture; and

(iii) temperature of reaction.

Formula	HO $(CH_2O)_n$ H (n = 6-100)
Formaldehyde content %(W/W)	91 - 99
Melting range (°C)	120 - 170
Free water content %(W/W)	0.2 - 4
Specific weight (g cm^{-3})	1.2 - 1.3
Flash point (°C)	71
Solubility in water (20°C)	dissolves slowly

Table 3.2 Properties of paraformaldehyde[a]

Formula	$(CH_2)_6 N_4$
Molecular weight	140.2
Specific weight (g cm^{-3})	1.39
Application of heat	sublimes at 270-280°C
Solubility (g/100g, 20°C)	
water	87.4[b]
ethanol	3.0
ethyl ether	0.08

[a] Values in Table 3.2 suggest that paraformaldehyde is not a defined compound.

[b] Solubility decreases with increasing temperature up to approximately 50°C (36).

(Data taken from references 32, 36 and 37).

Table 3.3 Properties of HMTA

The concept of functionality is also important in relation to the chemistry of phenolic resins. Formaldehyde has a functionality of two ($f_F = 2$) towards phenol; likewise phenol has a functionality of three ($f_P = 3$) towards formaldehyde, the reactive hydrogens at ortho- (2) and para- (4) ring positions.

The phenolic hydroxyl is not a functional group in this sense and the two meta-positions do not enter the reactions under the normal conditions; this requires specific catalysis and selectively substituted phenols. Stoichiometry requires a ratio of formaldehyde to phenol of 3/2 or a mole ratio $N_F/N_P = 1.5$. Under these conditions a fully crosslinked structure is possible. (In practice, the ratio N_F/N_P varies between 1 and 2.5).

The complexity of phenolic resins was pointed out by Megson and Hollingdale(40) when referring to novolaks. They estimated that for the average molecule of eight phenol rings (units), there exist 1,485 unbranched isomers; the total, inclusive of branched isomers was calculated to be around 12,000 isomers. In practice, however, there is selectivity in the reactions of formation as a result of differences in reaction of functional groups, and the number of isomers, and thus the complexity, is far less than predicted by theory(38).

Nevertheless, the systems are by no means simple and elucidation of the structures has yet to be determined. In other respects the potential of producing a variety of resins which would satisfy a wide range of customer's requirements is of great importance to the plastics industry.

3.4.1 Types of Phenolic Resins

There are basically two types of phenolic resins, resols and novolaks which have been described in several books(31, 32, 41-43). Phenolic resins that can cross-link into an infusible material on heating and without the addition of hardening agents, are widely referred to as 'one-step' resins(10). Resols fall into this category. In this respect novolaks may be appropriately termed 'two-step' resins. In figure 3.1 an outline of the processes resulting in resols and novolaks is shown.

The classification of phenolic resins into resols and novolaks is based on two reaction variables:

(i) mole ratio of formaldehyde to phenol (N_F/N_P); and
(ii) pH of reaction medium.

The reactions of phenol and formaldehyde are therefore conveniently classified under the type of catalyst used. i.e. whether alkaline or acidic. Catalysis in acidic

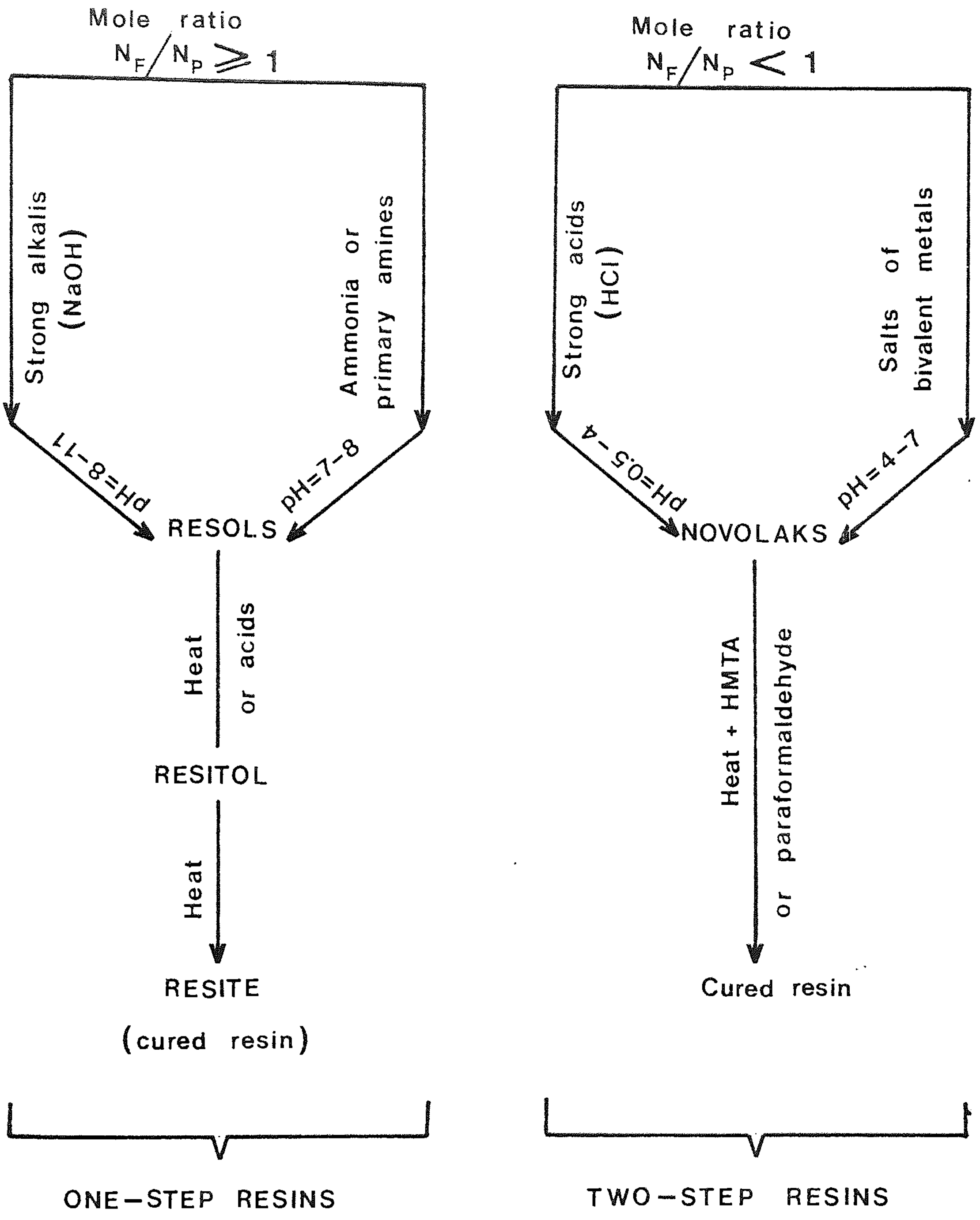


Figure 3.1 Phenolic resin processes.

(*Novolaks prepared at pH = 4-7 are usually called 'high-ortho' - novolaks because of the dominating ortho-ortholinkage in their structure).

medium will not be reviewed as it is beyond the scope of this project.

The alkali (and also the acid) catalysis is strongly influenced by formaldehyde equilibria (in aqueous and alcoholic solutions) and will be considered first.

3.4.2 Formaldehyde Equilibria

(i) Aqueous Media

Aqueous formaldehyde solutions contain the monomeric hydrate $CH_2O.H_2O$, of unknown structure usually assumed to be $HOCH_2OH$ - methyleneglycol (equation 3.4). In such solutions free formaldehyde is present in small amounts (< 0.1%) and is usually neglected in considerations of equilibria in reactions with active hydrogen; this, however may not be totally justified(38). Low molecular weight polymeric hydrates HO $(CH_2O)_nH$ also exist in aqueous solutions in equilibrium (equations 3.5 and 3.6)(36, 44, 45).

$$\underset{\text{(formaldehyde)}}{CH_2O} + \underset{\text{(water)}}{H_2O} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(Methylene glycol)}}{HOCH_2OH} \qquad (3.4)$$

$$\underset{\text{(methylene glycol)}}{n\,HOCH_2OH} \rightleftharpoons \underset{\text{(polyoxymethylene glycol)}}{HO(CH_2O)_nH} + (n-1)\,H_2O \qquad (3.5)$$

$$HOCH_2OH + HO(CH_2O)_nH \rightleftharpoons HO(CH_2O)_{n+1}H + H_2O \qquad (3.6)$$

The hydration of formaldehyde, equation (3.4) is rapid. The mole fraction of the monomeric hydrate decreases with increased formaldehyde concentration(36); the rate at which the equilibrium value is attained is temperature - and pH - dependent(44). It has been concluded(46) that the lowest velocity constant (k_1) for this reaction is about 10 s^{-1} at ordinary temperatures, and that $k_{dehyd.} = k_2 =$ 5.1×10^{-3} s^{-1} at pH 7 and 25°C.

Aqueous solutions of formaldehyde generally have a pH range 2.5 - 3.5. This acidic character is attributed to traces of formic acid, as a result of the oxidation of formaldehyde during its manufacture and also the Cannizzaro reaction.

$$\underset{\text{(formaldehyde)}}{2CH_2O} + \underset{\text{(water)}}{H_2O} \rightarrow \underset{\text{(formic acid)}}{HCOOH} + \underset{\text{(methanol)}}{CH_3OH} \qquad (3.7)$$

Neutral solutions become acid on standing and reach an 'equilibrium pH' range of 2.5 to 3.5.

Equations (3.5) and (3.6) represent equilibria of the polymerisation of methylene glycol. Polyoxymethylene glycols are formed by the progressive condensation of methylene glycol. Data on the distribution of methylene glycol and polymers (n = 2 - 10) at formaldehyde concentrations of 5-50% (W/W), is given by Walker(36, p.64). (See also ref. 38, p.167).

(ii) Hemiformal equilibria

A typical analysis of commercial aqueous formaldehyde solutions is shown in table 3.4. Methanol is present as a result of:

(i) the formaldehyde production from methanol;
(ii) the Canizzaro reaction, equation (3.7); and
(iii) deliberate addition.

Methanol favours the formation of hemiformals and related equilibria (equations (3.8) and (3.9)).

Table 3.4 Commercial formalin

Product →	(A)	(B)	(C)
Formaldehyde as $CH_2O^{(*)}$ (W/W)	37.0-37.3%	37.0-37.3%	49.75-50.25%
Methanol	3.0% max.	1.0% max.	1.5% max.
Formic acid	0.02% max.	0.02% max.	0.05% max.

(*) By analytical methods which do not distinguish hydrolysable derivates of CH_2O.

Source: Reference (38).

$$HOCH_2OH + CH_3OH \rightleftharpoons HOCH_2-O-CH_3 + H_2O \quad (3.8)$$

$$HO(CH_2O)_nH + CH_3OH \rightleftharpoons HO(CH_2O)_nCH_3 + H_2O \quad (3.9)$$

The effect of hemiformal equilibria on the kinetics of the reaction between formaldehyde and phenol under alkaline conditions has been considered by Zavitsas and his co-workers(44, 47).

The addition of methanol to commercial formaldehyde solutions is, therefore, significant as it changes the availability of methylene glycol (or formaldehyde) owing to the hemiformal formation. Methanol has a retarding effect on the reactions of formaldehyde with phenol.

It can therefore be seen that solutions (B) and (C) in table 3.4 can be used interchangeably since the mole ratios of methanol to formaldehyde (N_M/N_F) are almost equal. (Certain allowance for the higher concentration of CH_2O must be made). Interchanging (B) or (C) with (A) will require changes in catalysts, temperature of reaction and, in some cases, formaldehyde ratios.

3.4.3 Alkaline Catalysis : Strong alkalis

In the presence of strong alkalis (KOH, NaOH, Na_2CO_3 etc.) and with mole ratios $N_F/N_P \geqslant 1$ the reactions of phenol with formaldehyde have received a great amount of study(44, 47-55) and they are reasonably well understood.

Strong alkalis favour formation of water soluble resols; in contrast, ammonia and certain amines (particularly primary amines), although basic, cause a rapid loss in water solubility(42) and the resulting resols are soluble in alcohols (methanol, ethanol etc.). The initial reaction products are for both types of alkaline catalysts (strong or weak), the phenol alcohols. (In the case of ammonia, benzylamines are also formed).

3.4.3.1 Formation of methylol phenols

The methylol groups ($-CH_2OH$) formed initially, can be attached to the aromatic phenol ring in only three positions by electrophillic attack(56) (see figure 3.2).

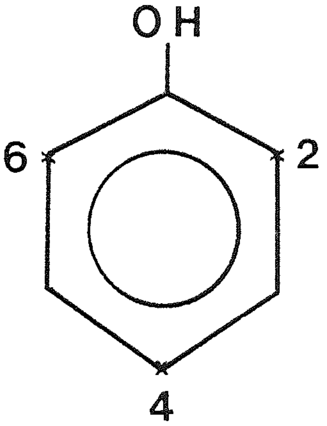


Figure 3.2 Points where formaldehyde adds to phenol.
2, 6 are ortho to the OH group
4 is para to the OH group.

At pH > 8 the formation of methylol phenols is fast and proceeds according to seven simultaneous routes shown in figure 3.3. Under conditions typical of resol synthesis, condensation to multinuclear products does not begin until after the degree of reaction of phenol is about 0.7(47).

Freeman and Lewis(48) were the first to describe the kinetics of the seven reactions (figure 3.3) using paper

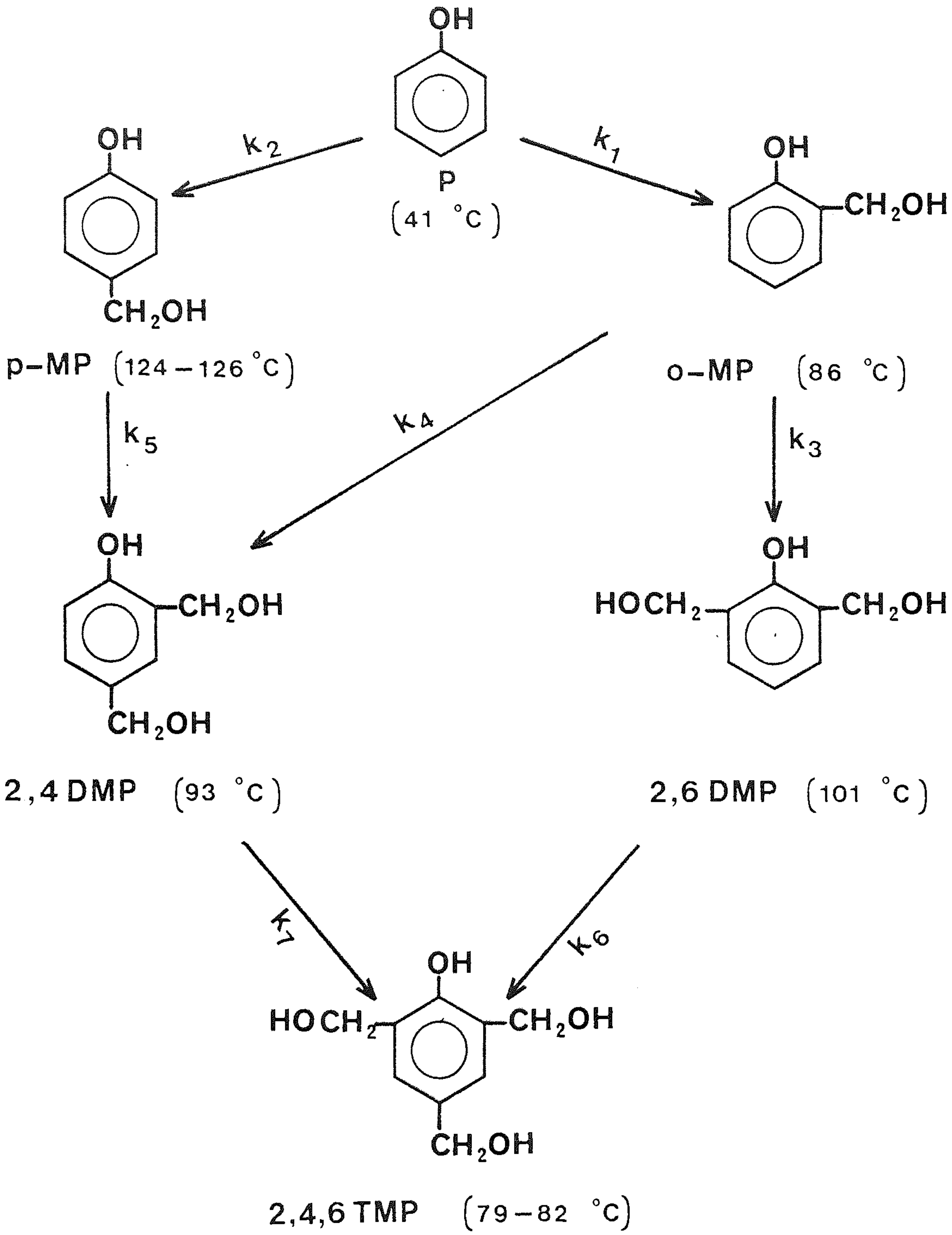


Figure 3.3 The initial reaction of formaldehyde and phenol under alkaline conditions (each step assumes addition of 1 mole of CH_2O)

Key:

P = Phenol
MP = Methylol phenol
DMP = Dimethylol phenol
TMP = Trimethylol phenol

(Figures in brackets denote melting points(32, 57)) chromatographic techniques. Simplified steps were used in order to calculate reaction rates. Hemiformals of the methylol phenols were not considered; their significance in phenol-formaldehyde chemistry was unknown at the time. The reaction conditions used of 30°C, pH > 11 and mole ratio of $N_F/N_P = 3$ are not typical of commercial practice. Their work, however, opened the path for Zavitsas and co-workers(44, 47, 49, 50) for a more thorough and rigorous analysis of the methylolation reactions to be undertaken. Relative reactivities, for reaction conditions similar to those of Freeman and Lewis, but at a pH = 8.5 are given in table 3.5.

Some of the conclusions reached by Zavitsas and co-workers are as follows: (see also(38))

(i) The reactions are second order.

(ii) The general expression for the overall reaction is:

$$\text{rate} = k \left[P^-\right] \left[HOCH_2OH\right]$$

where

k = reaction constant and,

$\left[P^-\right]$ = phenol anion concentration.

(iii) Concentration of reactive species depends upon the formaldehyde equilibria in aqueous media. At high dilution more formaldehyde as percent methylene glycol ($HOCH_2OH$) is available.

(iv) The hemiformal formed between formaldehyde and methylol phenols influence concentration of methylene glycol.

Table 3.5 Ortho-para relative reactivities

	Freeman and Lewis(a) (1954)	Zavitsas and Beaulieu(b) (1967)
P → O-MP	1.00	1.00
P → p-MP	1.18	1.42
O-MP → 2,6-DMP	1.66	2.49
O-MP → 2,4-DMP	1.39	1.80
p-MP → 2,4-DMP	0.71	1.07
2,6-DMP → 2,4,6-TMP	7.94	5.32
2,4-DMP → 2,4,6-TMP	1.73	1.27
k_1/k_2(b)	1.41	1.69
All data at pH	> 11	8.5
N_P/N_F	1/3	1/2
Reaction temperature	30°C	30°C

(a) From the data of Freeman and Lewis(48) as listed by Zavitsas (49, table II, column 3).

(b) Reference 50, table II, column 1.

(v) A low dielectric medium (high concentration of reactants) generally gives higher reaction rate constants.

(vi) The acid ionisation constants of methylol phenols (experimentally measured to be higher than that of phenol(58)) affect the reaction rates. A high ionisation constant (low pK_a) favours higher rates of reactions.

It can be seen from table 3.5 that the p-position in phenol shows a higher relative reactivity (1.42) than the o-position towards formaldehyde. However, o-MP is produced at a higher rate (k_1/k_2 = 1.69) since two o-positions are available.

The total relative reactivity of phenol at the start is 3.42, the sum of the two o- and one p-positions. The formation of 2,4-DMP and 2,6-DMP results in a total relative reactivity of 4.29, a value higher than that of the original phenol. This means that o-MP is formed first, and in this state will react with formaldehyde for the formation of 2,4- and 2,6-DMP's, and consequently of 2,4,6-TMP. Therefore, due to the marked tendency towards the formation of poly-alcohols, resols contain considerable amounts of unreacted phenol, even if a relatively high N_F/N_P is chosen.

The quantity of unreacted phenol in commercial resols may vary between 2 and 15%(59), and it could be as high as 20%(60).

Low reaction temperature, low mole ratio N_F/N_P, and strong alkaline catalysts tend to increase the amount of 'free' phenol(42).

Berlin and co-workers(61) examined the hardening of ammonium hydroxide (NH_4OH) catalysed resols. They studied the effect of free phenol on the structure of cured resin (C-stage), by using a resol with an initial free phenol content of 10%. This was compared to a similar resol but with the free phenol removed(62) prior to hardening. The resins were heated to 80°-175°C in a stream of argon. Their findings were:

(i) the presence of free phenol altered the reaction path resulting in a different structure of the final C-stage resin;

(ii) the mechanical properties, elastic modulus and compression and flexural strengths, were higher if free phenol was present in the A-stage resin;

(iii) a sharply defined exothermic peak with a maximum at 160°C was observed in contrast to the dephenolised resin which showed no distinct exothermic peaks; this masking of the exothermic reaction was attributed to the endothermic destruction of dimethylene ethers; and

(iv) during the thermal hardening, some of the free phenol and low molecular weight products were lost at temperatures between 40° and 100°C.

Other investigators(32), however, have suggested that the presence of free phenol in resols reduces the resin efficiency in technical processes, and it also constitutes an environmental hazard.

3.4.3.2 Formation of polynuclear compounds

While the initial reactions between phenol and formaldehyde proceed at a fast rate, condensation of the phenol alcohols, at temperatures between 60° and 100°C, into dinuclear and polynuclear compounds is a relatively slow process.

It was shown that at pH > 8 dihydroxydiphenylmethanes (DPM's) result(47, 52). Freeman and Lewis(48) suggested that DPM's are formed through condensation of methylol groups with evolution of formaldehyde (figure 3.4).

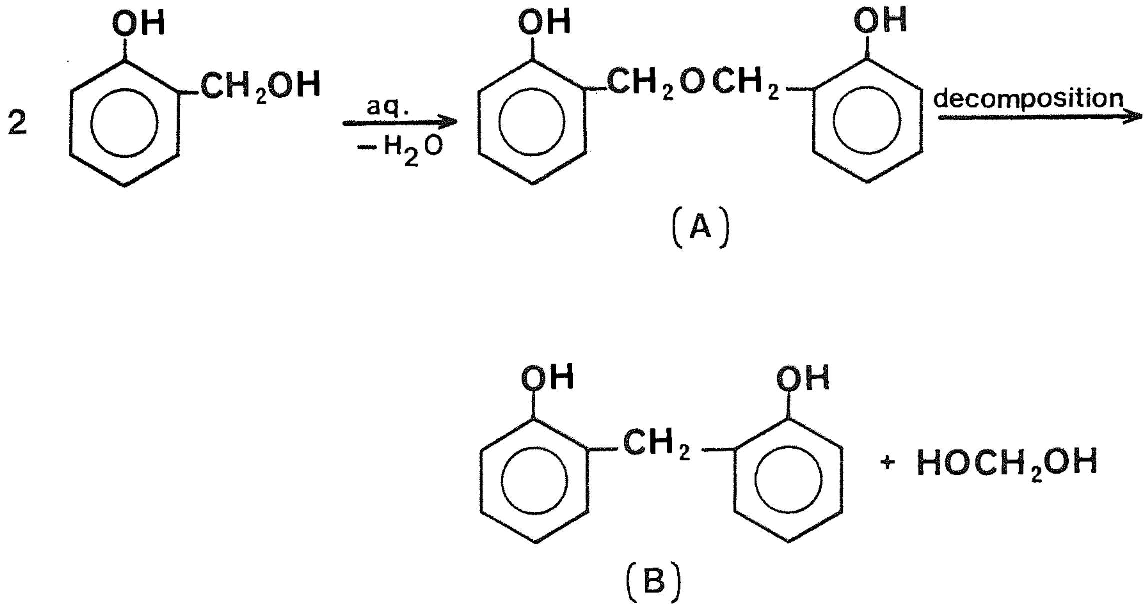


Figure 3.4 Formation of DPM through condensation of methylol phenols.

(Dihydroxydibenzyl ether (A) is more prevalent in neutral or weakly acidic conditions(32)).

The presence of methylolated DPM's in alkali-catalysed reactions is mainly due to the self condensation of the methylol phenols(51). They may also result from reactions of phenol with methylol phenols. This reaction is, however, slower than the self-condensation(51).

It may therefore be stated that a typical commercial resol is a complex mixture of mono-, di- and polynuclear phenolic bodies possessing reactive methylol groups. The polynuclear molecules derived from phenol alcohols will be mainly joined by methylene bridges, prior to neutralisation of the alkaline catalyst. Dimethyl ether linkages will be more prevalent if the resin is condensed under neutral conditions. The resol will also contain unreacted phenol and small quantities of water.

A typical structure of the polynuclear molecules present in a commercial resol is shown in figure 3.5(9).

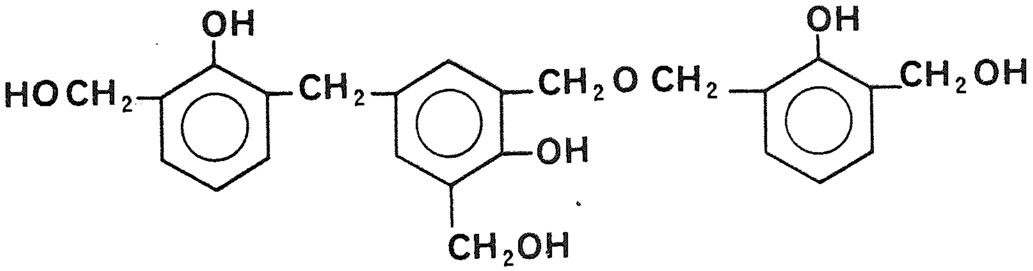


Figure 3.5 Structure of polynuclear products present in a typical commercial resol.

3.4.4 Alkaline catalysis : Ammonia

When aqueous ammonia (NH_3) is used as the catalyst, the resins formed are different in some of their characteristics from other alkali-catalysed phenol-formaldehyde resins. Some of the important differences are:(31, 42, 63)

(i) greater insolubility in water as compared with neutralised NaOH-catalysed resins;

(ii) higher average molecular weight; and

(iii) higher melting points.

Although the importance of NH_3-catalysed resols in varnishes in the production of industrial and decorative laminates is well recognised, their chemistry has received less attention than the strong alkali catalysis. The published work lacks detailed analytical treatment. Nevertheless, it is also well known that these resins are very complex.

The reaction in the pH range 7.0-7.3 was found to be kinetically of the first order by Tsuruta(64). This was confirmed by other investigators(65, 66, 67). Debing and co-workers(67) used HMTA instead of NH_3 for greater ease and accuracy of handling.

Catalysis by ammonia is through the adduct with formaldehyde, HMTA(57). Ammonia reacts almost instantaneously with formaldehyde (equation 3.10). The HMTA is formed via a methylol NH_3-derivative(32).

$$\underset{\text{(formaldehyde)}}{6CH_2O} \quad + \quad \underset{\text{(ammonia)}}{4NH_3} \quad \rightleftharpoons \quad \underset{\text{(HMTA)}}{(CH_2)_6N_4} \quad + \quad \underset{\text{(water)}}{6H_2O} \qquad (3.10)$$

The initial reaction products consist of a mixture of phenol alcohols (mono- and di-nuclear(68)), and hydroxybenzyl amines (di- and tri-nuclear(69, 70)). The structures of the amines are shown in figure 3.6. The presence of hydroxybenzylamines was also shown by the work of Chervinskaya and co-workers(71) using one-, and two-dimensional paper chromatography. The reaction was carried out with a 25% aqueous solution of ammonia, a mole ratio of formaldehyde to ammonia (N_F/N_A) of 3, and at temperatures between 35° and 80°C. The estimated amount of free phenol was 13.5%.

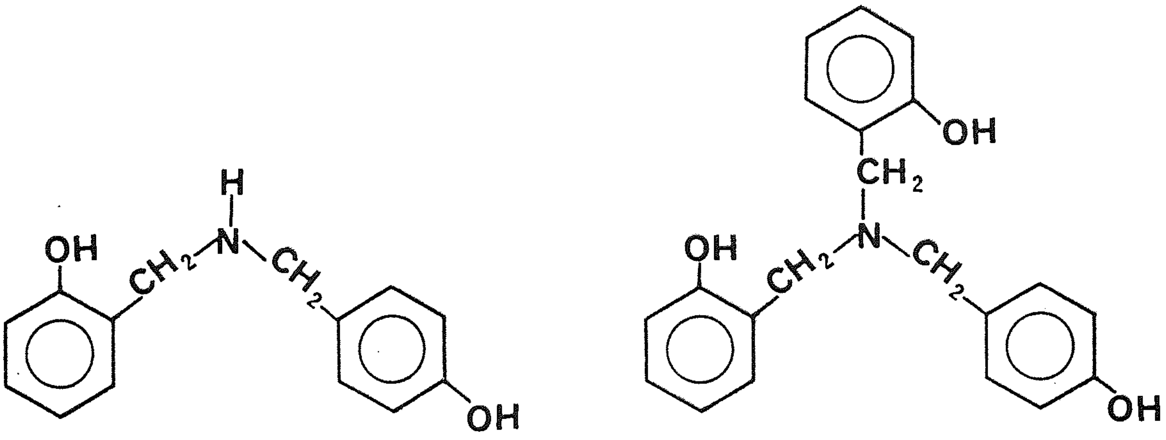


Figure 3.6 Hydroxybenzylamine structures.

The formation of di- and tri-hydroxybenzylamines could explain, partly at least, the greater insolubility shown by ammonia-catalysed resins, as these amines are themselves not readily soluble in water.

In discussing the characteristics of these resols, Calderbank(72) points out that the more ammonia is used the higher becomes the molecular weight and melting point which may be safely attained without crosslinking occurring. This may be due to the inhibition of crosslinkage by N-containing groups, such as $-CH_2NH_2$, which condense relatively slowly with loss of ammonia(31).

4. CURE OF PHENOLIC RESINS

4.1 Introduction

Phenolic resins are of practical use primarily as network polymers. In the preparation of most network polymers, the polymerisation reaction is carried out in at least two separate steps. The first step, the A-stage reaction is the preparation of a low molecular weight polymer also termed a prepolymer. The second step, the B-stage reaction, is the conversion of the prepolymer into a lightly crosslinked product; further reaction results in the formation of a highly crosslinked C-stage polymer structure.

The thermosetting process therefore, involves both physical and chemical changes which are interdependent. The physical transformations that take place, such as gelation and vitrification, are applicable to most thermosetting systems, but the chemistry of the crosslinking reactions will be discussed in relation to phenolic resins.

4.2 Physical transformations : Gelation and vitrification

Gelation and vitrification result from reactions which convert a fluid to a solid during the cure of thermosetting systems.

Gelation is associated with a marked increase in viscosity and a corresponding decrease in processibility. The viscosity approaches infinity or a sample fracture occurs at the gel point, as shown in figure 4.1(73). Beyond the gel point, the reaction proceeds

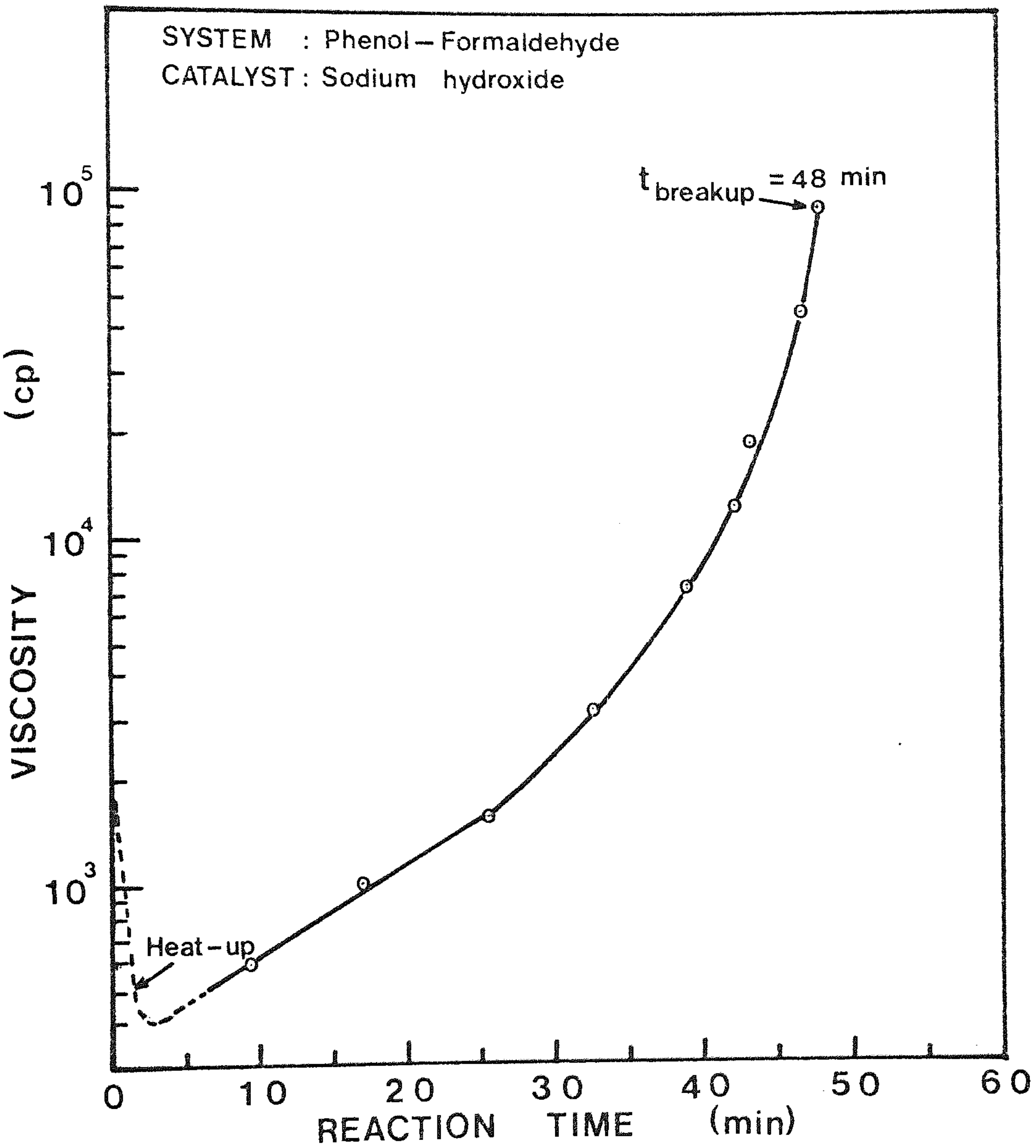


Figure 4.1 Viscosity versus cure time for a resol system at 100°C.

to the formation of a network structure with an increase in crosslink density, glass transition temperature and mechanical rigidity. The network structure will be a rubber (elastomer) at a given temperature if the segments between junction points of the network are flexible. If the segments are immobilised by further chemical reaction, or by cooling, the structure will change to a glassy (vitrified) state.

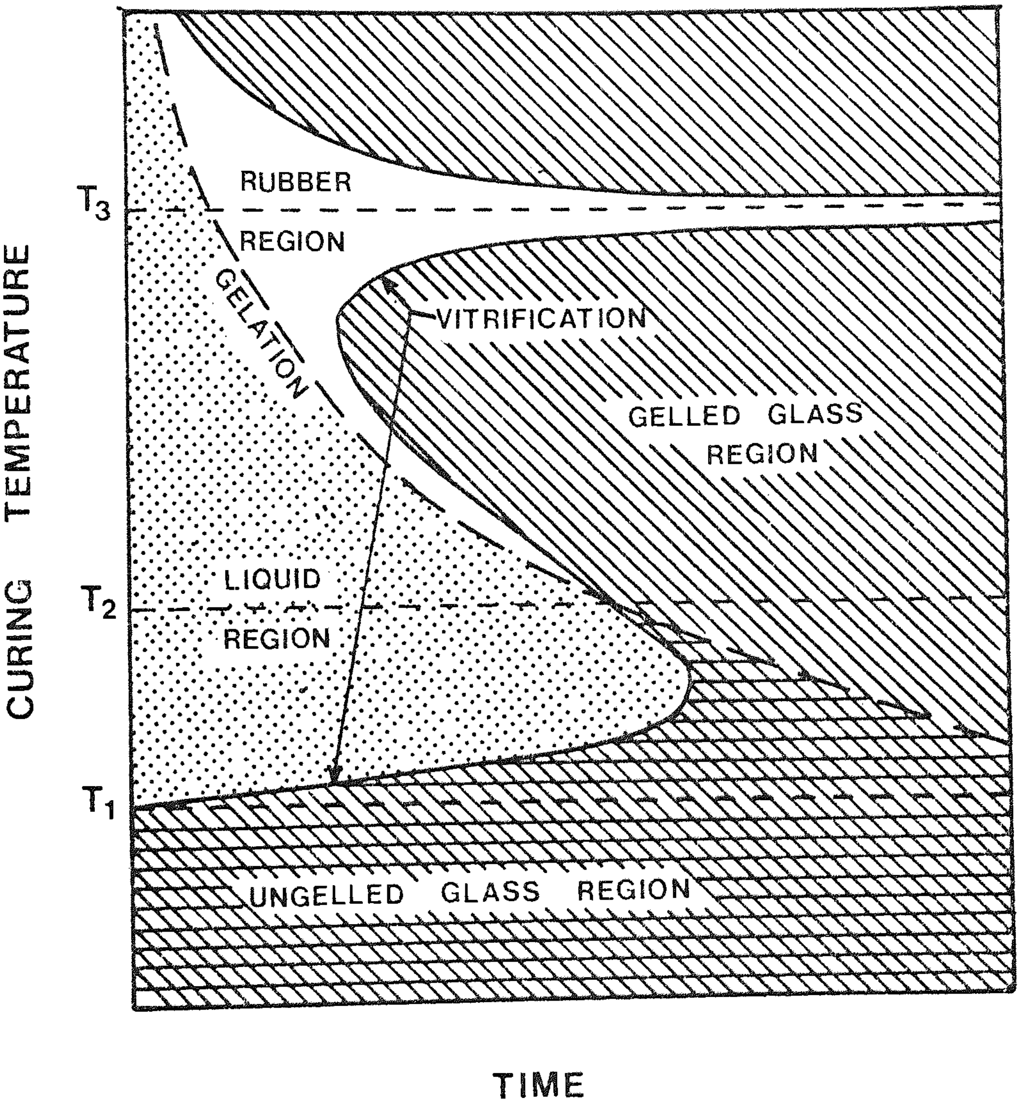
In thermosets vitrification generally follows gelation and occurs as a consequence of:(74)

(i) an increase in the average size of the molecules; and
(ii) the network becoming tighter through further crosslinking.

Vitrification can retard further reaction since in the glassy state the reaction is probably diffusion controlled(75). The overall transformation from liquid to gel to rubber to glass due to chemical reaction is termed 'cure'.

The thermosetting process can be characterised for a particular system by cure/phase diagrams which depict the different states encountered during cure. These diagrams are called Time-Temperature-Transformation (TTT) diagrams and a generalised example is presented in figure 4.2(74). It shows the four distinct material states; liquid, rubber, ungelled glass and gelled glass.

The phase diagram may be constructed by measuring the time to gelation and the time to vitrification versus the isothermal temperature of cure. A convenient technique is the Torsional Braid Analysis(76).



T_1 = glass transition temperature of reactants (or resins).

T_2 = temperature at which gelation and vitrification occur at the same time.

T_3 = maximum glass transition temperature of cured system.

Figure 4.2 Temperature-time relationships.

4.3 Chemical changes : Resol crosslinking reactions

4.3.1. Heat curing of alkali-catalysed resins

Heat curing is by far the more important hardening process for resols; it is directly related to the production of laminates. Cure of one-stage resins can also be affected by employing strong organic and inorganic acids(32, 77, 78).

Resols, formed in strong alkali-catalysed reactions of phenol and formaldehyde, are generally neutralised or made slightly acidic (pH 6-7) before the second stage crosslinking reaction is carried out(9, 16). The catalytic actions of ions such as Na^+ and K^+ is reduced and this results in an improved shelf life of the resin(79). Crosslinking is then effected by heating the mixture of mainly mono- and polynuclear methylol phenols, usually in the temperature range of 130°C - 160°C.

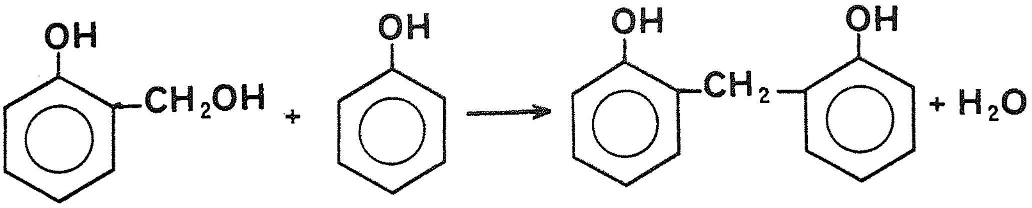
Heat curing is an extremely complex process. It involves a number of competing reactions which may be influenced by reaction conditions and also by the structure of the phenol used in the initial reaction stage(42). The essentially insoluble, and intractable structure of the final (cured) product is another complicating factor when studying the process. It has rendered standard analytical techniques ineffective. It is only comparatively recently that 'new' techniques, such as thermal analysis, have been employed which have enabled more comprehensive analysis to be made.

In the study of resol crosslinking reactions early workers employed various phenol alcohols as model compounds. Although some of their findings may not be directly applicable to the complex mixtures found in present day commercial resins, significant contributions were made towards clarification of the mechanism of cure.

These studies have shown that crosslinking takes place over two main stages and the reactions involved are temperature dependent(80, 81, 82). The first stage includes reactions up to a temperature of approximately 160°C. The second stage occurs in the temperature range of 160°-230°C. This classification is rather arbitrary and overlapping between the stages does occur. It presents however, the thermal curing process in a clear and also convenient form without over-simplifying the system. Figure 4.3 outlines the reactions that take place in both stages and which are relevant to commercial resin cure cycles. A detailed breakdown of all possible reactions is given by Martin(42).

4.3.1.1 First stage reactions(31, 41, 42, 83)

At temperatures up to approximately 160°C the major products are dihydroxydiphenylmethanes (DPM's) and dibenzyl ethers as shown in equations 4.1, 4.2 and 4.3.



(4.1)

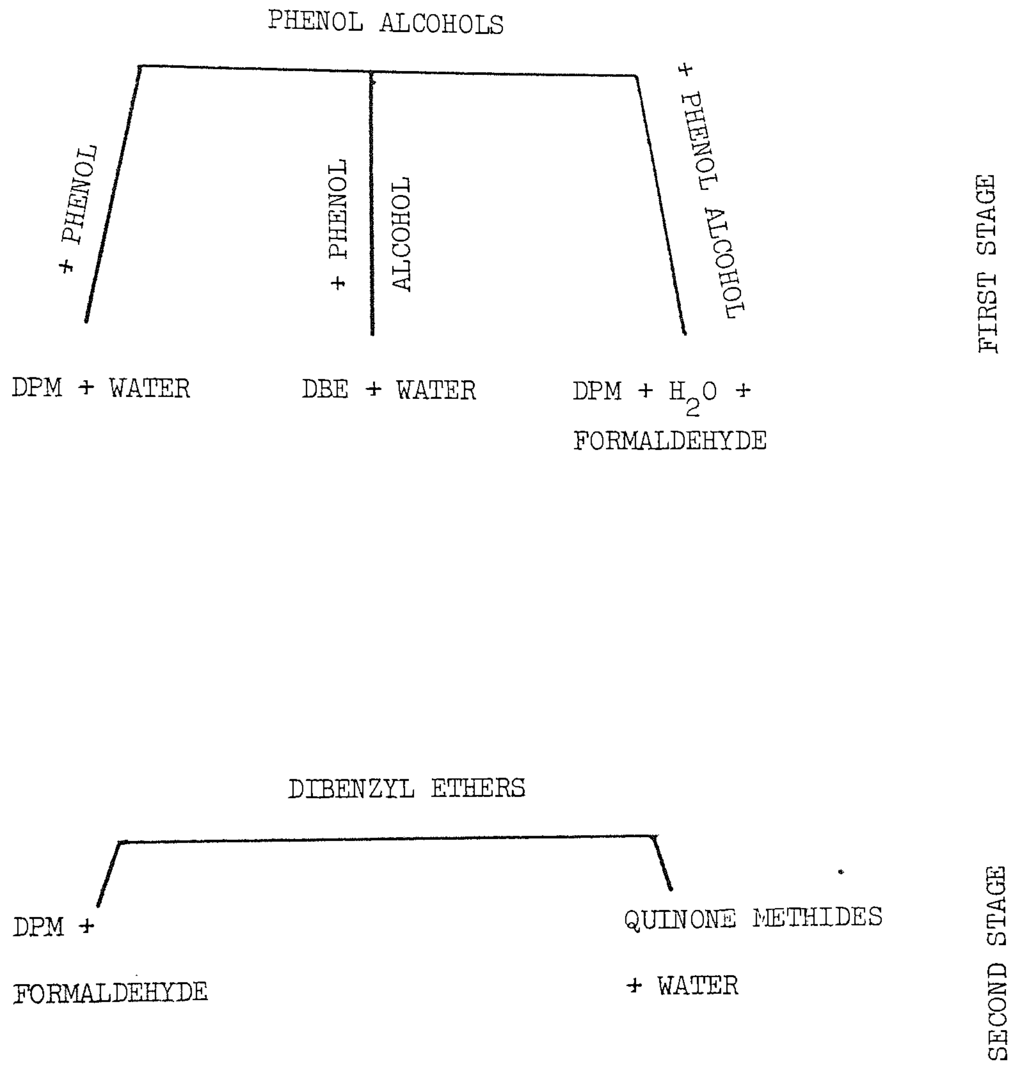
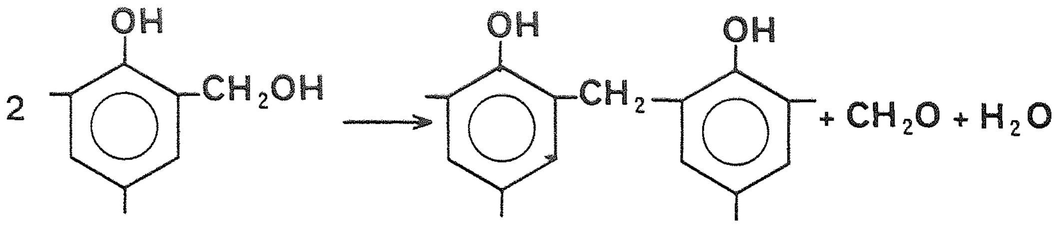


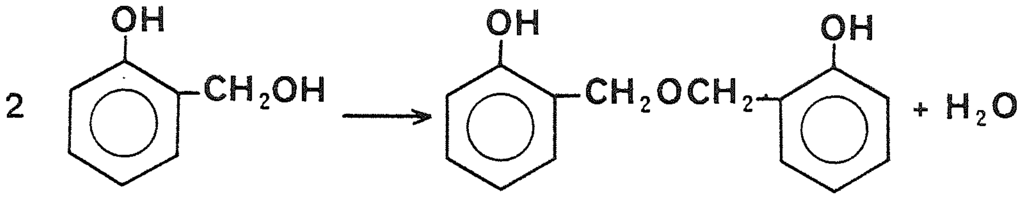
Figure 4.3 Crosslinking reactions of phenol alcohols

DPM = Dihydroxydiphenylmethane (diarylmethane)

DBE = Dihydroxydibenzyl ether



(4.2)



(4.3)

Formation of DPM's is favoured by alkalis and strong acids. Phenol monoalcohols having no active hydrogens are particularly susceptible to reaction 4.2 (Martin, references 56-58 p. 162). Under neutral or slightly acidic conditions ethers are the major products. The reactions in this stage are characterised primarily by:

(i) An increase in the molecular weight

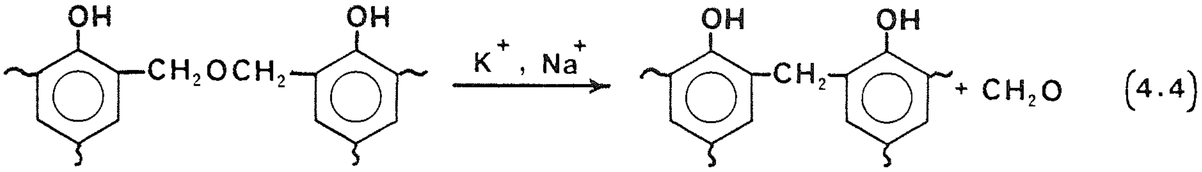
Using phenol dialcohols (molecular weight of less than 400), Zinke(80) obtained an increase in the molecular weight to about 1400. This increase was attributed to the formation of mainly ether-linked molecules.

(ii) Evolution of water

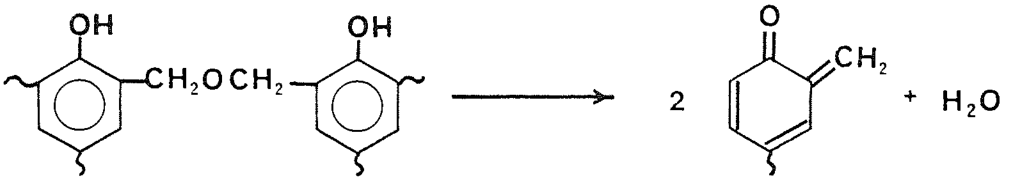
Water is produced in each of the three reactions described above. In the cure of phenol dialcohols, one mole of water is eliminated per mole of dialcohol(80).

4.3.1.2 Second stage reactions(31, 41, 42, 83)

The second stage of the thermal cure of phenol alcohols starts around 160°-170°C. Many of the reactions in this stage arise from the breakdown of the dibenzyl ethers to form DPM's and quinone methides (4.4, 4.5).



(4.4)



(4.5)

A number of simultaneous reactions occur at temperatures above 200°C and these involve the oxidation-reduction and polymerisation of quinone methides and related structures.

The second stage reactions are frequently accompanied by:

(i) A decrease in the molecular weight over the temperature range 160°-200°C. Above 200°C the molecular weight increases again(80);

(ii) an increase in water and formaldehyde resulting mainly from reactions 4.4 and 4.5; and

(iii) a colour change from yellowish to dark brown which has been attributed to the formation of the quinone methides.

4.3.1.3 Conflicting results

Previous work has established that although methylene and benzyl ether linkages may be formed simultaneously, ether formation is very largely eliminated under alkaline conditions(51). Under mildly acidic or neutral conditions, ether formation predominates(42).

Evidence for the relative tendency for ether or methylene formation with increasing temperature is not well established(42). Hanus and Fuchs(84) working with 2,6-dimethylol derivatives of para-substituted phenols, have shown that at temperatures up to about 150°C ether formation is the primary reaction. Adler and co-workers(85) however, have found that in some systems dibenzyl ether formation occurs subsequent to the formation of methylene bridges. Studies on commercial resols catalysed by sodium hydroxide (NaOH) or triethylamine (TEA), by King and co-workers(86), confirmed the proposition that ether formation (equation 4.3) is favoured at higher temperatures than methylene bridges.

It should therefore be emphasised that caution must be exercised as many of the conclusions have been drawn from work on model compounds and their validity on commercial resins may be questionable.

4.3.2 Heat curing of ammonia-catalysed resols

Although many commercial products are catalysed by means of ammonia, usually in the form of hexamethylenetetramine, no research work has been published in the literature. It is therefore assumed that the mechanism of cure is similar to that encountered when slightly alkaline, achieved with dilute alkaline systems, catalysis is employed. Similar products are anticipated, with the benzyl amines present also participating in the cure reactions.

4.4 Degree of cure

The properties of thermoset materials are intimately related to their formation (cure). Analysis of the cure process in order to establish the optimum conditions for cure is therefore of great importance. The most important factor controlling the physical properties of a given thermoset is the degree of cure (extent of crosslinking). For this reason considerable effort has been spent to quantify the amount of cure needed for the necessary property level.

For phenolic resins, chemical(87), physical(73, 88-93), electrical(94, 95) and thermodynamic(96, 97) properties have been examined in order to characterise the degree of cure. As cure proceeds various changes in the properties can be measured. The methods for studying cure have therefore taken the empirical character of maximising a particular property versus the conditions of cure.

Two types of tests have been employed to characterise the degree of cure(98). The first type determines conversion, which is the disappearance of reactive groups or the appearance of a particular structure. Typical tests for determining conversion involve infra-red or chemical analyses. For phenolic resins which can cure by different mechanisms depending on their structure and on the cure conditions, these methods provide useful information on the chemical structures formed during crosslinking.

The second type determines crosslinking, which is the coupling of the molecule into three dimensional networks through the reactive sites. Included in this category are thermoanalytical techniques such as DSC, DTA, DMA and others.

Those methods which follow only the degree of conversion do not completely characterise the degree of cure since they give no indication of the extent of crosslinking. However, it may be possible to relate the results to those methods that determine extent of crosslinking. Westwood(99) expressed infra-red and DSC data in terms of a percentage cure scale. Plotting one data against the other a linear relationship was obtained. Resols cured isothermally at 120°C and for various times were investigated.

4.4.1 Quantitative methods

A number of methods have been used to determine quantitatively the degree of cure for phenolics. The acetone-solubility test(100) is probably the most used method for determining the relative degree of cure in phenolic mouldings and laminated products. (A modification of this test for use with resins was introduced by Harbour(101)).

An instrumental method which is finding increasing use in the analysis of the cure process is Differential Scanning Calorimetry (DSC). DSC is proving to be a valuable thermoanalytical technique for investigating parameters associated with the crosslinking reactions of thermosetting resins and of products based on them. A number of workers have used DSC to investigate the cure of phenolic resins(96, 97, 99, 102).

The application of these methods in determining degree of cure is discussed in detail in Appendix A1.

5. LAMINATES

5.1 Composites

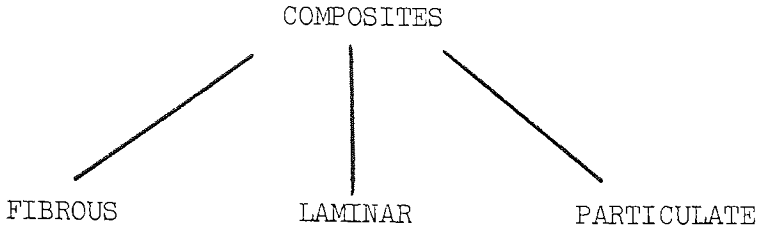
The great interest in composites today stems largely from the fact that demands on materials imposed by todays advanced technologies have become so diverse and so severe, that simple or one-constituent materials are no longer satisfactory. It is therefore frequently necessary to combine several materials into a composite to which each constituent contributes its share, and whose physical properties and technical performance are superior relative to the individual constituents.

5.1.1 Definition

A precise definition of composites is difficult to formulate but may be considered to be combinations of materials which differ in composition or form on a macroscopic scale(103,104). All of the constituents in the composite retain their identities and do not dissolve or otherwise completely merge into each other. This definition is not entirely precise, and it includes some materials often not considered to be composites. Furthermore, some combinations may be thought of as composite structures rather than composite materials. The dividing line is not sharp, and differences of opinion do exist(105).

5.1.2 Classification

Composites may be classified in a number of different ways, but in general three main categories are recognised and these are as follows:(103, 105, 106)



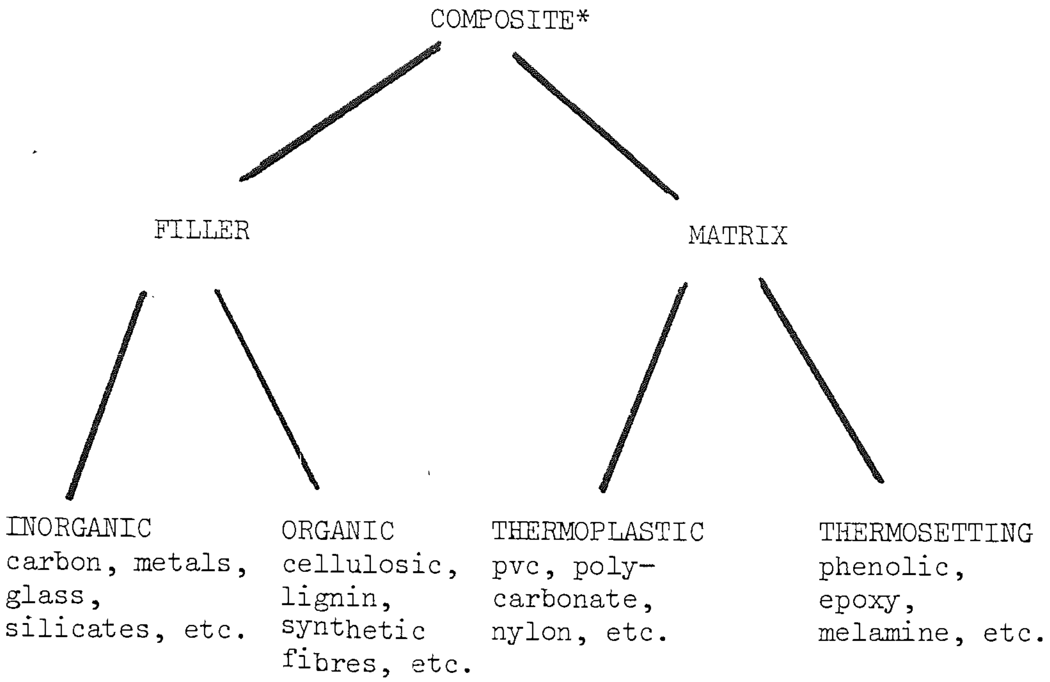
This classification is based on the form of the reinforcing constituent. Each of these categories has several sub-divisions:

Fibrous	The dispersed phase is composed of fibres usually bonded together by a continuous matrix (wood, filament wound structures etc.).
Laminar:	Composed of layers of materials. The bonding phase is discontinuous (plywood, paper, laminates etc.).
Particulate:	Composed of discrete particles, usually in a matrix. (Cement, various types of wood particle-board etc.).

Additional classes have also been suggested, and these include the skeletal and flake composites.

5.1.3 Basic Components

It can be seen from the above classification that each of the various types of composites consists of two basic components, namely a filler (fibrous, laminar, particulate), and a compatible matrix (binder). The main constituents may be further subdivided as follows:



(*This simplified classification is applicable to synthetic polymer composites).

A filler may be defined as a solid material, substantially inert chemically in a plastics material which improves specific properties and forms an essential part of the plastics composition(10). In the literature a large amount of published work has been devoted to the subject of fillers and reinforcements(9, 107-111).

Laminates comprise a family of laminar composites and consist of layers or laminae bonded by a suitable resin under the action of heat and pressure.

In laminates the fillers used are usually materials such as paper (cellulose, asbestos) or woven fabrics (cotton, glass) that are readily available in continuous form. In phenol-formaldehyde based laminates, the matrix is an alkali-catalysed resol, usually in liquid form.

5.2 Production of laminates

5.2.1 The resin matrix

The function of the resin matrix is to bind together and protect the filler, and so it influences directly the physical properties of the laminate. Although the properties of the laminate depend on the nature of both resin and filler, in general, a high resin content gives improved electrical properties and a low resin content gives higher mechanical properties(112).

5.2.1.1 Manufacture of resols

Commercial production of phenolic resols is carried out batchwise although a number of continuous processes have been described in the literature(113-116). Continuous production is appropriate for a large volume of a single product or minor variations of it but, the phenolic resin industry is characterized by a large variety of products where batch production is ideally suited. Nevertheless, continuous production of phenolic novolaks and particle-board resols has been reported(32). In the manufacture of resols, the phenol, formalin and alkaline catalyst are charged into a reaction still of the type shown diagrammatically in figure 5.1. The mixture is continuously stirred and its temperature raised to 70°-80°C by the application of heat. It is then refluxed for 1-3 hours

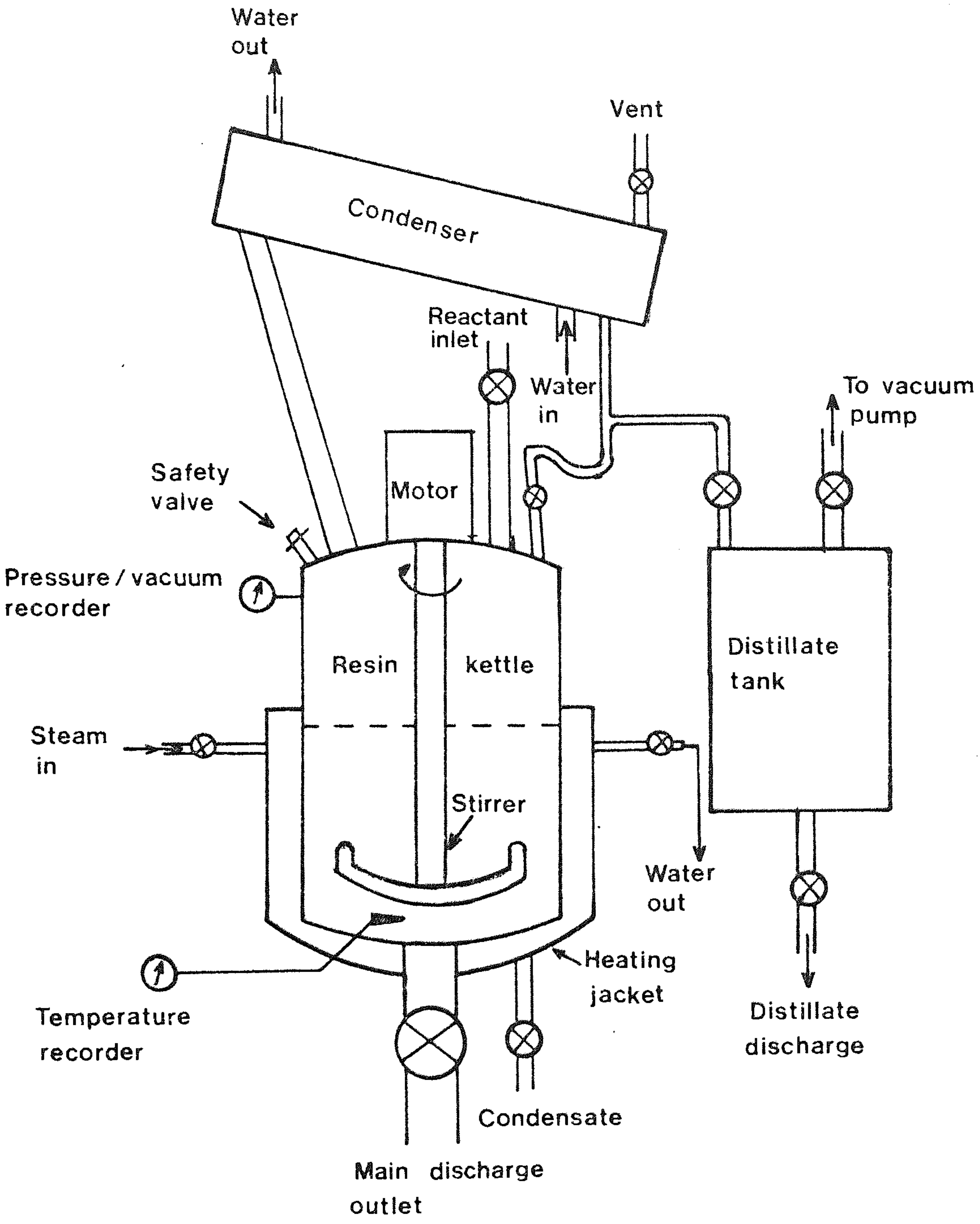


Figure 5.1 Typical batch production of phenolic resins.

before cooling to 50°-60°C, when water is distilled off under reduced pressure (30-50 mbar) to prevent heat hardening of the resin. The temperature is not allowed to exceed 70°C. Samples are withdrawn at regular intervals and tested for gel time. Other tests such as acetone or alcohol solubility, melting point, refractive index, viscosity, free phenol content or loss in weight on stoving at 135°C may be used to follow the reaction(9, 31, 57).

5.2.1.2 Water - and alcohol - soluble resols

Two classes of resol are generally distinguished: water-soluble resins which are usually catalysed by sodium hydroxide (NaOH) and alcohol-soluble resins which are prepared using aqueous ammonia (NH_3aq.) as catalyst.

The water-soluble resins are only partially dehydrated during manufacture to give an aqueous resin with a solids content of up to about 70%. The solution viscosity can critically affect the success in a given application(9). Water-soluble resols are used mainly for mechanical grade paper and cloth laminates and in decorative laminates.

In contrast to the NaOH-catalysed resols, the alcohol-soluble resins have good electrical properties. It has been shown that the presence of polar compounds such as sodium hydroxide has an adverse effect on the electrical properties(117, 118). This is thought to be due to ionisation in the absorbed water so increasing the number of charge carriers and therefore increasing the dielectric loss. When preparing ammonia-catalysed resols, the solvent, usually in the form of industrial methylated spirit (IMS), is added to the mixture when dehydration has been completed. The resulting blend (varnish) is then suitable for use in the production of paper- and fabric-based industrial laminates. The resin is now at the resol or A-stage.

5.2.2 The paper filler

Paper is a bonded random network of natural cellulosic fibres the tensile strength of which is appreciable, approaching that of hardened steel(119).

When paper is dried, water removal creates surface forces which bring the fibres into close contact with each other. The fibres adhere at the contact points because of the formation of intermolecular hydrogen bonds(119).

The covalent bond, a much stronger linkage than the hydrogen bond, is the dominating one within the macromolecules which compose each fibre. The chemical structure of cellulose is illustrated in figure 5.2.

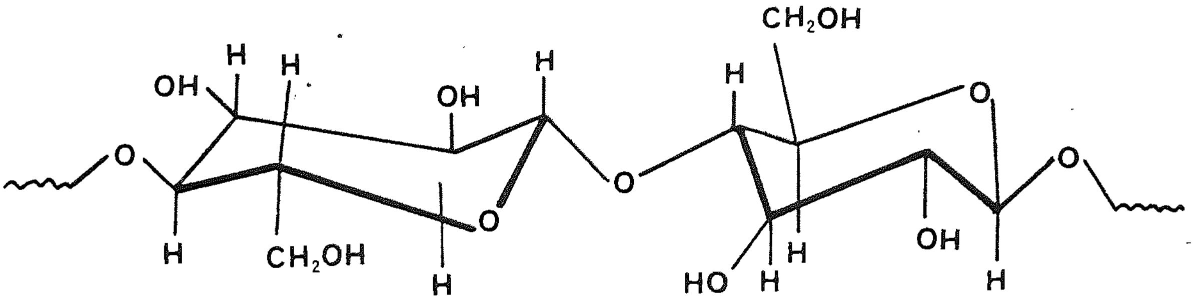


Figure 5.2 Structure of cellulose

It can be seen that the macromolecule possesses a high degree of hydrophilic character. This then lends chemical compatibility to the hydroxyl group-rich resol, thus increasing the ease with which the paper filler may be impregnated with resin. The resin distribution and possible interaction with the paper is considered more fully in another section.

In the production of paper laminates, various types of paper are used for different applications. Kraft papers constitute by far the largest proportion. Usually used in the unbleached condition, they are strong and can be very absorbent. Bleached kraft papers are usually employed when maximum strength is not required. Pigmented kraft paper and paper manufactured from cotton pulp is also used in certain applications.

5.2.3 Test methods

Several tests are applied by manufacturers of industrial laminates in the quality control of the raw materials; detailed descriptions will be found in the appropriate British Standard specification.

These tests are recommended by the various manufacturers of phenol-formaldehyde-based paper laminates and were employed in this research project.

5.2.4 Unit operations

The manufacture of most types of laminates includes basically the same unit operations. Essentially three stages are necessary, although many auxiliary stages are desirable. Figure 5.3 shows the various production stages.

The first operation consists of bringing the filler into contact with the resin solution (varnish); this is called impregnation or coating. The next step, taken immediately after impregnation has a dual function:

(i) to remove the solvent(s) from the impregnated web; and

(ii) to advance the polymerisation of the resin to a predetermined degree of cure (B-stage polymerisation). This is achieved by drying the wet material in a heated enclosure. The combined operations of impregnation and drying are called 'treating'.

Following these operations the treated material or 'prepreg' is then guillotined into pieces of convenient size. To make a sheet of the laminate the appropriate number of prepreg layers is stacked between the platens of a heated hydraulic press. After being subjected to heat and pressure, the resin becomes thermoset (C-stage) and the individual layers are bonded together to form an almost homogeneous solid sheet.

Each of the main stages, impregnation, drying and pressing will be considered fully in subsequent sections.

5.2.5 Impregnating devices (120)

5.2.5.1 Dip-and-flow

The oldest and simplest of the impregnating devices utilises

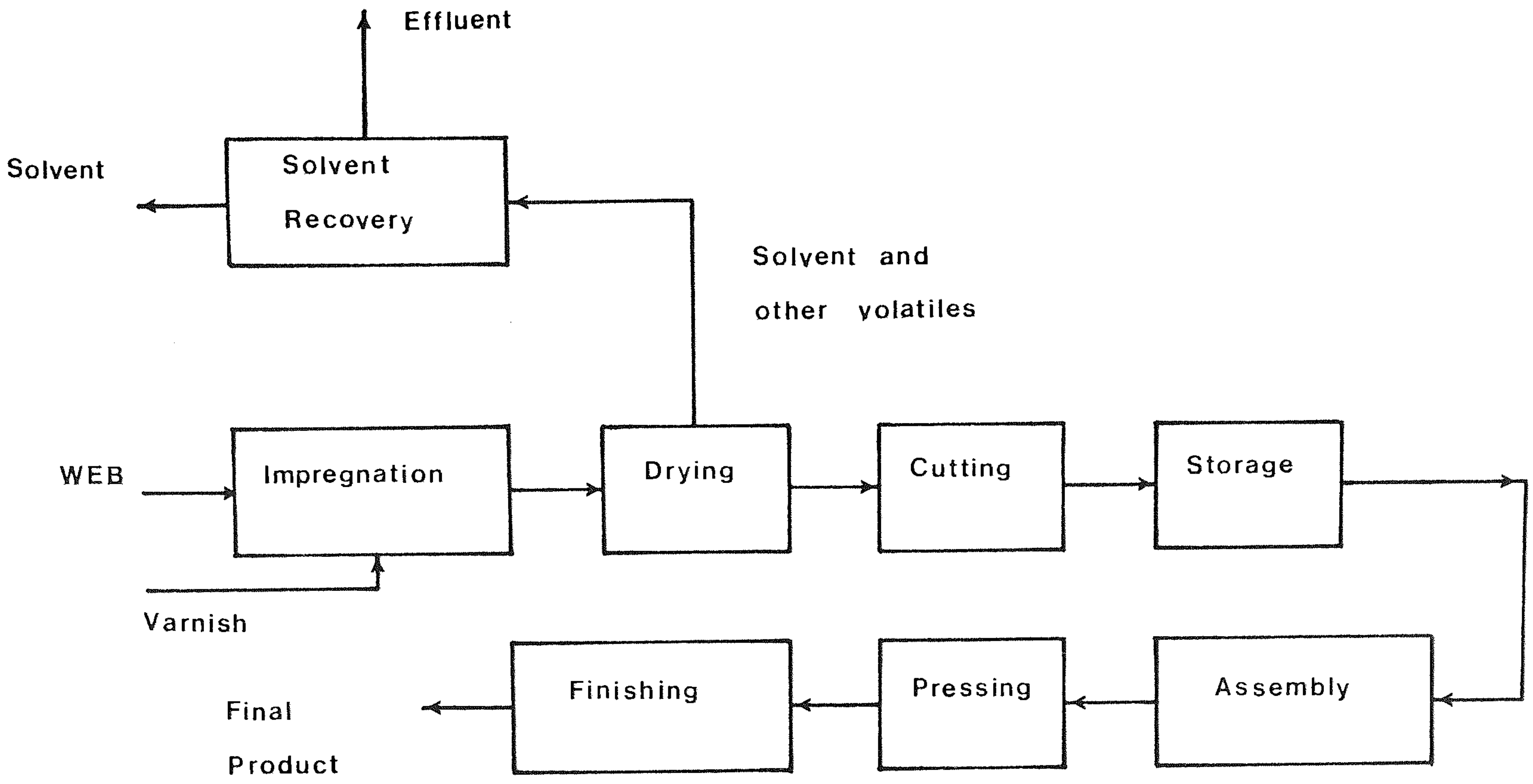


Figure 5.3 Block diagram for laminated plastics.

the 'dip-and-flow' method as shown in figure 5.4. The substrate passes through a bath containing the varnish, becomes saturated and the excess drains off during the upward travel. The amount of varnish applied depends entirely upon the drainage which is controlled by the viscosity of the solution, the thickness (caliper) or porosity of the substrate and the volatility of the solvent.

5.2.5.2 Dip-and-scrape

In the 'dip-and-scrape' technique (figure 5.5) the excess varnish is removed by a scraper. The scraper may be a sharp-edgedknife or large radius rod, or any one of several varieties. More than one scraper may be used. Figure 5.5 shows a single immersion arrangement used in the application of a heavy coating on only one side of the filler. Adhesive sheets and surface sheets for industrial laminates are commonly made this way.

In most cases however, the roller is fully immersed in the varnish so that both faces of the substrate are in contact with the solution, that is, double immersion takes place. When operating at high speeds (0.15 - 1.5 ms^{-1} web speed), the resin pick up can be controlled by the residence time in the bath. To accomplish this the immersion pan is 1.2 to 1.8 m deep and the immersion roller can be raised or lowered with respect to the varnish level to adjust residence time. Resin concentration and varnish temperature also provide simple controls on resin pick up(121); they are normally adjusted to compensate for each other.

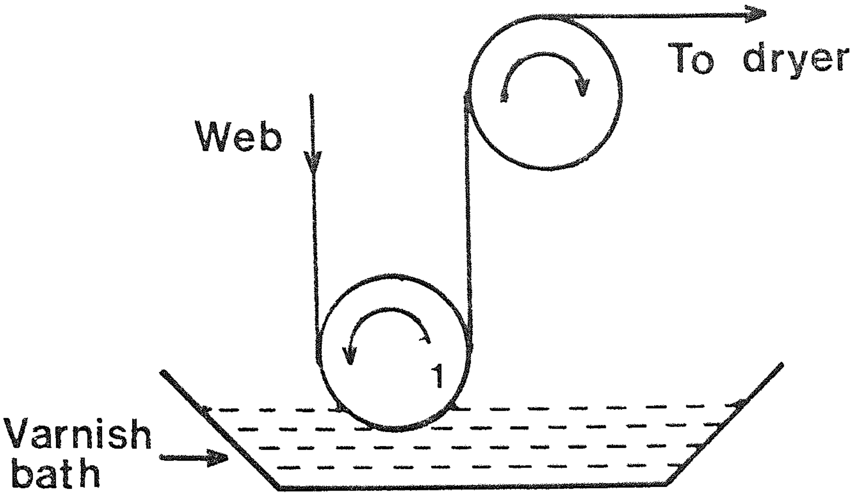


Figure 5.4 Dip-and-flow method for impregnation. 1, immersion roller.

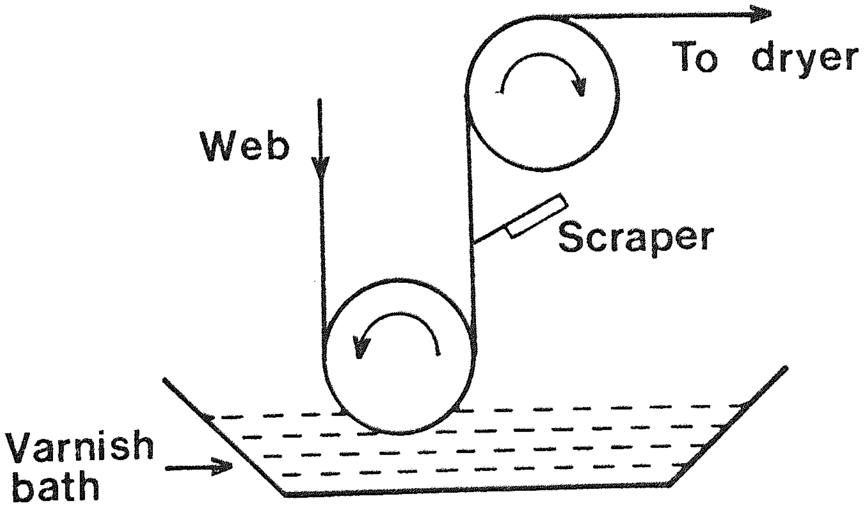


Figure 5.5 Single immersion impregnation bath.

5.2.5.3 Dip-and-meter

This is probably the most popular impregnating device. It is basically a variation of the dip-and-scrape method with the scraper replaced by the metering rollers (figure 5.6). In this arrangement the rollers are chromium-plated, accurately ground hardened steel. They are mounted on bearings and may be adjusted with respect to the separation of their long axes. The use of metering rollers gives greater control over the amount of varnish deposited on the substrate than does the typical dip-and-scrape device.

5.2.5.4 Reverse-roller coater

Reverse-roller coating gives the most uniform coat and it is entirely unaffected by variations in the caliper of the substrate, the accuracy being dependent upon that to which rollers 1, 2 and 3 in figure 5.7 are ground.

It is the most precise coating arrangement. Its operation is simple. Roller 1 picks up varnish and transfers it to roller 2. Rollers 1, 2 and 3 are ground smooth and accurately to about ± 0.0025 mm on 250 mm diameter. The opening between 1 and 2 is carefully adjusted to admit only the exact amount of varnish desired, and the excess flows back into the varnish bath. The remaining varnish is carried to the substrate, the film thickness controlled by roller 3. Roller 4 is a resilient material which assures good contact.

The peripheral speeds of rollers 2 and 4 may be the same, in which case the varnish is deposited on the substrate at

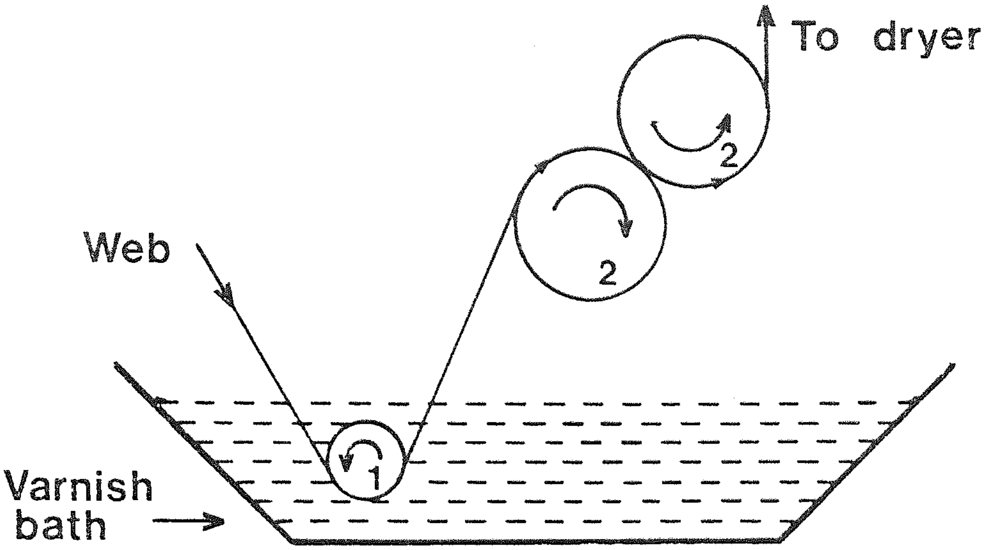


Figure 5.6 Metering roller method for impregnation.
1, immersion roller; 2, metering rollers.

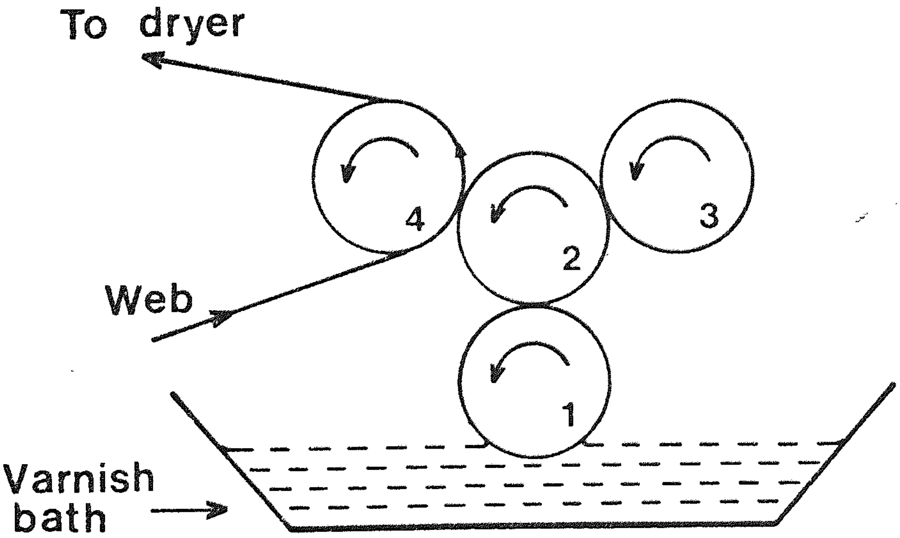


Figure 5.7 Four-roller-reverse coating.
1, furnishing roller; 2, applicator roller;
3, metering roller; 4, backing roller.

the same rate that it leaves the opening between rollers 2 and 3. If roller 4 rotates faster or slower than 2, the film applied will be respectively stretched or compressed.

The reverse-roller coating technique will apply varnishes having a wide range of viscosities. It can therefore be used with high viscosity solutions which results in a true surface coating, or it can be employed with dilute solutions where penetration of the substrate may be desired.

The reverse-roller has found wide application in the area of decorative laminates. Phenolic-impregnated kraft paper used for decorative laminates requires a resin content of 30-35% (W/W). In this range, the paper saturates satisfactorily by means of any of the dipping methods or by coating. When reverse-roller coating is employed, it is possible to use a higher resin concentration which results in faster feed rates since less solvent must be evaporated. The paper however, must have a good absorption rate and the resin should be of a low degree of condensation to provide quick penetration.

5.2.5.5 Other impregnating devices

(i) Substrates of low absorbency

For substrates of low absorbency a typical impregnating machine will usually be equipped with a variable dip system as shown in figure 5.8. This permits the 'breathing' distance for the substrate to be varied from 2 to 7.5 m(122).

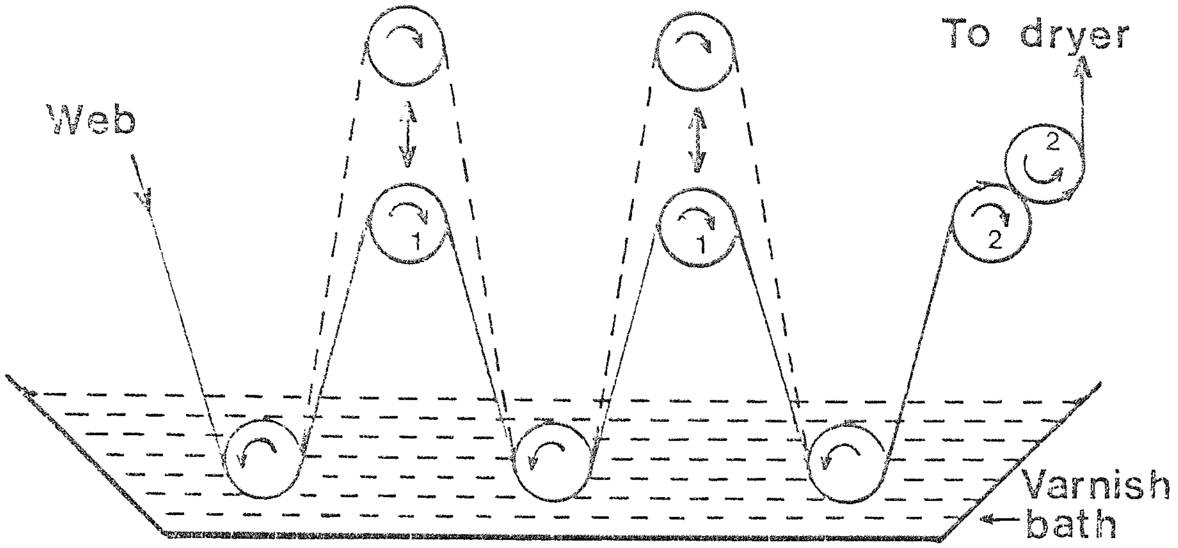


Figure 5.8 Impregnating low absorbency substrate.
1, vertically adjustable guiding rollers;
2, metering rollers.

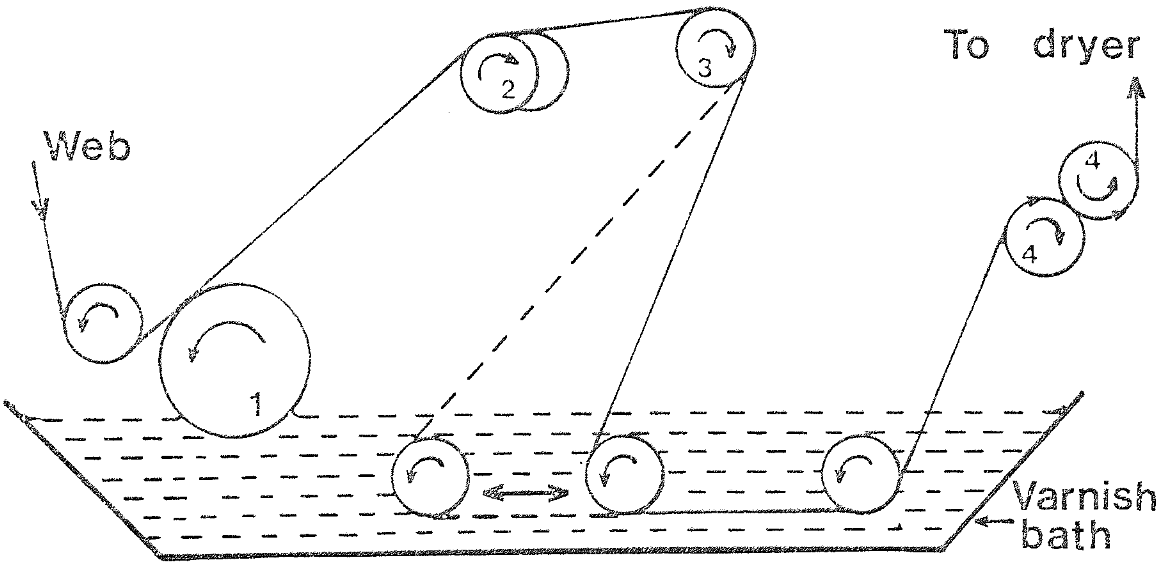


Figure 5.9 Impregnation with 'prewetting'.
1, prewetting roller; 2, web expander roller;
3, web breathing roller; 4, metering rollers.

(ii) Impregnation with pre-wetting

In certain applications particularly when high resin contents (55–65% - dry basis) are desired, 'total' penetration can be achieved by pre-wetting the substrate on one side prior to submerging it in the varnish bath. It is very important that enough web travel time (breathing time) is provided between these two operations to permit the varnish to displace all remaining air from the web(32, 122). Figure 5.9 illustrates this type of impregnation. The distance between the pre-wetting and immersion rollers is adjusted to correspond to the desired feed rate. For high feed rates the distance between these two rollers is increased so that the residence time is decreased.

5.2.6 Dryers

The design of the drying plant may take two forms: either vertical or horizontal arrangements.

5.2.6.1 Vertical dryers

These are economical in floor space, but the oven length is usually limited by the wet strength of the substrate particularly if it is paper. Long unsupported web would also limit the width which can be impregnated without wrinkling. A schematic diagram of a vertical type dryer is shown in figure 5.10.

One of the main problems which is encountered in vertical dryers is the deflection of the hot web around the 'sky

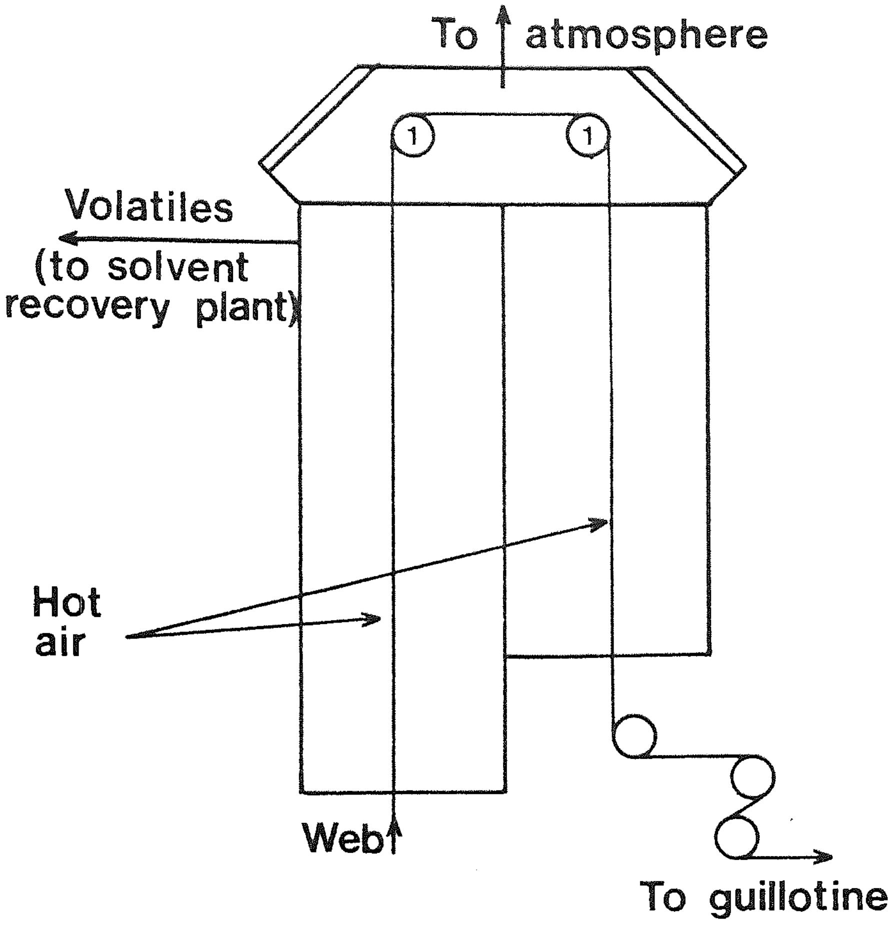


Figure 5.10 Vertical drying arrangement.
1, sky rollers (fixed).

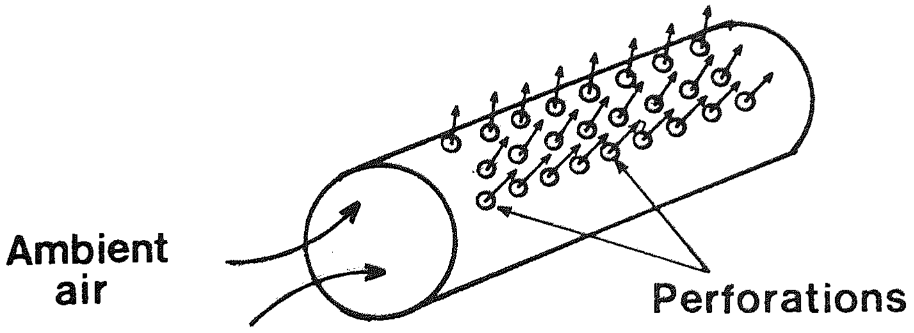


Figure 5.11 Sky roller.

rollers', also known as 'top rollers'. In order to provide floatation of the web and to prevent it from coming into contact with the sky rollers, ambient air is injected through holes situated at the top of each roller, as shown in figure 5.11. Periodic cleaning of the rollers is necessary as the holes tend to get blocked from resin dripping; sometimes however, breakdown of the web does occur when the web comes into contact with rollers and sticks onto their surfaces. Heated air is introduced in order to drive off the solvent and advance the polymerisation to the B-stage.

In order to minimise drying variations between the centre and edges of the web, due to the 'chimney' effect, heating is usually supplemented by steam-heated radiant panels.

After impinging on the web, the air together with the absorbed volatiles is collected by centrifugal fans. A large part is sent to the solvent recovery plant, and the rest vented to the atmosphere.

The volatiles evolved during the drying operation consist of solvent(s), water of condensation, water bound in the original web and other constituents of the resin.

5.2.6.2 Horizontal dryers

These are more efficient than vertical type dryers and can be operated at very high speeds ($> 3\ \mathrm{ms}^{-1}$). To meet the needs for drying a variety of resins, a modular construction is utilised which implies availability of large floor space.

Each drying section may be either 4 or 6 m in length and equipped with its own circulating fan, temperature controls, and exhaust fan.

One of the most commonly used horizontal dryers is the conveyor type dryer (figure 5.12). The web rests upon bars perpendicular to the web length and often fitted with small projections (on coiled springs) which reduce the contact between substrate and conveyor bars(121). Often the conveyor moves at a speed greater than the web to minimise further the local contact between web and conveyor bars. However, even with these measures, the resin tends to stick to the support bars and adds to the bar mark problems. The frequency of substrate breakdown also increases(122).

Another type of horizontal dryer which has gained wide popularity in recent years is the 'floating dryer'. These dryers offer true floatation of the web, therefore eliminating many of the problems found with conventional dryers.

The air circulating blower is equipped with a variable speed drive which delivers the hot air to the nozzles in the range of 10 to 40 ms^{-1}. The air nozzles are located within 25 to 50 mm of the web and assure that the web floats steadily and with minimum vibration between the upper and lower air cushions (figure 5.13). With the hot air in such close proximity to the web surface, the saturated film (boundary layer) on the resin surface is destroyed and rapid

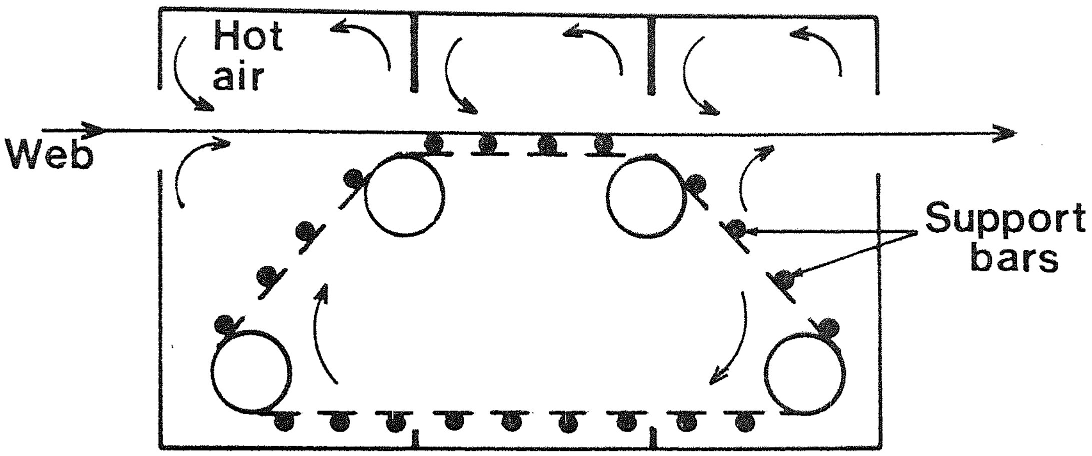


Figure 5.12 Conveyer type dryer.

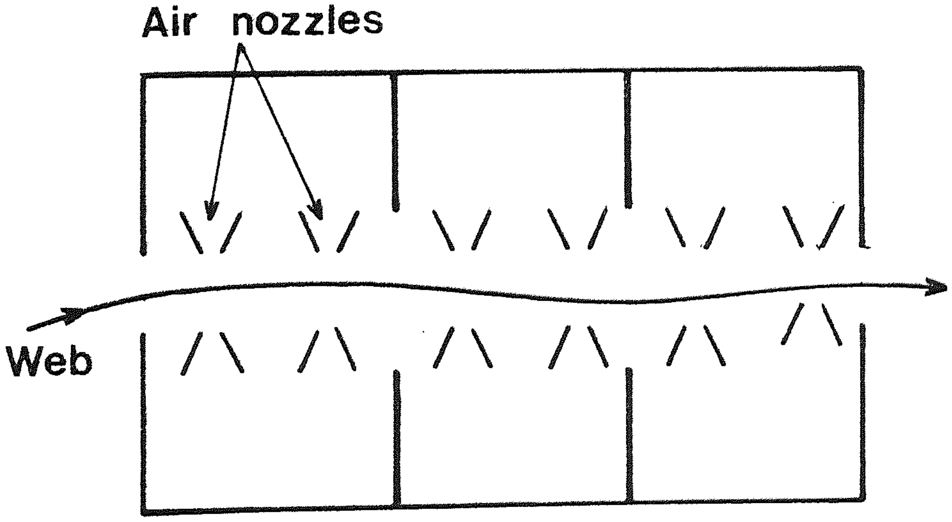


Figure 5.13 Floating dryer.

evaporation of the solvent is achieved without disturbing the even resin distribution(122).

By using infinitely adjustable air velocity in connection with temperature changes, it is possible to influence volatility and resin flow (important parameters in the final cure stage) without changing the dryer operating speed. A rise in temperature and reduction of air velocity reduces flow, and lowering the temperature and increasing the air velocity increases flow, and in neither case will volatility change substantially(122).

5.2.7 Presses

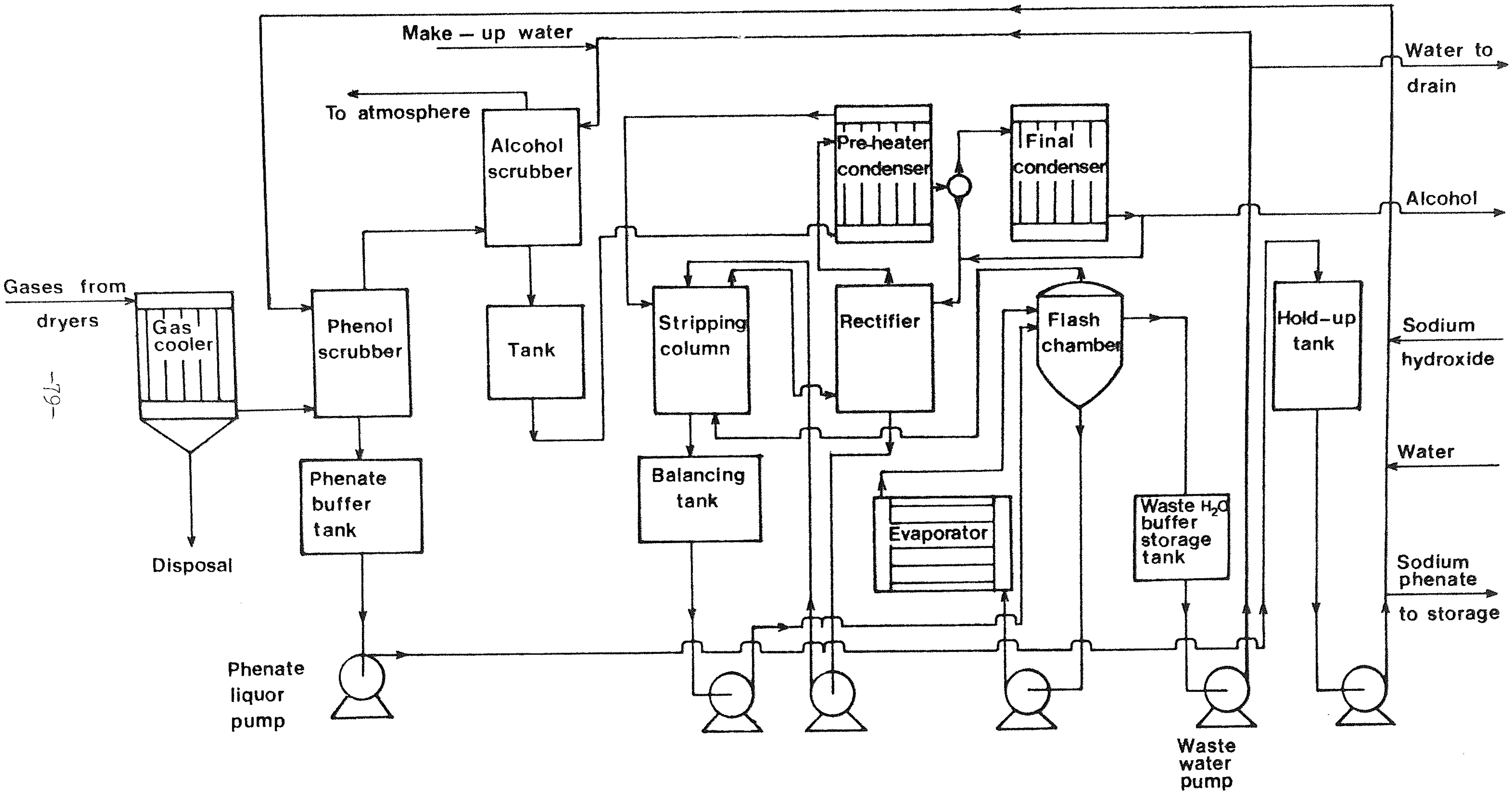
The presses used to produce the cured composite in sheet, slab, tube or rod form are mainly upstroke multi-daylight hydraulic presses with platens heated with steam, oil or hot water under pressure and at temperatures mainly in the range 150°-160°C. Modern laminating presses may have as many as 22 openings for sheet sizes up to 1.5 x 3.7 m. Since each press could produce up to 14 laminates per opening, a total of 1709 m^2 of laminate is possible in each press cycle. For a cycle of 90 minutes, 19 m^2 $min.^{-1}$ can be produced. Assuming a 1.5 m width and converting to lineal metres per minute required to yield 19 m^2 it can be shown that a continuous press operation would be required to run at 12.7 m $min.^{-1}$ to equal this output. It is mainly for this reason that batch laminating continues in popularity in the industry of high pressure laminates.

5.2.8 Ancillary stages

5.2.8.1 Solvent recovery plant

With processes which utilise alcohol-soluble ammonia-catalysed resols, it is usually normal practice to recover the alcohol. The exhaust gases from the dryers will contain air, water and various phenols (constituents of resin) in addition to the solvent(s). Small amounts of ammonia may also be present. If however, water-soluble resols are employed or if the recovery of the solvent(s) is not feasible or it is uneconomical, the volatiles may be treated by a variety of methods. These methods include microbial degradation, combustion (thermal or catalytic), chemical scrubbing and others(32).

Chemical scrubbing with sodium hydroxide has commonly been adopted in combination with the solvent recovery plant. A block diagram of the combined processes is shown in figure 5.14. Hot gases (> 100°C) from the production dryers enter the gas coolers to condense any low volatility components and pass into the phenol scrubbers. In these units the phenols are selectively absorbed by a sodium hydroxide liquor which runs into the phenate buffer tank. It is then pumped away intermittently by the phenate liquor pump to the holding tank from where it is recirculated to the phenol scrubbers. Water and sodium hydroxide may be added as required. Part of the phenate liquor is withdrawn to storage.



Fogure 5.14 Alcohol recovery and phenol treating plant.

The vapours from the phenol scrubbers are pressurised and passed to the alcohol scrubbers into which water is pumped. This absorbs the alcohol which was not absorbed in the phenol scrubbers, to produce a dilute alcohol solution. This solution is sent to the stripping and rectifying columns where the alcohol is concentrated to the desired level. It may then be sold to the resin manufacturers for the preparation of the various varnishes.

The solvent recovery plant represents a considerable capital investment, and with alcohol recovery in the region of 50% (based on initial input to the dryers), it is clearly an area where an economic improvement may be necessary.

5.2.8.2 Storage of treated material

After the treating (impregnation and drying) stage the web may be rolled again or cut into sheets of appropriate size for pressing. The rolls may be stored in a controlled-humidity area (relative humidity is usually below 10%) to preserve electrical properties by minimising atmospheric moisture absorption, or to retain the flow conditions in the resin as they existed at the time of treating. The temperature of the storage area is not very important for materials treated with phenolic and melamine-formaldehyde resins. Ambient temperatures of 30°C can be tolerated for 2-4 weeks. Dust-free atmosphere may be necessary however for certain types of melamine-impregnated papers used in decorative laminates(123).

Upon removal from storage the treated rolls are cut into sheets on rotary knives. Often several rolls will be mounted simultaneously so that many sheets are generated at a single cut. This procedure serves to mix material from several rolls, hence contributes to increased uniformity. These sheets (prepregs) are then stored on shelves which are clearly labelled to enable easy identification when assembled.

In decorative laminates, it is normal practice to cut the material into sheets as it issues from the treating machine. The exit end of such machines incorporates sophisticated cutting, separating and stacking devices, since kraft-phenolic decorative filler may be treated at very high speeds (3 - 3.6 ms^{-1})(121).

5.2.8.3 Assembly of prepregs

The number of prepregs required to produce a laminate of specified thickness is selected by weighing. The prepregs are then assembled in a cross-plied configuration; that is the machine direction of each ply is rotated through 90° relative to that of each adjacent ply. This is designed to increase uniformity in the properties of the cured laminate. The prepregs are placed between stainless steel sheets (press plates) which will provide the required finish on the laminates.

It is noteworthy that during the assembly of the plies that constitute the different sets, and due to the fact that the different plies do not have exactly the same length and width, each ply is arranged over the other with two perpendicular sides coinciding with the relevant sides of the adjacent sheets. The excess length and width of the plies is left on the opposite perpendicular sides. This operation minimises the waste in the quantity of material trimmed from the pressed laminated panel.

5.2.8.4 Finishing

Generally, industrial laminates require little finishing after pressing. Each panel is usually trimmed on all sides to remove flash and that portion of the assembly which was not under pressure. Individual plies are cut slightly larger (6 to 12 mm) than the press plate. In some cases other finishing operations such as sanding may be carried out.

Upon completion of finishing, other operations such as fabrication (machining, punching etc.) may follow. Inspection and physical testing of the final product is carried out in parallel to the above operations so that quality control specifications are maintained.

6. IMPREGNATION

6.1 Definition

The impregnation process is the first major stage in the production of laminates. It involves the continuous application of varnish to a moving substrate and it may be represented schematically as shown in figure 6.1.

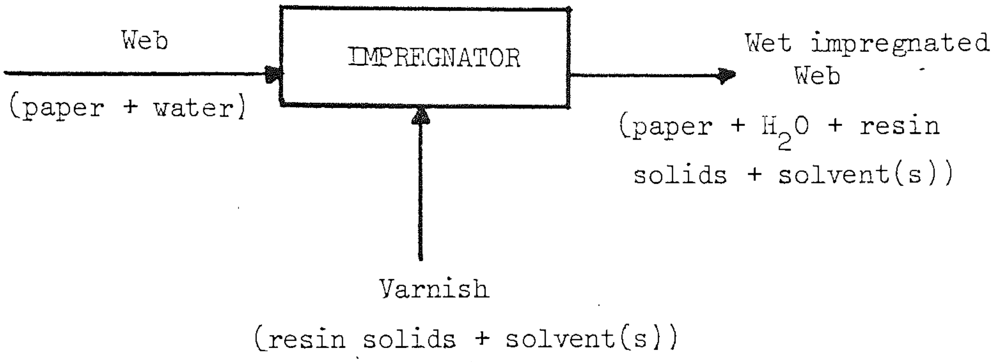


Figure 6.1 The impregnation process.

Although the terms 'impregnation and 'coating' are frequently used synonymously, impregnation implies that substantial penetration of the substrate takes place.

The main objectives of impregnation are:-

(i) to bring the filler (substrate) into direct contact with the varnish;

(ii) to ensure a uniform distribution of varnish on the substrate; and

(iii) to control the amount of varnish pick-up.

The function of the solvent present in the varnish is two-fold:-

(i) to act as the carrier of the resin solids (non-volatile matter); and

(ii) to aid the penetration of the substrate.

6.2 Paper-resin interactions

If a paper-plastic composite is to be successful, the adherence of the polymer to the substrate has to be very intimate. Thus, in the manufacture of phenolic resin-paper laminates it is expected that, on a physical basis, the resin should intrude through the pores of the surface into the interior of the sheet, fill the voids, move readily along the unbonded fibres, and be permanently retained by them.

Addition of resin beyond the minimum required for filling all voids results in a reduction in tensile strength and embrittlement of the laminate; a reduction in laminate density also results because the percentage of cellulose decreases at the expense of the added resin of lower density(124). However, water absorption decreases with increasing resin content and therefore electrical properties are in general enhanced.

It is not entirely clear whether the bond produced between resin and paper is of a physical or chemical nature or both. Preliminary experimental work has indicated the existence of hydrogen bonding between the hydroxyl-rich paper and resin(125).
It is certain in any case that the resin has to be accepted by

the paper surface and good contact between the two phases achieved. If this is not produced, the resin will not be able to spread and migrate into the depth of the sheet or it will not be retained strongly enough; then, at the lamination stage the resin will escape freely from the paper.

6.2.1 Liquid penetration into paper

The actual mechanism by which liquids penetrate paper is complex. The possible paths have been summarised by Nissan(126) as:-

(i) Liquid penetration through the pores by capillary flow;
(ii) liquid movement through the pores by surface diffusion;
(iii) liquid movement through the fibres by various processes;
(iv) vapour phase movement through the pores.

It is often pointed out that the actual mechanism is a combination of all four paths, with one path being the rate determining stage.

The rate and extent to which a resin system penetrates into the fibre structure of paper (or cloth) is a function of many resin variables such as viscosity, polarity, interfacial tension, molecular weight, solvent type, temperature(127) and pressure, as well as a large number of paper variables such as degree of hydration, fibre length, void concentration and density(128). The swelling action of the solvent employed to carry the resin will have a significant effect on the degree of penetration. Non-polar liquids do not interact with the fibre, which do not swell, and neither absorb into it, at least to any great extent(129). In addition, they usually wet the fibre surface easily and have a low vapour pressure. The result is that the only real path for penetration is capillary flow through the pores - a relatively simple process.

At the other end of the scale the highly polar compounds such as water and methanol have a high swelling action on the fibres. Only a few organic compounds have been reported to swell cellulosic materials to a greater extent than water and these are:- formic acid, formamide, the lower primary amines, and pyridine and its related compounds(130). Although non-polar systems do not penetrate fibres themselves, they can replace polar liquids in which they are soluble.

The penetration of kraft papers by phenolic resins has been investigated by Cook(131).

Penetration times were found to decrease rapidly with increase of moisture content in paper up to 7 - 9% approximately. In contrast, increase in the water of the varnish caused a slight reduction in rate of penetrability(132). Marton and Crosby(133) studied paper-phenolic resins interaction by means of contact angle measurements between varnish and paper, and of sonic velocity of impregnated sheets. It was found that the rougher felt side always absorbed more resin although it shows a higher contact angle compared to the wire side.

6.2.2 Resin distribution

In the final analysis, the paper–resin interaction at the impregnation stage will have to be related to the physical properties of the final product and how these are affected. The work of Marton and Crosby(134) has shown that a uniform distribution of resin inside the paper was a pre-requisite to the formation of a 'good quality laminate'. It also showed that some of the voids had become larger, and even new ones have been formed as a result of the flow of varnish between the bonded fibre surfaces and subsequent scission of bonds. As a consequence the thickness (bulk) of the impregnated sheet increased.

When the treated paper is cured under pressure, the fluidised resin flows into all available voids. The excess that cannot be accommodated is squeezed out. This suggests that as swelling increases and possible new voids are formed, more resin can be accommodated within the structure of the fibres producing a more uniform resin distribution. As a result of this, a higher proportion of the initial resin may be retained within the laminate at the pressing stage which could have an effect on the water absorption – an important property in electrical laminates.

It is known that solutions, such as varnishes, may act differently in their swelling action (and penetration) than does the pure solvent(130). In some cases the rate of penetration is materially decreased even though the final equilibrium swelling may be increased(135). An increase of residence time in the solution is therefore required to bring about a similar degree of swelling as the solvent.

On the basis of the foregoing discussion it was decided to examine the effect, if any, of immersion time on the water absorption and insulation resistance of the laminate. For a meaningful comparison of results, it is necessary that for a given immersion time, volatile content should be within specification, whilst resin content variation should be small at any particular level of varnish loading.

6.3 Experimental investigation of impregnation

6.3.1 Materials

In all experimental runs pure unbleached kraft paper was used, obtained from a single paper roll chosen at random from a batch of twenty-five.

The phenolic varnishes used in the impregnation experiments were obtained from two different batches (blends), selected for having small variation in their properties. They were stored at temperatures below $-2^{o}C$ and equilibrated to room temperature before use. Some of the characteristic properties of the kraft papers and varnish blends are shown in table 6.1.

6.3.2 Impregnation and drying

All paper samples were hand impregnated and varnish pick-up was controlled by passing the wet sheets through metering rolls. Resin and volatile content were determined following the drying operation (see Chapter 7).

PAPER		VARNISH	A	B
Grammage ($g\ m^{-2}$)	97	SP. Gravity @ $15^{\circ}C$	1.036	1.034
Caliper (mm)	0.165	SP. Gravity @ $25^{\circ}C$	1.029	1.027
Apparent Density ($g\ cm^{-3}$)	0.554	Solids Content @ $110^{\circ}C$ (%)	48.19	48.03
Moisture Content (%)	3.77± 0.2	Gel Time @ $130^{\circ}C$ (min)	16.47	16.63
α - Cellulose Content (%)	92	Viscosity @ $25^{\circ}C$ (mPas)	34	32
Ash Content (%)	0.26	H_2O Tolerance (%)	10	10

Table 6.1 Properties of paper and varnish blends

6.3.3 Lamination and property tests

Lay-ups, comprising of four treated sheets each, were pressed in an electrically heated press at 150°C and for 75 minutes cure time. Water absorption and insulation resistance tests were carried out according to BS 2782.

6.3.4 Preliminary work

An extensive amount of preliminary work was undertaken in order to establish the drying times necessary to give volatile content values that lie within the specification limits of 2.5% and 4%. Using paper sheets measuring 45.7 x 45.7 cm, it was found that at 150°C drying times between 3.5 and 6.5 minutes were adequate.

The preliminary work also showed that at a given roll gap (within the range examined) the resin content variation with immersion time was less than 4%.

6.3.5 Procedure

Briefly, the experimental procedure was as follows:- Eight sheets measuring 45.7 x 45.7 cm were cut from the paper roll. Two of these were used for moisture content determination.

The remaining six samples were used in the impregnation experiments. This constituted a run. Each sheet was quickly but carefully, placed in a large tray (76 x 60 x 10 cm) containing the phenolic varnish at room temperature. Immersion time was defined as the period between complete immersion and withdrawal from the impregnating bath. The wet paper was then slowly passed through the metering rolls set at a pre-determined gap; this operation took approximately 10 seconds to complete. (Preliminary work had shown that it was necessary to keep the rolls wet just before and during the impregnation period for reproducible results). This procedure was repeated for the rest of the samples. Two of the dried sheets were used for resin and volatile content determinations. In each run, fresh varnish was used.

6.4 Results and discussion

Table 6.2 shows the results of resin and volatile content determination at various immersion times and roll gap settings. As expected, higher resin contents are obtained with increased roll gap. At the individual settings there is some variation in resin content at different immersion times, but it is considered to be within experimental errors.

Although the volatile content is within the specification limits, its variation is large enough to exclude any determination of resin flow at the lamination stage and therefore of the resin retained in each board. Results would have been meaningless.

The results of the physical property tests are presented in table 6.3; these show that:-

(i) in general, the amount of water absorbed decreases with increased resin content, due to the relative increase in the proportion of the less hydrophylic component (resin);

(ii) insulation resistance increases with resin content in the range of roll gap settings between 0.254 mm to 0.356 mm; and

IMMERSION TIME (s)	RESIN CONTENT (%)				VOLATILE CONTENT (%)			
6	42.10	46.11	48.18	52.07	3.33	2.86	2.76	3.92
30	42.94	46.37	49.12	52.41	3.40	2.92	3.15	3.01
90	43.62	46.30	49.36	53.27	3.30	3.56	3.69	3.09
180	43.75	46.56	49.76	53.48	3.61	3.64	2.96	3.12
ROLL GAP (mm) →	0.254 (a)	0.305 (b)	0.356 (c)	0.406 (d)	(a)	(b)	(c)	(d)

Drying time @ 150°C = 3.5 - 6.5 min.

Table 6.2 Resin and volatile content variations

IMMERSION TIME (s)	WATER ABSORPTION (mg)				INSULATION RESISTANCE (10^{10} ohms)			
6	72	60	49	36	0.23	0.60	1.8	1.11
30	63	53	37	29	0.57	0.79	6.2	8.9
90	62	52	36	29	0.50	0.91	6.5	6.2
180	62	53	36	30	0.46	0.93	8.4	7.8
ROLL GAP →	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)

Table 6.3 Variation of physical properties with immersion times.

(Nominal thickness of laminates at respective roll gap settings are: 0.47, 0.49, 0.51, 0.54 mm).

(iii) at immersion times greater than 6 seconds both water absorption and insulation resistance are greatly enhanced at any particular roll gap setting.

It should be noted that a residence time of 6 seconds, is usually employed at production cycles of paper laminates. Porosity (expressed in $cm^3 min^{-1}$) determinations of several sheets before and after treating were also conducted and these are detailed in Appendix A2.

These results are however inconclusive due to the large variations obtained for each sample examined. Assuming that the small differences in resin content at a particular roll gap setting have a negligible effect on the porosity values, they do indicate a general trend of lower porosity at immersion times above 6 seconds.

6.5 Conclusions

The impregnation work has indicated that increased residence times above 6 seconds have a beneficial effect on the water absorption and insulation resistance of the final product. The improvements, on the physical properties may be due to better distribution and higher retention of resin, although this has not been established.

7. DRYING

7.1 Definition and objectives

The drying operation forms an integral part of the treating process. It may be defined according to the diagram in figure 7.1.

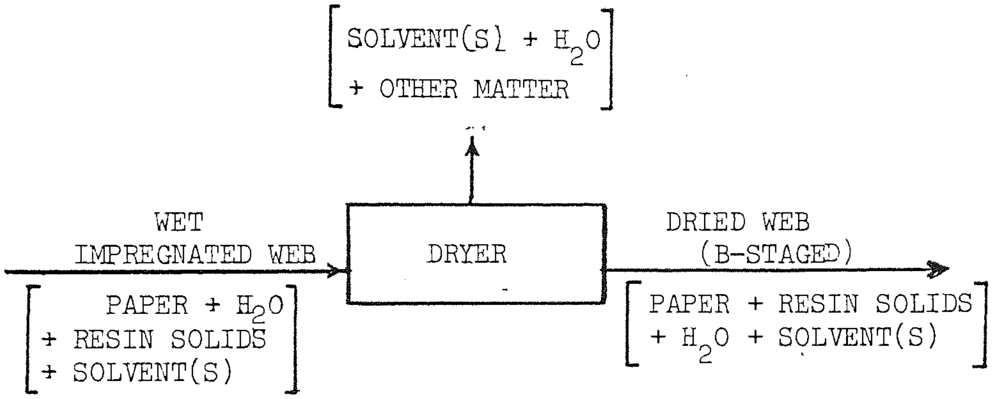


Figure 7.1 Schematic diagram of the drying process.

The main objectives of drying are:

(i) To remove the solvent(s) from the impregnated web; and

(ii) to advance the polymerisation of the resin to a predetermined degree of reaction (B-stage) as measured by various tests. (In this respect the dryer may be thought of as a 'continuous reactor').

At the dryer exit, the treated web usually passes over snubber rollers (figure 7.2) which draw the web from the dryer and maintain any desired tension in the web. The tension at A and B can be of entirely different magnitudes.

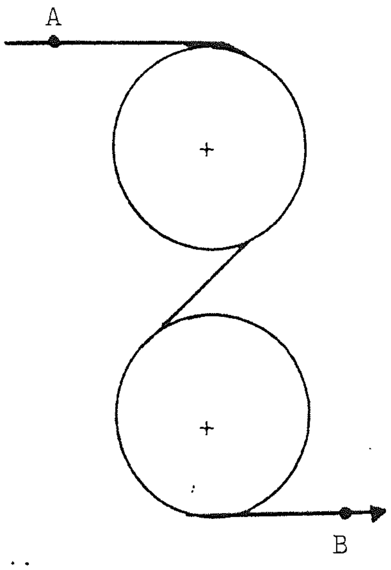


Figure 7.2 Snubber rollers.

(A and B are points of tension application.)

7.2 B-stage characterisation

It is important that the material leaving the treating stage (impregnation + drying) is in a precisely defined state of semi-cure (B-stage). The resin must be capable of being softened by heat and consolidated by pressure. In the pressing stage if the level of B-staging is 'too high', pressing may be impossible; by contrast, 'very low' levels of B-staging could result in a resin-starved, dry and inferior laminate due to excessive resin flow at the final pressing stage.

There is no fundamental method of measuring the state of semi-cure, also sometimes referred to as 'greenness'. To date, the generally accepted methods of characterising B-staged thermosetting prepregs are usually isothermal end-point property determinations. Volatile content and resin flow are the classic examples. With these methods however only an indirect measure of the state of semi-cure can be obtained.

7.2.1 Volatile content

From a 250 mm square prepreg sample, two test pieces measuring 125 mm square each are cut and weighed. The test pieces are then dried in a laboratory oven at 150 ± 2.5°C for a period of 5 minutes, allowed to cool in a dessicator and re-weighed (W_4).

The volatile content (y) is expressed as the percentage decrease in weight:

$$\%\, y = \frac{(\text{Original treated weight} - \text{dried weight})}{\text{original treated weight}} \times 100 \qquad (7.1)$$

Precautions should be taken to prevent absorption of atmospheric moisture by the dried samples, as this would affect the results.

7.2.2 Prepreg resin flow

This test employs a series of 125 mm square pieces cut from the treated web and then assembled together to form a small lay-up which is pressed for a period of 10 minutes under standard laminating conditions. In effect, a small laminate is made. During this procedure, some of the resin flows and forms a bead (flash) around the edge of the laminate. Upon cooling to room temperature, the resin bead may be broken away and discarded.

The percentage reduction in prepreg weight due to resin flowing beyond the laminate boundaries is calculated as:

$$\% F = \frac{(W_i - W_F)}{W_i} \times 100 \qquad (7.2)$$

where:

F = resin flow (%)

W_i = initial weight of all test pieces (g)

W_F = final weight of consolidated sheet after pressing and removal of bead (g)

It is a common practice to adjust the drying operation to yield the degree of flow desired, and this is used as the basis for the production of the larger sheets. Since the prepreg resin flow test is carried out on small specimens and under standard production conditions, large errors could result when evaluating materials to be laminated in large industrial panels on the basis of this test. This was shown by the work of Roller(136) on epoxy prepregs. Several simple experiments indicated the large magnitude of errors encountered when the pressures were not approximately scaled and the geometry factor also considered.

7.2.3 Other methods

Several other techniques have also been applied for the determination of B-staged resins cure advancement in addition to or in conjunction with the methods described above.

Chang(137) reported results obtained on the determination of resin cure in phenolic prepregs. His method was based on the solubility of the resin in an acetone-water mixture as the measure of cure.

The technique of infra-red spectrophotometry has been used by several workers, and phenolic resin cure indices have been defined based on various infra-red band ratios. These have included the Marquardt Index(138), the Infra-red Polymerisation Index(138) and the U.S. Polymeric Index(139). As cure progressed changes in the band ratios were observed. However, none of these indices behaved satisfactorily in that data points were scattered and did not fall on a smooth curve.

More recently differential scanning calorimetry has been used to characterise B-staged epoxy and polyimide prepregs in terms of kinetic and thermodynamic parameters(140).

A powerful technique directly related to the lamination process, involved resin characterisation data that could describe a B-stage epoxy material via the viscosity-time-temperature interactions(141). Mathematical models in the form of a dual Arrhenious equation were developed in order to describe the resin behaviour under isothermal and non-isothermal conditions.

The application of these techniques has been mainly in research and development rather than as quality control tests in production cycles. This is particularly true for the small industrial concerns, where thermoanalytical instruments such as DSC represent a considerable investment in both capital and skilled labour costs, and full justification for their use has not been realised.

Therefore, the volatile content and resin flow methods still play an important part in the production of industrial laminates. In particular, resin and volatile content are used extensively as control parameters in the treating process.

7.3 Control of the treating stage

In the impregnation and drying operations it is important to control:

(i) The amount of resin applied to the web;

(ii) the degree to which it is dried (removal of solvents); and

(iii) the degree to which the resin is reacted (level of B-stage).

Objective (i) is carried out by measuring the resin content (R). (ii), and to a certain extent (iii) are measured by volatile content (V). Resin flow (F) may give additional information on the degree of reaction reached by the prepregs.

Resin and volatile contents may be determined by off-line destructive testing of samples or by on-line measurements.

7.3.1 Off-line testing : Conventional system

Resin content (R_1)

The first step is to establish the weight of the raw paper from measurements of the untreated paper weight and its moisture content (equation 7.3).

$$P = W_1 (1 - M) \tag{7.3}$$

where:

P = untreated (raw) paper weight (g)
W_1 = untreated paper weight (g)
M = moisture fraction of untreated paper.

Resin content represents the increase in weight due to varnish addition and it is expressed as a percentage of the treated paper weight (W_3):

$$\% R_1 = \frac{(W_3 - P)}{W_3} \times 100 \tag{7.4}$$

The quantity W_3 is determined by weighing a sample cut from the treated web as it issues from the dryer exit.

Equations 7.3 and 7.4 may be combined to give:

$$\% R_1 = \frac{\left(W_3 - W_1 (1 - M)\right)}{W_3} \times 100 \tag{7.5}$$

Alternatively, a 'resin ratio' may be considered which, in terms of the above nomenclature, may be defined as:

$$\% R_1' = \frac{(W_3 - P)}{P} \times 100 \tag{7.6}$$

This is a more fundamental expression and is especially useful when the resin ratio departs substantially from 1:1(121). If the resin content (R_1) is as high as 75% or as low as 25% a very large change in the resin ratio (R_1') will appear as a relatively small change in resin content, simply because of the mathematical properties of the two expressions.

For example, if R_1 = 75% then a 30% change in R_1' will produce an equivalent change of just over 9% in R_1.

In the above expressions the weight of the treated paper (W_3) includes residual solvent(s) that remain in the web after the drying operation.

Volatile content (V_1)

The determination of volatiles is made upon the same specimen used to measure resin content, and it is calculated according to equation 7.1.

$$\% \ V_1 = \frac{(W_3 - W_4)}{W_3} \times 100 \qquad (7.7)$$

where W_4 is the dried weight defined in Section 7.2.1.

7.3.1.1 Control limitations

Percent resin (R_1) and volatile contents (V_1) are used to determine and control the amount of resin and residual volatiles respectively in the treated paper.

Both percentage calculations (equations 7.4 and 7.7) are therefore based on the same common weight (W_3). A deviation in the treated weight (W_3) may necessitate that either of the following actions be taken:

(i) Adjust impregnator in order to bring the percent resin content (R_1) to the product specification. This usually requires adjusting the gap between the metering rollers;

(ii) adjust the speed of impregnation or the drying rate in order to bring the percent volatile content (V_1) to the product specification.

However, taking action (ii) which changes W_3, would also change R_1. Similarly, following action (i) would result in changes in V_1. Therefore, there is an interaction of resin and volatile contents and this limits the controllability of the process. It may be necessary to specify wider limits for both R_1 and V_1 so that an acceptable variation due to their interaction could be accommodated. Adopting this approach may lead to increased product costs due to increased tolerances. Also, lamination may be affected which would result in products of inconsistent properties. Skillful operators could remedy this to some extent.

An alternative approach is to use on-line measurement techniques in conjunction with automatic feedback control which could be based on a computer system.

7.3.2 On-line testing : Alternative systems

A system that could provide continuous and accurate measurements of resin and volatile contents should, in theory at least, improve quality control and result in a treated material of greater uniformity at a lower unit cost.

Such systems have been employed in the laminating industry and they have found particular use in the field of decorative laminates where high speed impregnators and dryers (2.5 - 5 ms^{-1}) would require such controls, since manual determination would be slow, if at all possible(121, 142).

Weight information can be obtained by using thickness gauges(143). Beta and infra-red are typical examples. These gauges actually measure weight per unit area, or density, and they will work satisfactorily for materials whose density is constant or a known variable. For other materials such as foams, they will, in general, fail to provide satisfactory operation(144).

Moisture determination may be accomplished by infra-red gauges or other suitable instruments which measure a particular property, for example dielectric constant.

7.3.2.1 Control parameters

For control purposes, the resin and volatile contents are expressed as ratios according to the following equations:

$$\% \text{ Resin } (R_2) = \frac{\text{Resin solids weight}}{\text{Raw paper weight}} \times 100 \qquad (7.8)$$

$$\% \text{ Volatile } (V_2) = \frac{\text{Residual volatile in treated paper}}{\text{Raw paper weight}} \times 100 \qquad (7.9)$$

Percent resin (R_2)

The raw paper weight is given by equation 7.3.

$$P = W_1 (1 - M) \qquad (7.3)$$

Phenolic varnishes consist of 45 to 60 percent resin solids (non-volatile matter) in an appropriate solvent base (alcohol, water or a mixture of the two). The weight of the varnish added to the web is found by weighing the web immediately after impregnation and then subtracting the weight of the web prior to impregnation.

$$\text{Varnish added} = W_2 - W_1 \qquad (7.10)$$

where:

W_2 = weight of wet impregnated web (g)

The weight of the resin solids on the web is calculated from equation 7.11.

$$\text{Resin solids weight} = (W_2 - W_1) \times S \qquad (7.11)$$

where:

S = percent resin solids, determined according to BS 2782 : Part 1 : 1970 : Method 107B or by any other approved method.

The desired resin ratio is calculated by substituting equations 7.3 and 7.11 into equation 7.8.

$$\therefore \% R_2 = \frac{(W_2 - W_1) S}{W_1(1-M)} \times 100 \qquad (7.12)$$

Percent volatile (V_2)

The weight of the solvents remaining in the web after the drying operation are found by subtracting the weight of the resin solids and raw paper from the weight of the treated paper (W_3).

$$\text{Residual solvents} = W_3 - ((W_2 - W_1)S + W_1 (1-M)) \qquad (7.13)$$

Therefore, from equation 7.9 we have:

$$\% V_2 = \frac{\left(W_3 - \left((W_2 - W_1)S + W_1 (1 - M)\right)\right)}{W_1 (1 - M)} \times 100 \qquad (7.14)$$

The two measurement and control techniques used in the treating process are depicted in figure 7.3.

The conventional system is shown on the upper portion (figure 7.3 is a slightly different version of figure 4 in reference 142).

7.3.2.2 Remarks

There are several points of interest regarding the application of an on-line control system and these may be summarised as follows:

(i) When calculating percent resin and volatile (equation 7.12 and 7.14), it is assumed that the raw paper weight (P) and percent resin solids (S) are not affected by the high

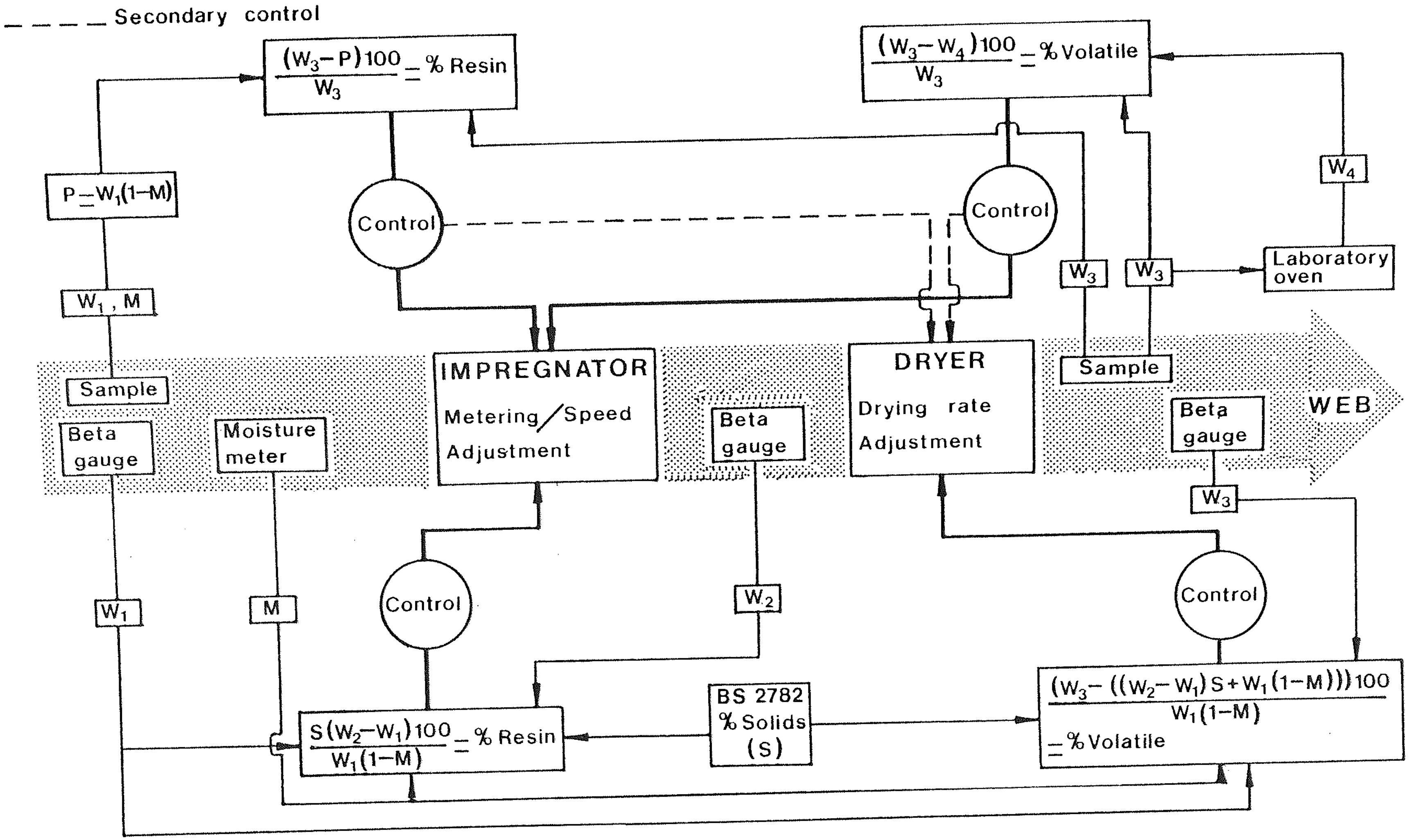


Figure 7.3 Off-line and on-line techniques for controlling the treating process.

temperatures used in the dryer (up to 180°C). For the raw paper this may be true since residence times are usually small (< 10 minutes); for resin solids this has not been established. It should be remembered that the resin solids determination is carried out at 110°C (sometimes at 130°C) and not at the dryer conditions. Variation in S which is not accounted for, would result in incorrect percent volatile.

(ii) Percent resin solids (S) is also assumed to be constant within a given varnish batch, but this is unlikely to be true. This may be overcome by carrying out a large number of determinations so that resin solids can be expressed in a statistical form that would represent possible variation in a given batch. An alternative and less time consuming approach is to continuously monitor resin solids using instrumental techniques.

(iii) In cases where double impregnation is required so that enhanced properties in the final product can be obtained, continuous monitoring of moisture (M) would no longer be applicable since the treated web will also contain additional volatiles. It may be possible to use percent volatile values derived during the first impregnation with appropriate corrections for absorbed atmospheric moisture.

(iv) Corrections in the moisture content (M) of the untreated paper may also have to be applied to account for the effects of changes in the relative humidity in production environments.

(v) From equation 7.14 it can be seen that the value of V_2 represents 'total' volatiles and it may be different to that of V_1 which indicates residual volatiles after a period of 5 minutes at 150°C. Tests would be required to establish the V_2 values that correspond to current control limits for V_1.

(vi) Finally, it should be recognised that consistent results can only be obtained if an accurate and uniform operation is shown by both impregnator and dryer.

7.4 Temperature zones in dryers

Modern dryers will have at least two independantly controlled temperature zones; frequently four or more will be used. With vertical dryers usually four zones are employed as shown in figure 7.4. The temperatures shown will usually vary with ambient conditions.

Zones 1 and 2 are used to heat the web and drive off solvent(s) in the constant-rate portion of the drying schedule. In zones 3 and 4 most of the solvent(s) has evaporated and the resin has reacted to a pre-determined B-stage level. More volatiles from the condensation reactions will be produced in these zones.

Air is the usual drying medium, and it is heated to temperatures of 135°-150°C as it passes through a heater bank. Additional heat is provided by steam-heated radiant panels. In horizontal dryers it is common to employ a series of ducts and baffles for distribution of the hot air stream over the surface of the web(121).

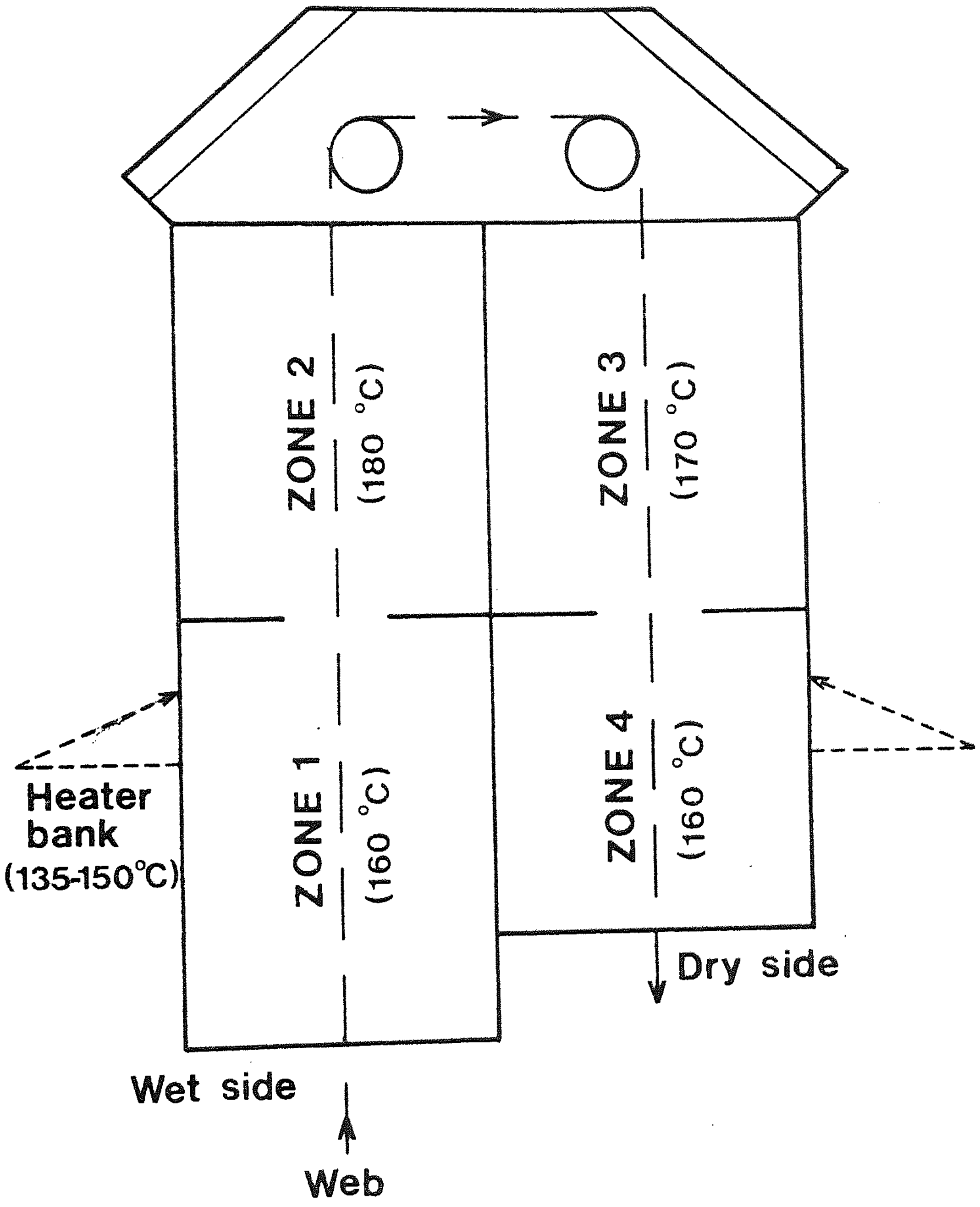


Figure 7.4 Temperature zones in a vertical dryer.

At the inlet to the dryer, the air impinges on the web after passing through a perforated plate. Air velocity through the perforations is between 0.3-0.45 ms^{-1}. The air velocity and high temperature driving force results in rapid removal of volatile matter.

7.5 Volatile emissions

7.5.1. Varnish constituents

The ammonia-catalysed phenolic varnish will normally consist of:

(i) Mixtures of mono- and poly-alcohols;
(ii) Mixtures of di- and tri-hydroxybenzyl amines;
(iii) Free phenol;
(iv) Industrial methylated spirit (mainly ethanol);
(v) Moisture.

(i), (ii) and (iii) will constitute the resin solids or 'non-volatile matter'. In addition to the moisture present in the varnish, the paper web will contain 'bound' moisture in the region of 4-6% (W/W). Additional moisture will also be produced as a result of condensation reactions during the drying operation. Some of these reactions have been discussed in Chapter 4.

The free phenol content of typical varnishes used in this work, determined by gas chromatography (GC) (Appendix A3), was found to be between 7.0% and 8.5% (W/W). Phenol boils at 182°C, but the presence of water creates an azeotropic mixture of 89% (W/W) phenol and 11% (W/W) water that boils at 160°C. Azeotropic data does not exist for phenol alcohols and water, but such a relationship may be expected to exist since the two conditions necessary for the formation of an azeotrope, dissimilarity of the compounds and difference in boiling points are present(145).

7.5.2 Migration during drying

At 15°C, 8.2 g. of phenol are soluble in 100 g. of water(37). Monoalcohols and other low molecular weight phenolic species are also expected to be soluble in water although to a possibly lesser degree. Water tolerance values for phenolic varnish of 10% are typical. (When exceeding these values resin precipitation results).

When the varnish is subjected to sudden heat, surface evaporation of alcohol and water takes place. Free phenol and other low molecular weight species - wanted matter - evaporate with the water according to relative concentrations of 'monomers' and water(79). Movement of moisture (and alcohol) within the substrate also takes place by two distinctly different processes(146). It moves en masse carrying all dissolved and suspended matter with it, and it moves by liquid diffusion. More resin is therefore brought to the paper surface by the former process. Even when higher molecular weight, water-insoluble structures are formed via the curing reactions, it is possible that migration of these species due to steam distillation by partial pressures can take place.

The portion of the resin driven off with the water and alcohol is commonly referred to as 'blue smoke'(79, 147). The blue smoke consists of free phenol and then increasing molecular weight species. The solvent recovery, and the treatment of these phenolic oligomers has been considered in Chapter 5.

7.5.3 Estimation of resin losses

There is virtually no published work on resin losses as a result of the drying process. Henderson's work(147) on water-based sodium hydroxide-catalysed resols relates to volatile emissions at 105°C and 177°C, and concentrates on the effect of resin-preparation variables (reflux time, catalyst concentration etc.) and the possible adjustments necessary to minimise these emissions.

It was therefore decided to determine experimentally resin solids loss in a series of static drying tests on phenolic impregnated paper samples. Two different drying modes were examined:

(i) 'Slow drying from ambient temperature to approximately 140°C;

(ii) Rapid drying carried out isothermally at 135°C - the minimum temperature existing at the inlet to the dryer.

With the conventional off-line testing control methods, it is impossible to determine resin losses in the production equipment since measurements of varnish loadings prior to drying are not required. This may be a major and costly drawback if losses in wanted material are excessive but could be minimised without prejudicing process efficiencies. Estimation of resin losses may also be justified on this basis.

7.6 Drying experiments

7.6.1 Designation of experiments

A total of nine experimental runs were carried out, five of these in the slow and four in the rapid drying modes designated SD and RD respectively.

In each run, three batches (A,B,C) of five samples each were employed, so that the designation B_8 refers to the second batch and sample number 8. (see results in Appendix A3).

7.6.2 Materials

The substrate was pure unbleached kraft paper used in production cycles.

The phenolic varnish was used 'as supplied' without further modification. A number of 'blends', each conforming to raw material specifications, were employed since only small quantities of varnish could be stored at any given time. These were kept in a freezer at temperatures less than $-2^{\circ}C$.

The storage containers were equilibrated at room temperature for about two hours before opening in order to prevent condensation of moisture from the air.

Some of the characteristic properties of the various varnish blends are presented in table 7.1.

7.6.3 Experimental set-up

7.6.3.1 Oven

A large oven 1.92 x 1.57 x 1.89 m was used in all drying experiments. Air was blown over electric heaters, arranged in parallel, situated at the back of the oven between real and false walls.

The air was drawn by an electric fan (0.746 kW, 151 rad s^{-1}) through a duct at the top of the oven, and it could be recirculated or vented to the atmosphere. During the course of the experimental work, the facility for venting was fully opened so that only a minimum air re-circulation was allowed for.

The oven was calibrated over a temperature range of 70°-160°C using a factory-calibrated temperature recorder (Appendix A3).

7.6.3.2 Temperature recorder

The oven temperature was monitored at three locations using a Cambridge potentiometric multipoint temperature recorder (0°-200°C) in conjunction with copper/constantan thermo-

EXPERIMENTAL RUN	VARNISH BLEND NO.	SOLIDS CONTENT*		GEL TIME AT 130^{o}C (min)	WATER TOLERANCE AT 25^{o}C (%)
		(a) (%)	(b) (%)		
SD1	I	49.73	48.37	16.58	10.1
SD2	II	49.71	47.38	15.93	9.9
SD3	II	49.71	47.38	15.93	9.9
SD4	III	48.43	48.75	15.53	10.1
SD5	I	49.73	48.37	16.58	10.1
RD1	III	48.43	48.75	15.53	9.9
RD2	I	49.73	48.37	16.58	10.1
RD3	I	49.73	48.37	16.58	10.1
RD4	I	49.73	48.37	16.58	10.1

* After heating for two hours at 110^{o}C.
(a) - measured data
(b) - supplier's data

Table 7.1 Characteristic properties of the phenolic varnish blends.

couples. A manual balancing rheostat allowed any necessary standardisation and calibration to be carried out.

7.6.3.3 Balance

An Avery balance, readily available, was modified so that handling of both wet and dry paper samples could be easily accommodated. The balance, marked in 0.01 g. divisions, was calibrated with weights accurate to three decimal figures.

7.6.3.4 Stop-watch

Stop watches accurate to 0.05 seconds were used.

7.6.4. Experimental procedure

The experimental procedure involved a series of clearly defined stages, closely followed in each run.

7.6.4.1 Paper samples

The paper samples measured 25 x 25 cm. In each run eighteen samples were cut from six large paper strips (123 x 35 cm); only the central portion of the strips was utilised in order to minimise 'end effects'. From these, three samples were chosen at random for moisture content determinations. These results were used to calculate a mean moisture content applicable to all experimental runs.

7.6.4.2 Weighing of untreated samples

Prior to weighing, each sample was clearly numbered in accordance with the designation described earlier for easy identification. They were then weighed by suspending them from similarly marked metal hooks, previously weighed.

7.6.4.3 Impregnation

Prior to impregnation in a hand operated impregnating machine the roll gap was set to 0.38 mm using a feeler gauge. The setting was checked a minimum of three times by turning the metering rolls through 180° and re-setting.

Starting with batch A each sample was hand impregnated at one minute intervals, and then suspended from metal rods using the appropriate hooks.

7.6.4.4 Weighing of wet samples

When impregnation was completed, the wet samples were weighed also at one minute intervals. In order to minimise handling of the wet papers, a long pair of laboratory tweezers was used throughout the weighing period for lifting each sample from its hook.

7.6.4.5 Drying

Immediately after weighing, the samples were quickly but carefully placed into the oven in a parallel arrangement and adequate spacing to avoid any contact between samples during drying. For the SD mode the oven was initially at room temperature, usually between 16 and 20°C; for the RD mode it was maintained at 135 ± 2°C.

At pre-determined time intervals each batch was quickly withdrawn and at the same time the temperature of the oven was recorded. Zero drying time was defined as the time at which each batch was introduced into the oven.

7.6.4.6 Weighing of treated samples

Samples removed from the oven were allowed to cool in large dessicators prior to weighing. Because of the small volume: surface area ratios (< 0.01 cm), the cooling period necessary was brief (approximately five minutes for an entire batch). After cooling they were weighed quickly in order to minimise moisture absorption. The metal hooks were also separately re-weighed and any increase in weight due to resin deposition was allowed for in the subsequent calculation of the treated paper weight.

From each batch two samples were taken for volatile content determinations. These were conducted at the completion of each drying run.

7.7 Results and discussion

The results of the drying experiments are presented in tabulated form in Appendix A3.

7.7.1 Resin and volatile content

Figure 7.5 shows the variation of resin and volatile content with drying time. Equations 7.4 and 7.7 were used in the determination of these parameters.

Both resin and volatile content decrease with increasing

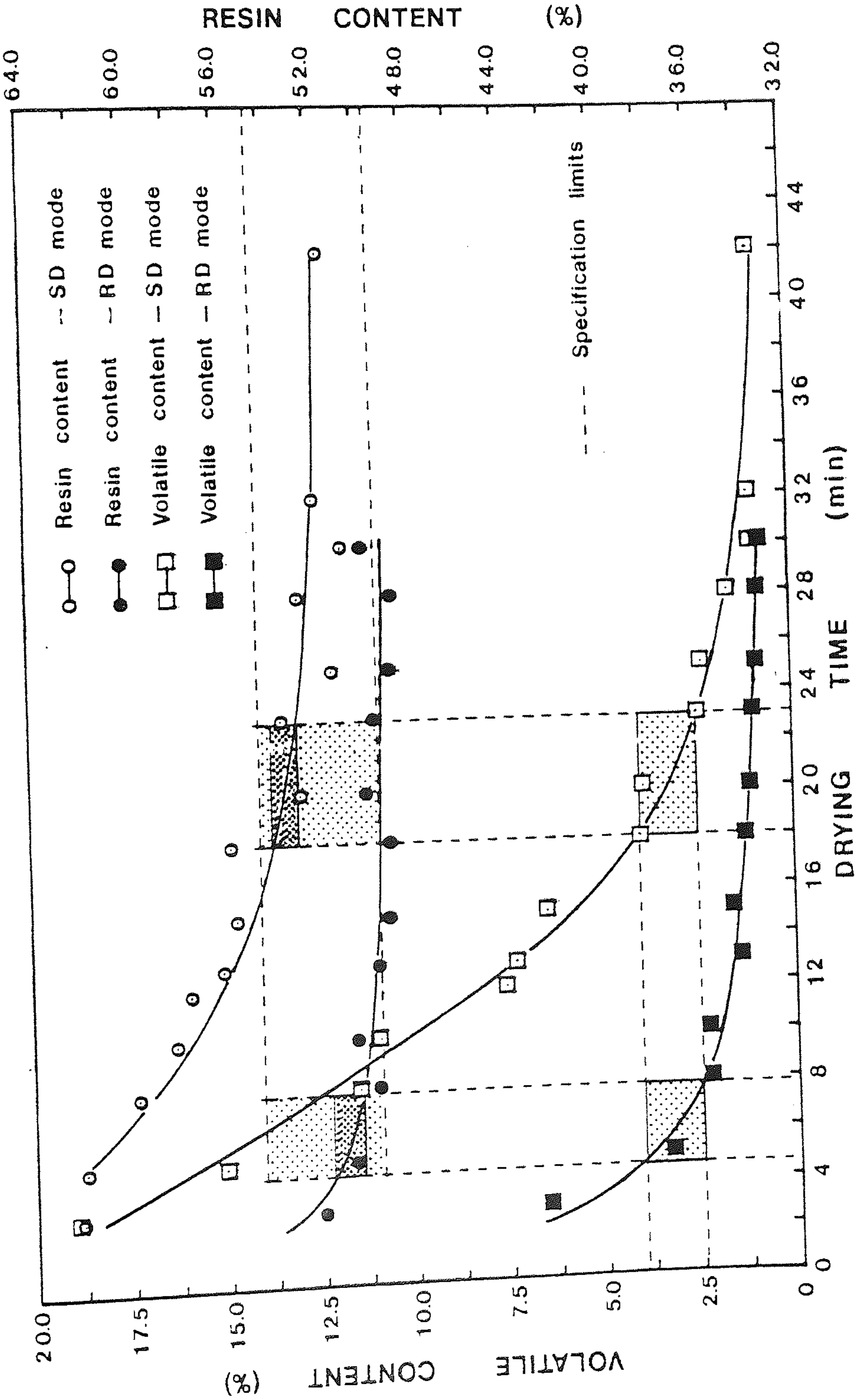


Figure 7.5 Variation of volatile and resin content with drying time.

drying time. In the RD mode the resin content approaches a steady value of 49% in just 30 minutes; in the SD mode however, a constant value of 51.5% is reached after 40 minutes of drying time, a difference of 2.5%.

In contrast, the difference in the volatile content curves is only 0.6% after 30 minutes, decreasing with increased time. It is expected that for large values of time t, this difference will become zero and both curves will approach zero values.

Figure 7.5 is taken as the basis for the comparison of the weight losses incurred as a result of the drying process. The volatile content specifications (2.5% - 4%) are used as the main criterion. At the 2.5% limit, the drying times for the SD and RD modes are 23 and 7.8 minutes respectively. At the 4.0% value, times of 18 and 4.5 minutes are obtained.

It is clear from the plots that the corresponding resin contents, shown in the dark shaded areas, which lie between the volatile limits are situated near the upper (SD mode), and near the lower (RD mode) resin content specifications of 54.5% and 49.5%.

Table 7.2 summarises some of these results; also shown are the mean temperatures corresponding to the drying times.

7.7.2 Weight loss (L)

(i) Basis : Varnish weight

The percent weight loss based on the varnish pick-up

DRYING MODE →	SD	RD	SD	RD	SD	RD
VOLATILE CONTENT SPECIFICATION LIMITS (%)	DRYING TIME (MIN)		RESIN CONTENT (%)		TEMPERATURE (°C)	
2.5	23	7.8	52.8	50.4	135	135
4.0	18	4.5	54.0	51.6	125	135

Table 7.2 Operating parameters during drying.

may be defined as follows:

$$\% \text{ Weight loss} = \frac{(\text{wet paper weight} - \text{treated paper weight})}{\text{varnish weight}} \times 100$$

$$\text{i.e.} \quad \% L_V = \frac{(W_2 - W_3)}{W_2 - W_1} \times 100 \qquad (7.15)$$

(ii) Basis : Wet paper weight

Alternatively, the weight loss may be expressed in terms of the weight of the wet impregnated samples to allow for variation in the paper weight W_1.

Therefore,

$$\% L_W = \frac{(W_2 - W_3)}{W_2} \times 100 \qquad (7.16)$$

The weight loss calculated from equations 7.15 and 7.16 is plotted versus the drying time in figure 7.6(a) and (b). In both plots, the loss in weight increases with time in a non-linear form.

In figure 7.6(a), the difference in weight loss between the SD and RD modes reaches a maximum of 31% after about 3 minutes of drying time, decreasing to a value of about 5.5% after 30 minutes. More importantly however, at the 2.5% and 4% volatile content levels the difference is 6% and 7% respectively. Similar arguments apply to figure 7.6(b). In this case the net losses are 3.5% and 4.5%. The smaller values may be explained in terms of the mathematical properties of equations 7.15 and 7.16 as follows:

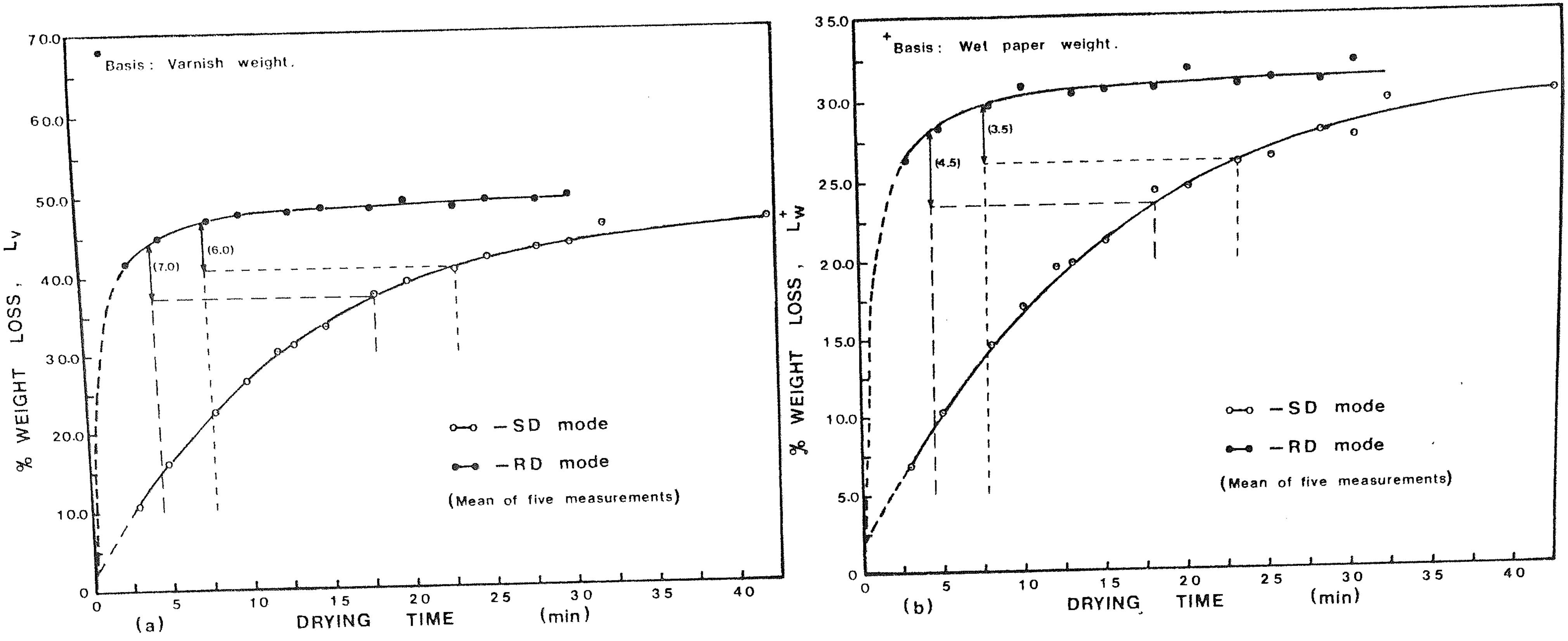


Figure 7.6 Weight loss as a function of drying time.

Assuming that W_2 and W_1 are constant in both the SD and RD modes, then at any given drying time the (mean) value of W_3 is always smaller for the latter mode.

Therefore:

$$(L_v)_{RD} - (L_v)_{SD} = \frac{(W_3)_{SD} - (W_3)_{RD}}{W_2 - W_1} \qquad (7.17)$$

Similarly:

$$(L_w)_{RD} - (L_w)_{SD} = \frac{(W_3)_{SD} - (W_3)_{RD}}{W_2} \qquad (7.18)$$

Since W_2 is always greater than W_1 it follows that the result for equation 7.18 will always be smaller than that of equation 7.17.

It should be noted that both curves of figure 7.6 do not pass through zero weight loss when extrapolated to zero drying time. The weight loss at t = 0 is due to solvent evaporation prior to introduction of the samples into the oven.

For accurate weight loss data it therefore became necessary to apply corrections to the results obtained.

7.7.3 Correction to 'zero' drying time

Several experiments were carried out in order to determine the reduction in varnish weight due to solvent evaporation at ambient conditions prior to drying; they are described in Appendix A3 together with the mathematical treatment of the data obtained and the relevant corrections applied.

The corrected values of weight loss as a function of drying time are depicted in figure 7.7(a), (b). The shape and form of the curves is similar to those in figure 7.6, the main difference being that they have now been shifted to lower values in a non-uniform fashion. The net weight loss for the SD and RD modes is indicated on the plots. Table 7.3 summarises some of the results obtained from the plots in figures 7.6 and 7.7. Although these differences are smaller in comparison to the uncorrected data, they are still significant.

The results clearly indicate that, drying in the RD mode will produce prepregs that will retain a lower proportion – up to 5% (W/W) – of the varnish present at the time of introduction into the dryer. On the basis of these calculations, however, it is difficult to estimate the amount of resin solids lost (or retained) in relation to the original varnish solids.

An alternative approach to weight loss determinations is to use the weight of the solids present in the varnish at the impregnation stage.

7.7.4 Determination of resin solids loss

The weight of resin solids retained in each treated sample may be calculated and compared to the initial solids content of the varnish. All calculations related to resin solids determination are presented in Appendix A3; only the results will be discussed in this section.

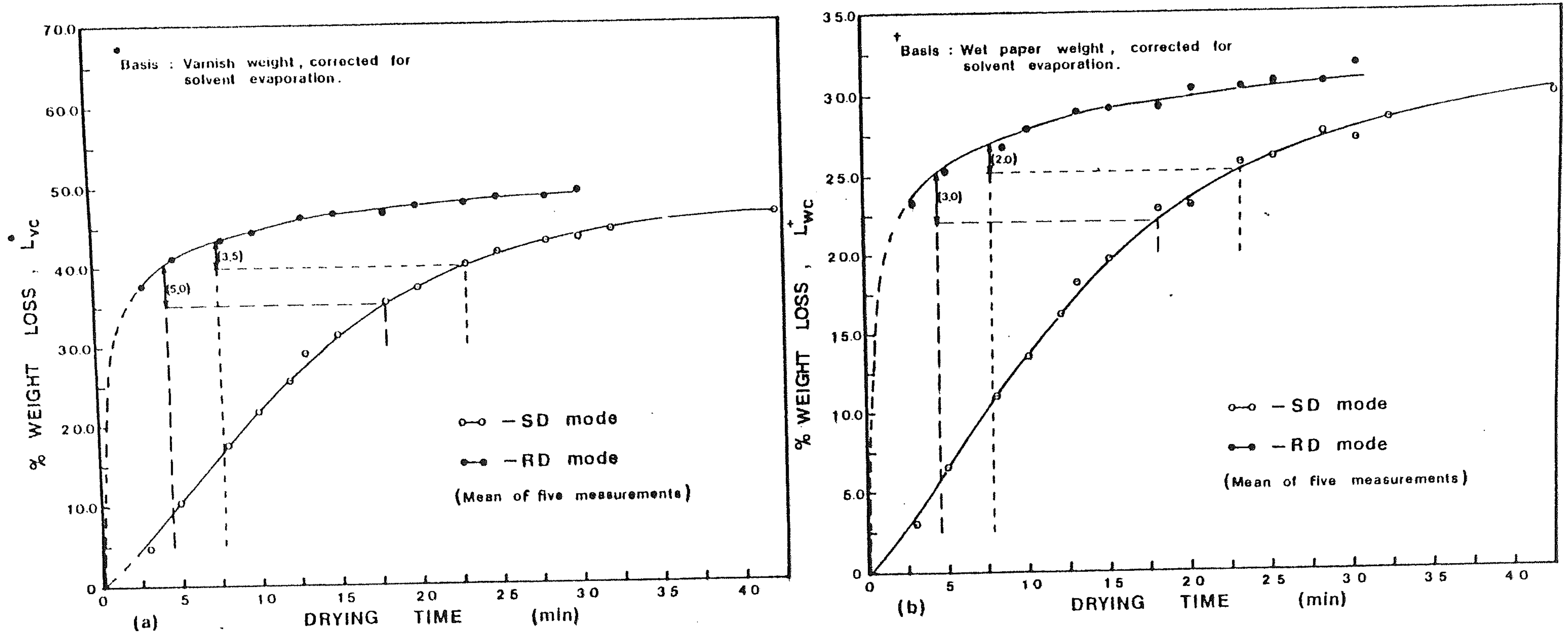


Figure 7.7 Weight loss corrected for solvent evaporation.

VOLATILE CONTENT SPECIFICATIONS (%)	% WEIGHT LOSS (Basis : Varnish)				% WEIGHT LOSS (Basis : Wet paper)			
	L_v		L^*_{vc}		L_w		L^*_{wc}	
2.5	41.0	47.0	39.9	43.4	26.2	29.7	25.0	27.0
4.0	37.2	44.2	35.3	40.3	23.5	28.0	22.1	25.1
Drying mode →	SD	RD	SD	RD	SD	RD	SD	RD

* Corrected for solvent evaporation prior to drying.

Table 7.3 Weight loss results.

The ratio (β) of solids weight at time t to the initial solids weight is plotted in figure 7.8 as a function of drying time. Two types of curves are shown for each mode of drying.

The curves plotted in full line (——) are based on varnish I (table 7.1) which was used in the experiments carried out in order to establish weight losses due to solvent evaporation prior to drying. The rest of the plots (·—·—) are obtained when the resin solids of the individual varnishes (table 7.1) are considered in the relevant calculations. (In each case the initial varnish solids are based on measured data, (a) in table 7.1).

According to the data in figure 7.8, samples experience loss in resin solids, irrespective of the drying mode, which increases with drying time. In obtaining these results it was assumed that initial varnish solids remain constant throughout the drying operation. This may be true in the early part of the process; in the latter stages, condensation reactions will produce a reduction in resin solids since more free phenol will be consumed and an increase in volatile matter - mainly water and ammonia. The effect would be a shift of the plots in figure 7.8 to relatively higher β values. The important considerations here are the relative changes in solids weight rather than the absolute values reached at the end of the treating process.

These results, determined at the appropriate volatile

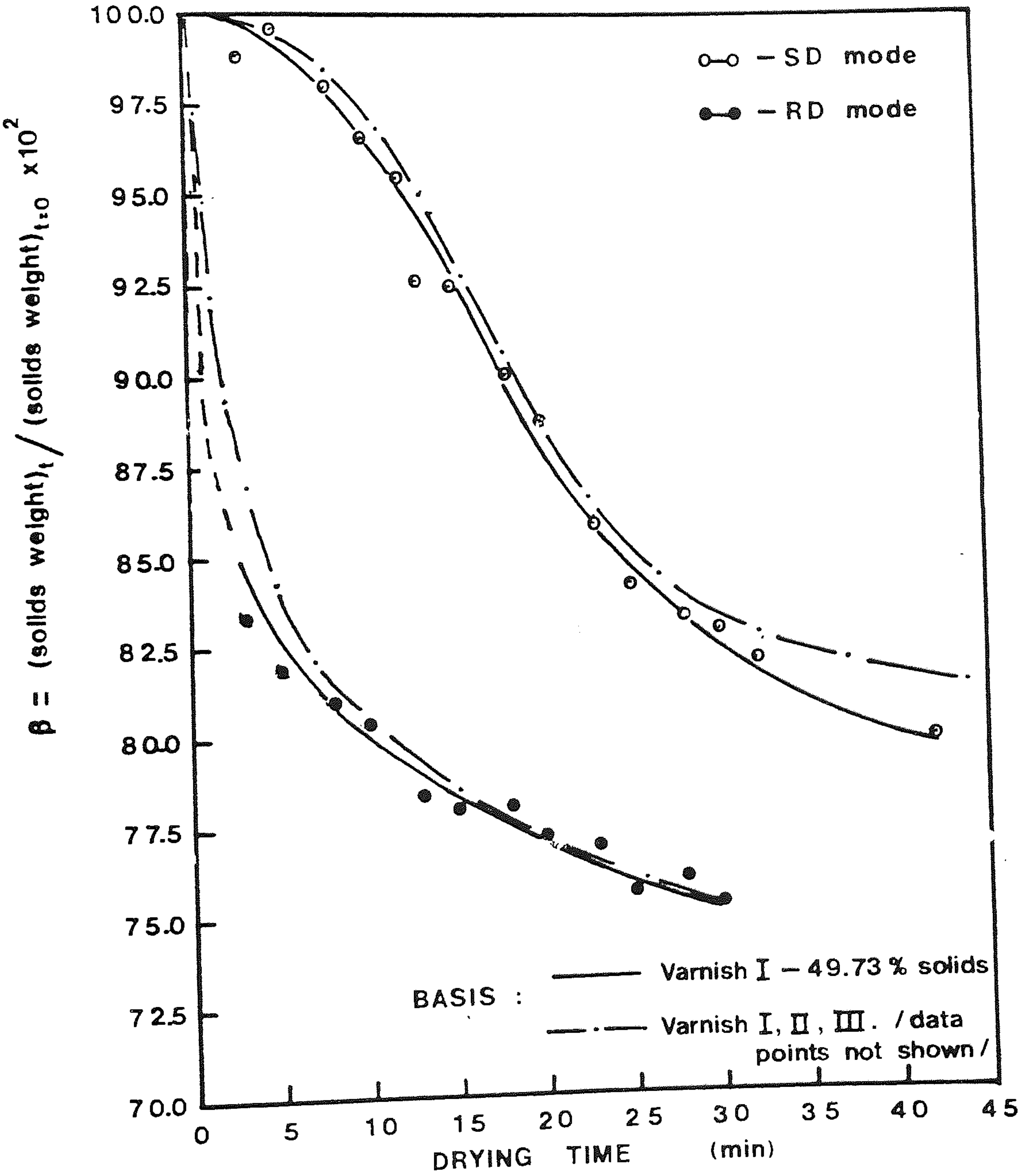


Figure 7.8 Proportion of solids in prepregs as a function of drying time.

content limits are shown in table 7.4. Samples dried in the RD mode lost up to 6.5% (W/W) more of the original solids - a significant proportion.

7.7.5 Application

The main objective of the static drying tests was to determine whether significant losses in resin matter occur as a result of rapid heating at high temperatures. This has been conclusively established. In actual drying practice these losses are expected to be even higher since substantially higher temperatures are used (up to 180°C).

The results therefore indicate 'minimum' losses. Even so, these could amount to significant financial losses unless action is taken to minimise them.

Several options exist.

(i) Lower temperatures in the dryer may be adopted, particularly in zones 1 and 2 in figure 7.4. Air temperatures in the range of 90° - 110°C would be adequate for solvent evaporation at the inlet. The increase in residence time as a result of lowering the temperature driving force can be overcome by increasing air flow rates and/or by utilising a better distribution of the available air flow. Consequent reduction in throughput rate would then be small.

For air flow impinging normal to the surface from slots, nozzles or perforated plates, the heat-transfer

DRYING MODE →	SD	RD	SD	RD
VOLATILES →	2.5%		4.0%	
β_1^* (Basis : Varnish I)	0.858	0.810	0.897	0.832
β_2^* (Basis : Varnish I, II, III)	0.865	0.815	0.907	0.847
$\frac{(\beta)_{RD}}{(\beta)_{SD}} = \frac{(\text{solids weight})_{RD}}{(\text{solids weight})_{SD}}$	0.944	0.942	0.928	0.934

$$* \beta = \frac{(\text{solids weight})_t}{(\text{solids weight})_{t=0}}$$

Table 7.4 Weight of resin solids

coefficient (h) is given by(37):

$$h = \alpha G^{0.78} \tag{7.19}$$

where:

h = Heat-transfer coefficient ($Wm^{-2}K^{-1}$)

G = air mass velocity ($kg\ m^{-2}s^{-1}$)

α = empirical constant ($J\ kg^{-1}K^{-1}$)

(α is dependent on plate open area, hole or slot size, and spacing between the plate, nozzle, or slot and the heat-transfer surface; G is based on the total heat-transfer area).

An increase in air mass velocity may result in vibration of the web inside the dryer which could increase the incidence of web breakage leading to delays in production runs. Correct distribution of air on both sides of the web via externally located extractor fans may remedy this.

Drying of alcohol-based phenolic varnishes require that the lower explosive limits (LEL) are not exceeded. Currently, drying is carried out at about 30% of LEL. Since the treated web can retain more resin solids at the lower temperatures, it should be possible to use lower varnish loadings at the impregnation stage without changing the resin content of the prepregs. This would allow increases in air flow rates without the risk of exceeding the LEL limits.

(ii) Lower levels of free phenol in the varnish should result in lower resin solids losses, since phenol is expected to represent the highest proportion of resin loss.

(iii) Faster curing systems may also contribute to lower resin losses since higher molecular weight species insoluble in water would quickly form. In this case, rapid cooling of the web may be necessary in order to stop resin advancement to a possible ruinous degree.

7.7.6 Percentage flow and physical property tests

In order to obtain additional information on the level of B-staging of samples dried in the SD and RD modes, and also to ascertain whether any difference in properties of laminates based on these samples exists, percent flow and physical property tests were carried out.

Percent flow was measured according to the method in section 7.2.2. Briefly, it involved impregnation of fresh samples using varnish I and subsequent drying in both modes. In each run the samples were withdrawn from the oven in two batches and at the following times:

RD mode - 5 and 7 minutes
SD mode - 19 and 21 minutes

Each run was repeated. Volatile and resin content were determined as previously shown.

Percent flow was calculated according to equation 7.2.

The prepregs produced were laminated under standard conditions into sheets of 1.5 mm nominal thickness. They were then tested for water absorption and insulation resistance. (The laminating conditions and physical property determinations are fully discussed in Chapter 8.)

The experimental results together with some of the prepregs characteristics are shown in table 7.5. They show that for both drying modes the percent flow is within 2.7% and 4.3%. For these types of laminates no specification exists but percent flow can vary from 1% to 5%(148).

The percent flow results in conjunction with volatile content show (indirectly) that the level of B-staging for samples dried in the SD and RD modes is similar and within production limits. Chemical characterisation was not attempted and it is not always required for quality control.

Due to the small number of physical property tests carried out, no firm conclusions can be drawn from these results. It may be stated that the results are comparable to production laminates of similar nominal thickness.

7.8 Conclusions

The experimental work on the drying of phenolic varnish impregnated paper has shown that:

(i) Rapid heating at 135°C causes significant losses in resin solids (wanted matter). In contrast, samples dried in a slow mode retained up to 6.5% more resin;

DRYING MODE	DRYING TIME (min)	VOLATILE CONTENT (a) (%)	RESIN CONTENT(a) (%)	FLOW (%)	WATER ABSORPTION(b) (mg)	INSULATION RESISTANCE(b) (10^{10} ohms)
SD	19.5	3.12	53.7	3.6	58.4	7.40
	21.5	2.96	53.0	2.9	57.8	7.57
RD	5.0	3.01	50.8	2.7	62.1	4.32
	7.0	3.46	51.2	4.3	60.6	3.94

(a) Mean of four determinations.

(b) Mean of six determinations.

Table 7.5 Results of percent flow and physical property tests.

(ii) phenol, and low molecular weight oligomers are thought to be the main constituents of the resin lost;

(iii) the level of B-staging (semi-cure) as measured by volatile content and percent flow was shown to be within acceptable limits for samples dried at lower temperatures. Physical property values were also within specifications;

(iv) the use of lower temperatures necessitates larger residence times. An increase in air flow rate in conjunction with better distribution is a possible option for minimising the increase in residence time.

8. LAMINATION

8.1 Definition and objectives

The final essential stage in the production of laminates is the laminating (pressing or moulding) stage. Anything else subsequent to this step may be considered as a finishing operation.

The process of lamination may be defined schematically as shown in figure 8.1.

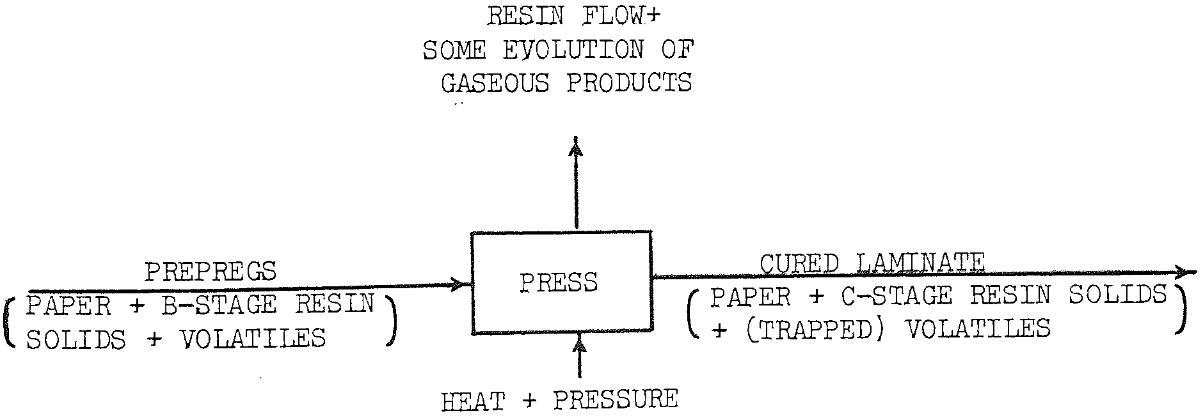


Figure 8.1 The lamination stage

For a particular resin-filler system, the main objectives of lamination are:

(i) to advance the polymerisation of each prepreg to the final C-stage; and

(ii) to effect bonding of the individual layers into a composite possessing uniform characteristics and optimum properties throughout.

8.2 Cure of laminates

8.2.1 Cure cycle

For the production of laminates in sheet form, prepregs with a specified resin and volatile content are assembled into a standard production sequence, and the entire pack is inserted between the platens of a steam-heated hydraulic press. The maximum number of sheets that may be loaded per daylight is mainly determined by the nominal thickness and the curing conditions of each laminate. Where a combination of sheet thickness is to be pressed in one daylight, the total (combined) sheet thickness usually does not exceed 20 mm.

Lamination is carried out according to what is sometimes referred to as the 'hot press' cycle,that is,the press platens are at the cure temperature (150 ± 5°C) during the insertion of the lay-up. The press is then closed and maximum pressure (5.5 - 7.6 MPa) is applied.

As the temperature of the B-stage prepregs in the lay-up is increased, the phenolic resin at first liquifies and flow occurs. Liquifaction is followed by gelation and vitrification (see section 4.2). At the end of the heating period, the press is cooled with water prior to the removal of the laminate in order to reduce blistering and warping which may be caused from thermal stresses set-up during heating. The pressure is maintained at the same level throughout the cure cycle.

8.2.2 Thermal characteristics

The final properties of each laminate produced are mainly governed by the degree of cure. In practice the conditions for complete crosslinking are not attempted for economic and other reasons, since, because of vitrification, the polymerisation reaction becomes diffusion controlled and curing may never go to completion; the extent of reaction will depend upon the temperature-time history. Even under laboratory conditions complete cure, resulting in the maximum number of chemical crosslinks possible, is hardly ever obtained(98).

The curing reaction of most thermosets is exothermic. Since polymers exhibit low thermal conductivity, temperature variations within the lay-up can be expected. For thick laminates in particular, temperature differences may be considerable. It is therefore quite likely that the extent of crosslinking may vary with the differing local thermal histories within the laminate and that the local properties may also vary. It may be possible therefore, that this variation can be controlled by controlling the curing temperature environment and the cure time. Clearly, heat transfer, reaction kinetics, and degree of cure information must be considered if a realistic approach to a comprehensive analysis of the lamination process is to be made.

There are a number of descriptive reports in the literature concerning the theory of reaction moulding processes, but there are only a few analytical studies of the problems of non-uniform reaction due to both heat transfer and the reaction exotherm during these processes.

Knappe et al(149) applied transient heat transfer concepts to the curing of unsaturated polyester and phenolic resin moulding compounds. Hills(150) reported some transient heat transfer calculations used to predict cure development in thick sections of rubber moulding. Engelmaier and Roller(151) also used transient heat transfer along with a time and temperature-dependent viscosity to model thickness changes in epoxy-based multilayer printed wiring boards (MLBs). Aung(152) applied numerical techniques to model the temperature distribution in MLB lay-ups. Close agreement was found between predicted and experimental results for five- and fifteen-layer MLBs. Recently, Pusatcioglu and co-workers(153) developed a mathematical model in order to predict the temperature gradients produced during casting of a general-purpose unsaturated polyester. The agreement between the predicted and experimental results was quite satisfactory over almost the entire reaction time interval - total cure time was approximately 22 minutes.

With respect to paper-based phenol formaldehyde laminates no published work was found regarding the temperature distribution during lamination, and also on the possible variation in the properties which might result from different cure histories.

There is clearly a need for an investigation into the thermal characteristics of the lamination stage. This could provide the basis for a better understanding of the curing process for phenolic laminates, and an improvement in both the economics of the process and the properties of the final product may be possible from such an undertaking.

8.3 Aims

Due to the importance ascribed to the lamination stage, a considerable effort was directed to this part of the project. The main objectives of this work are:

(i) to thermally characterise the lamination process in terms of the temperature distributions which lay-ups experience during the cure cycle;

(ii) to evaluate the possible variation in the properties within the laminate which may result from different cure histories; and

(iii) to propose an alternative cure cycle which would result in improved process economics and/or properties of the final product.

8.4 Proposed plan of work

The proposed plan of the experimental work is outlined in figure 8.2 and it consists of two main parts:

Part 1 : Preliminary work

The preliminary work involved the following:-

(i) calibration of press temperature regulators;

(ii) measurement of temperature distribution in each platen;

(iii) tests to ensure that the thermocouples embedded in prepregs held firmly during measurements;

(iv) determination of the temperature profiles during the lamination of lay-ups measuring 25 x 25 cm. Four sheet thicknesses were investigated: 0.32 cm, 1.27 cm, 2.54 cm and 5.1 cm.

Each laminate was produced in a single loading operation; sheet thickness combinations were not pressed. For the 0.32 cm thick sheets this procedure is inconsistent with normal practice - usually three such sheets would be loaded into a daylight. It was however justified on the basis that at this stage of the experimental work, identical pressing conditions were necessary so that a direct comparison of the temperature profiles of each laminate could be made.

A small electrically heated press was employed for the lamination measurements. Several factors contributed in selecting the press and these include the following:-

(i) Availability. The press was used for light work such as resin-flow experiments on new products;

(ii) Convenience. The press was situated in the development

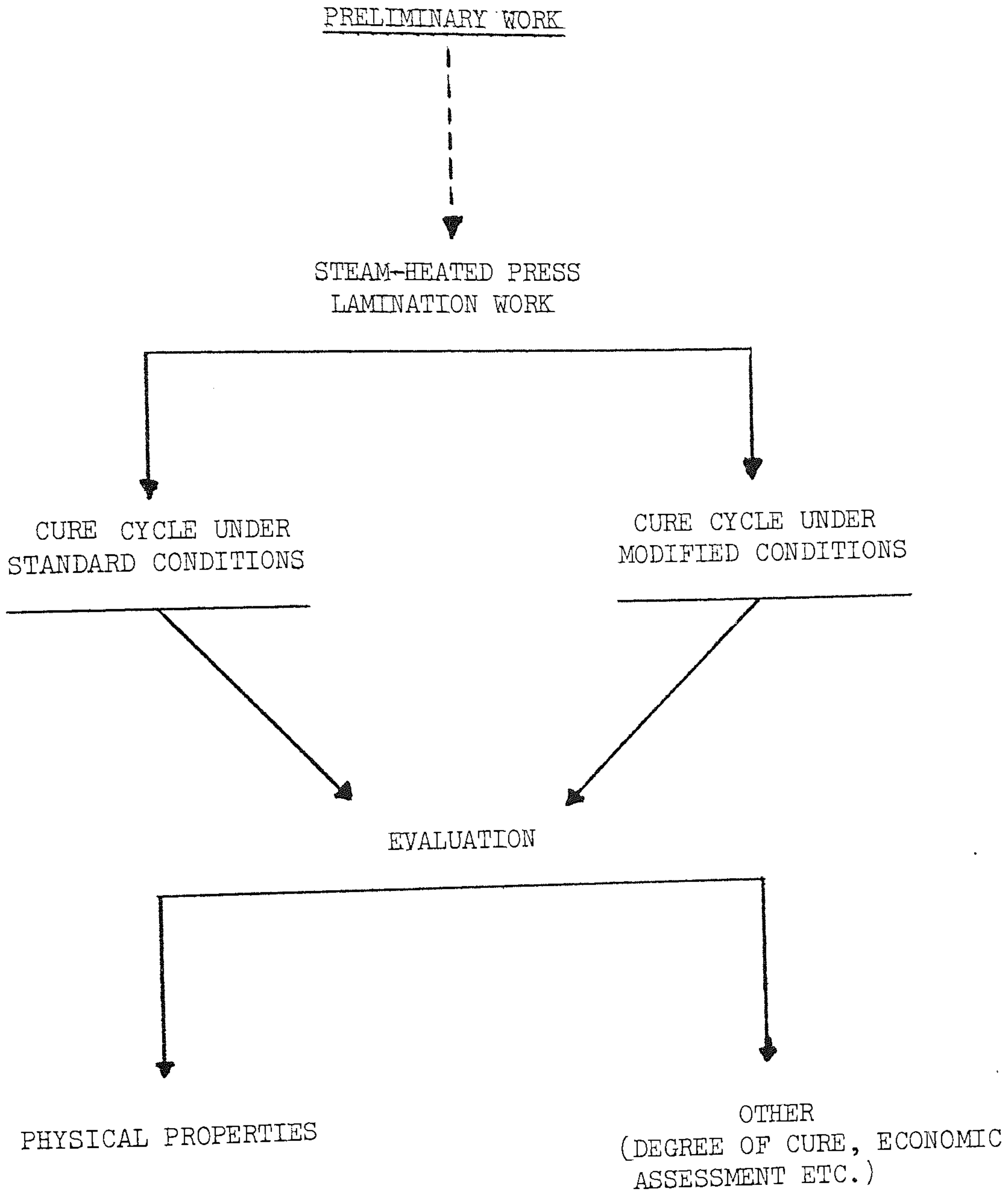


Figure 8.2 Schematic diagram of proposed plan of experimental work.

laboratory area with facilities for impregnation, drying, cutting etc; and

(iii) Adequate instrumentation. Each platen was independently controlled by simple on-off temperature regulators using thermocouple probes embedded in each platen.

Part 2 : Lamination on a steam-heated press

The work on the larger (47.6 x 47.6 cm) steam-heated press constituted the bulk of the experiments. On the basis mainly of the results obtained in the preliminary work, further detailed tests were carried out and these involved:

(i) determination of the temperature distributions for laminates cured under (a) standard and (b) modified cure cycles;

(ii) evaluation of the physical properties and of the degree of cure of laminates for each mode of operation - a and b;

(iii) economic assessment of the modified cycle and its effect on production costs.

Since most laminates of this type are at present produced on steam-heated presses, the results from this part of the experimental work may be considered directly applicable.

8.5 Experimental

8.5.1 Materials

The resols and paper base used throughout the course of the experimental work conformed to the raw materials specifications. Their characteristic properties have been cited in the impregnation and drying sections (Chapters 6 and 7 respectively). Storage conditions for the resols have also been discussed previously.

8.5.2 Experimental set-up

The experimental set-up for the temperature measurements consisted of the press, thermocouples, and a Comark electronic thermometer with a selector unit for up to a maximum of twenty thermocouple inputs.

All prepreg lay-ups were fitted with Chromel/Alumel (Ni-Cr/Ni-Al) thermocouples 0.376 mm in diameter placed between the prepreg sheets. The thermocouples were prepared using the STP Dynatech welder (model 125 SRL) which utilises an argon-arc welding technique. More than two hundred thermocouples were made this way. Calibration over the temperature range of interest was carried out in a constant temperature bath. Batches of ten thermocouples were used in each calibration.

Each thermocouple junction was carefully positioned in the centre of the square prepregs, to assure the measurement of only z (thickness) - direction temperature gradients. In order to determine the temperature gradients in the x and y directions (parallel to the press platen surface), additional thermocouples were placed at various x, y positions. Thin strips of high temperature glass cloth electrical tape, measuring approximately 0.6 x 0.3 cm were used to firmly attach each 'leg' of the thermocouples' junctions onto the surface of the prepreg (Sellotape was also used with similar results).

The use of the adhesive tape was found:

(i) to hold the position of each junction quite satisfactorily;

(ii) to facilitate handling of the large number of thermocouples which were employed in each run; and

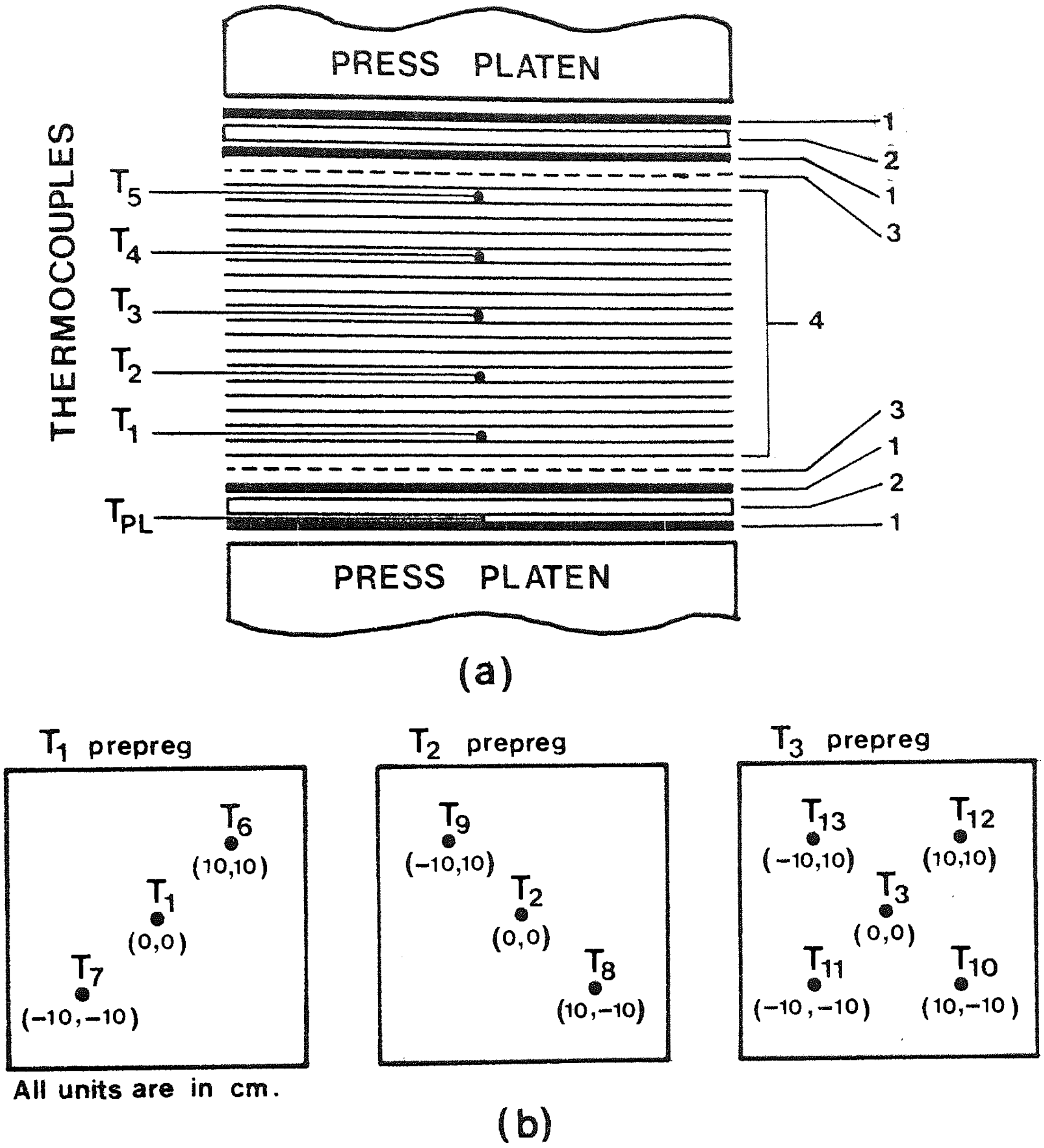
(iii) not to alter the characteristics of the lay-ups during the cure cycle. (The maximum area covered by the glass-tape strips was estimated to be less than 0.05% of the total surface area of the prepregs used in any one experiment).

The Chromel/Alumel wires projecting from the lay-up were insulated with silicon-impregnated glass sleeving, 2 mm in diameter, and connected to the Comark selector unit via terminal blocks and compensating cables. The terminal blocks were securely fixed on a wooden strip and clearly labelled.

A typical experimental arrangement is presented in figure 8.3. The position of the thermocouples in the z-direction was identical in all experiments (electric- and steam-heated press lamination). The x, y positions shown are typical of the preliminary work only.

8.5.3 Experimental procedure

A general procedure was set out and it was closely followed



All units are in cm.

KEY

1 – Stainless steel plates

2 – Padding (corrugated paper or cardboard bonded with fabric-based phenolic prepregs)

3 – Release film (polyvinyl fluoride or polyester)

4 – Prepregs

Figure 8.3 Thermocouple arrangement in lay-up. (a) z-direction; (b) x,y-directions (electric press work only).

in each experiment. Resin content, volatile content, and the laminating conditions in general were in accordance with production specifications.

8.5.3.1 Impregnation and drying

Pure unbleached kraft paper, 0.178 mm (7 mil) in thickness was cut into strips measuring 110 x 60 cm. Two-three paper strips were taken at random for moisture determinations. Each strip was then hand-impregnated with phenolic varnish. Batches of up to fourteen sheets each were dried in an oven at a constant temperature of 140 ± 1°C. In order to minimise atmospheric moisture absorption, the resin and volatile content tests were carried out immediately after drying. Any batch of prepregs with resin and/or volatile content outside the specifications was discarded.

Following the drying operation each strip was cut into square sheets using the appropriate template. End-effects were minimised by discarding a minimum of five centimetres from each side of the prepreg strips. The prepregs were carefully wrapped in black polythene bags and stored in a cool and dark place prior to pressing. They were usually pressed within seven days of impregnating.

8.5.3.2 Assembly

The number of prepreg sheets required to make a given thickness of finished laminate was determined by weighing (table 8.1). The sheets were then assembled in a cross-

NOMINAL THICKNESS (mm)	25 x 25 cm (Kg)	45.7 x 45.7 cm (Kg)
3.0	0.27	0.89
12.75	1.14	3.76
25.4	2.28	7.50
51.0	4.57	15.10

Table 8.1 Weights of prepregs for producing laminates of given nominal thickness. (These weights are for guidance purposes only and apply to prepregs which have the following specifications:

(i) resin content: 49.5 - 54.5%

(ii) volatile content : 2.5 - 4.0%)

plied configuration by rotating the machine direction of each ply through 90° relative to that of each adjacent ply.

The stack of treated sheets including the attached thermocouples was placed between sheet metal plates. The plates were stainless steel with the brush-polished surfaces in contact with the plies so that a 'satin' finish would be obtained. Before use the plates were thoroughly cleaned, and care was taken to exclude any foreign matter. Any hard particles left on the metal surface would mark the laminate and dent the plate, such a dent being reproduced on the surface of every laminated sheet which is subsequently pressed by the same metal. With the padding (mainly used to improve distribution of pressure) and release film in position the lay-up was ready for pressing.

8.5.3.3 Pressing

The press was maintained at 150 ± 3°C for a minimum of one hour prior to lamination. It was then loaded and a pressure (on the laminate) of 7.33 MPa was applied. The force required to be delivered by the hydraulic ram was calculated according to the following equation:

$$p_L = \frac{F_H}{a_L} \qquad (8.1)$$

where:

p_L = pressure applied on lay-up (Pa)

F_H = force delivered by hydraulic ram (N)

a_L = surface area of lay-up in contact with lower platen (m^2)

For p_L = 7.33 MPa and $a_L = 6.25 \times 10^{-2}$ m^2 then F_H was set at 4.58×10^5 N.

At the end of the curing period the heating was turned off and cooling water was immediately passed through the platens, still maintained under the same pressure.

The insertion time, sometimes known as operator-press time lag (o-p lag), that is the time between insertion of the lay-up into the press and application of the maximum pressure, was kept minimum and in the range of 30-40 seconds. This compares well with production o-p lags in the range of 30-60 seconds.

Temperature readings to within 0.5°C were then taken for both the heating and cooling periods. Zero time was defined as the time immediately prior to the insertion of the lay-up. The time taken to record each set of temperature readings was noted. The following sequence was used during each run.

First set : $T_1, T_2, \ldots\ldots, T_{n-1}, T_n$

Second set : $T_n, T_{n-1}, \ldots\ldots, T_2, T_1$

Third set : $T_1, T_2 \ldots\ldots, T_{n-1}, T_n$ etc.

(Corrections were applied to the measurements taken when subsequently plotted in graph form in order to account for the time taken to record each set.)

The room temperature (near the press) was also taken before and after each run and the average value noted.

The temperature of each platen was continuously measured using 0.63 mm diameter Copper/Constantan (Cu/Con) thermocouples inserted together with each thermal regulator probe. A third Cu/Con thermocouple was used for cross-checking purposes and was inserted as shown in figure 8.3. A temperature chart recorder (Cambridge Instruments) was employed for these measurements. Most experiments carried out in the preliminary work were repeated in order to assess the reproducibility of the results.

8.5.4 Preliminary work

The results of the temperature measurements during lamination of 25 x 25 cm lay-ups using the electric press are presented in this section. The rest of the preliminary work is described in Appendix A4.

8.5.4.1 Results and discussion

The experimental results are presented in graphical form in figures 8.4 to 8.11.

Figures 8.4 and 8.5 refer to the temperature distribution in prepreg layers for a lay-up of cured thickness of 3.38 mm. Figure 8.4(a) shows the temperature histories in the z (thickness) direction from both the centre prepreg and for the prepreg nearer to the lower

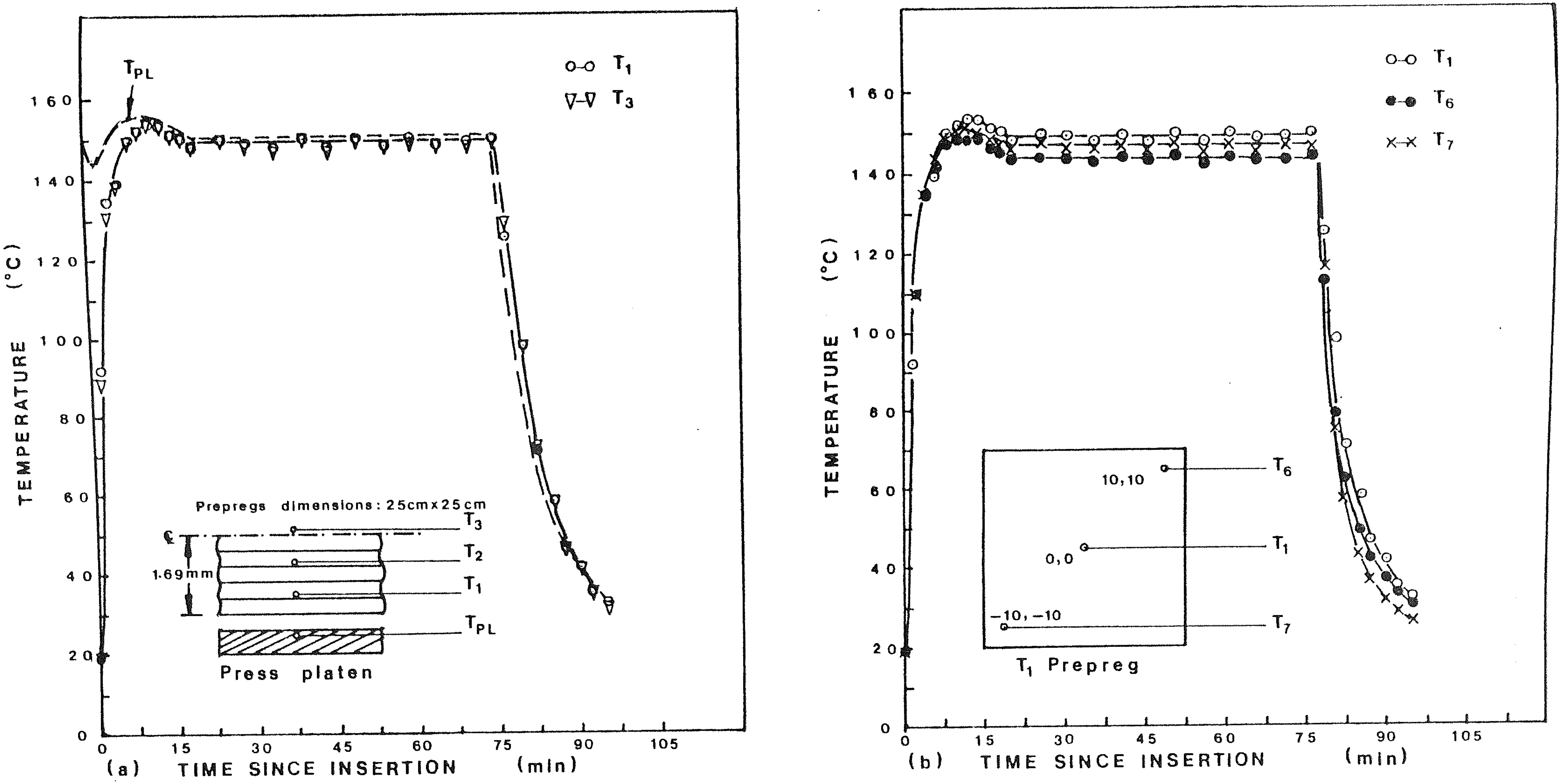


Figure 8.4. Temperature histories of a lay-up of 3.38 mm cured thickness. (a) z-(thickness) direction; (b) x,y-directions for T_1 prepreg. (o-p lag = 30 s).

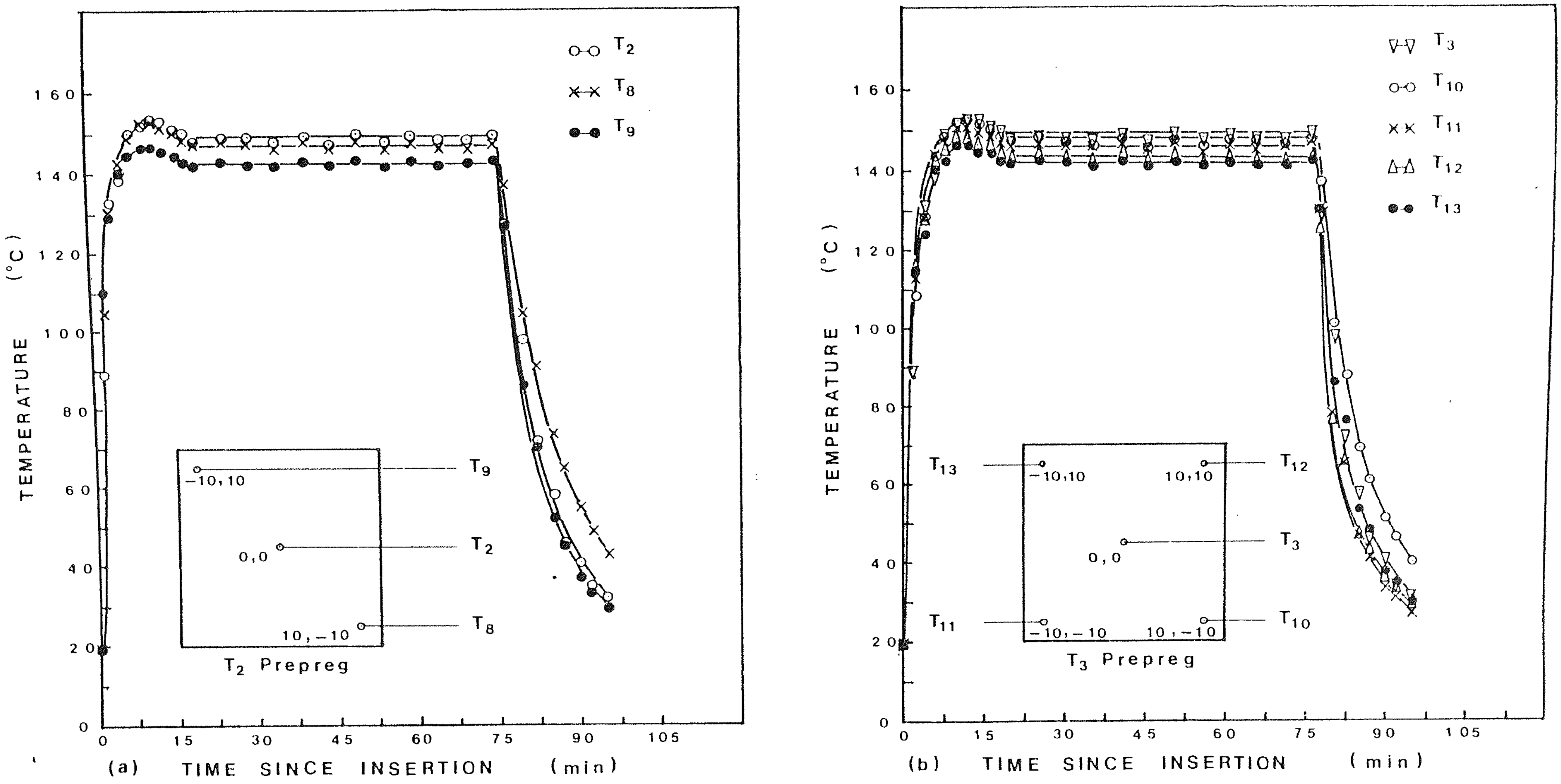


Figure 8.5 Temperature histories of a lay-up of 3.38 mm cured thickness. (a) T_2 prepreg; (b) T_3 prepreg.

heating platen. (T_3 and T_1 respectively). It can be seen that there is no discernible difference in the temperatures of these layers during both the heating and cooling periods.

The slight temperature peak which occurs after 12 minutes of heating time is partly due to the exothermic heat of reaction and partly due to the controlling action of the thermal regulators. As the cold lay-up was placed between the already hot platens of the press, it resulted in a slight drop in the temperature of the platens (T_{PL}). This caused overshooting of the set temperature of 150°C, and up to 5°C overshoot was a typical value.

Figures 8.4(b) and 8.5(a),(b) show the temperature histories at various positions in the x,y directions (parallel to the platen surface) in prepregs T_1, T_2 and T_3. All three prepregs experience differing temperature histories at x, y positions in both the heating and cooling cycles. However, these differences are mainly due to the press platens heating characteristics and they have been observed during the press-temperature calibration.

Figure 8.6 refers to the lay-up of nominal cured thickness of 12.75 mm. The temperature variation in the z-direction between prepregs T_1 (nearer the platen) and T_6 (centre of lay-up) is more pronounced and a temperature difference of approximately 60°C is reached two minutes after insertion of the lay-up. In contrast to the

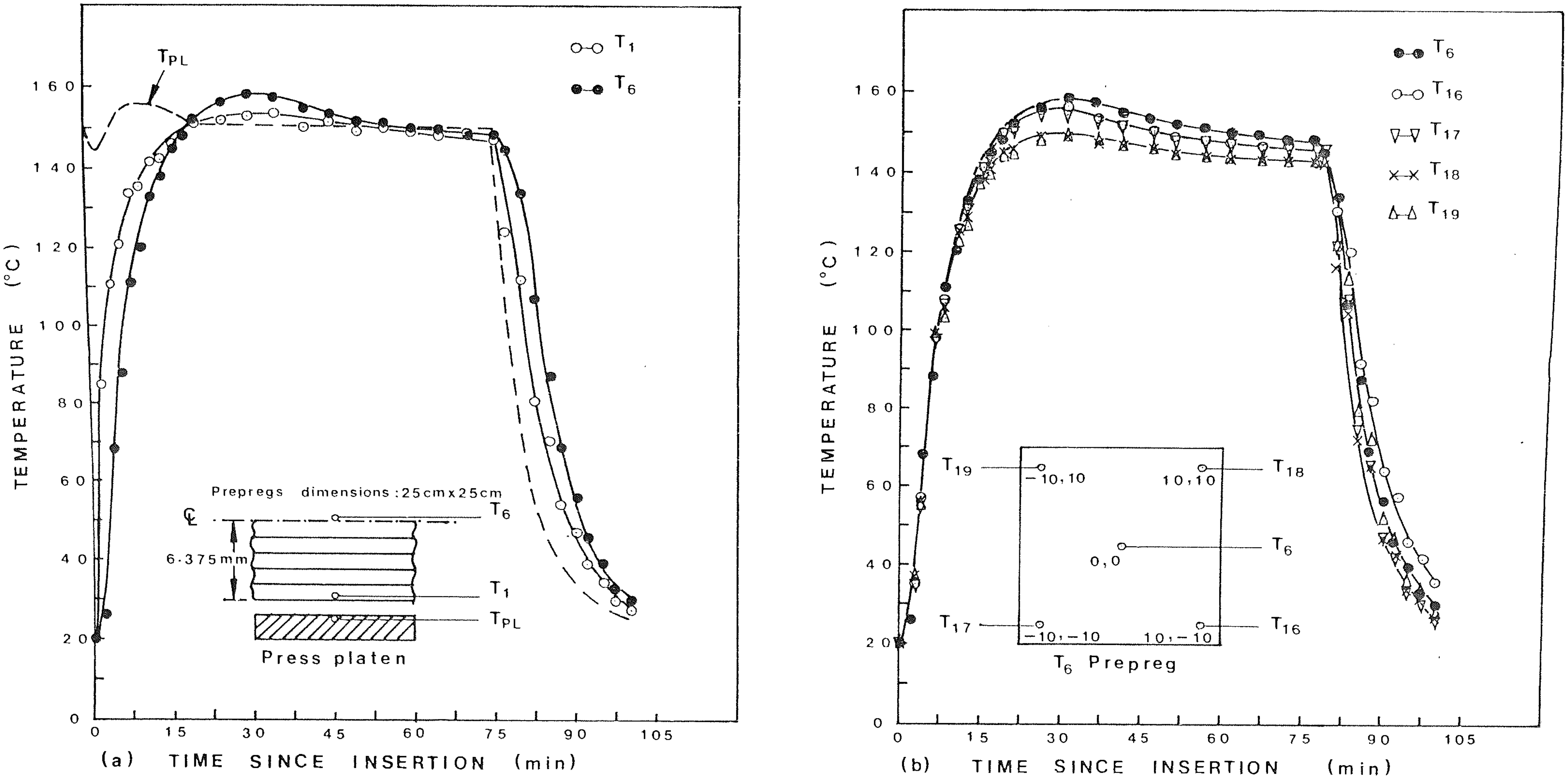


Figure 8.6 Temperature histories of a lay-up of 12.75 mm cured thickness.
(a) z-direction; (b) x,y-directions for T_6 prepreg.
(o-p lag = 30 s).

previous run a maximum temperature of 158.5°C occurs after 30 minutes of heating, due solely to the exothermic heat generated in the centre of the lay-up. The exotherm contributes in producing temperature differences at the various x,y positions larger than can be accounted for by the platens heating characteristics. This is shown in figure 8.6(b).

The temperature distribution for a lay-up with a cured thickness of 25.5 mm is depicted in figures 8.7 to 8.9. Only temperature histories of the T_1 and T_6 prepregs are shown since in all cases the temperature variation of the other prepregs are enveloped by these histories.

The maximum temperature difference between T_1 and T_6 occurred approximately 8 minutes after the lay-up insertion and reached 92°C. Due to the exothermic effects the temperature of T_6 (centre layer) peaked at 171.5°C after 66 minutes of heating, which is a rise of 21.5°C above the mean cure temperature of 150°C. The temperature variation during cooling is however less pronounced.

Temperature differences in the x,y directions (8.7(b)) are also large reaching a maximum of 23°C in the T_6 prepreg. As previously argued, the exothermic heat is the major factor causing the temperature differences observed.

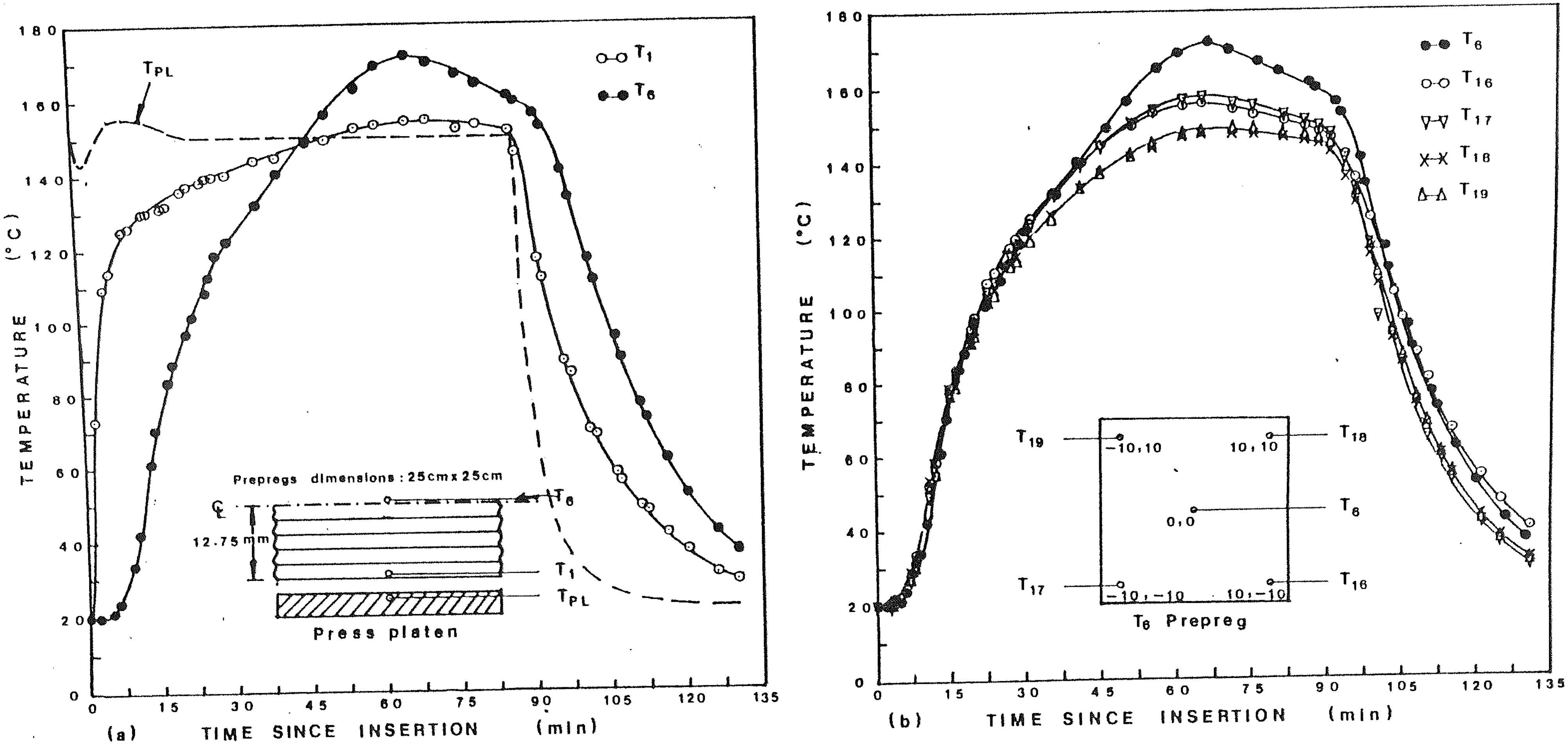


Figure 8.7 Temperature histories of lay-up of 25.5 mm cured thickness.
(a) z-direction; (b) x,y-directions for T_6 prepreg.
(o-p lag = 37 s).

Figure 8.8 shows the temperature histories in the z-direction as a function of the location of thermocouples with the time as a parameter. It shows clearly the layer-to-layer variation in temperature as a direct result of the physical thickness imposed by the number of prepregs in the lay-up. High initial heat-up rates are experienced (up to 26°C min^{-1} for T_1) and it results in the non-linearity of the temperature profiles.

Within 24 hours of the completion of the curing cycle the 25.5 mm thick laminate was reheated under identical conditions, but for a slightly shorter cooling time. The same thermocouples already embedded in the laminate were employed. The temperature histories for the T_1 and T_6 prepregs are plotted in figure 8.9 (broken lines) together with the thermal histories of the same prepregs taken from the figure 8.7(a) plots.

It is interesting to note that for the T_6 prepreg the thermal histories - curing (●-●) and cured (■ - - - ■) - are nearly parallel to one another during the first 30 minutes of heating and after an initial time offset. This thermal lag represents a time-shift of 5.5 to 6.5 minutes and it is probably largely due to thickness reduction as a result of resin flow during the early part of the curing cycle. Assuming that the thermal diffusivities of the cured and curing prepregs are similar, this time lag is equivalent to an overall thickness reduction of 0.8 - 0.9 cm.

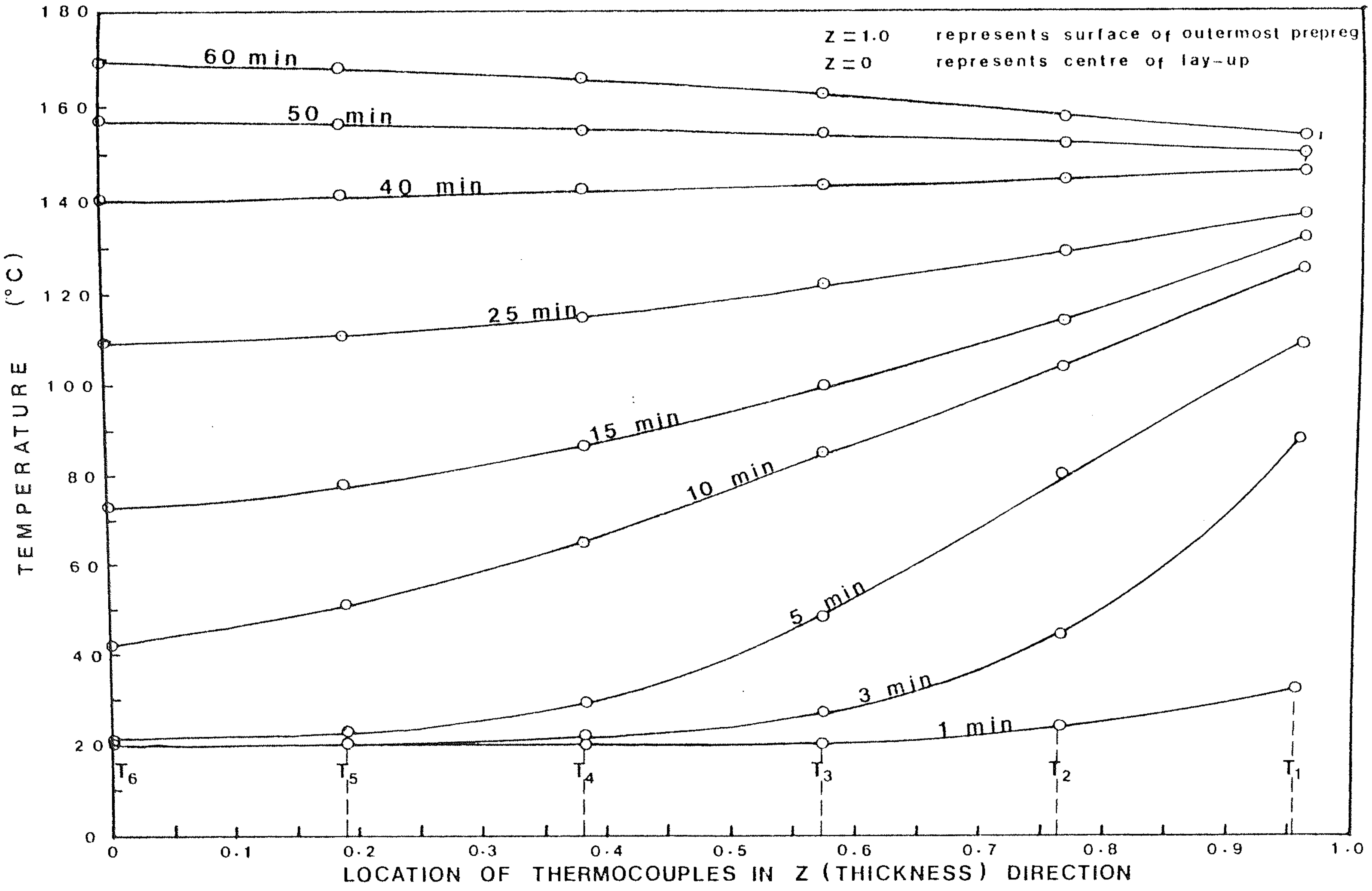


Figure 6.8 Temperature as a function of thermocouple location for a lay-up of 25.5 mm cured thickness.

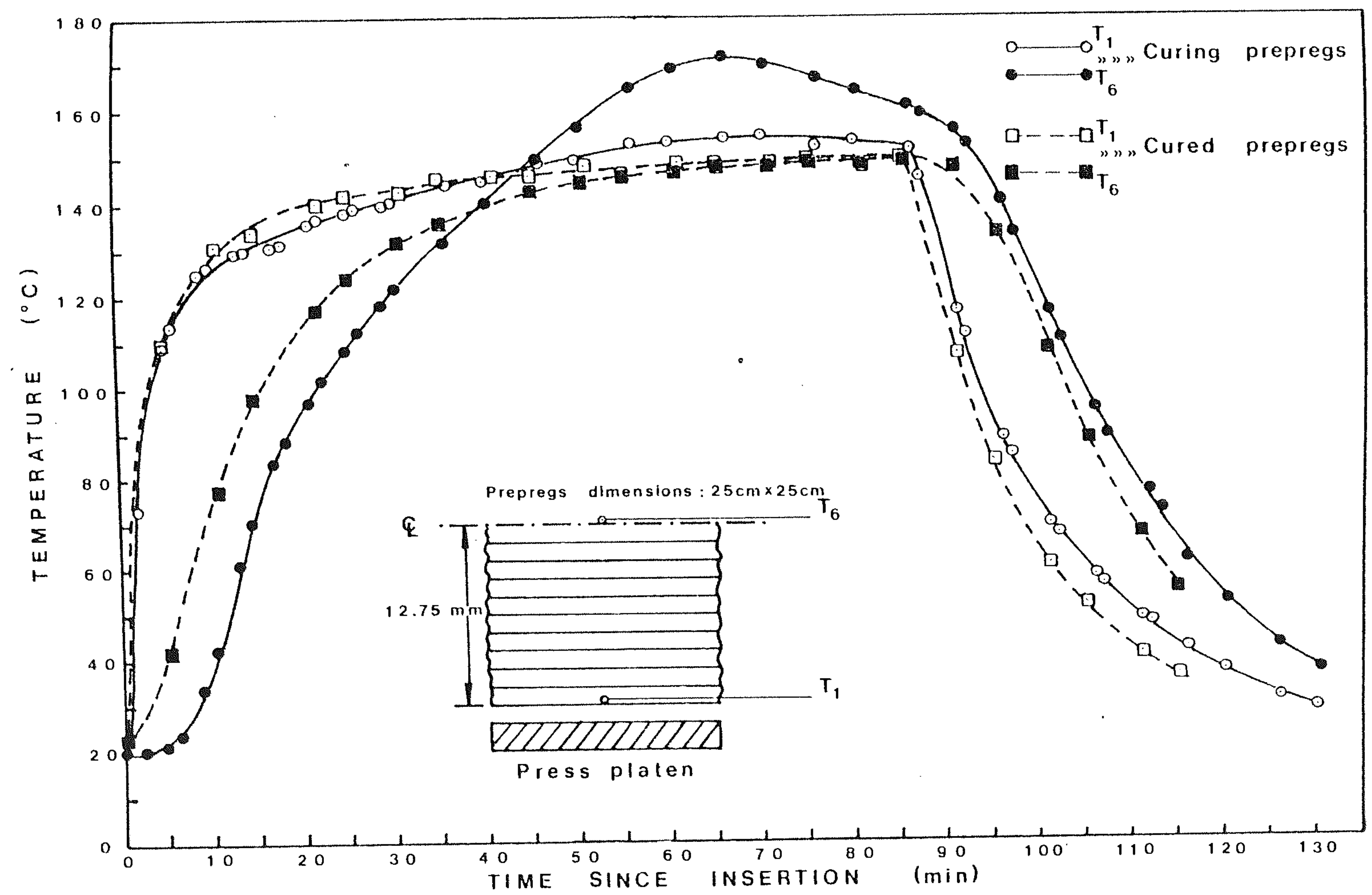


Figure 8.9 Temperature distribution in a lay-up of 25.5 mm cured thickness. (i) during lamination (solid lines); and (ii) when re-heated under identical cure conditions (broken lines).

Finally, figures 8.10 and 8.11 present the temperature profiles for a lay-up with a cured thickness of 51 mm. The temperature distribution in the z-direction is shown in figure 8.10(a). It can be seen that an enormous thermal lag exists between the T_1 and T_6 layers which also extends over the cooling period. A maximum temperature difference of 110.5°C was recorded between the two prepregs 18 minutes after insertion of lay-up. The exothermic heat produced resulted in a temperature rise for T_6 of 35.5°C above the mean cure temperature.

The temperature variation in the x,y directions for the T_6 prepreg is shown in figure 8.10(b). Although the difference in temperatures between T_6 and the other four thermocouples is large (up to 57°C between T_6 and T_{19}) relatively small variation occurs between each temperature of thermocouples T_{16} to T_{19}. This is mainly due to the fact that cooling has been applied well before the exotherm was fully developed, and the temperature histories are still at the early part of the cycle. Longer heating would certainly have produced similar effects as with the other laminates. More importantly however, is that none of the four thermocouples (T_{16} - T_{19}) reached the cure temperature, the worst case being that of T_{18} and T_{19} reaching a maximum temperature of only 132°C.

Figure 8.11 shows the temperature histories of the prepregs as a function of thermocouple location in the lay-

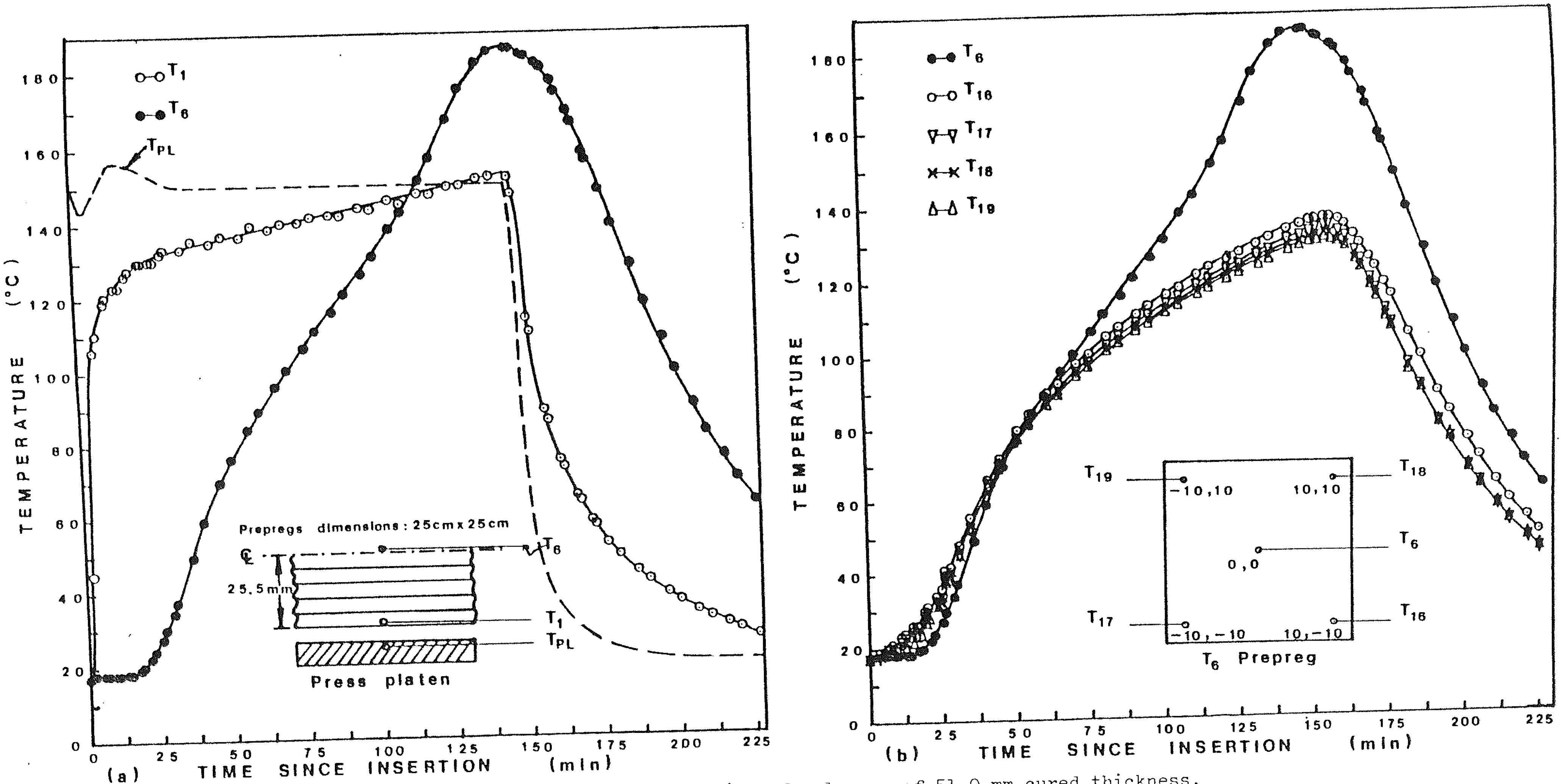


Figure 8.10 Temperature histories of a lay-up of 51.0 mm cured thickness.
(a) z-direction; (b) x,y-directions for T_6 prepreg.
(o-p lag = 30 s).

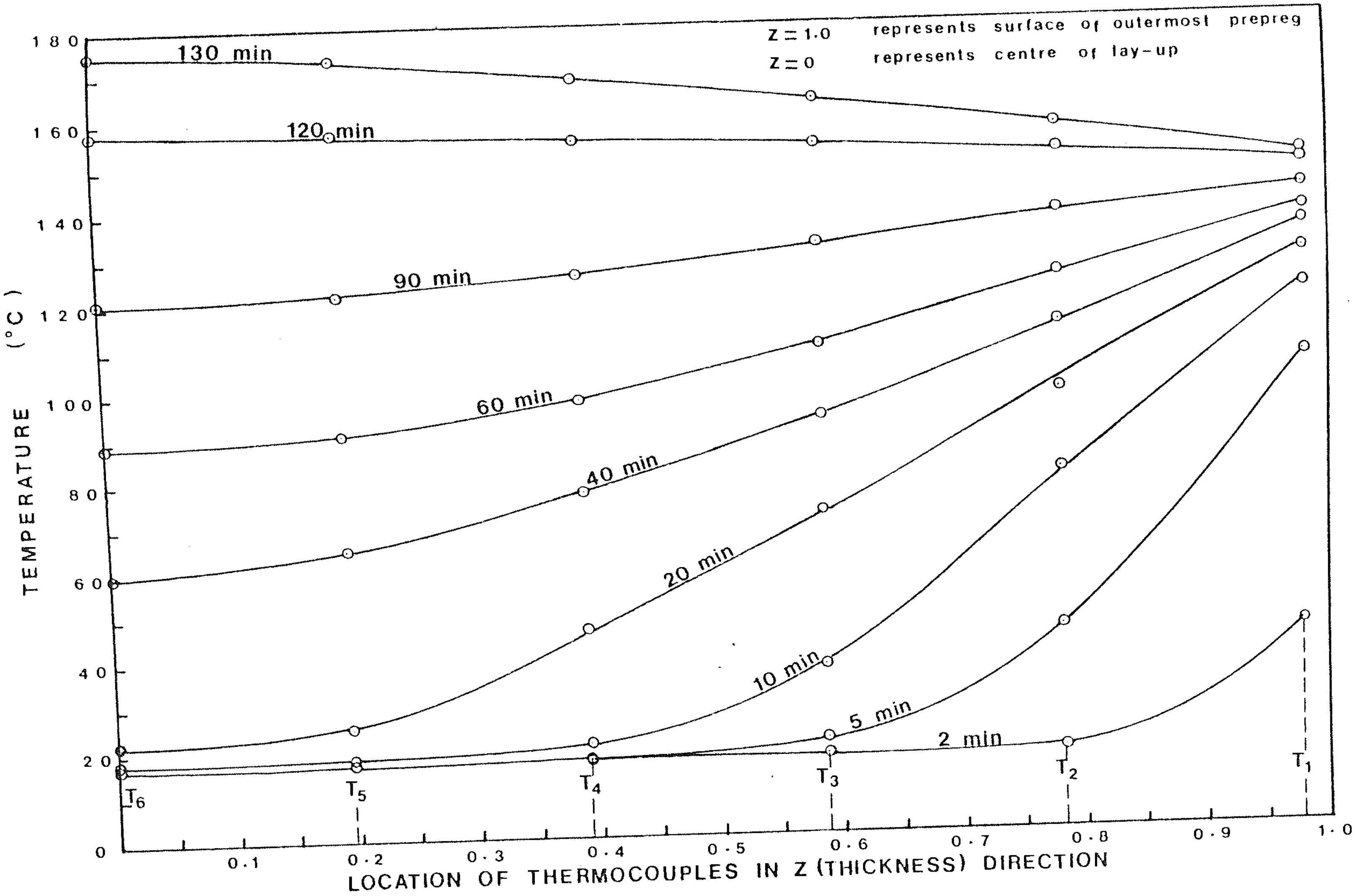


Figure 8.11 Temperature as a function of thermocouple location for a lay-up of 51.0 mm cured thickness.

up. The initial heat-up rates for the layers nearer the platens, although significant (18°C min^{-1} maximum) are smaller in comparison to those of figure 8.8, because of the increased thickness.

The first three experimental runs up to and including laminate thickness of 25.5 mm were repeated. Small variations in the results obtained under nominally identical conditions and press control settings were observed. The likely major cause of these variations is an insufficient sensitivity of the press controls with respect to temperature. In general however, it was found that the results were well reproduced with a maximum temperature deviation of ± 2°C over the entire cure cycles.

8.6 Lamination on a steam-heated press

The lamination experiments carried out on the steam-heated press involved mainly lay-ups of nominal cured thickness of 2.54 cm. This is usually the maximum thickness for paper-phenolic sheet laminates although fabric-based phenolic laminates are produced having nominal thickness of 23 cm or even higher.

Two series of laminates were produced and these were designated 'S' (standard cure) and 'M' (modified cure). Each series comprised three laminates measuring 45.7 x 45.7 cm and one laminate measuring 40.6 x 40.6 cm.

8.7 Press calibration

The press platen calibration is described in Appendix A4.

8.8 Experimental set-up

The experimental set-up employed for the measurement of the temperature distributions during lamination (series S and M) has been described in Section 8.5.2. Some minor modifications were made however, regarding the thermocouples lay-out.

The number of thermocouples used for the temperature determination in the z (thickness) direction was reduced to three - T_1, T_2, and T_3 in figure 8.3(a). Due to the symmetry of the system only the temperature histories in the one-half of the lay-up, in this case the lower half, were measured.

The thermocouples placement in the x, and y (parallel to the platen) directions was confined to the centre layer (T_3 prepreg). By placing the thermocouples in one-half of the T_3 prepreg it was possible to use the other half of the lay-up (being free of any thermocouples) in the physical properties evaluation tests. Figure 8.12 shows the position of the thermocouples relative to the steam passages configuration of the lower press platen; the upper platen's configuration was identical. Although every possible effort was made to ensure exact positioning of each lay-up on the lower platen, some variations could have occurred.

Scale : 1 cm ≡ 4 cm

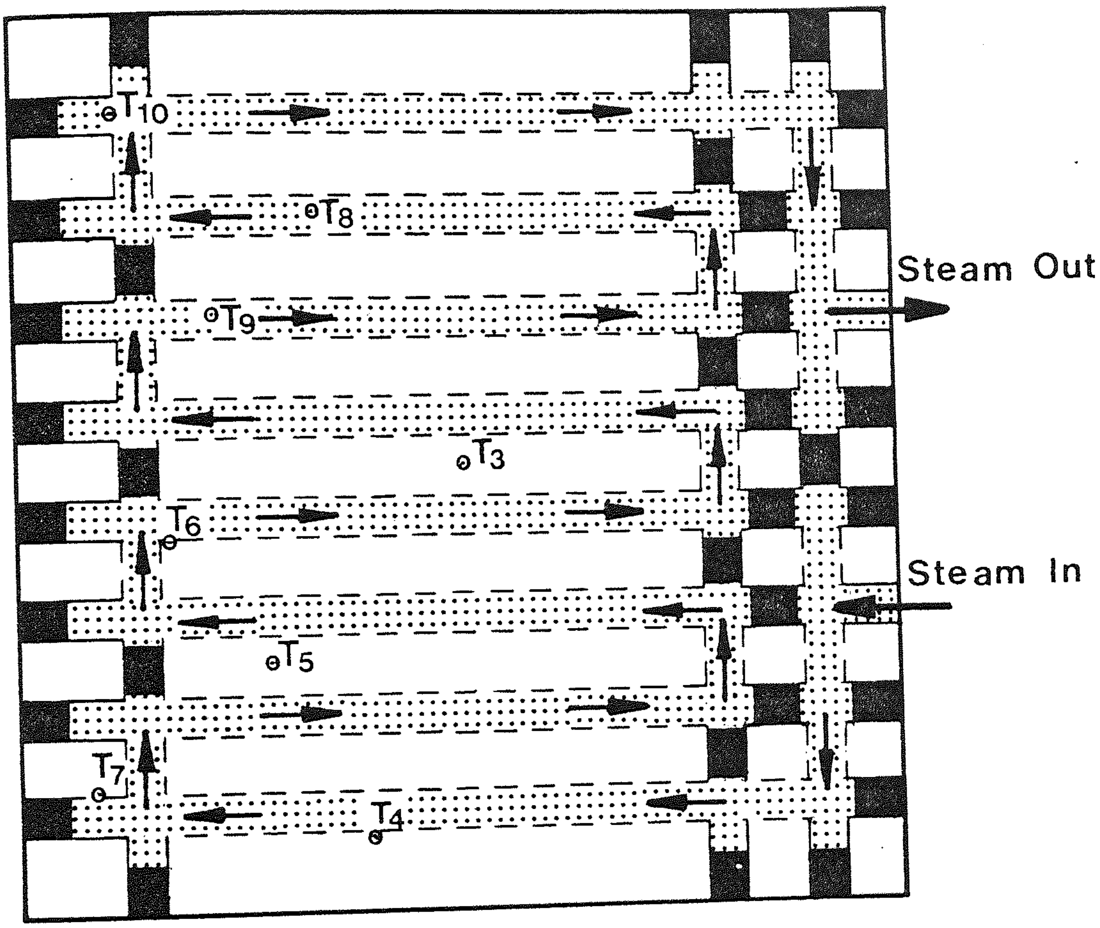


Figure 8.12 Typical position of thermocouples relative to the press platen configuration. (All thermocouples are located in the T_3 prepreg - centre layer; x,y coordinates can be found in subsequent plots).

KEY

▨ – Steam passages , 1.91 cm diameter.

■ – Plugs , 2.54 cm long .

o – Thermocouples for $45.7 \times 45.7\ cm^2$ and $40.6 \times 40.6\ cm^2$ lay – ups.

8.9 Experimental procedure

The laminates designated S1 and M1 were produced using kraft paper which had been treated according to the experimental procedure set out in Section 8.5.3. The rest of the laminates, S2 to S4 and M2 to M4, were made using freshly cut paper prepregs which were obtained from production cycles so that the lamination experiments could be speeded-up. Both sets of prepregs conformed to required specifications on the resin and paper characteristics including resin and volatile contents. No significant differences were observed in the temperature histories or physical properties of laminates made from either the production prepregs or the hand-impregnated ones. As in previous experiments, each laminate was produced in a single loading operation under an applied pressure on the laminate of 7.33 MPa calculated according to equation 8.1. Table 8.2 summarises some of the characteristics of the lay-ups including the curing conditions.

For the S-series laminates the curing conditions were in accordance with standard production specifications as applied to the pressing of lay-ups with a final (cured) thickness of 2.5 cm. Regarding the cooling period the time allowed was arbitrary since this is normally related to platen temperature.

For the M-series laminates heating was stopped when the temperature in the centre layer (T_3) reached the cure temperature of 150°C, approximately 40 minutes after insertion of the lay-up. An intermediate (transition) period of 15 minutes duration then

DESIGNATION	SIZE (cm x cm)	NOMINAL CURED THICKNESS (cm)	PAPER PREPREGS		CURE CONDITIONS$^{(a)}$	
			TYPE	NUMBER PER LAY-UP	HEATING TIME (min)	COOLING TIME (min)
S1	45.7 x 45.7	2.56	Hand-impregnated	178	85	30
S2	45.7 x 45.7	2.56	Production cycles	178	85	30
S3	45.7 x 45.7	2.57	Production cycles	178	85	30
S4	40.6 x 40.6	2.52	Production cycles	175	85	30
M1	45.7 x 45.7	2.55	Hand-impregnated	175	55$^{(b)}$	30
M2	45.7 x 45.7	2.54	Production cycles	179	55$^{(b)}$	30
M3	45.7 x 45.7	2.55	Production cycles	179	55$^{(b)}$	30
M4	40.6 x 40.6	2.52	Production cycles	179	55$^{(b)}$	30

(a) Cure temperature = 150 ± 1°C; applied pressure on laminate = 7.33 MPa

(b) This includes a period of 15 min prior to cooling, during which the steam has been turned off.

Table 8.2 Some characteristics of the lay-ups. (Insertion time was in the range of 33 ± 2 s).

followed so that the heat generated by the exothermic reaction could be utilised. At the end of this period cooling was applied in the usual way, that is by passing cold water through the steam passages.

At the completion of each run the laminates were wrapped in black polythene sheet and stored in a dark, cool place. When all eight laminates were finally produced they were trimmed round the edges and then carefully cut through the middle using a circular saw. The parts which were free of thermocouples were cut into samples of the appropriate dimensions so that testing of the physical properties could be carried out.

8.10 Testing of laminates

8.10.1 Conditioning of test specimens

As most laminated plastics are sensitive to both temperature and humidity, conditioning of the specimens is important otherwise the basis of comparison is lost. All samples were therefore conditioned prior to testing in a humidity chamber maintained at 50 ± 2°C and 50 ± 5% relative humidity. The duration of the conditioning of the test pieces was 24 ± 1 hours.

8.10.2 Physical properties

The basic and optional requirements for phenolic resin bonded paper sheets for electrical applications are described in BS 5102 : 1974. The relevant specifications which are applicable to the paper laminates produced in this work are covered by type 1 sheets in the above British Standard.

As a full range of tests was not possible due to the limited number of samples available, three tests were initially applied to the laminates of both series S and M. The tests, cross-breaking strength, insulation resistance, and water absorption were chosen on the basis that they would adequately represent the mechanical, electrical and physical properties of the laminates(154).

(i) Cross-breaking strength (BS 2782 : method 304E)

The cross-breaking or flexural strength test is carried out at a temperature of 23 ± 5°C. The flexural strength is the maximum load sustained by the specimen when subjected to a bending force and it is calculated by means of the following formula.

$$S_F = 1.5 \times 10^6 \frac{F_L \, l}{B \, d^2} \qquad (8.2)$$

where:

S_F	=	flexural strength	(Pa)
F_L	=	load at fracture	(N)
l	=	distance between supports	(mm)
B	=	width of test piece	(mm)
d	=	thickness of test piece	(mm)

The flexural strength, sometimes called the modulus of rupture(155), gives an indication of the elastic characteristics of the material. The test is simple to apply and serves the purpose of checking the consistency of material against a specification value.

(ii) Insulation resistance (BS 2782 : method 204C)

The insulation resistance between two electrodes that are in contact with, or embedded in a specimen, is the ratio of the voltage applied to the electrodes to the total current between them.

$$R_i = \frac{e}{I} \qquad (8.3)$$

where:

R_i = insulation resistance (ohms)

e = potential difference (volts)

I = direct current (amps)

The insulation resistance is measured one minute after a potential difference of 500 ± 10 V has been applied between the electrodes. The test is carried out in an atmosphere of not more than 75% relative humidity and at an ambient temperature of 15-35°C.

Insulation resistance is of great importance in determining the suitability of a material as an electrical insulator.

(iii) Water absorption (BS 2782 : method 502F)

The water absorption of a material is determined by immersing a test sample in distilled water maintained at a temperature of 23 ± 0.5°C. The duration of the test is 24 ± 1 hours. The difference in weights before and after immersion is the amount of water absorbed by the specimen, and it is usually expressed in mg.

For thick specimens, the amount of water absorbed over the immersion period of 24 hours is probably a relatively small proportion of the saturation quantity, as equilibrium may take several months to be reached(31, 118). The test is thus a measure not of total absorption but of its rate.

It should be emphasised that for this test in particular, conditioning the samples prior to exposure is very important as failure to do so may lead to significant errors in the interpretation of the results(156).

8.10.3 Specimens

Since by its very nature a laminated material is anisotropic, the test pieces are usually obtained by cutting the laminate in the lengthwise and crosswise directions. (Lengthwise means the machine direction of the paper from which the laminate is made; crosswise is perpendicular to the lengthwise direction). In this way a more representative value of the property under test may be obtained.

In this work the test specimens for the physical properties described above were obtained in accordance with the cutting diagram shown in figure 8.13. For the laminates measuring 40.6 x 40.6 cm (S4 and M4), trimming of the edges was kept to a minimum so that the dimensions of samples for flexural strength tests could be accommodated.

As it can be seen from figure 8.13 each set of test pieces was designed to provide property information in a specific area of the laminate. The actual distance between the centre set and the ones at each edge is smaller than shown in the diagram, when allowance is made for the thickness of the saw blade (3 mm) used for cutting the samples.

8.10.4 Other tests

Several other tests were also carried out to enable a more detailed comparison of the physical properties of the two sets of laminates to be made. These tests included the following:

(i) determination of acetone-soluble matter (BS 2782 : part 4, method 451 A, 1978).

(ii) determination of free phenols (BS 2782 : part 4, method 451 E, 1978).

(iii) determination of formaldehyde (BS 2782 : part 4, method 451 G, 1978).

(iv) determination of pH of water extract (BS 2782 : part 4, method 451 K, 1978).

(v) determination of density (BS 2782 : part 6, method 620 A, 1980).

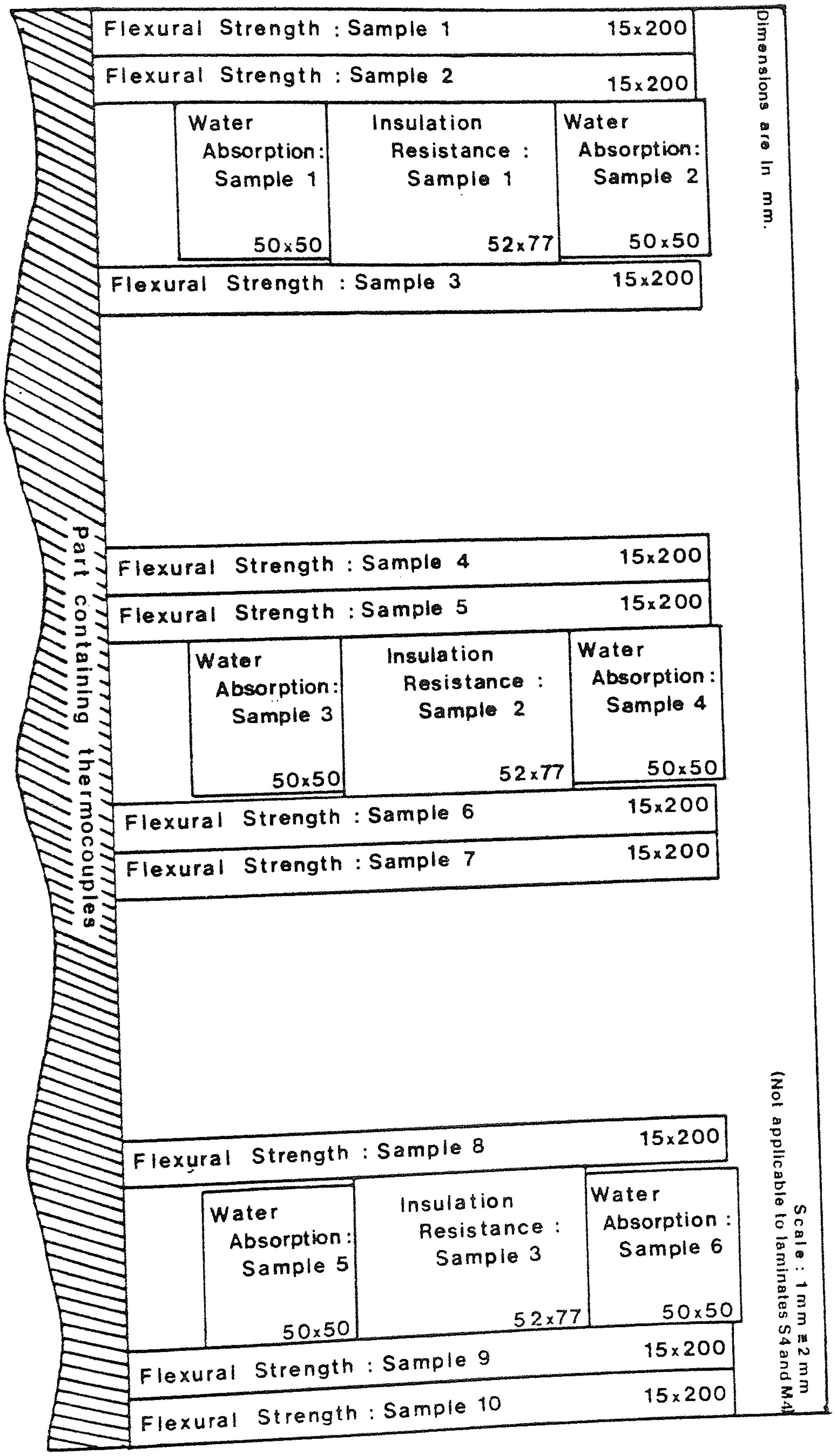


Figure 8.13 Cutting lay-out of test pieces for the physical property evaluation tests.

8.11 Results and discussion

8.11.1 Temperature histories

Figures 8.14 to 8.16 summarise in graphical form the temperature histories determined during the lamination runs on the steam-heated press. Detailed tabulation of the experimental results may be found in appendix A4.

Figures 8.14(a), (b) show the temperature distribution of a typical lay-up (S2) pressed under standard cure conditions, and which had a final thickness of 25.4 mm. A maximum temperature difference between outer (T_1) and centre (T_3) layers of 89°C was recorded 6 minutes after the lay-up insertion in the press - figure 8.14(a). The temperature of T_3 peaked at 186°C after 60 minutes of heating, a rise of 36°C above the cure temperature. The maximum temperature of 186°C is higher than the equivalent peak temperature of 171.5°C reached by the 25.5 mm thick laminate which was made under similar conditions on the electric press (see also figure 8.7). This is probably due to the different lay-up volume : lay-up surface area ratios (V_L/A_L). This ratio was calculated as 0.91 cm and 1.14 cm for the electrically- and steam-heated laminates respectively. The smaller V_L/A_L value indicates that the heat generated by the exothermic crosslinking reaction (volume effect) will dissipate relatively faster towards the outer prepregs and the environment by conduction (surface effect) and by convection as a result of which a lower peak temperature is obtained.

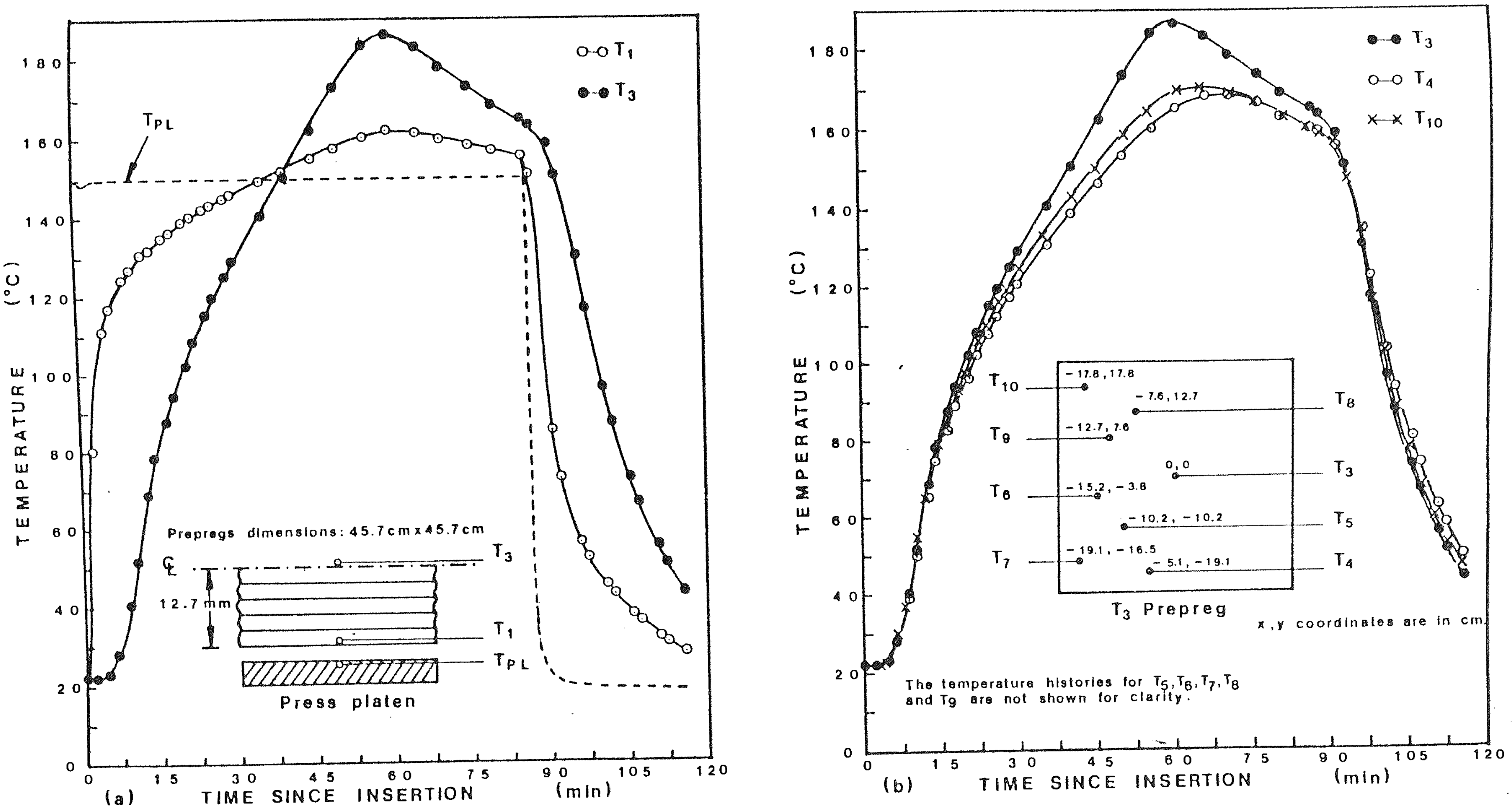


Figure 8.14 Temperature histories of a typical lay-up (S2) during lamination on a steam-heated press. (a) z-direction; (b) x,y-directions. (Insertion time is 31 s)

Figure 8.14(b) shows the temperature variation in three locations with different x, y coordinates in the T_3 prepreg. Since the configuration of the steam passages was known (figure 8.12), significant temperature variations were only expected to occur in the y-direction. These temperature differences are relatively small in the early part of the heating period - maximum of 6°C between T_3 and T_4 after 20 minutes - , becoming significant in the latter stages, reaching a maximum of 23°C after 55 minutes of heating.

Although the area directly heated by steam was estimated at 32% of the total press platen area, the temperature variation between T_3 and thermocouples T_5, T_6, T_8, T_9 is relatively small throughout the cure cycle. Therefore, the observed temperature variation as shown in figure 8.14(b) is probably due to heat losses to the environment by convection (edge effects) which results in T_4, T_7 and T_{10} exhibiting lower temperatures. Another possible factor affecting temperatures near the edges is that higher resin flow is experienced at these locations resulting in a relatively low exothermic heat being generated since the resin content is reduced.

In figure 8.15(a), (b) the temperature histories of a typical lay-up (M2) which was pressed under a modified cure cycle is presented. The temperature variation in the z - (thickness) direction between T_1 and T_3 prepregs is shown in 8.15(a). The following may be of interest:

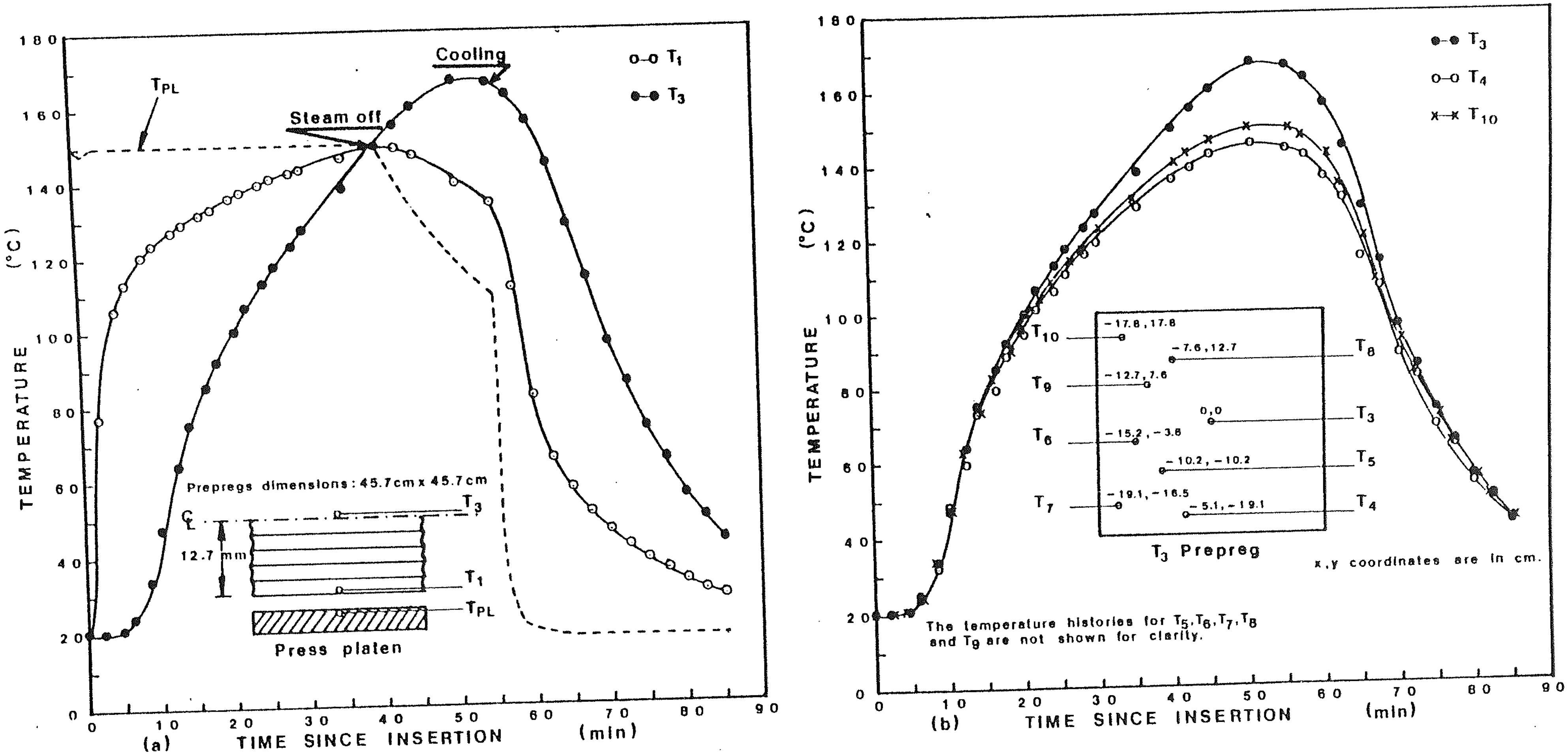


Figure 8.15 Temperature histories of a typical lay-up (M2) during lamination on a steam-heated press. (a) z-direction; (b) x,y-directions. (Insertion time = 31 s).

(i) The difference in temperature between centre and outer prepregs during the 'normal' heating (first 40 minutes) and cooling periods (55-85 minutes) is similar to lay-ups cured under standard conditions;

(ii) during the 'transition' period in which the steam is turned off (40-55 minutes) cooling of the press platen is almost linear with a mean cooling rate of about $3^{\circ}C\ min^{-1}$. For the T_1 prepreg the difference between the cooling and exothermic heat effects is relatively small, so that T_1 is being cooled at a lower rate; and

(iii) the maximum temperature of $167^{\circ}C$ reached by the centre prepreg respresents a rise of $17^{\circ}C$ above the cure temperature which is about half the temperature rise experienced by the laminates cured under standard conditions (figure 8.14).

The temperature histories in the x, y-directions are shown in figure 8.15(b). A maximum temperature difference between T_3 and T_4 of $23^{\circ}C$ was recorded 54 minutes after lay-up insertion. As with the previous runs, the thermocouples nearer the edges of the lay-up exhibited the lowest temperatures in the T_3 prepreg, with T_4 and T_7 not reaching the cure temperature. Although the temperature histories in the other prepregs were not monitored, from the work on the electric press it may be reasonable to assume that similar temperature variations can be expected.

The temperature profiles in the x, y-directions for the smaller laminates S4 and M4 are presented in figure 8.16(a) and (b). The purpose of producing these laminates was mainly to investigate whether an improvement in the temperature characteristics could be brought about. By using smaller lay-ups the area of the platen with the larger heat losses, that is the edges, estimated to be approximately 400 cm^2 could be 'excluded' from the cure process.

From the temperature histories in figures 8.16 it can be seen that some improvement was achieved during the cooling period where the temperature variation in the x, y-directions is almost negligible. For the rest of the cure cycle the temperature differences in the T_3 prepreg are relatively large. This may be at least in part the result of keeping the thermocouples' x, y-coordinates and their position relative to the steam passages unchanged, so that a comparison with the profiles of the other runs could be made. This meant however, that the locations of T_4, T_7 and T_{10} in figure 8.16 was nearer the edges of the lay-up relative to the other lay-ups.

Another factor that may have influenced the temperature variation in both S4 and M4 laminates was that,by using smaller laminates an additional area of 400 cm^2/platen was exposed to ambient conditions and therefore to larger heat losses by natural convection.

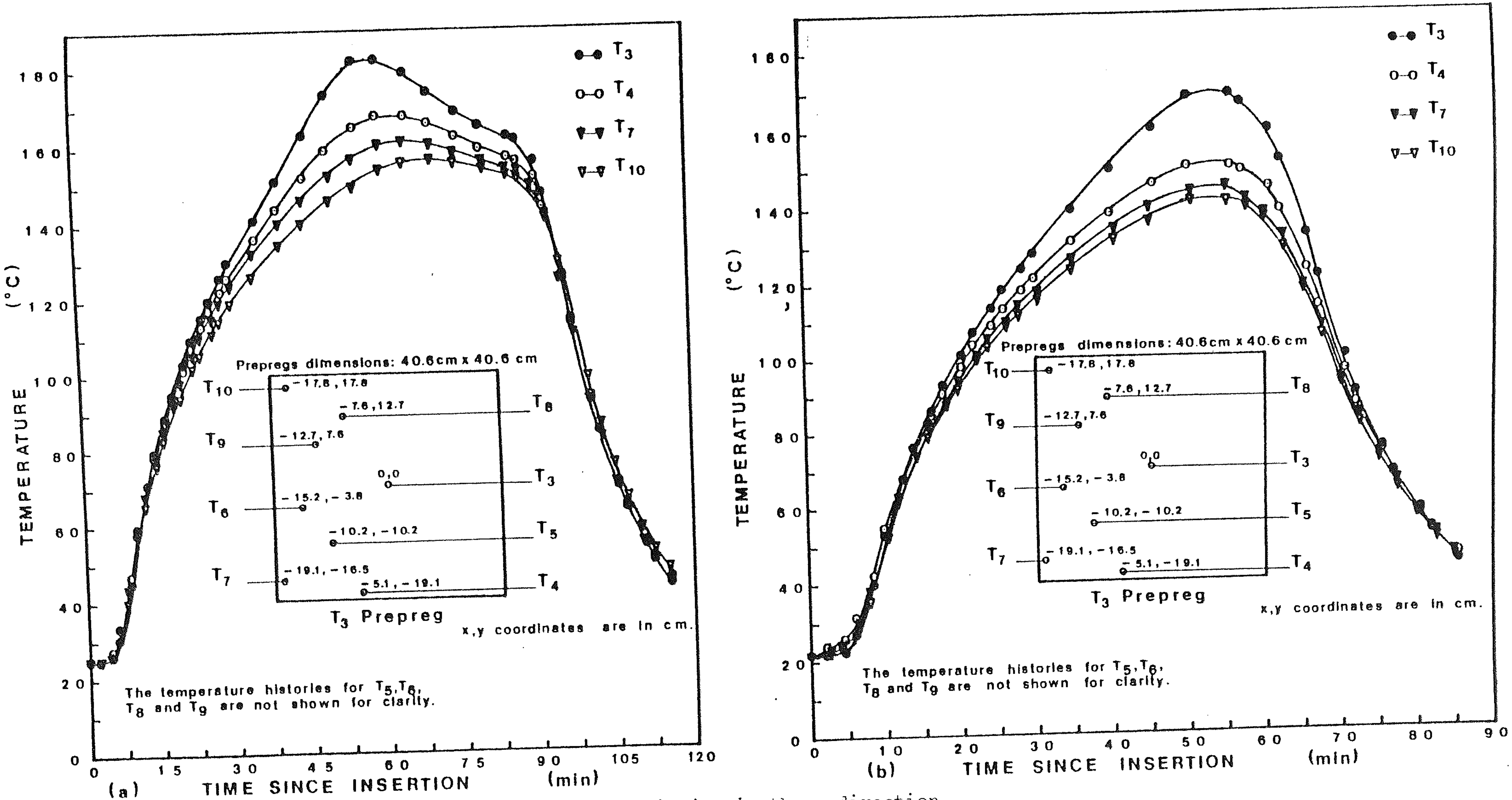


Figure 8.16 Temperature variation in the z-direction. (a) cured under standard conditions (S4); (b) cured under modified conditions (M4).

The effects of the V_L/A_L ratio to the rate of heat dissipation are expected to be similar with the larger laminates since its numerical value of 1.13 cm is about the same.

A summary of some of the thermal characteristics of the various lay-ups observed during the lamination process is presented in table 8.3.

8.11.2 Properties

8.11.2.1 Characteristics of prepregs

Table 8.4 shows the percent volatile and resin content of the prepregs used in the production of the experimental laminates; also shown is the percent moisture content of the untreated kraft paper which was determined according to procedures discussed previously.

Although both volatile and resin contents were within the specification range for paper-phenolic laminates, it can be seen from table 8.4 that for the laminates M1 to M4 the volatile content is consistently higher than that of the laminates S1 to S4. This situation was quite accidental but, it has been argued that higher volatile contents could affect the dielectric properties of the laminates(1). In general, a reduction in the electrical properties can be expected with increasing volatile content because of the higher dielectric constants which the solvent(s) and moisture - the main constituents - possess.

LAY-UPS	SIZE (cm x cm)	PEAK TEMPERATURE IN T_3 PREPREG. (^{o}C)	MAXIMUM TEMPERATURE DIFFERENCE RECORDED DURING THE HEATING PERIOD		(a) V_L/A_L (cm)
			z-direction (^{o}C)	x,y-directions in T_3 prepreg. (^{o}C)	
S2	45.7 x 45.7	186 (60)	89 (6)	23 (55)	1.14
M2	45.7 x 45.7	167 (54)	89 (6)	23 (54)	1.14
S4	40.6 x 40.6	182.5 (60)	82 (6)	32.5 (55)	1.13
M4	40.6 x 40.6	169 (55)	86 (6)	28 (55)	1.13
Electrically treated	25 x 25	171.5 (66)	92 (8)	23 (60)	0.91

(a) Volume/surface area. This ratio affects the rate of heat dissipation.

Table 8.3 Summary of temperature characteristics of lay-ups with a nominal cured thickness of 25.4 mm.
(Values in brackets indicate the corresponding times over which the observations were made).

LAY-UP	PAPER MOISTURE CONTENT[a] %	PREPREGS VOLATILE CONTENT[b] %	PREPREGS RESIN CONTENT[c] %
S1	4.56	2.55	52.20
S2	4.41	3.06	52.70
S3	4.35	3.18	52.09
S4	4.67	2.72	52.25
M1	4.76	3.55	50.94
M2	4.70	3.74	51.17
M3	5.02	3.47	49.88
M4	4.93	3.86	52.57

[a] Mean value of five measurements.

[b] Mean value of ten measurements.

[c] Mean value of five measurements.

Table 8.4 Lay-up characteristics prior to lamination.

The paper moisture content varied in the range 4.68 ± 0.34% which is not unusual. A variation of 4 ± 3% was found throughout a number of rolls of kraft paper(142); such extreme distribution of moisture was not observed in any of the experiments in this work.

8.11.2.2 Flexural strength

The flexural strength results are shown in table 8.5. The values of all the samples tested are at least 50% higher than the required specification value of 85 MPa. The modified cure cycle seems to have produced no deterioration (or improvement) in the flexural strength results of the samples tested.

In general, the results of the specimens M1 - M4 are relatively more consistent when compared to the specimens S1 - S4. Uniformity in any physical property is a desirable characteristic, provided that the specifications are met or even exceeded. Table 8.7 provides basic statistical data for the flexural strength (and water absorption) measurements. It can be seen that variation in the results occurs between the different laminates and also between the different samples within each laminate. For S3 in particular, the standard deviation is very large.

The method for carrying out flexural strength tests (BS 2782 : 304E) has been followed closely, and any errors in the measurements are expected to affect all the

SAMPLE[a]	FLEXURAL STRENGTH OF EXPERIMENTAL LAMINATES[b] (MPa)							
	S1	S2	S3	S4	M1	M2	M3	M4
1	188	171	171	161	189	179	180	163
2	190	178	131	167	172	183	185	184
3	184	173	153	162	178	171	178	163
4	180	180	164	165	172	176	181	171
5	182	180	158	157	169	184	177	177
6	182	172	159	146	185	181	183	173
7	183	183	161	160	169	173	168	166
8	168	183	176	143	189	174	170	161
9	182	176	185	161	182	175	189	179
10	188	159	181	153	190	178	189	163

[a] See also Figure 8.13.

[b] Minimum specified value is 85 MPa (BS 5102 : 1974).

Table 8.5 Results of flexural (cross-breaking) strength tests.

results in a similar fashion. Since absolute values are of secondary importance when comparing the two sets of laminates (series S and M), other factors that may have influenced the results will be considered.

One of the main factors that could have a significant contribution to the flexural strength values is the moisture content of the prepregs(1, 157, 158). The proportion of moisture present in the volatile content of the treated paper was shown to affect the mechanical properties of the laminates(157); flexural and tensile strength values were found to decrease from 4 to 6% for each unit change in the percent moisture content.

During the pressing stage, moisture (and other volatiles) is produced as a direct consequence of the crosslinking reactions which are temperature dependent (Chapter 4). From the temperature profiles obtained (section 8.11.1) it was found that the various lay-ups experienced different thermal histories in both the z- and x, y-directions. (This variation in temperature was observed to occur not only between prepreg layers, but also between individual laminates in each series, although to a much smaller degree. This latter variation was mainly due to small differences in the laminating conditions, for example in the room temperature, and insertion time). Since little of the moisture escapes during the laminating stage(1), it may be reasonable to assume that the moisture distribution (profiles) would also vary.

The observed differences in the flexural strength could be explained therefore, at least in part, in terms of the moisture distribution.

8.11.2.3 Water absorption

The results of the water absorption tests are presented in table 8.6, with statistical data provided in table 8.7.

The results show clearly that the water absorption values of laminates S1 - S4 are significantly higher than the values of M1 - M4, the difference in some samples being of the order of 200% or more. Although the mean values of the S-series specimens are below the specification of 219 mg, some samples have exceeded this value, whilst others are very close to it.

As with the flexural strength tests, the results of the M-series specimens are generally more uniform with smaller deviations from the means. Laminates S4 and M4 show the largest spread in the water absorption figures in their respective series S and M.

A limited number of experiments were carried out with the main purpose of investigating the moisture content of specimens as a function of time. The specimens from previous water absorption tests were used. The following test procedure was adopted.

(i) Each specimen was weighed and then dried at 50 ± 1°C

SAMPLE[a]	WATER ABSORPTION OF EXPERIMENTAL LAMINATES[b] (mg)							
	S1	S2	S3	S4	M1	M2	M3	M4
1	180	195	211	163	84	79	81	97
2	173	220	195	210	88	78	77	105
3	175	209	198	134	87	86	85	84
4	179	182	180	202	93	84	83	105
5	184	215	192	139	88	84	79	100
6	164	233	186	212	88	81	81	113

[a] See also Figure 8.13

[b] Maximum specified value is 219 mg for 25 mm thick test pieces (BS 5102 : 1974)

Table 8.6 Results of water absorption tests.

(Samples' thicknesses were in the range of 25.44 ± 0.40 mm. (BS 5102 permits tolerance in the range ±0.85 mm for 25.0 mm thick paper-phenolic laminates)).

PROPERTY	LAMINATE	BASIC STATISTICS			
		MEAN	STANDARD DEVIATION	MINIMUM VALUE	MAXIMUM VALUE
FLEXURAL STRENGTH (MPa)	S1	182.7	6.11	168	190
	S2	175.5	7.23	159	183
	S3	163.9	15.65	131	185
	S4	157.5	7.89	143	167
	M1	179.5	8.58	169	190
	M2	177.4	4.35	171	184
	M3	180.0	7.10	168	189
	M4	170.0	8.03	161	184
WATER ABSORPTION (mg)	S1	175.8	6.97	164	184
	S2	209.0	18.21	182	233
	S3	193.7	10.67	180	211
	S4	176.7	35.85	134	212
	M1	88.0	2.89	84	93
	M2	82.0	3.16	78	86
	M3	81.0	2.83	77	85
	M4	100.7	9.81	84	113

Table 8.7 Statistical data derived from flexural strength and water absorption tests.

under vacuum (660 mbar) until the moisture content of two successive weighings was 5 mg or less - this figure was arbitrarily chosen;

(ii) the dried specimen was placed in a dessicator for 24 hours, after which its dry weight W_d was determined; and

(iii) the specimen was then immersed in a constant temperature bath (23 ± 0.5°C) containing distilled water and its weight W was recorded as a function of time.

The results of this investigation are shown in tables 8.8 and 8.9. The percent weight change (moisture content) $\% M_s = \frac{(W_s - W_d)}{W_d} \times 100$ is plotted versus $(\text{time})^{0.5}$, as illustrated in figure 8.17; also shown on the same plot is the weight change $\Delta W = W_s - W_d$ (mg). Presenting the data in terms of percentage weight change could sometimes lead to misleading conclusions. This is because for a given weight of water absorbed, the percentage change of weight depends upon the density of the material; the heavier the material the less is the apparent absorption. In this work, it was found that specimens M1 - M4 exhibited higher densities although the difference in the density values was not significant (less than 2% maximum).

Since the tests were carried out over a relatively short period, figure 8.17 represents 'rates' of water absorption rather than of total water content. It is clear however,

TIME		% WEIGHT CHANGE$^{(a)}$, M_s x 10^2			
(MIN)	(MIN)$^{0.5}$	S1$^{(b)}$ (6)	S2 (4)	M2 (3)	M3 (5)
3	1.73	2.79	3.62	0.98	1.10
5	2.24	3.58	4.19	1.29	1.37
10	3.16	4.48	5.37	1.64	1.57
20	4.47	5.63	6.63	2.06	2.02
30	5.48	6.86	7.41	2.13	2.36
40	6.33	6.54	7.89	2.47	2.34
50	7.07	7.25	8.73	2.73	2.60
60	7.75	7.69	8.99	2.75	2.87
70	8.37	7.69	9.22	2.81	2.83
80	8.94	8.81	10.76	3.34	3.26
90	9.49	9.11	10.97	3.82	3.39
100	10.00	9.17	10.32	3.28	3.47
110	10.49	9.70	11.11	3.79	3.66
120	10.95	9.65	11.20	3.64	3.72
130	11.40	9.68	11.78	3.85	3.80
140	11.83	9.93	11.69	3.85	3.88
150	12.25	10.03	12.05	4.16	3.80
160	12.65	10.16	11.83	4.18	3.85
170	13.04	10.28	12.46	4.30	3.95
180	13.42	10.64	12.51	4.23	4.17
190	13.78	10.68	12.60	4.35	4.10

$$^{(a)}\% \ M_s = \frac{\text{(Weight of specimen - weight of dry specimen)}}{\text{Weight of dry specimen}} \times 100$$

(b) Numbers in brackets refer to the test specimens

Table 8.8 Percent weight change due to water absorption.

TIME		WEIGHT CHANGE$^{(a)}$, ΔW (mg)			
(MIN)	(MIN)$^{0.5}$	S1$^{(b)}$ (6)	S2 (4)	M2 (3)	M3 (5)
3	1.73	24.0	31.3	8.6	9.7
5	2.24	30.8	36.3	11.3	12.1
10	3.16	38.6	46.5	14.4	13.8
20	4.47	48.5	57.4	18.1	17.8
30	5.48	59.1	64.2	18.7	20.8
40	6.33	56.3	68.3	21.7	20.6
50	7.07	62.4	75.6	24.0	22.9
60	7.75	66.2	77.8	24.2	25.3
70	8.37	66.2	79.8	24.7	24.9
80	8.94	75.9	93.2	29.4	28.7
90	9.49	78.5	95.0	33.6	29.9
100	10.00	79.0	89.4	28.8	30.6
110	10.49	83.5	96.2	33.3	32.3
120	10.95	83.1	97.0	32.0	32.8
130	11.40	83.4	102.0	33.8	33.5
140	11.83	85.5	101.2	33.8	34.2
150	12.25	86.4	104.3	36.6	33.5
160	12.65	87.5	102.4	36.7	33.9
170	13.04	88.5	107.9	37.8	34.8
180	13.42	91.6	108.3	37.2	36.8
190	13.78	92.0	109.1	38.2	36.1

(a) ΔW = weight of specimen - weight of dry specimen (mg).

(b) Numbers in brackets refer to the test specimens.

Table 8.9 Weight change (ΔW) as a function of time.

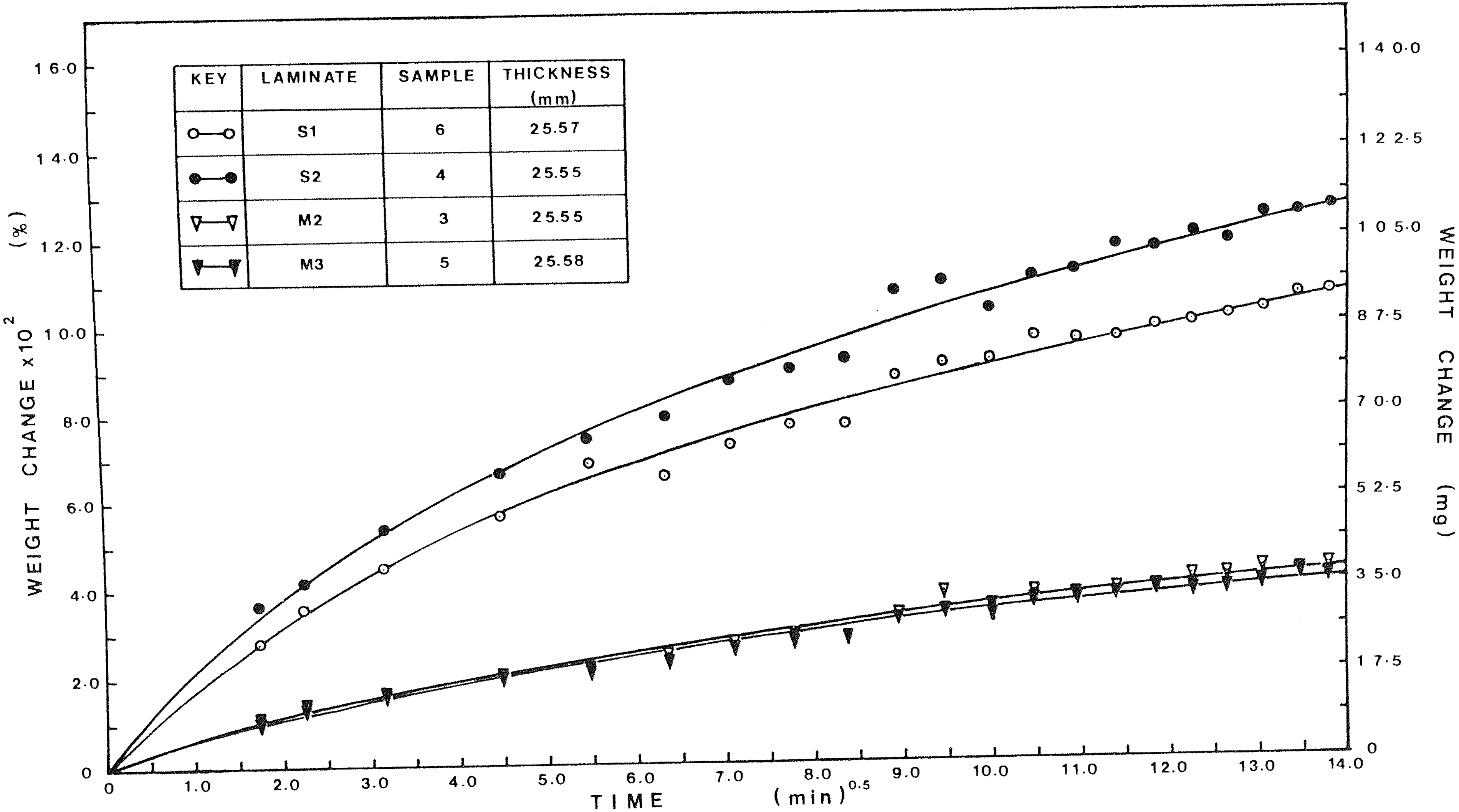


Figure 8.17 Weight change as a function of time. (distilled water at 23 ± 0.5 °C).

that for the specimens being tested the rate of water absorption for S1 and S2 is about 2 to 3 times higher than that of M2 and M3.

The water absorption process for all samples tested is said to be 'Fickian', even though only a very small part is represented by figure 8.17; other thermosetting resin composites have also shown similar behaviour(156, 159, 160).

When a composite material is immersed in a liquid or exposed to an environment of constant temperature, the moisture content of the material during absorption (or desorption) is given by:(160)

$$M_s = J \; (M_m - M_i) + M_i \qquad (8.4)$$

where:

M_s = moisture content (%)
M_i = initial moisture content (%)
M_m = maximum (saturation) moisture content (%)
J = a time-dependent parameter

$$\simeq 1 - \exp\left(- 7.3 \; \left(\frac{Dt}{d^2}\right)^{0.75} \right) \qquad (8.5)$$

where:

D = mass diffusivity ($mm^2 \; s^{-1}$)
d = specimen thickness (mm)

For the moisture content versus time tests, $M_i \simeq 0$ and therefore

$$M_s = J \; M_m \qquad (8.6)$$

For the water absorption tests M_i is not known. However, it is likely that $M_m >> M_i$ and therefore for these tests and for large t, the initial moisture content is unlikely to influence the diffusion significantly. For small values of t, M_i contribution will be important. It should be emphasised that in applying equation 8.4 it is assumed that the initial moisture distribution inside the specimen is uniform. Conditioning test pieces of large thickness is not expected to bring about uniform moisture content in the specimen over a short period of 24 hours - the time of conditioning. Since, for reasons discussed earlier, the samples tested, in particular S1 - S4, may exhibit significant moisture content variation, this could have influenced the water absorption results.

An increased affinity for water as shown by the laminates of S-series may be due to the fact that these experienced higher temperatures and for longer periods of time during lamination, which may have rendered the cellulose 'dry' and more susceptible to increased water absorption. It is known that the action of high temperatures produces profound changes in cellulose(161). The extent of these changes depends not only on the temperature of heating but also on its duration, the degree of polymerisation (DP) of cellulose and the composition of the surrounding medium, increasing considerably in the presence of moisture and air. When cellulose is heated in the temperature range of 120° - 240°C, at first depolymerisation occurs, and then at the higher temperatures dehydration and alteration of the repeating unit of macromolecullar cellulose chain takes place(161).

The water absorption figures for laminates M1 - M4 are 'unusually' low, and it is comparable to values shown by specimens of 10-12 mm thickness. It is possible that, as a result of immersion in water, leaching out of low molecular weight components, initially present in the resin, could have taken place. Glass-reinforced polyester resin composites (1 mm thick) were shown to experience loss in weight - up to 0.53% at 20°C - after immersion in water for 15 days(162). However, leaching out effects arising from possible hydrolysis of the resin are not expected after only 24 hours immersion and for samples of such thickness. This was confirmed by further experimental evidence presented in Appendix A4.

8.11.2.4 Insulation resistance

The results of the insulation resistance measurements are given in table 8.10. All specimens tested show values which are at least 3.5 times higher than the specification value of 0.1×10^{10} ohms.

It is interesting to note that for each laminate the insulation resistance for the central specimen (sample 2 in table 8.10 and figure 8.13) is consistently higher

SAMPLE[a]	INSULATION RESISTANCE OF EXPERIMENTAL LAMINATES (b) (10^{10} ohms)							
	S1	S2	S3	S4	M1	M2	M3	M4
1	1.72	1.07	1.46	0.47	0.86	0.89	1.38	1.04
2	2.05	1.29	1.73	0.78	1.07	1.17	1.75	1.31
3	1.42	0.97	1.36	0.53	0.82	0.98	1.63	0.99

[a] See also Figure 8.13.

[b] Minimum specified value is 0.1 x 10^{10} ohms (BS 5102 : 1974).

<u>Table 8.10</u> Results of insulation resistance tests.

relative to that of the other two samples 1 and 3. Although the number of samples tested was small, it does tend to indicate that for this test the position of the samples on the original laminate may be significant.

It is known that electrical conduction in plastics is an ionic process(118, 163) which depends on the number of ions formed during cure. However, conduction in a polymer is also dependent on ion mobility(164). Mobility is proportional to the reciprocal of the system viscosity. As the crosslinking advances, the viscosity increases and ion mobility decreases.

Since the insulation resistance tests were carried out after the test pieces have been immersed in distilled water for 24 hours, it would be expected that specimens S1 - S4 would have a higher moisture content than the other specimens. The water would cause additional ionisation, or it would merely increase the mobility of the ions already present. The insulation resistance of these samples should therefore be much lower relative to that of M1 - M4. This has not been observed. Higher degree of crosslinking (section 8.11.3) may have offset the effect of absorbed moisture on the electrical resistance.

It should be remembered that the insulation resistance is measured over a small portion of the sample - the electrodes being placed approximately 25 ± 1 mm apart and normal to the plane of the specimen - and since the moisture content is expected to be non-uniform (particularly for S1 - S4), this could account for the variation in the results.

8.11.2.5 Permittivity and power-factor

(Relative) permittivity or dielectric constant and power factor tests are of particular importance in laminates for electrical applications. They are included in the basic requirements specified by BS 5102 : 1974 and the test procedure is given in considerable detail in BS 2067 : 1953.

The permittivity of a material is defined as the ratio of the capacitance of a condenser containing the material relative to the capacitance of an equivalent vacuum (or air for most practical purposes). The power-factor ($\tan \delta$) is usually expressed as:

$$\tan \delta = \frac{\kappa''}{\kappa'} \tag{8.6}$$

where:

δ = phase displacement angle (rad)

κ'' = loss factor or loss index, and is a measure of the A.c. conductance of the medium

κ' = permittivity or dielectric constant.

Permittivity and power-factor depend upon the nature of the dielectric medium and upon the frequency of the applied electromagnetic field. For phenolic resins the power factor (and to a lesser degree the permittivity) is also temperature dependent(118).

Values of permittivity may give information regarding the water content of a plastic material(117), for water has a high dielectric constant of 80 (cf. 2-6 for most plastics). It follows that the absorption of water by such materials causes an increase in permittivity. Measurements of permittivity may also provide an indication of the manner in which the water is distributed throughout the material, since water in the form of spherical droplets has an effect different from that produced in the form of adsorbed films or long filaments(165).

Permittivity and power-factor tests were carried out for all the laminates in accordance with the method in BS 2067 :1953. The test pieces, in the form of discs 53 ± 1 mm in diameter, were obtained from freshly cut rectangular pieces by utilising the part of the original laminate which contained the thermocouples. The rectangles were cut from a thermocouple-free area, identical in all laminates. Three layers (parallel to the laminae) of equal thickness were cut from each rectangular piece. From these, the discs were machined out by reducing the thickness on both sides of each layer to a suitable value (1.81 ± 0.02 mm). The reduction of both sides of each layer was necessary so that comparable test results could be possible. Figure 8.18 is a schematic representation of the discs used in the permittivity and power factor tests.

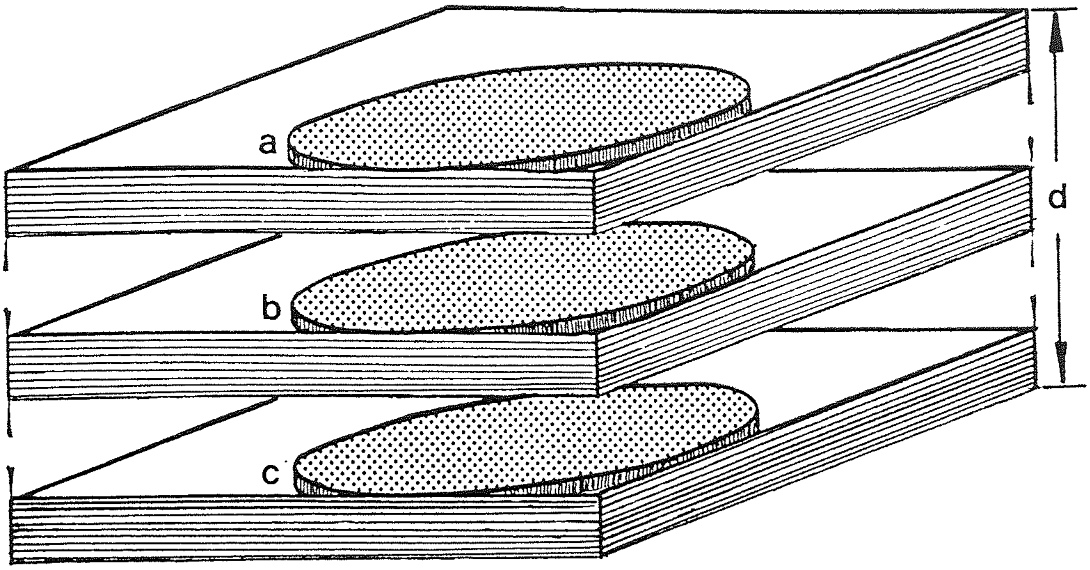
The results obtained (table 8.11) indicate that:

(i) For each series, the middle discs have consistently higher values than the other two discs, for both power-factor and permittivity;

(ii) for the S-series specimens the permittivity values are significantly higher than those based on the M-series; and

(iii) no significant variation in the power factor was found between each set of results.

The higher permittivity results for S1 - S4 could be indicative of higher moisture content. The explanation for this may be given in terms of the z-direction profiles determined during the lamination process. Higher temperatures and longer heating times have been experienced by these laminates. This is particularly true for the prepregs in and around the central plane of each lay-up (both series), and it is reflected in the permittivity results. In addition to the increased moisture with increasing temperature, the moisture distribution would be non-uniform as a consequence, at least to a large extent, of the x, y- temperature distributions.



a — upper disc
b — middle disc
c — lower disc
— thickness = 1.81 ± 0.02 mm

d — nominal thickness = 25.4 mm

Figure 8.18 Location of test discs for permittivity and power-factor.

TEST / LAMINATE	POWER-FACTOR[a] ($\tan \delta \times 10^2$)			PERMITTIVITY[b] (κ')		
	UPPER DISC	MIDDLE DISC	LOWER DISC	UPPER DISC	MIDDLE DISC	LOWER DISC
S1	3.47	3.56	3.50	5.23	5.36	5.29
S2	3.51	3.63	3.56	5.35	5.50	5.26
S3	3.48	3.64	3.53	5.26	5.40	5.28
S4	3.56	3.64	3.49	5.40	5.55	5.34
M1	3.50	3.54	3.49	4.49	4.97	4.56
M2	3.43	3.53	3.46	4.50	4.63	4.55
M3	3.52	3.56	3.45	4.63	4.70	4.67
M4	3.32	3.39	3.36	4.79	4.95	4.82

[a] Maximum specified value is 4.5×10^{-2} at 1 MHz (BS 5102 : 1974)

[b] Maximum specified value is 5.70 at 1 MHz (BS 5102 : 1974)

Table 8.11 Power-factors and relative permittivities at 1 MHz and 21°C.

Taylor(95) measured in situ the permittivity of 2.16 mm thick phenolic-paper laminates in the temperature range of 135° - 160°C, frequency of 1MHz, and cure times of up to 50 minutes. His results showed that permittivity increased with increasing temperature. Thermal degradation was believed to be the cause for the increase in permittivity at 160°C from 5.42 to 5.56 after 10 and 40 minutes cure respectively.

Further evidence for the increase in permittivity with increase in moisture content was shown when comparing the results of specimens dried for 72 hours at 50°C under vacuum and after being immersed in water for 24 hours. The test pieces were taken from specimens already tested; testing of dry samples was preceeded by cooling in a dessicator for a minimum of 2 hours.

The results are presented in table 8.12. It is clear that after immersion in water both power-factor and permittivity showed an increase in comparison to the values of the specimens in the 'dry state'. The increase in permittivity for S1 - S4 is about three times that of M1 - M4.

It should be emphasized that different results would have been obtained at different frequencies of the applied electromagnetic field used in these tests but the appropriate British Standard test was used during the research project. It is known that the effect of water

LAMINATE	WATER ABSORBED$^{(a)}$ (mg)	POWER-FACTOR (tan δ x 10^2)$^{(b)}$			PERMITTIVITY (κ')$^{(b)}$		
		DRIED	AFTER IMMERSION IN WATER	PERCENT INCREASE	DRIED	AFTER IMMERSION IN WATER	PERCENT INCREASE
S1	49.6	3.12	3.45	10.6	4.32	5.63	30.3
S2	48.5	3.14	3.37	7.3	4.29	5.60	30.5
S3	56.4	3.13	3.74	18.4	4.26	5.61	31.7
S4	54.9	3.06	3.55	16.0	4.37	5.66	29.5
M1	32.6	2.99	3.32	11.0	4.21	4.51	7.1
M2	32.3	3.01	3.31	9.9	4.19	4.57	9.0
M3	34.1	2.99	3.32	11.0	4.22	4.52	7.1
M4	36.8	3.04	3.35	10.2	4.28	4.73	10.5

(a) After immersion in water for 24 hours, following the drying period.

(b) According to the method in BS 2067 : 1953.

Table 8.12 Power-factors and permittivities at 21°C for pre-dried specimens.

absorption on the dielectric properties of paper-phenolic laminates is more evident at frequencies below 1 MHz, and that at higher frequencies additional factors such as dipole orientation polarization of hydroxyl groups become significant(166).

8.11.3 Other tests

The results of additional tests carried out on all laminates are shown in table 8.13.

8.11.3.1 Acetone-soluble matter

The acetone-solubility test has been discussed in Appendix A1. It may be noted that in this work a sample from each laminate was reduced to powder by drilling, during which operation temperatures of up to 75°C were recorded with a thermocouple. High temperatures ($> 130^{\circ}C$) would influence the degree of cure by inducing further crosslinking.

Acetone-soluble matter (E) and relative degree of cure (D_c) were calculated according to equations A1.1 and A1.2 in Appendix A1. The results show that for laminates M1 - M4 the acetone-soluble matter is almost twice as high as that of S1 - S4. However, the (relative) degree of cure D_c remained within acceptable levels.

8.11.3.2 Free phenols and formaldehyde

As a direct consequence of lower degree of cure, the free phenols and free formaldehyde content of M1 - M4 is higher

LAMINATE	ACETONE-SOLUBLE MATTER[(a)] E (%)	(RELATIVE) DEGREE OF CURE D_c = 100-E (%)	FREE PHENOLS[(a)] (%)	FREE FORMALDEHYDE[(a)] (%)	pH OF WATER EXTRACT	DENSITY[(a)] AT 20°C (kg m^{-3})
S1	3.52	96.48	0.251	0.0066	7.60	1366.3
S2	3.52	96.48	0.204	0.0055	7.60	1368.8
S3	3.26	96.74	0.208	0.0063	7.40	1367.3
S4	3.57	96.43	0.208	0.0055	7.20	1359.3
M1	6.56	93.44	0.754	0.0205	7.75	1382.1
M2	6.53	93.47	0.758	0.0228	7.55	1381.6
M3	6.51	93.49	0.691	0.0211	7.60	1381.6
M4	6.61	93.39	0.667	0.0196	7.40	1376.1

[(a)] Mean of two values.

Table 8.13 Results of miscellaneous tests.

than those of S1 - S4. The evaluation of free phenols in a moulded article is of interest where the possibility of contamination of foodstuffs in contact with the article has to be considered. In such cases, the recommended maximum amount is 0.5% free phenols.

It may be possible to bring about a reduction in free phenols in the final product, if resins containing small amounts ($<$ 5%) are utilised. This however has not been investigated.

8.11.3.3 pH of water extract

The pH values of all specimens tested were found to be in the range 7.5 ± 0.3.

8.11.3.4 Density at 20°C (Immersion method)

From table 8.13 it can be seen that the density results obtained are uniform within each set of laminates, but that differences between each set do exist. Slightly lower values are shown by the smaller laminates S4 and M4 in their respective series. Any effects due to water absorption are considered to be negligible since immersion times were small (less than one minute).

The density of cellulose is 1520-1550 kg m^{-3} and that of cured phenolic resin 1270-1280 kg m^{-3}(155). The density of paper is less than that of cellulose because of the presence of air. (In this work the nominal density of kraft papers used was 550 kg m^{-3}). The density therefore of a paper laminate will be between 1270 and 1550 kg m^{-3}

and it will depend upon the resin content, decreasing linearly when the resin content of the prepregs is increased above an optimum value of 21% by weight(167).

Another factor that could affect the density of the laminates is the resin flow during the pressing stage. It has been shown(136) that the flow of resin during lamination of epoxy-based multilayer printed wiring boards (MLBs) is a complex process involving the interaction of time, temperature, pressure, resin chemorheology, and geometry. For a given resin-paper system, and with constant level of B-staging and laminating conditions, any changes in the resin flow may be a result of large temperature gradients, usually developed in thick lay-ups. As a consequence of this, higher resin flow would result in laminates of lower resin to paper ratios and hence increased density.

Although the resin flow during the experimental runs was not quantified, visual examination of the laminates after each pressing operation did not show any significant variation due to resin flowing out beyond the laminate boundaries.

8.12 Discussion and conclusions

8.12.1 Basis for a modified cure cycle

Preliminary work on the small electrically-heated press has identified that large temperature variations occurred during lamination under standard conditions, particularly for thick laminates. In addition, centre layers experienced temperatures well in excess of the specified cure temperature of 150° C.

Since the degree of cure is strongly dependent upon temperature and time, sustained large temperature differences would lead to different degrees of cure within the lay-up. Resin flow may also be affected by the temperature gradients produced, and so it may be concluded that variation in the degree of cure (and also resin flow) would result. As a direct consequence of this, 'local' property variation may also be experienced and a product of non-uniform properties will result for a given system.

The modified cycle, applied during the main phase of the experimental work, had the following main objectives:

(i) Reduction in the maximum temperature experienced by the innermost layers;

(ii) reduction in the cure time;

(iii) reduction in the temperature difference over and above the cure temperature between the inner and outer prepregs; and

(iv) improvement in x,y-directions temperature profiles.

Both (i) and (ii) were achieved by controlling the cure environment mainly through utilisation of the exothermic heat developed in the lay-ups during the pressing stage.

For (iii) the temperature differences when compared to lay-ups cured under standard conditions remained unchanged. However, through shorter cure times these differences only materialise to a large extent near the completion of the heating period and therefore were only sustained for short periods.

There was a small improvement in the x,y-direction temperature profiles during the cooling period when using smaller lay-ups (S4 and M4). Otherwise objective (iv) was not met successfully, but the use of a suitably designed enclosure, for a press, to reduce heat losses should be carefully considered. More effective use could then be made of the exotherm.

8.12.2 Improvements in the physical properties

An inherent property of the modified cycle was a reduction in the amount of water (and of other volatiles) which is evolved during cure. The consideration of moisture evolution combined with the characteristic thermal profiles, provided the central argument in the analysis of the results of the physical property tests.

The results indicated that:

(i) Water absorption of the test samples was reduced by 43-61% (based on mean values);

(ii) permittivity values were decreased by a significant amount of about 12%; and

(iii) flexural strength, insulation resistance, and power-factor remained unaltered, but exhibiting a higher degree of uniformity.

8.12.3 Production costs

For lay-ups (25.0 mm thick) cured under standard conditions the 'steaming' period, that is the time during which steam is continuously supplied to the platens, is 85 minutes. For the modified cycle this period is only 40 minutes, although the actual heating is 55 minutes duration. This represents a reduction in steam-heating consumption of almost 53%.

The overall cure times (heating + cooling) is also reduced from 115 to 85 minutes or 26%. On this basis, for a single press with a total of 10 loadings/day, production could be increased to just over 13 loadings/day. Over a year this would represent a significant increase.

8.12.4 Optimum cure conditions

Lamination of phenolic composites as a technique is governed by empirical rules which have evolved over many years by trial and error. Laminating conditions are kept as consistent as possible once they are established over a wide range of different types of laminates.

For the lamination process, time, temperature and chemo-rheological aspects are the main characteristic parameters. A comprehensive analysis of the process would require a detailed understanding of the relationships between these variables. Optimum cure conditions that would lead to products of consistent properties may then be possible.

The modified cycle proposed, is only a small step towards fulfilling these objectives. Its application to the pressing of combination of sheet thicknesses has not been examined. Preliminary work on a phenolic-fabric laminate (25.0 mm thick) based on the shorter cure cycle showed that improvements in the properties can be produced (see Appendix A4).

It is anticipated that, in the future, the lamination process will undergo a radical change. Fully automatic presses under the control of microprocessor technology would enable data based on thermal, chemical (cure kinetics) and rheological (viscosity, resin flow, gelation) behaviour to be incorporated, so that a programmed and cost-effective process can be achieved.

9. IN SITU POLYMERISATION

9.1 Introduction

In high-pressure laminating industries the treating and pressing stages are of paramount importance. Another significant stage which has received little attention in the literature is the solvent recovery and associated effluent treatment plant. In processes which employ organic solvent-based phenolic resins solvent recovery forms an integral and necessary part of the process.

However, with process efficiencies small (in the region of 50% solvent recovery), alternative approaches have been considered. Water-soluble resins are an obvious and attractive solution to the problem, and these have found wide application in decorative laminates and also in laminates for mechanical applications. Water-soluble phenolic resins are usually catalysed by sodium hydroxide and have a high methylol content and a lower average molecular weight when compared to ammonia-catalysed resols(9, 32).

Laminates incorporating water-soluble resols have inferior electrical properties compared with alcohol-based ones. Therefore, a solventless process will only provide an alternative route to laminate production if the properties of the final product can be maintained at normal specifications.

9.2 Alternative processes

Several processes (including solventless) have been studied in the past but their application has been very limited. These have mainly taken the form of introducing the resin into the sheet while it is on the paper-making machine(1) and they include the following:

(i) direct addition to the furnish;
(ii) wet-web treatment; and
(iii) treatment after partial drying.

Another approach considered was the introduction of solid resin to the substrate in powder form.

9.2.1 Direct addition to the furnish

This may be carried out in the beater or the stock chest during paper production and is sometimes known as the 'premix' method. Aniline-formaldehyde(168) and lignin resins(169, 170), as well as phenolic resins(171) have been employed. The reaction takes place in a vessel containing the beaten paper pulp and after suitable treatment the mixture of pulp and resin is made into paper which can be subsequently laminated. 'Prepregs' containing between 40-60% (W/W) resin can be made by this process.

The essential characteristics of a resin for beater addition are that it is water-insoluble and can be retained mechanically, or by chemical or colloidal attachment to the fibres. These include finely divided phenolic resins which may be added as such, or as water-dispersions, phenolic resin solutions or emulsions(1).

9.2.2 Wet-web treatment

The web may be treated after forming on the wire but before it has reached the dryer section at which point it contains large quantities of water. This necessitates the use of water-solutions or emulsions.

Papers produced by this method are fully saturated presenting some difficulties when trying to achieve uniform drying without excessive cure of the high resin content substrates.

9.2.3 Treatment after partial drying

This may be carried out by substituting an impregnating bath for the sizing tub, positioned about half-way through the dryer section. Water (or organic solvent) solutions or emulsions may be applied. The solvents however must be of low boiling point and therefore of higher costs. This method can only be applied economically to large runs of a single type.

9.2.4 The dry process

In the dry process the resin is applied to the web in powder or granular form. NH_3-catalysed resols can be utilised as solids of low meting range (40° - $60^\circ C$) fused by subsequent heating.

With the dry process the costs of the solvent recovery plant and the solvent itself are saved. However, this process is essentially a coating operation with little or no penetration of the substrate by the resin which may result in technically inferior laminates compared to the varnish-based ones.

A further drawback is that solid resins of uniform properties are difficult to produce although significant improvements have been made with continuous production of resols, and recently with the 'new' class of phenolic resins known as phenolic thermospheres (PTS) produced by suspension polymerisation(172).

9.3 In situ polymerisation

Another route which has not been considered before, or which has not been reported in the literature, is polymerisation of the phenolic resin in situ. This is in effect analoguous to a continuous resin production with the paper web acting as the supporting reaction medium. The main difference is that the reaction is not stopped at the resol stage, but it is further advanced to the recitol or B-stage.

9.3.1 Preliminary evaluation

The preliminary evaluation was in the form of experimental observations on several small (25 x 25 cm) laminates prepared at different drying and pressing conditions.

9.3.1.1 Experimental

The composition of the reactants in all experimental runs was as follows:

Phenol	- 94 g (1 mol)
aqueous formaldehyde (37% (W/W))	- 122 g (1.5 mols)
aqueous ammonia (s.g. 0.88)	- 4-5 g

Solid phenol was heated to 50° - 55°C until liquid, and maintained at that temperature. Formalin was then added and the mixture stirred for approximately 5 minutes. At this temperature, the reaction of phenol and formaldehyde is negligible.

After addition of ammonia, the mixture was quickly and carefully poured into the impregnation tray. Kraft paper samples were hand-impregnated, taking the necessary safety precautions due to the toxic nature of all reactants present in the solution.

Drying was carried out in the usual manner. Lay-ups made up of three treated samples each were pressed at 150°C and 7.33 MPa applied pressure on the laminate.

Table 9.1 summarises the experimental conditions including the corresponding observations.

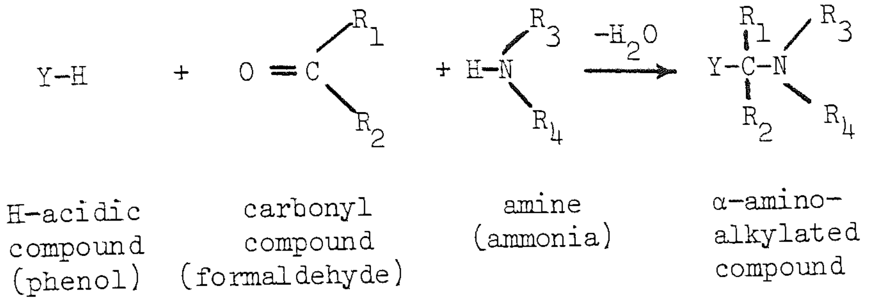
9.3.1.2 Chemical aspects

The chemistry of ammonia-catalysed resols has been briefly discussed in Chapter 3. The reaction between phenols, aldehydes and amines can be treated as aminoalkylation(32) according to the reaction sequence shown in equation (9.1).

BOARDS	DRYING CONDITIONS		CURING TIME* (min)	COMMENTS
	TEMPERATURE (°C)	TIME (min)		
A	90	10	60	Both boards showed yellow colouration with some brown patches near the edges indicating resin formation. Easily delaminated. No flow occurred.
B	90	15	60	
C	100	20	65	Yellow-orange colouration in the centre of the boards. Significant resin formation in the rest of the boards resulting in hard, clear laminated structures. No delamination. No resin flow.
D	100	30	65	

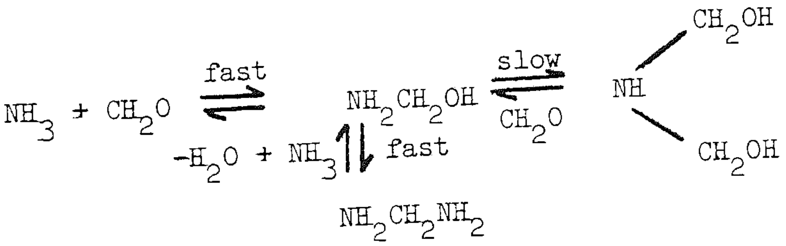
* at 150°C and 7.33 MPa

Table 9.1 Laminate production by polymerisation in situ.



(9.1)

In the presence of amines the carbonyl component is confronted with two nucleophiles. For this reason it must be determined whether formaldehyde reacts with the phenol or with the amine first. The formation of HMTA from formaldehyde and ammonia is a very fast reaction in which the formation of the bis-hydroxymethylamine (reaction 9.2) is the slowest and, therefore, rate determining step(173). (The formation of HMTA was observed in all the experimental runs). In diluted aqueous systems, the reaction stops at the stage of the α-aminoalcohols.



(9.2)

The hydrolysis of HMTA also leads to similar aminomethylated products so that HMTA may be used instead of ammonia. It may even be possible to replace the formaldehyde, or at least part of it, with HMTA and add small quantities of water.

The use of HMTA as the reagent and/or catalyst in polymerisation in situ experiments would greatly reduce the amount of water required to be evaporated during the treating process. It would also allow higher loadings at the impregnation stage since the proportion of solids in the mixture would be increased.

9.3.2 Discussion

When considering the polymerisation of phenolic resins in situ certain important points need to be given particular attention:

(i) The treating stage

This stage will assume an even greater importance than at present. Since the reaction is mainly a surface phenomenon it is analoguous to continuous production of resins as thin films and as such, small temperature variations may have an adverse effect on the curing characteristics of the resin produced. Experimental work will be necessary to establish optimum conditions and the temperature zones necessary to carry out the polymerisation. Cooling of the web at the dryer exit in order to retard further curing should not present any problems.

(ii) Residence time

The residence time in the dryer will also have to be determined experimentally. It has been shown that the initial addition and condensation reaction can be completed within 80 s at 140° - 180°C in the continuous production of resins 4 mm thick(174). Subsequent dehydration time was less than 45 s.

Heating may be accomplished by a combination of forced convection and radiation. Air recirculation would be possible without any danger of explosion limits being exceeded, since water will be the main volatile component. More efficient use of the drying medium will thus be possible. (Lower temperatures would be necessary at the dryer inlet to minimise loss of phenol through azeotropic distillation).

(iii) Impregnation

Impregnation can be accomplished in a similar manner as currently in use. The reactants and catalyst may be pre-mixed prior to the impregnation or the web can be exposed to the catalyst in a subsequent impregnation stage after it has been treated with the reactants. The use of HMTA would be the preferred catalyst and may also be used interchangeably with formaldehyde and ammonia.

9.3.3 Conclusion

This brief examination of phenolic resin polymerisation in situ cannot lead to any firm conclusions at this stage. The results show that the proposed process is, at least, chemically feasible. Further experimental work will be necessary to establish technical and economic feasibility at optimum conditions.

10. FURTHER WORK

Suggestions for further work are as follows:

(i) The modified cycle proposed for the pressing stage should be further examined so that the optimum timing for closing down the steam supply to utilise the exotherm, and opening the cooling water supply at the end of cure can be established. It is envisaged that ultimately a fully controlled and programmable cure cycle may be possible.

(ii) A thermal enclosure to insulate the press should be considered in order to minimise heat losses from both the lay-up and press platens. This should improve the x, y temperature variation particularly near the edges of the lay-up where cure temperatures are usually not attainable. Less of the final product would then be below specification and more would be useful.

(iii) The application of the modified cycle to fabric-based laminates will need further investigation. The cycle may prove to be particularly useful in lay-ups of thickness greater than 25.5 mm so that full utilisation of the large exotherms can be obtained.

(iv) With reference to the drying stage, more investigation of the potential extra costs would be required if lower temperatures in conjunction with increased air flow rates and better distribution are to be employed. The use of on-line testing may be necessary if a close and continuous monitoring of the impregnation (varnish loading) and drying parameters is to be achieved.

(v) The use of in situ polymerisation should be further studied in greater detail in order to identify major technical problems. The physical properties of laminates produced by such a process will need to be determined and production costs assessed.

With the introduction of solid resins of uniform physical properties such as phenolic thermospheres, the dry process employing highly absorbent substrates may need to be re-appraised.

APPENDIX A1

A1.1 Methods for determining degree of cure

A1.1.1 The acetone-solubility test(100)

The acetone-solubility test is a gravimetric method for the determination of the amount of matter that can be extracted by acetone, at a temperature near its boiling point (56.5°C), from a finely ground sample of a phenolic moulding. The test is used for determining the relative degree of cure of phenolic mouldings made from a given material. It has found wide application in the plastics industries and it is a standard test used to measure the degree of cure of laminated products based on phenolic resins.

The method involves the hot extraction of acetone-soluble matter from a representative sample of the material. The extraction is usually carried out in a Soxhlet-type apparatus and the duration is six hours. At the end of the extraction period the acetone is evaporated by heating the residue in an oven at a temperature of 50 ± 2°C.

A1.1.1.1 Expression of results

The amount of acetone-soluble matter (E) in the sample expressed as a percentage is given by:

$$\%E = \frac{m_1}{m_o} \times 100 \qquad (A1.1)$$

where:

m_o = mass of sample (g)

m_1 = mass of dry extract (g)

The degree of cure (D_c) also expressed as a percentage, is:

$$\% D_c = 100 - E \qquad (A1.2)$$

For a given system, the cure temperature and time are the most important factors which influence degree of cure. With samples which have been heated at different temperatures and times, the degree of cure as calculated from equation A1.2 can be expressed in graphical form. Figure A1.1 shows the type of plots that may be obtained(87).

A1.1.1.2 Discussion

The acetone-solubility test is a simple method requiring only accurate weight measurements. The main assumption is that, a 'fully' cured sample (D_c = 100%) is completely insoluble in acetone. However, when employed as a quality control test, no distinction can be made between a sample which has been cured 'fully' and an 'overcured' one. The acetone soluble matter would be zero, indicating a degree of cure of one hundred per cent for both samples.

In order to eliminate errors resulting from overcuring, it may be possible to normalise all samples using as a basis the total extractables of an uncured sample.

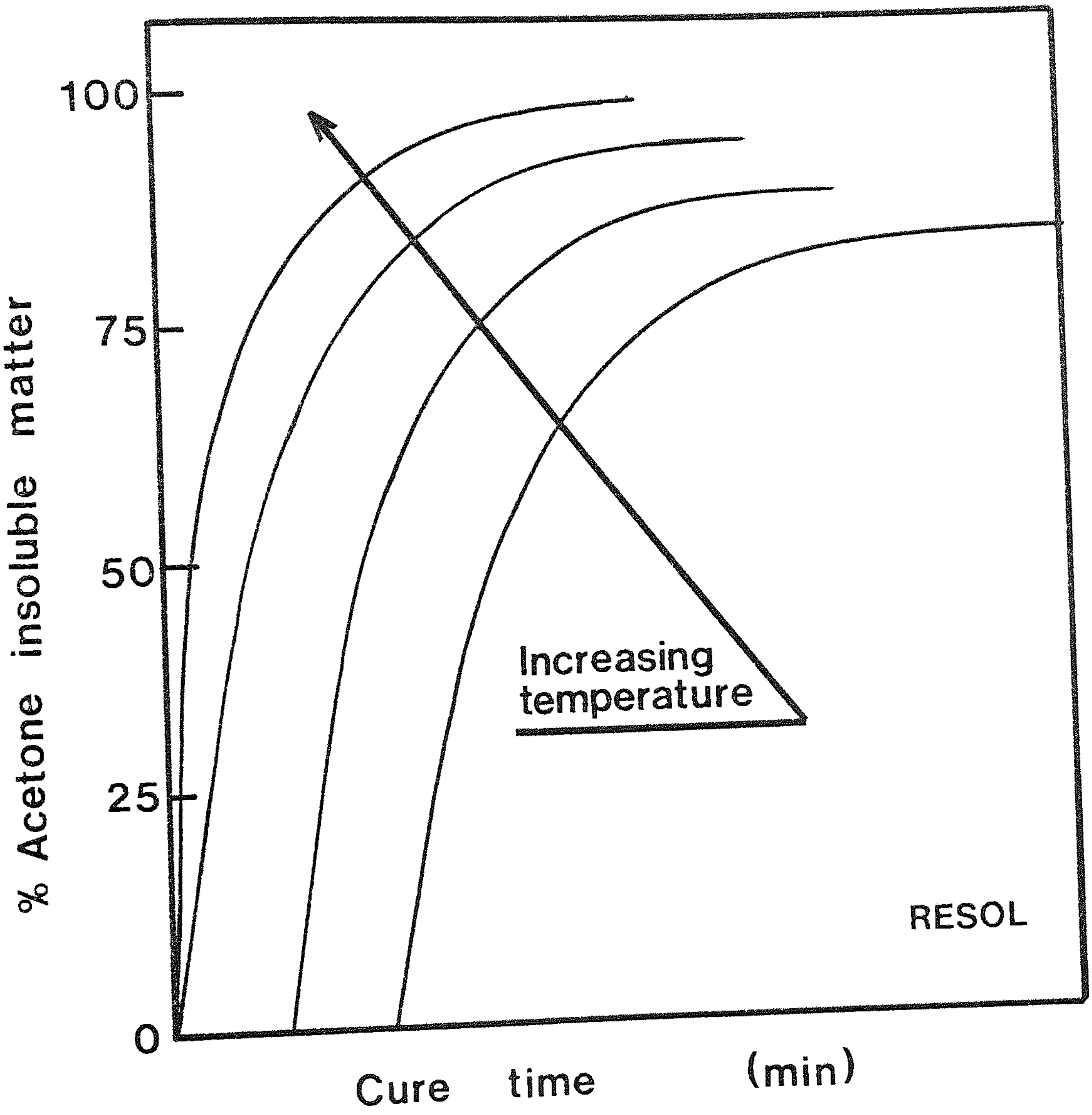


Figure A1.1 Acetone insolubility as a function of time and temperature.

For laminated products it may be feasible to use as a basis an impregnated sample previously dried at ambient conditions to remove the solvent.

The degree of cure normalised is therefore expressed as a percentage according to the following equation.

$$\%\ \text{normalised}\ D_c = \left(\frac{E_1 - E_2}{E_1}\right) \times 100 \qquad \text{(A1.3)}$$

where E_1 and E_2 are the acetone extractables for the uncured and cured samples respectively.

The value of E_1 should be less than one hundred per cent, otherwise similar arguments as for the 'overcured' samples can be applied. If E_1 = 100% then it would be necessary to heat the uncured sample until E_1 falls just below this value.

In the quality control of phenolic mouldings, the acetone solubility test is sometimes used in conjunction with the Hot Indentation Method (HIM). A calibration curve is established by correllating the results of both techniques(97). Once the calibration plot is established, the HIM is then used as the main test for determining the degree of cure for hardened samples, as it only requires 10-15 minutes in comparison to 8-10 hours for the acetone-solubility test.

A1.1.2 Differential Scanning Calorimetry (DSC)

Modern differential scanning calorimeters are designed to determine the enthalpies of any process in which heat is either absorbed or evolved. The DSC is therefore employed to measure the exothermic heat associated with the cure of phenolics. A basic assumption made is that, for a given material the heats of reaction are directly proportional to the apparent extent of residual cure and that the fraction cured is therefore proportional to the area of the generated exotherm.

The degree of cure may be determined by either a series of scans or by just a single one. Both of these methods have been used to study the curing process for phenolic resins.

A1.1.2.1 Degree of cure from a series of DSC scans

For an exothermic reaction, the DSC measures the rate of heat produced (dH/dt), as a function of temperature and time.

To determine the degree of cure for a system, the calorimeter is used in the temperature-scanning (dynamic)mode. The following procedure may be adopted.

An uncured sample (s_1) is heated at a constant heating rate ($d\theta/dt$) until the thermogram generated is complete; that is the recorder pen returns to the initial base line. The area bound by the exotherm represents the overall heat of reaction ΔH_o (figure A1.2).

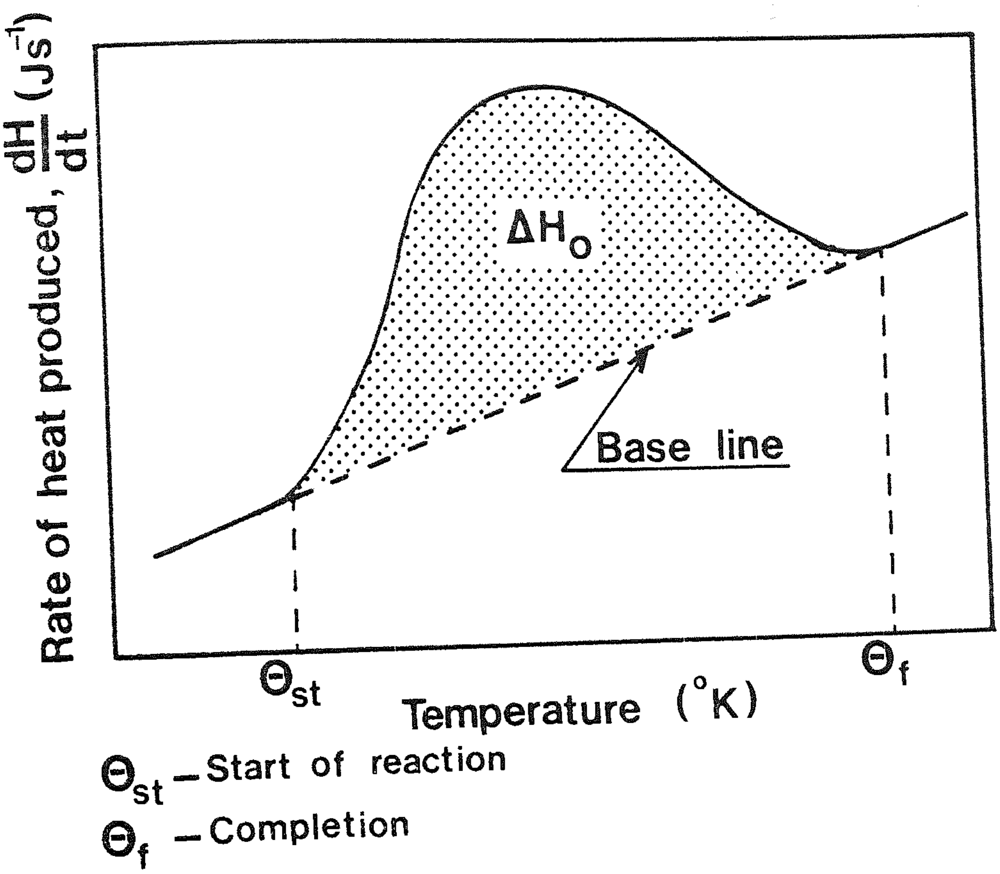


Figure A1.2 DSC trace of an uncured sample. (exothermic reaction)

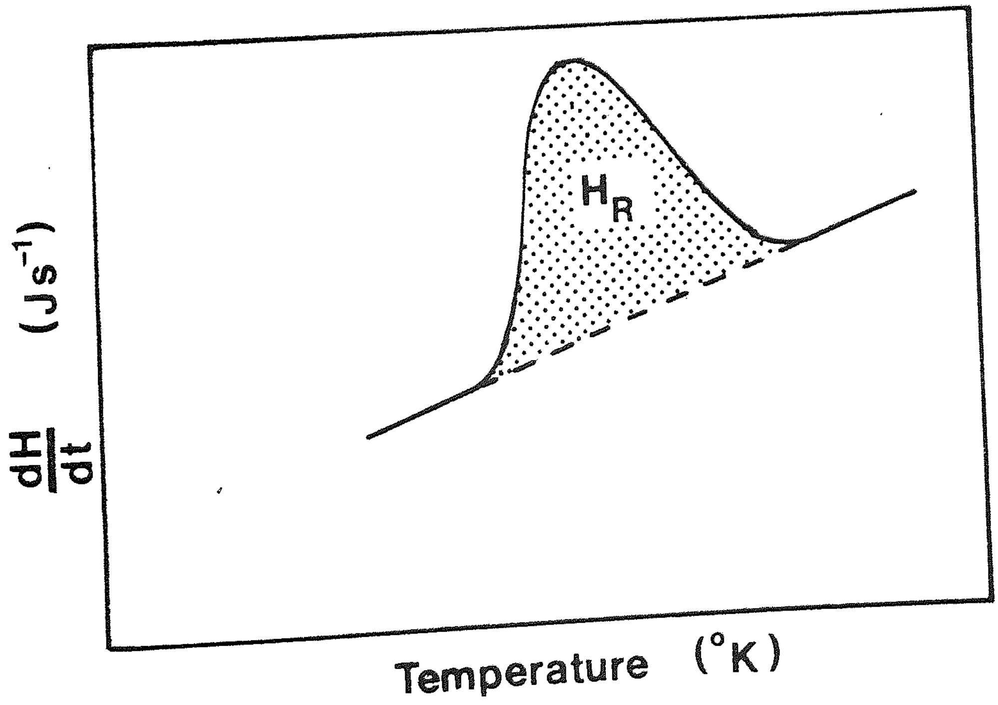


Figure A1.3 DSC trace of a partially cured sample.

A second sample (s_2) is cured by heating it at a temperature θ_1 ($\theta_{st} < \theta_1 < \theta_f$) and time t_1. This may be carried out in the calorimeter, employed in the isothermal mode. Alternatively the curing may be carried out in an oven under controlled conditions. The cured sample s_2 is then scanned at the same heating rate ($d\theta/dt$), in order to determine the residual heat of reaction (H_R) as shown in figure A1.3.

The degree of cure of sample s_2 at θ_1 and t_1 is given by:

$$\% \; D_c \Big|_{\theta_1, t_1} = \left(\frac{\Delta H_o - H_R}{\Delta H_o}\right) \times 100 \qquad \text{(A1.4)}$$

The above procedure is then repeated with other samples which have been heated at various cure temperatures and times. Optimum curing conditions may be obtained from plots of percent cure versus time and temperature.

A1.1.2.2 Degree of cure from a single DSC Scan

The technique which utilises a number of dynamic scans is experimentally time consuming. Methods for obtaining degree of cure from reaction kinetics data using one DSC scan greatly decreases the time necessary for analysis and they have been reported in the literature(96, 175-177).

The working equations consist of the general n^{th} order rate equation and the Arrhenius equation. The general rate expression is:

$$\frac{df}{dt} = k\,(1-f)^{n} \qquad (A1.5)$$

where:

f = fractional extent of conversion

k = rate constant for the reaction (s^{-1})

n = reaction order

The fractional extent of conversion ranges from zero to one and is defined as: (see figure A1.4)

$$f = \frac{H}{\Delta H_o} \qquad (A1.6)$$

where:

H = partial heat of reaction, at a given temperature (Jg^{-1})

ΔH_o = overall heat of reaction for complete crosslinking (Jg^{-1})

The rate constant k (θ) can be expressed in terms of parameters obtained from the DSC scan and subsequently related to the activation energy E_a and frequency factor A of the Arrhenius equation.

Substituting equation (A1.6) into equation (A1.5) and solving for the rate constant k in logarithmic form yields the following expression.

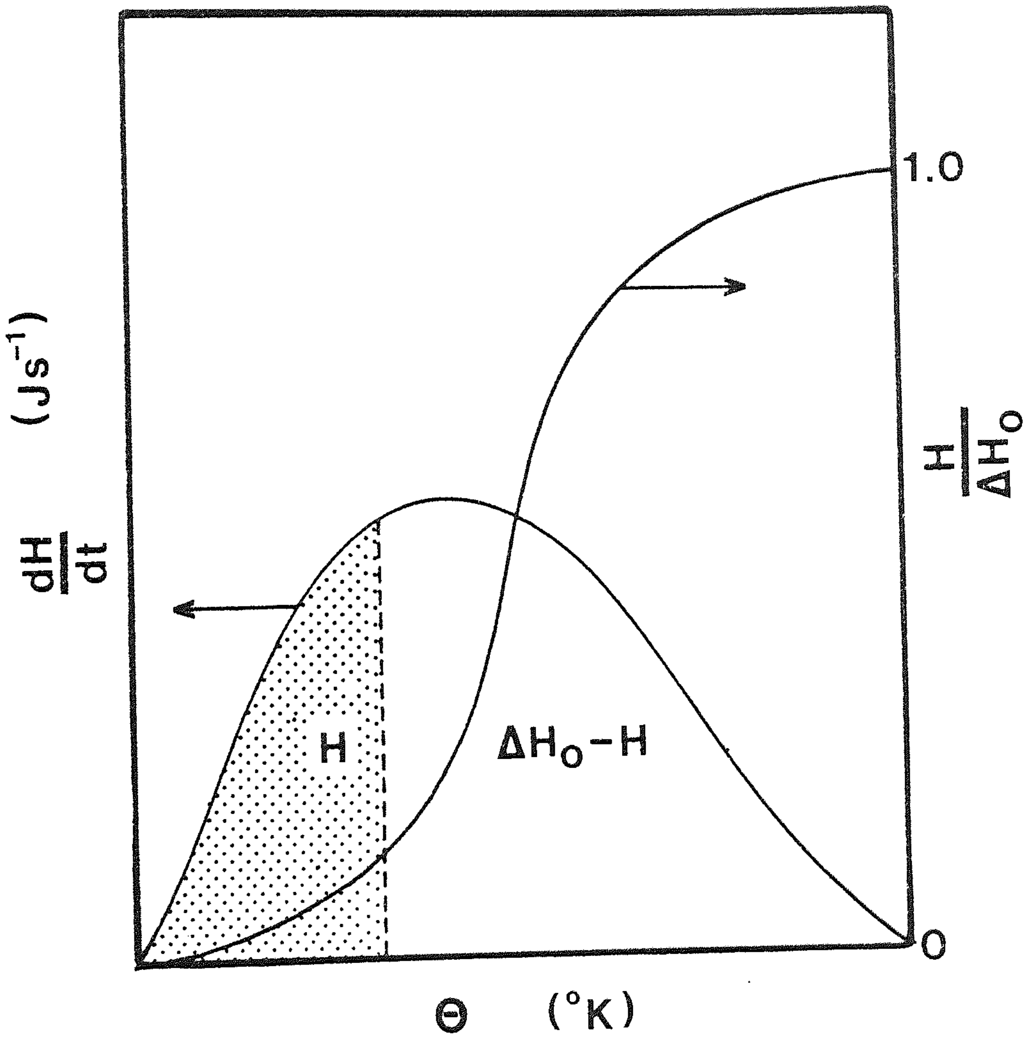


Figure A1.4 DSC trace for an exothermic reaction.

$$\ln k = \ln \left(\left(\frac{dH}{dt}\right) / \frac{(\Delta H_o - H)^n}{(\Delta H_o)^{n-1}} \right) \qquad (A1.7)$$

All the quantities on the right hand side of equation (A1.7), with the exception of reaction order n, are observable.

The Arrhenius equation is:

$$k = A \exp(-E_a/R_G\theta) \qquad (A1.8)$$

$$\text{or } \ln k = \ln A - \frac{E_a}{R_G\theta} \qquad (A1.9)$$

where:

A = Arrhenius frequency factor (s^{-1})

E_a = activation energy (J $mole^{-1}$)

R_G = gas constant (J $mole^{-1}$ $^oK^{-1}$)

Substituting equation (A1.9) into equation (A1.7) yields the working equation (A1.10).

$$\ln A - \frac{E_a}{R_G\theta} = \ln \left(\left(\frac{dH}{dt}\right) / \frac{(\Delta H_o - H)^n}{(\Delta H_o)^{n-1}} \right) \qquad (A1.10)$$

The correct order of reaction (n) is selected by evaluating the linearity of the Arrhenius plot. A series of Arrhenius plots are generated by varying the order of reaction (n) in equation (A1.10). The correct value of n is that which gives the highest correlations coefficient of the least squares fit of the ln k versus $1/\theta$ curve. The value for n is then substituted into equation (A1.10) to obtain the activation energy and Arrhenius frequency factor.

Having obtained the kinetic parameters relating to the overall crosslinking process, the degree of cure (extent of crosslinking) is calculated as a function of time or temperature. This involves integration of equation (A1.5) to yield the following expression.

$$f = 1 - \left((n-1)kt \right)^{1/1-n} \tag{A1.11}$$

For the case where n = 1, integration of equation (A1.5) gives:

$$f = 1 - \exp(-kt) \tag{A1.12}$$

(f is usually multiplied by 100 to give a percentage cure scale which extends from 0 to 100 percent).

A1.1.2.3 Discussion

There are several assumptions implicit in the DSC method which utilises a single scan to obtain degree of cure via kinetic data. These are:

(i) A single type of crosslinking reaction with a characteristic ΔH value occurs over the range of temperature involved in the DSC scan; therefore the area under the curve will always be directly proportional to the number of crosslinks formed (extent of cure);

(ii) the area under the curve has no contribution from thermal phenomena other than crosslinking.

Both of these assumptions apply equally to the methods which employ a series of scans or a single one. They are necessary if progress is to be made, but caution must clearly be exercised in the interpretation of results; and

(iii) the predicted values of the degree of cure are independent of scan speed (heating rate) $d\theta/dt$.

Work on phenolic-paper composites by Kay and Westwood(96) has shown that, calculations of the extent of crosslinking expected for a particular thermal cure cycle produced results in good agreement, no matter at what scan speed the data were obtained. However, the rate constants determined were not entirely independent of scan speed. Attempts to eliminate this discrepancy by the method proposed by Prime(178) were not successful. They suggested that the constant values of percentage cure obtained at various scan speeds was due to 'internal compensation' between k and n values.

Crane et al(179) working on the curing of epoxy-phenolic adhesives claimed that, whilst in principle a single DSC scan at a constant rate is sufficient to define E_a and n for the curing system, a more comprehensive evaluation is provided by the use of multiple scan rates to isolate a single value of E_a/n for the system.

Despite the simplifying assumptions which the method of a single DSC scan involves, useful kinetic and degree of cure data may be obtained. This information could be used to provide quantitative analysis of the curing process of thermosetting polymers.

It should also be emphasized that in experimental studies by DSC, relatively small quantities of resin (or prepregs) are used (20-30 mg). This results in a defined, reproducible, and uniform distribution of degree of cure over the sample volume. However, in industrial productions the conditions of uniform heating of the material are usually never obtained, and local temperature variations (which can be significant) do occur. (see Chapter 8).

The use of dynamic-static experiments(180) represents a more realistic approach to the characterisation of the thermosetting process as found in industrial practice.

APPENDIX A2

A2.1 The Bendtsen Smoothness and Porosity tester

The Bendtsen tester allows measurements of roughness (reciprocal of smoothness) and porosity (expressed as air flow rate) on paper or thin boards to be made. The tester, when used in the 'porosity mode', measures the volumetric air flow ($cm^3\ min^{-1}$) which is passing through a well defined area of the paper. The oil-free air flow is delivered to the measuring gauge by a small compressor designed specifically for this purpose.

Model 6 (Andersson & Sorensen), employed in the porosity determination, was equipped with three rotameters in the following range:
(i) 5-150; (ii) 50-500; (iii) 300-3000 ($cm^3\ min^{-1}$).

Manostat weights which ensured a constant over-pressure at the measuring point were also provided.

A2.2 Porosity determinations

A2.2.1 Experimental procedure

Treated (dried) and unimpregnated paper samples measuring 12 x 12 cm were used throughout. Side 1 was arbitrarily defined as the outer surface of the paper roll from which the samples were originally cut. Each sample was marked for easy identification. (The treated specimens were taken from the sheets used in the impregnation work). Twelve measurements were taken, 6 on each side. Porosity determinations were confined to the higher-resin content runs which are relevant to production specifications.

The Bendtsen tester was calibrated by replacing the porosity gauge with a capillary tube (supplied by the manufacturer). The air flow rate was adjusted until the rotameter reading was within 3% of that printed on the capillary tube.

The measuring gauge was re-connected, and the sample was inserted between the two planes of the gauge. Hand-pressure was then applied and held until a constant reading was shown by the relevant rotameter. Five more determinations were made over the rest of the area of the specimen. This procedure was repeated on the reverse side.

A2.2.2 Results

The results are presented in table A2.1; only mean values are shown.

It was found that, although reproducibility was relatively good (within ± 1%), for a given sample there was large variation in the measurements obtained.

The variation is particularly large in the treated samples as it can be seen from table A2.2. This may be due to the non-uniform hand-impregnation, since unimpregnated papers in general, show relatively small variation.

IMMERSION TIME (s)	POROSITY** (cm^3 min^{-1})			
	SIDE 1	SIDE 2	SIDE 1	SIDE 2
0*	943	955	930	953
6	200	218	160	188
30	120	130	97	108
90	136	116	70	98
180	107	119	104	88
ROLL GAP (mm) →	0.356 (c)		0.406 (d)	

* Unimpregnated kraft paper.
** Mean of twelve determinations.

Table A2.1 Porosity results at various immersion times.

IMMERSION TIME (s)	SIDE 1		SIDE 2		SIDE 1		SIDE 2	
	Standard deviation. (cm^3 min^{-1})	Coefficient* of variation. (%)	Standard deviation. (cm^3 min^{-1})	Coefficient of variation. (%)	Standard deviation. (cm^3 min^{-1})	Coefficient of variation (%)	Standard deviation. (cm^3 min^{-1})	Coefficient of variation (%)
0	56.7	6.0	15.2	1.6	17.9	1.9	10.3	1.1
6	32.7	16.4	21.6	9.9	17.3	10.8	7.5	4.0
30	4.1	3.4	4.2	3.2	2.9	3.0	12.6	11.7
90	15.0	11.0	16.5	14.2	10.0	14.3	14.7	15.0
180	19.0	17.8	19.9	16.7	5.0	4.8	10.2	11.6
Roll Gap (mm) →	0.356 (c)				0.406 (d)			

* Coefficient of variation = $\frac{\text{standard deviation}}{\text{mean}} \times 100\%$

Table A2.2 Statistical data derived from impregnation experiments.

Nevertheless, the results in table A2.1 indicate that lower porosity values are obtained at immersion times above 6 seconds.

It is not possible to draw any firm conclusions from the available data. Further experimental work, and perhaps a rigorous statistical analysis are required in order to establish whether porosity measurements as a technique, can be used to study resin distribution in papers.

APPENDIX A3

A3.1 Initial data

The initial data obtained for all drying experiments (SD and RD mode) are shown in tables A3.1 to A3.9. Also shown are the results of the resin and volatile content determinations.

The mean ambient temperature and relative humidity (not shown) were 18°C and 65% respectively.

A3.2 Weight corrections to 'zero' drying time

A3.2.1 Solvent evaporation

In each experimental run (SD and RD mode), the duration of impregnating and weighing periods was 15 minutes each. At the completion of the weighing period all samples were introduced into the oven. Therefore, although individual samples were subjected to equal time intervals between impregnation and weighing, at the time of introduction into the oven the samples experienced different exposure times to ambient conditions. This is shown schematically in figure A3.1.

Since solvent continuously evaporated from the surfaces of the wet samples, this variation in time between weighing and drying must be allowed for so that each sample can be related to the appropriate starting condition at 'zero' drying time, that is 30 minutes after the start of impregnation. What is therefore required is the varnish weight (also wet paper weight)

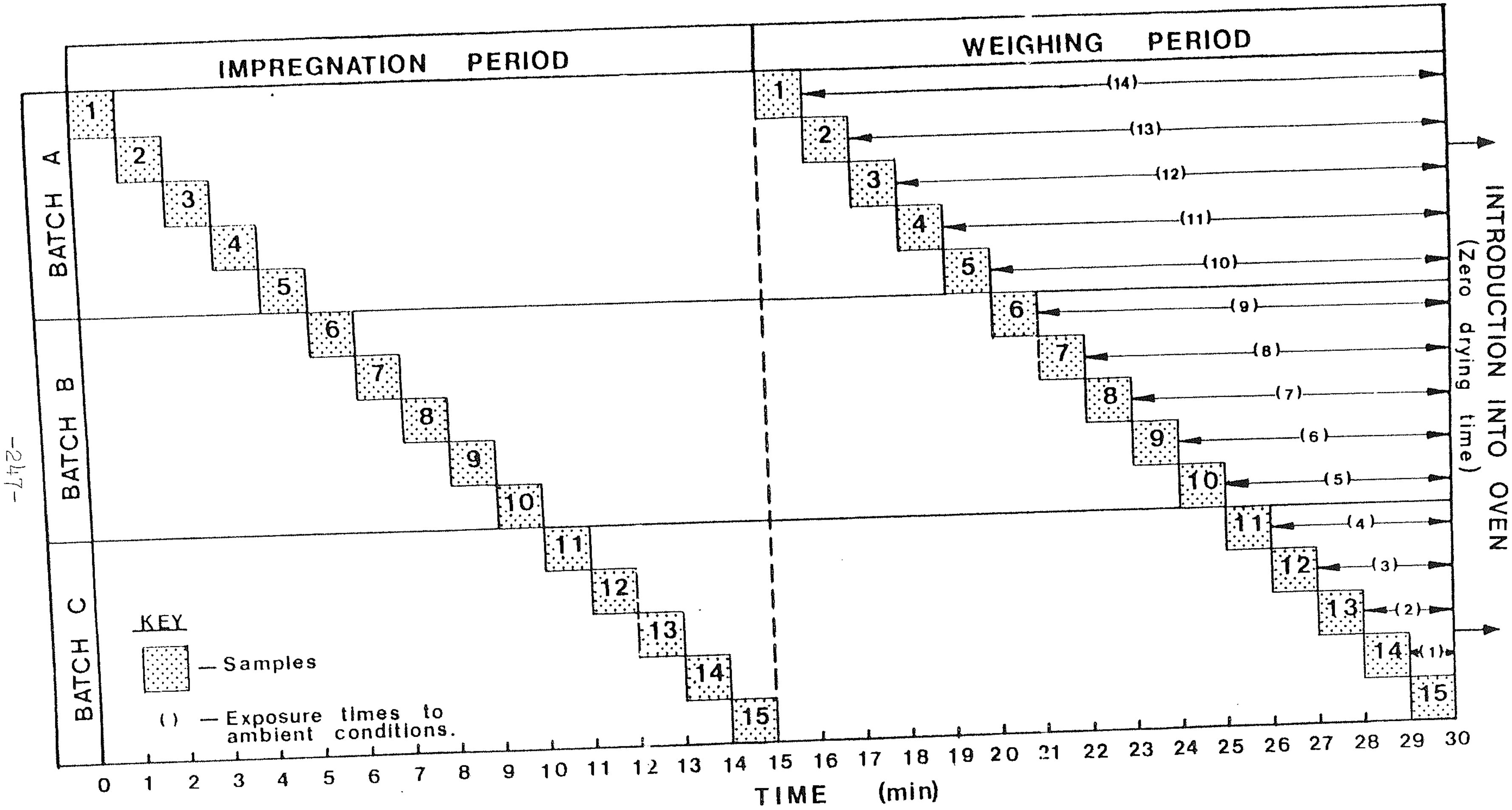


Figure A3.1 Time elapsed since impregnation of samples.

at t = 30 minutes for each sample.

Data necessary for these corrections was obtained from a series of experiments which measured reduction in varnish (and wet paper) weight as a result of solvent evaporation.

A3.2.2 Experimental procedure

Three experimental runs were carried out using 25 x 25 cm paper samples. Blend I (see main text table 7.1) was used throughout since it was a typical blend in the drying experiments.

Each run consisted of five samples. These were impregnated at one minute intervals and subsequently weighed also at one minute intervals over a period of 70 minutes while exposed to the atmosphere. The time elapsed since impregnation was therefore the same for all samples.

A3.2.3 Results

The results of these experiments are presented in tables A3.10 - A3.12. Figure A3.2(a),(b) shows typical plots for samples exposed to ambient conditions. (The data points have been taken from sample 1 (o-o), 8 (●-●), and 15 (x-x)).

Although ambient temperature and relative humidity were not controlled, the variation in both parameters was relatively small during the course of the experiments and mean values similar to those in the drying

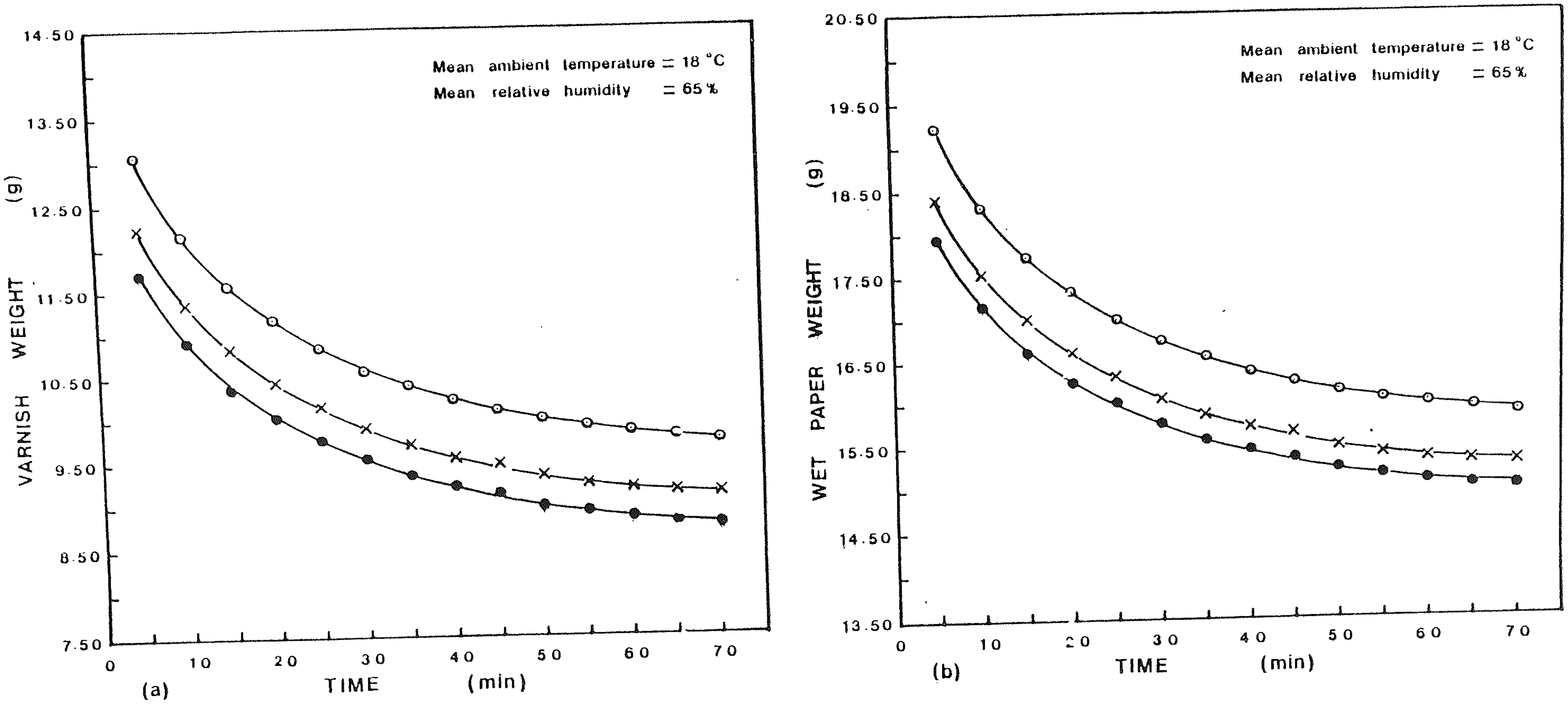


Figure A3.2 Weight change versus time for samples at ambient conditions. (a) varnish; (b) wet paper.

experiments were recorded.

A3.2.4 Weight ratio (r)

In order to obtain an equation which would closely represent the data in tables A3.10 - A3.12, a weight ratio (r) was defined as:

For sample i

$$r_i = \frac{(\text{weight})_i\big|_t}{(\text{weight})_i\big|_{t=5}} \qquad (A3.1)$$

The mean value is:

$$\bar{r} = \frac{1}{15}\sum_{i=1}^{15} r_i \qquad (A3.2)$$

A3.2.5 Polynomial regression

The experimental values of $\bar{r}$ are presented in table A3.13. In figure A3.3 the ratio r is plotted as a function of time for both varnish and wet paper.

Fourth order polynomial equations were fitted through the data points.

$$\bar{r} = a_o + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 \qquad (A3.3)$$

The polynomial regression was carried out using a Hewlett-Packard HP-85 desktop computer utilising available programs which employ a least-squares method.

The values of the coefficients in equation A3.3 are as follows:

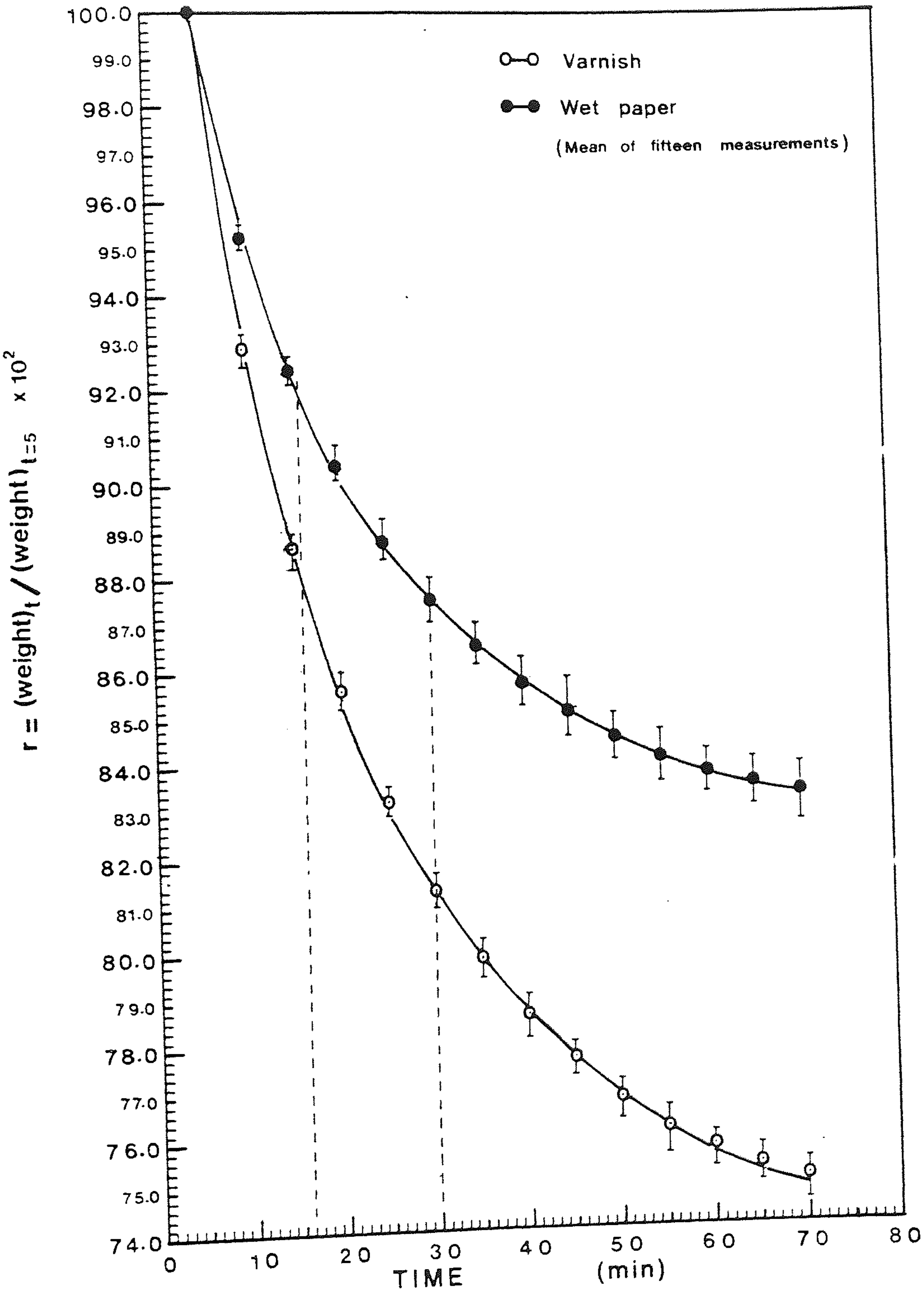


Figure A3.3 Weight ratio (r) as a function of time.
(Points o–o and ●–● shown are $\bar{r}$-values)

Coefficients	Basis : Varnish weight	Basis: Wet paper weight
a_o	1.08161	1.05460
a_1	-1.93815×10^{-2}	-1.29571×10^{-2}
a_2	5.28653×10^{-4}	3.53402×10^{-4}
a_3	-7.22493×10^{-6}	-4.82599×10^{-6}
a_4	3.80886×10^{-8}	2.54127×10^{-8}

Corellation coefficients of 0.999 were obtained in both cases, indicating an 'excellent fit'.

The calculated values of $\bar{r}$ from equation A4.3 are also shown in table A3.13. Using these values, corrected weights for varnish (W_{vc}) and wet paper (W_{2c}) at 'zero' drying time can be calculated (tables A3.14 - A3.22). Weight corrections are only required over the time range of interest, that is 16-30 minutes in figure A3.1.

Using W_{vc} and W_{2c}, weight loss can then be obtained for each sample treated in either SD or RD mode. Weight loss results (L_{vc}, L_{wc}) are also shown in tables A3.14 - A3.22 together with weight loss obtained from the initial 'uncorrected' data (tables A3.1 - A3.9).

A3.3 Specimen calculation

Calculations for weight loss using corrected weight data will be shown with reference to sample B_6, SD-1.

(i) Corrected varnish weight (W_{vc})

In terms of the nomenclature in figure A3.1, the varnish weight for sample B_6 is:

$$W_v \equiv W_v\Big|_{t=21} = 10.59 \text{ g (from table A3.1)}$$

The required varnish weight at t = 30 (W_{vc}) is obtained by making use of the definition of r.

Therefore,

$$W_{vc} = \left[\frac{\bar{r}\,\big|_{t=30}}{\bar{r}\,\big|_{t=21}}\right] \text{ x } W_v\Big|_{t=21}$$

From table A3.13 (varnish basis) :

$$\bar{r}\Big|_{t=21} = 0.8482$$

$$\bar{r}\Big|_{t=30} = 0.8123$$

$$\therefore \quad W_{vc} = \frac{0.8123}{0.8482} \text{ x } 10.59 \quad \text{(g)}$$

$$\underline{\underline{W_{vc}}} = 10.14 \text{ g (shown in table A3.14)}$$

(ii) Corrected wet paper weight (W_{2c})

W_{2c} is similarly calculated.

$$\underline{\underline{W_{2c} = 16.29 \text{ g}}}$$

(iii) Weight loss

For sample B_6, SD-1:

$$L_{vc} = \frac{(W_{2c} - W_3)}{W_{vc}} \times 100\%$$

where W_3 = treated paper weight (table A3.1)

$$\therefore \quad L_{vc} = \frac{(16.29 - 13.44)}{10.14} \times 100\%$$

$$\underline{\underline{L_{vc} = 28.11\%}}$$

Similarly

$$L_{wc} = \frac{(W_{2c} - W_3)}{W_{2c}} \times 100\%$$

$$= \frac{(16.29 - 13.44)}{16.29} \times 100\%$$

$$\underline{\underline{L_{wc} = 17.50\%}}$$

Both of these results are shown in table A3.14.

A3.4 Resin solids of treated samples

A3.4.1 Weight of varnish solids

For any sample i the weight of varnish solids (g) immediately following impregnation is given by equation A3.4.

$$(W_{vs})_i = \left[\frac{\bar{r}|_{t=o}}{\bar{r}|_{t=30}}\right] \times (W_{vc})_i \times \frac{S}{100} \qquad (A3.4)$$

where:

W_{vs} = weight of varnish solids at t=o (g)

W_{vc} = corrected varnish weight at t=30 (g)

S = % solids

= 49.73 for varnish I.

$$\bar{r}|_{t=o} = 1.08161$$

$$\bar{r}|_{t=30} = 0.8123$$

For each batch A,B,C mean values for W_{vs} are obtained.

$$\bar{W}_{vs} = \frac{1}{5}\left(\sum_{i=1}^{5} (W_{vs})_i \right) \quad (g) \qquad (A3.5)$$

A3.4.2 Weight of resin solids

The weight of resin solids in a treated sample i (g) may be found as follows:

$$(W_{ds})_i = \left((W_3)_i \left(1 - \frac{V}{100}\right) \right) - (W_1)_i \qquad (A3.6)$$

where:

W_{ds} = solids weight in treated samples (g)

W_3 = treated paper weight (g)

W_1 = paper weight (g)

V = % volatile content (obtained from figure 7.5 in the main text at the corresponding drying time for each batch).

Therefore,

$$\bar{W}_{ds} = \frac{1}{5}\left(\sum_{i=1}^{5} (W_{ds})_i \right) \quad (g) \qquad (A3.7)$$

The proportion of resin solids to varnish solids is:

$$\beta = \frac{\bar{W}_{ds}}{\bar{W}_{vs}} \qquad (A3.8)$$

Using the solids content (S) of either varnish I (employed in all solvent evaporation experiments) or of the individual varnishes I, II, III in equation A3.3, β_1 and β_2 are obtained respectively (table A3.23).

A3.4.3 Specimen calculation

Consider batch B, SD-1 (drying time = 13 minutes) and solids content of varnish I.

Using equation A3.4 the values of W_{vs} for each sample in batch B are given below:

Samples	W_{vs} (g)
B_6	6.71
B_7	6.73
B_8	6.94
B_9	6.85
B_{10}	7.03

$$\therefore \quad \bar{W}_{vs} = 6.85 \text{ g}$$

From figure 7.5 at drying time = 13 minutes

$y = 7.3\%$

From equation A3.6 the individual W_{ds} are calculated.

Samples	W_{ds} (g)
B_6	6.31
B_7	6.32

B_8	6.34
B_9	6.22
B_{10}	6.54

$$\therefore \underline{\underline{\bar{W}_{ds} = 6.35}} \quad g$$

$$\text{Therefore,} \quad \beta_1 = \frac{6.35}{6.85}$$

$$= \underline{\underline{0.927}}$$

A3.5 Oven temperature calibration

The calibration of the oven temperature is shown in figure A3.4. Copper-constantan thermocouples in conjunction with a temperature recorder (Cambridge Instruments) were employed at three different locations inside the oven. The thermocouples were pre-calibrated over the temperature range of interest using a constant temperature bath accurate to ± 0.5°C.

A3.6 SD mode heating curve

The mean oven temperature for samples dried in the SD mode is plotted versus drying time in figure A3.5

A3.7 The determination of free phenols by GC(181)

A3.7.1 Principle:

A standard solution of phenol is analysed by gas chromatography (GC) using an internal standard technique. After the addition of the internal standard to the unknown sample, the mixture is

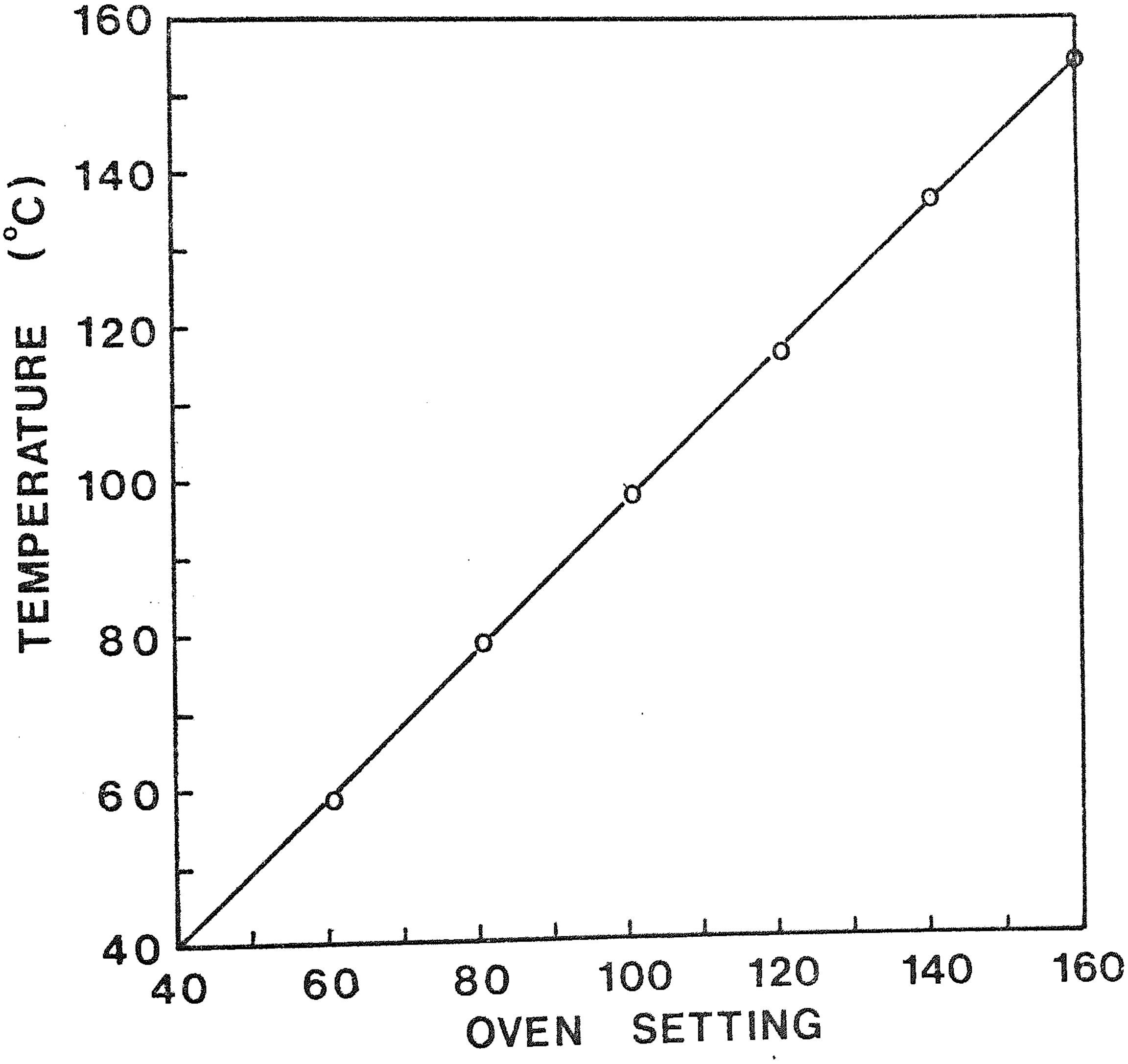


Figure A3.4 Oven temperature calibration.

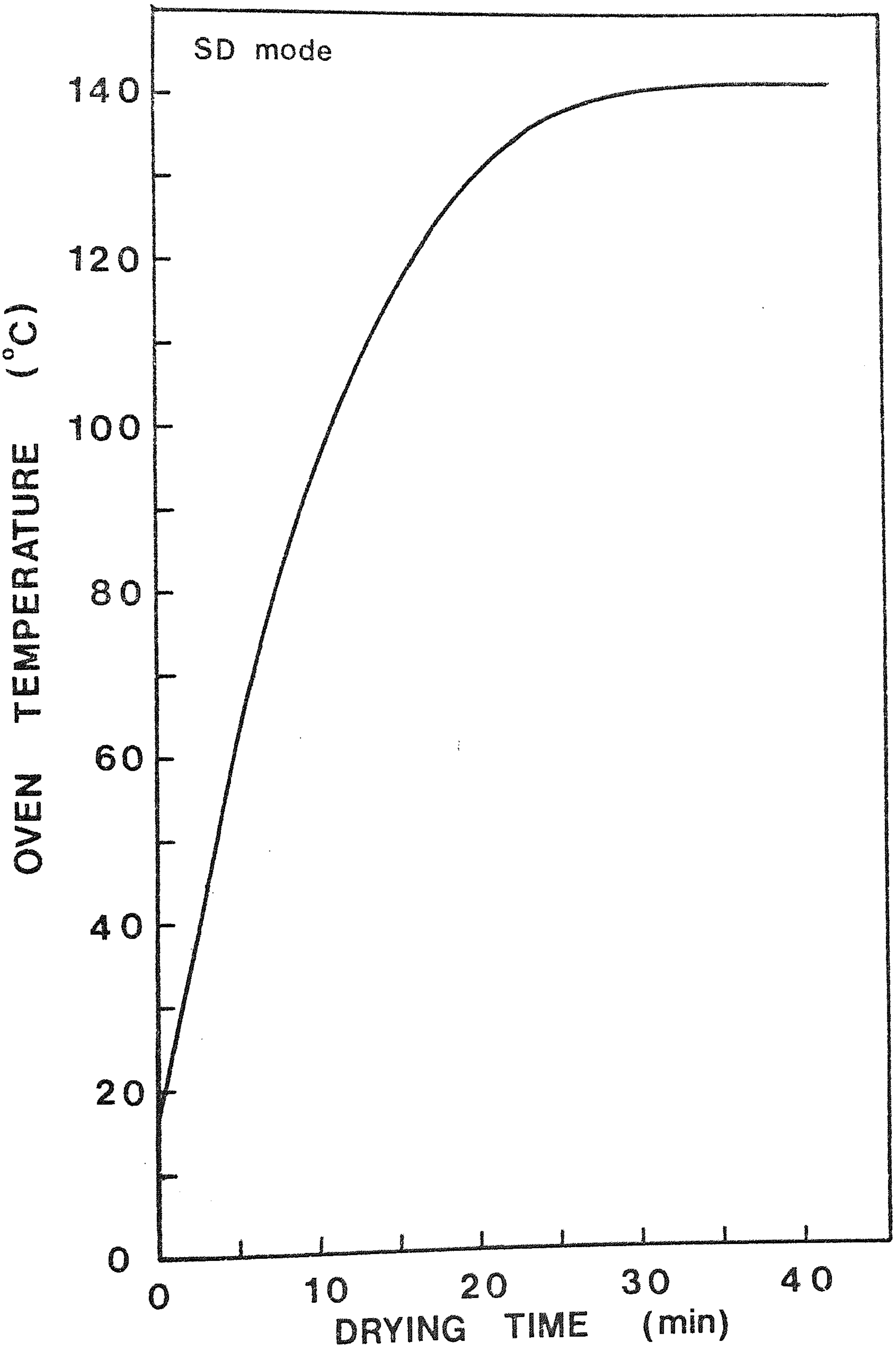


Figure A3.5 Mean oven temperature for the SD mode drying experiments.

subjected to an extraction process using an aqueous/ ether mixture with the resulting ether layer being chromatographed as before. Using a response factor calculated from the standard solution, the free phenol content of the unknown is calculated from the chromatograph of the sample.

A3.7.2 Reagents

(i) Diethyl ether
(ii) meta-cresol
(iii) phenol
(iv) N/1 NaOH
(v) N/1 H_2SO_4

The reagents may be of analytical or technical grade.

A3.7.3 Typical conditions

Column - 10% Apiezon L
Programme - 80° - 225°C at 8°C min^{-1}
Injectors - 200°C
Carrier gas - Nitrogen at 35-40 ml min^{-1} flow rate
Attenuation - 4×10^2 or 32×10^2

A3.7.4 Method

Weigh out, accurately, between 1.0 and 1.5 g of the varnish into a 90 x 155 mm pyrex test tube and about 0.1 - 0.15 g of m-cresol, accurately weighed as internal standard.

To the tube add 8 ml of distilled water, three drops of N/1 NaOH and 10 ml of diethyl ether. Seal the tube with a rubber bung and shake, gently at first, releasing the pressure at intervals, then vigorously for 5 minutes or until the resin has completely dispersed between the two phases. (In the case of solid resins the shaking time is usually of the order of about 20 minutes). Remove the rubber bung, add a piece of litmus paper and N/1 H_2SO_4 dropwise until the aqueous layer is acidic. Reseal the tube and shake for a further 5 minutes.

After allowing the two phases to separate, remove the ether layer by means of a pipette and transfer it to a screw-capped phial. With the GC set up as indicated earlier, chromatograph 1 µl of the ether solution using a syringe.

Standards are made by weighing out, accurately, 0.1 - 0.15 g each of the phenol and m-cresol and carrying through the above procedure.

A3.7.5 Calculations

(i) Response factor

$$\text{Response factor} = \frac{\text{Area of m-cresol in std}}{\text{Area of phenol in std}} \times \frac{\text{Wt. of phenol in std}}{\text{Wt. of m-cresol in std}}$$

(ii) Free phenol content

$$\%\ \text{Free phenol} = \frac{\text{Area of phenol in sample}}{\text{Area of m-cresol in sample}} \times \frac{\text{Wt. of m-cresol in sample}}{\text{Wt. of resin taken}} \times \text{Response factor} \times 100$$

A3.7.6 Results

The results of free-phenol content of typical varnishes used throughout the experimental work are given below:

Varnish	% free-phenol
A	7.99
B	8.38
C	7.10
D	7.84

MODE - RUN : SD-1

MEAN MOISTURE, M = 4.20%

TABLE A3.1

VARNISH I

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	3	49	6.21	16.79	10.58	15.61	61.88	
A_2	3	49	6.22	16.74	10.52	15.59	61.77	
A_3	3	49	6.21	16.79	10.68	15.68	62.05	
A_4	3	49	6.21	17.09	10.88	15.88	62.53	18.48/18.53
A_5	3	49	6.14	16.74	10.60	15.62	62.36	18.72/19.23
B_6	13	109	6.15	16.74	10.59	13.44	56.18	7.32/ 7.56
B_7	13	109	6.19	16.74	10.55	13.49	56.04	7.23/ 7.17
B_8	13	109	6.22	17.03	10.81	13.55	56.01	
B_9	13	109	6.19	16.81	10.62	13.39	55.71	
B_{10}	13	109	6.21	17.04	10.83	13.75	56.73	
C_{11}	23	135	6.23	17.24	11.01	12.77	53.25	
C_{12}	23	135	6.23	17.50	11.27	12.97	53.97	2.58/ 2.34
C_{13}	23	135	6.15	17.31	11.16	12.76	53.84	2.67/ 2.41
C_{14}	23	135	6.23	17.22	10.99	12.72	53.07	
C_{15}	23	135	6.18	17.21	11.03	12.67	53.28	

MODE - RUN : SD-2

MEAN MOISTURE, M = 4.20%

TABLE A3.2

VARNISH II

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	5	65	6.26	17.95	11.69	15.98	62.45	15.13/14.87
A_2	5	65	6.15	16.93	10.78	15.24	61.35	15.25/15.19
A_3	5	65	6.13	17.42	11.29	15.64	62.47	
A_4	5	65	6.22	17.50	11.28	15.64	61.89	
A_5	5	65	6.20	17.20	11.00	15.51	61.70	
B_6	15	116	6.22	16.65	10.43	13.06	54.36	
B_7	15	116	6.20	17.78	11.58	13.91	57.30	
B_8	15	116	6.23	16.89	10.66	13.35	55.28	6.38/ 6.76
B_9	15	116	6.20	16.99	10.79	13.43	55.77	6.55/ 6.21
B_{10}	15	116	6.23	16.81	10.58	13.21	54.81	
C_{11}	25	138	6.26	16.69	10.43	12.28	51.14	
C_{12}	25	138	6.26	16.72	10.46	12.29	51.18	
C_{13}	25	138	6.24	16.84	10.60	12.38	51.70	
C_{14}	25	138	6.26	16.67	10.41	12.33	51.34	2.75/ 2.30
C_{15}	25	138	6.30	16.97	10.67	12.40	51.29	2.46/ 1.72

MODE - RUN : SD-3

MEAN MOISTURE, M = 4.20%

TABLE A3.3

VARNISH II

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	8	86	6.30	17.92	11.62	15.23	60.34	11.87/11.35
A_2	8	86	6.31	17.36	11.05	14.97	59.65	11.67/11.09
A_3	8	86	6.31	17.55	11.24	14.92	59.52	
A_4	8	86	6.23	17.18	10.95	14.76	59.55	
A_5	8	86	6.22	17.58	11.36	14.92	60.05	
B_6	18	125	6.25	18.07	11.82	13.63	56.05	4.15/4.02
B_7	18	125	6.15	17.48	11.33	13.30	55.71	
B_8	18	125	6.18	17.80	11.62	13.37	55.72	
B_9	18	125	6.18	17.58	11.40	13.37	55.72	3.82/4.01
B_{10}	18	125	6.24	17.76	11.52	13.35	55.21	
C_{11}	28	140	6.22	17.69	11.47	12.75	53.25	1.76/1.84
C_{12}	28	140	6.27	17.55	11.28	12.72	52.75	
C_{13}	28	140	6.30	17.92	11.62	12.75	52.63	
C_{14}	28	140	6.26	17.56	11.30	12.70	52.76	
C_{15}	28	140	6.23	17.19	10.96	12.39	51.82	1.26/1.55

MODE - RUN : SD-4

MEAN MOISTURE, M = 4.20%

TABLE A3.4

VARNISH III

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	10	97	6.15	17.11	10.96	14.19	58.49	10.48/11.10
A_2	10	97	6.07	16.82	10.75	13.88	58.07	
A_3	10	97	6.19	17.15	10.96	14.19	58.21	
A_4	10	97	6.18	16.85	10.67	14.05	57.86	
A_5	10	97	6.18	16.97	10.79	14.08	57.95	11.21/11.14
B_6	20	130	6.20	16.55	10.35	12.51	52.52	
B_7	20	130	6.19	16.68	10.49	12.52	52.64	3.88/ 4.00
B_8	20	130	6.10	16.35	10.25	12.33	52.64	
B_9	20	130	6.09	16.41	10.32	12.33	52.72	4.27/ 3.52
B_{10}	20	130	6.07	16.43	10.36	12.43	53.18	
C_{11}	30	140	6.22	16.57	10.35	12.03	50.46	
C_{12}	30	140	6.10	16.37	10.27	11.91	50.97	1.07/ 0.96
C_{13}	30	140	6.12	16.44	10.32	11.98	51.09	0.98/ 0.84
C_{14}	30	140	6.22	16.81	10.59	12.07	50.62	
C_{15}	30	140	6.13	16.59	10.46	11.95	50.88	

MODE - RUN : SD-5

TABLE A3.5

VARNISH I

MEAN MOISTURE, M = 4.20%

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	12	105	6.14	17.57	11.43	14.08	58.24	7.63/ 7.81
A_2	12	105	6.16	16.55	10.39	13.35	55.81	7.55/ 7.21
A_3	12	105	6.15	17.02	10.87	13.76	57.19	
A_4	12	105	6.19	17.52	11.33	14.17	58.15	
A_5	12	105	6.21	17.76	11.55	14.15	57.95	
B_6	32	141	6.19	17.06	10.87	12.03	50.71	
B_7	32	141	6.19	17.75	11.56	12.53	52.67	1.13/ 1.03
B_8	32	141	6.11	17.57	11.46	12.21	52.09	1.05/ 1.03
B_9	32	141	6.11	17.67	11.56	12.29	52.40	
B_{10}	32	141	6.12	17.45	11.33	12.27	52.24	
C_{11}	42	141	6.11	17.29	11.18	12.06	51.49	
C_{12}	42	141	6.07	17.23	11.16	12.00	51.50	
C_{13}	42	141	6.11	17.31	11.20	12.08	51.57	0.98/ 0.90
C_{14}	42	141	6.18	17.51	11.33	12.22	51.55	
C_{15}	42	141	6.18	17.54	11.36	12.23	51.59	0.83/ 1.11

MODE - RUN : RD-1

MEAN MOISTURE, M = 4.20%

TABLE A3.6

VARNISH III

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	3	135	6.10	16.45	10.35	12.17	52.01	
A_2	3	135	6.14	16.36	10.22	12.02	51.08	
A_3	3	135	6.15	16.85	10.70	12.33	52.23	6.30/ 6.33
A_4	3	135	6.13	16.75	10.62	12.33	52.39	6.74/ 6.66
A_5	3	135	6.21	17.00	10.79	12.53	52.51	
B_6	13	135	6.20	17.11	10.91	11.85	49.87	
B_7	13	135	6.20	16.86	10.66	11.68	49.14	1.28/ 1.70
B_8	13	135	6.19	16.89	10.70	11.82	49.83	
B_9	13	135	6.19	16.69	10.50	11.74	49.49	1.38/ 1.32
B_{10}	13	135	6.18	16.92	10.74	11.71	49.44	
C_{11}	23	135	6.18	16.86	10.68	11.72	49.49	1.00/ 1.07
C_{12}	23	135	6.21	16.92	10.71	11.75	49.36	
C_{13}	23	135	6.26	17.09	10.83	11.88	49.49	
C_{14}	23	135	6.22	17.33	11.11	11.92	50.00	0.91/ 1.04
C_{15}	23	135	6.18	17.13	10.95	11.78	49.75	

MODE - RUN : RD-2

MEAN MOISTURE, M = 4.20%

TABLE A3.7

VARNISH I

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	5	135	6.23	16.69	10.46	12.00	50.25	
A_2	5	135	6.20	16.69	10.49	11.98	50.42	3.26/ 2.97
A_3	5	135	6.20	16.91	10.71	12.06	50.75	
A_4	5	135	6.22	16.73	10.51	11.97	50.21	3.51/ 3.47
A_5	5	135	6.19	16.85	10.66	12.11	51.03	
B_6	15	135	6.19	16.72	10.53	11.66	49.14	1.60/ 1.80
B_7	15	135	6.16	16.51	10.35	11.45	48.47	
B_8	15	135	6.18	16.95	10.77	11.74	49.57	
B_9	15	135	6.19	16.98	10.79	11.76	49.57	
B_{10}	15	135	6.18	16.62	10.44	11.53	48.66	1.34/ 1.72
C_{11}	25	135	6.20	16.61	10.41	11.50	48.35	
C_{12}	25	135	6.16	16.54	10.38	11.43	48.38	
C_{13}	25	135	6.07	17.11	11.04	11.60	49.83	
C_{14}	25	135	6.11	16.31	10.20	11.29	48.18	0.88/ 0.89
C_{15}	25	135	6.07	16.73	10.66	11.52	49.48	0.98/ 0.83

MODE - RUN : RD-3

MEAN MOISTURE, M = 4.20%

TABLE A3.8

VARNISH I

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	8	135	6.23	16.76	10.53	11.78	49.32	2.01/ 2.14
A_2	8	135	6.16	16.64	10.48	11.76	49.83	
A_3	8	135	6.22	16.64	10.42	11.74	49.23	2.46/ 2.43
A_4	8	135	6.23	16.73	10.50	11.76	49.23	
A_5	8	135	6.18	17.04	10.86	11.89	50.21	
B_6	18	135	6.18	16.79	10.61	11.56	48.79	
B_7	18	135	6.16	16.92	10.76	11.66	49.40	1.06/ 1.25
B_8	18	135	6.15	16.62	10.47	11.50	48.78	
B_9	18	135	6.18	16.67	10.49	11.64	49.14	
B_{10}	18	135	6.19	16.56	10.37	11.58	48.79	1.19/ 1.45
C_{11}	28	135	6.18	16.68	10.50	11.53	48.66	1.01/ 0.68
C_{12}	28	135	6.15	16.66	10.51	11.43	48.47	0.87/ 0.85
C_{13}	28	135	6.09	16.71	10.62	11.46	49.13	
C_{14}	28	135	6.11	16.56	10.45	11.44	48.86	
C_{15}	28	135	6.08	16.32	10.24	11.34	48.68	

MODE - RUN : RD-4

MEAN MOISTURE, M = 4.20%

TABLE A3.9

VARNISH I

BATCH	DRYING TIME t (min)	MEAN OVEN TEMPERATURE T (°C)	PAPER WEIGHT W_1 (g)	WET PAPER WEIGHT W_2 (g)	VARNISH WEIGHT $W_v = W_2 - W_1$ (g)	TREATED PAPER WEIGHT W_3 (g)	RESIN CONTENT R (%)	VOLATILE CONTENT V (%)
A_1	10	135	6.20	17.26	11.06	11.97	50.38	
A_2	10	135	6.22	17.33	11.11	12.03	50.46	
A_3	10	135	6.22	17.45	11.23	12.07	50.62	
A_4	10	135	6.22	17.34	11.12	12.00	50.33	2.42/ 2.54
A_5	10	135	6.22	17.55	11.33	12.10	50.74	2.19/ 2.05
B_6	20	135	6.19	17.14	10.95	11.76	49.57	
B_7	20	135	6.18	17.36	11.18	11.80	49.83	
B_8	20	135	6.20	17.34	11.14	11.76	49.49	1.10/ 1.11
B_9	20	135	6.24	17.43	11.19	11.92	49.83	
B_{10}	20	135	6.15	17.68	11.53	12.04	51.08	1.07/ 1.18
C_{11}	30	135	6.21	17.49	11.28	11.89	49.96	0.71/ 0.72
C_{12}	30	135	6.20	17.62	11.42	11.96	50.33	
C_{13}	30	135	6.14	17.50	11.36	11.81	50.21	
C_{14}	30	135	6.10	17.29	11.19	11.74	50.26	0.95/ 0.83
C_{15}	30	135	6.11	16.96	10.85	11.55	49.35	

RUN 1

TABLE A3.10

EXPOSURE TIME t (min)	WET PAPER WEIGHT W_2 (g)					VARNISH WEIGHT W_v (g)				
5	19.22	18.08	18.07	18.59	19.13	13.07	11.94	11.85	12.45	12.98
10	18.31	17.24	17.26	17.70	18.20	12.16	11.10	11.04	11.56	12.05
15	17.73	16.76	16.75	17.14	17.66	11.58	10.62	10.53	11.00	11.51
20	17.32	16.36	16.39	16.77	17.25	11.17	10.22	10.17	10.63	11.10
25	16.99	16.07	16.11	16.48	16.95	10.84	9.93	9.89	10.34	10.80
30	16.73	15.87	15.89	16.24	16.70	10.58	9.73	9.67	10.10	10.55
35	16.55	15.67	15.72	16.05	16.54	10.40	9.53	9.50	9.91	10.39
40	16.38	15.55	15.58	15.92	16.35	10.23	9.41	9.36	9.78	10.20
45	16.25	15.42	15.46	15.78	16.23	10.10	9.28	9.24	9.64	10.08
50	16.15	15.33	15.36	15.69	16.10	10.00	9.19	9.14	9.55	9.95
55	16.07	15.25	15.27	15.65	15.99	9.92	9.11	9.05	9.51	9.84
60	16.01	15.18	15.21	15.60	15.95	9.86	9.04	8.99	9.46	9.80
65	15.95	15.12	15.15	15.54	15.89	9.80	8.98	8.93	9.40	9.74
70	15.89	15.09	15.13	15.51	15.86	9.74	8.95	8.91	9.37	9.71
SAMPLES →	1	2	3	4	5	1	2	3	4	5

RUN 2

TABLE A3.11

EXPOSURE TIME	WET PAPER WEIGHT					VARNISH WEIGHT				
t (min)	W_2 (g)					W_v (g)				
5	18.82	17.97	17.95	18.45	18.26	12.60	11.78	11.71	12.30	12.11
10	17.89	17.16	17.15	17.53	17.41	11.67	10.97	10.91	11.38	11.26
15	17.38	16.64	16.61	17.00	16.88	11.16	10.45	10.37	10.85	10.73
20	17.03	16.32	16.26	16.63	16.52	10.81	10.13	10.02	10.48	10.37
25	16.68	16.02	16.02	16.35	16.25	10.46	9.83	9.78	10.20	10.10
30	16.43	15.81	15.78	16.11	16.01	10.21	9.62	9.54	9.96	9.86
35	16.26	15.64	15.58	15.94	15.84	10.04	9.45	9.34	9.79	9.69
40	16.11	15.50	15.46	15.77	15.68	9.89	9.31	9.22	9.62	9.53
45	15.97	15.39	15.37	15.68	15.55	9.75	9.20	9.13	9.53	9.40
50	15.88	15.28	15.23	15.56	15.46	9.66	9.09	8.99	9.41	9.31
55	15.78	15.21	15.16	15.50	15.37	9.56	9.02	8.92	9.35	9.22
60	15.76	15.13	15.10	15.43	15.34	9.54	8.94	8.86	9.28	9.19
65	15.71	15.10	15.04	15.40	15.28	9.49	8.91	8.80	9.25	9.13
70	15.68	15.07	15.02	15.36	15.25	9.46	8.88	8.78	9.21	9.10
SAMPLES →	6	7	8	9	10	6	7	8	9	10

RUN 3

TABLE A3.12

EXPOSURE TIME t (min)	WET PAPER WEIGHT W_2 (g)					VARNISH WEIGHT W_v (g)				
5	18.92	19.03	19.60	18.88	18.40	12.79	12.89	13.26	12.68	12.23
10	18.00	18.12	18.62	17.94	17.52	11.87	11.98	12.28	11.74	11.35
15	17.47	17.60	18.10	17.43	17.00	11.34	11.46	11.76	11.23	10.83
20	17.08	17.20	17.68	17.02	16.61	10.95	11.06	11.34	10.82	10.44
25	16.78	16.89	17.36	16.72	16.33	10.65	10.75	11.02	10.52	10.16
30	16.54	16.63	17.12	16.48	16.07	10.41	10.49	10.78	10.28	9.90
35	16.36	16.48	16.89	16.31	15.88	10.23	10.34	10.55	10.11	9.71
40	16.20	16.29	16.74	16.15	15.72	10.07	10.15	10.40	9.95	9.55
45	16.08	16.14	16.61	16.03	15.66	9.95	10.00	10.27	9.83	9.49
50	16.00	16.05	16.50	15.92	15.50	9.87	9.91	10.16	9.72	9.33
55	15.91	15.97	16.38	15.87	15.41	9.78	8.83	10.04	9.67	9.24
60	15.85	15.90	16.34	15.81	15.37	9.72	9.76	10.00	9.61	9.20
65	15.81	15.86	16.27	15.78	15.33	9.68	9.72	9.93	9.58	9.16
70	15.77	15.82	16.22	15.74	15.31	9.64	9.68	9.88	9.54	9.14
SAMPLES →	11	12	13	14	15	11	12	13	14	15

TABLE A3.13

TIME t (min)	$\bar{r}$ values			
	Basis : Varnish weight		Basis : Wet paper weight	
	Experimental	Calculated	Experimental	Calculated
5	1.0000	0.9970	1.0000	0.9981
10	0.9287	0.9338	0.9524	0.9558
15	0.8863	0.8874	0.9241	0.9248
16	-	0.8797	-	0.9197
17	-	0.8726	-	0.9149
18	-	0.8659	-	0.9104
19	-	0.8596	-	0.9062
20	0.8557	0.8539	0.9037	0.9023
21	-	0.8482	-	0.8986
22	-	0.8431	-	0.8952
23	-	0.8382	-	0.8919
24	-	0.8337	-	0.8889
25	0.8320	0.8295	0.8875	0.8861
26	-	0.8255	-	0.8834
27	-	0.8217	-	0.8809
28	-	0.8182	-	0.8786
29	-	0.8149	-	0.8763
30	0.8127	0.8123	0.8749	0.8742
35	0.7983	0.7983	0.8653	0.8652
40	0.7859	0.7873	0.8570	0.8580
45	0.7764	0.7778	0.8508	0.8516
50	0.7677	0.7691	0.8449	0.8458
55	0.7612	0.7613	0.8405	0.8406
60	0.7568	0.7549	0.8376	0.8364
65	0.7528	0.7511	0.8349	0.8338
70	0.7501	0.7517	0.8331	0.8341

MODE - RUN : SD-1

TABLE A3.14

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v L_v (%)	BASIS : W_2 L_w (%)	WET PAPER WEIGHT W_{2c} (g)	VARNISH WEIGHT W_{vc} (g)	BASIS : W_{vc} L_{vc} (%)	BASIS : W_{2c} L_{wc} (%)
A_1	11.15	7.03	15.96	9.77	3.58	2.19
A_2	10.93	6.87	16.00	9.79	4.19	2.56
A_3	10.39	6.61	16.12	10.02	4.39	2.73
A_4	11.12	7.08	16.49	10.28	5.93	3.70
A_5	10.57	6.69	16.22	10.08	5.95	3.70
B_6	31.16	19.71	16.29	10.14	28.11	17.50
B_7	30.81	19.42	16.35	10.17	28.12	17.49
B_8	32.19	20.44	16.69	10.48	29.96	18.81
B_9	32.20	20.35	16.53	10.35	30.34	19.00
B_{10}	30.38	19.31	16.81	10.61	28.84	18.20
C_{11}	40.60	25.93	17.06	10.83	39.61	25.15
C_{12}	40.20	25.89	17.37	11.14	39.50	25.33
C_{13}	40.77	26.29	17.22	11.08	40.25	25.90
C_{14}	40.95	26.13	17.18	10.96	40.69	25.96
C_{15}	41.16	26.38	17.21	11.03	41.16	26.38

MODE - RUN ; SD-2

TABLE A3.15

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v	BASIS : W_2	WET PAPER WEIGHT	VARNISH WEIGHT	BASIS : W_{vc}	BASIS : W_{2c}
	L_v (%)	L_w (%)	W_{2c} (g)	W_{vc} (g)	L_{vc} (%)	L_{wc} (%)
A_1	16.85	10.98	17.06	10.79	10.01	6.33
A_2	15.68	9.98	16.18	10.04	9.36	5.81
A_3	15.77	10.22	16.73	10.59	10.29	6.52
A_4	16.49	10.63	16.88	10.66	11.63	7.35
A_5	15.36	9.83	16.66	10.46	10.99	6.90
B_6	34.42	21.56	16.20	9.99	31.43	19.38
B_7	33.42	21.77	17.36	11.16	30.91	19.67
B_8	33.21	20.96	16.55	10.33	30.98	19.34
B_9	32.99	20.95	16.71	10.51	31.21	19.63
B_{10}	34.03	21.42	16.58	10.36	32.53	20.33
C_{11}	42.28	26.42	16.52	10.26	41.33	25.67
C_{12}	42.35	26.50	16.59	10.34	41.59	25.92
C_{13}	42.08	26.49	16.76	10.52	41.64	26.13
C_{14}	41.69	26.04	16.63	10.38	41.43	25.86
C_{15}	42.83	26.93	16.97	10.67	42.83	26.93

MODE - RUN : SD-3

TABLE A3.16

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v	BASIS : W_2	WET PAPER WEIGHT	VARNISH WEIGHT	BASIS : W_{vc}	BASIS : W_{2c}
	L_v (%)	L_w (%)	W_{2c} (g)	W_{vc} (g)	L_{vc} (%)	L_{wc} (%)
A_1	23.15	15.01	17.03	10.73	16.78	10.57
A_2	21.63	13.77	16.59	10.29	15.74	9.77
A_3	23.40	14.99	16.85	10.54	18.31	11.45
A_4	22.10	14.09	16.57	10.35	17.49	10.92
A_5	23.42	15.13	17.03	10.81	19.52	12.39
B_6	37.56	24.57	17.58	11.32	34.89	22.47
B_7	36.89	23.91	17.07	10.92	34.52	22.09
B_8	38.12	24.89	17.45	11.26	36.23	23.38
B_9	36.93	23.95	17.29	11.11	35.28	22.67
B_{10}	38.28	24.83	17.52	11.28	36.97	23.80
C_{11}	43.07	27.93	17.51	11.29	42.16	27.18
C_{12}	42.82	27.52	17.42	11.15	42.15	26.98
C_{13}	44.49	28.85	17.83	11.54	44.02	28.49
C_{14}	43.01	27.68	17.52	11.26	42.81	27.51
C_{15}	43.80	27.92	17.19	10.96	43.80	27.92

MODE - RUN : SD-4

TABLE A3.17

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v L_v (%)	BASIS : W_2 L_w (%)	WET PAPER WEIGHT W_{2c} (g)	VARNISH WEIGHT W_{vc} (g)	BASIS : W_{vc} L_{vc} (%)	BASIS : W_{2c} L_{wc} (%)
A_1	26.64	17.07	16.26	10.12	20.46	12.73
A_2	27.35	17.48	16.07	10.01	21.88	13.63
A_3	27.01	17.26	16.47	10.28	22.18	13.84
A_4	26.24	16.62	16.26	10.08	21.93	13.59
A_5	26.78	17.03	16.44	10.26	23.00	14.36
B_6	39.03	24.41	16.10	9.91	36.23	22.30
B_7	39.66	24.94	16.29	10.11	37.29	23.14
B_8	39.22	24.59	16.03	9.93	37.26	23.08
B_9	39.54	24.86	16.14	10.06	37.87	23.61
B_{10}	38.61	24.35	16.21	10.15	37.24	23.32
C_{11}	43.87	27.40	16.40	10.19	42.89	26.56
C_{12}	43.43	27.25	16.25	10.15	42.76	26.71
C_{13}	43.22	27.13	16.36	10.25	42.73	26.77
C_{14}	44.76	28.20	16.77	10.56	44.51	28.03
C_{15}	44.36	27.97	16.59	10.46	44.36	27.97

MODE - RUN : SD-5

TABLE A3-18

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v L_v (%)	BASIS : W_2 L_w (%)	WET PAPER WEIGHT W_{2c} (g)	VARNISH WEIGHT W_{vc} (g)	BASIS : W_{vc} L_{vc} (%)	BASIS : W_{2c} L_{wc} (%)
A_1	30.53	19.86	16.70	10.55	24.83	15.69
A_2	30.80	19.34	15.81	9.67	25.44	15.56
A_3	29.99	19.15	16.34	10.20	25.29	15.79
A_4	29.57	19.12	16.90	10.71	25.49	16.15
A_5	31.26	20.33	17.21	10.99	27.84	17.78
B_6	46.27	29.48	16.60	10.41	43.90	27.53
B_7	45.16	29.41	17.33	11.14	43.09	27.70
B_8	46.77	30.51	17.22	11.11	45.10	29.09
B_9	46.54	30.45	17.38	11.26	45.20	29.29
B_{10}	45.72	29.69	17.22	11.10	44.60	28.75
C_{11}	46.78	30.25	17.11	11.00	45.91	29.52
C_{12}	46.86	30.35	17.10	11.03	46.24	29.83
C_{13}	46.70	30.21	17.22	11.12	46.22	29.85
C_{14}	46.69	30.21	17.47	11.29	46.50	30.05
C_{15}	46.74	30.27	17.54	11.36	46.74	30.27

MODE - RUN : RD-1

TABLE A3.19

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v L_v (%)	BASIS : W_2 L_w (%)	WET PAPER WEIGHT W_{2c} (g)	VARNISH WEIGHT W_{vc} (g)	BASIS : W_{vc} L_{vc} (%)	BASIS : W_{2c} L_{wc} (%)
A_1	41.35	26.02	15.64	9.56	36.30	22.19
A_2	42.47	26.53	15.63	9.51	37.96	23.10
A_3	42.24	26.83	16.18	10.04	38.35	23.80
A_4	41.62	26.39	16.16	10.04	38.15	23.70
A_5	41.43	26.29	16.47	10.26	38.40	23.92
B_6	48.21	30.74	16.65	10.45	45.93	28.83
B_7	48.59	30.72	16.47	10.27	46.64	29.08
B_8	47.38	30.02	16.56	10.37	45.71	28.62
B_9	47.14	29.66	16.41	10.23	45.65	28.46
B_{10}	48.51	30.79	16.69	10.52	47.34	29.84
C_{11}	48.13	30.49	16.68	10.51	47.19	29.74
C_{12}	48.27	30.56	16.79	10.59	47.59	30.02
C_{13}	48.11	30.49	17.00	10.75	47.63	30.12
C_{14}	48.70	31.22	17.29	11.08	48.47	31.29
C_{15}	48.86	31.23	17.13	10.95	48.86	31.23

MODE - RUN : RD-2

TABLE A3.20

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v L_v (%)	BASIS : W_2 L_w (%)	WET PAPER WEIGHT W_{2c} (g)	VARNISH WEIGHT W_{vc} (g)	BASIS : W_{vc} L_{vc} (%)	BASIS : W_{2c} L_{wc} (%)
A_1	44.84	28.10	15.86	9.66	39.96	24.34
A_2	44.90	28.22	15.95	9.77	40.64	24.89
A_3	45.29	28.68	16.24	10.05	41.59	25.74
A_4	45.29	28.45	16.14	9.93	42.99	25.84
A_5	44.47	28.13	16.33	10.14	41.62	25.84
B_6	48.05	30.26	16.27	10.08	45.73	28.33
B_7	48.89	30.65	16.12	9.97	46.84	28.97
B_8	48.38	30.74	16.61	10.44	46.65	29.32
B_9	48.38	30.74	16.70	10.51	47.00	29.58
B_{10}	48.76	30.63	16.40	10.22	47.65	29.70
C_{11}	49.09	30.77	16.44	10.24	48.24	30.05
C_{12}	49.23	30.90	16.41	10.26	48.54	30.35
C_{13}	49.91	32.20	17.02	10.96	49.45	31.85
C_{14}	49.22	30.78	16.27	10.17	48.97	30.61
C_{15}	48.87	31.14	16.73	10.66	48.87	31.14

MODE - RUN : RD-3

TABLE A3.21

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v	BASIS : W_2	WET PAPER WEIGHT	VARNISH WEIGHT	BASIS : W_{vc}	BASIS : W_{2c}
	L_v (%)	L_w (%)	W_{2c} (g)	W_{vc} (g)	L_{vc} (%)	L_{wc} (%)
A_1	47.29	29.71	15.93	9.72	42.70	26.05
A_2	46.57	29.33	15.90	9.76	42.42	26.04
A_3	47.03	29.45	15.98	9.78	43.35	26.53
A_4	47.33	29.71	16.14	9.92	44.15	27.14
A_5	47.22	30.22	16.51	10.33	44.72	27.98
B_6	49.29	31.15	16.33	10.16	46.95	29.21
B_7	48.89	31.09	16.52	10.37	46.87	29.42
B_8	48.90	30.81	16.29	10.15	47.19	29.41
B_9	47.95	30.17	16.39	10.22	46.48	28.98
B_{10}	48.02	30.07	16.34	10.16	46.85	29.13
C_{11}	49.05	30.88	16.51	10.33	48.21	30.16
C_{12}	49.76	31.39	16.53	10.39	49.09	30.85
C_{13}	49.44	31.42	16.63	10.54	49.05	31.09
C_{14}	49.00	30.92	16.52	10.42	48.75	30.75
C_{15}	48.63	30.52	16.32	10.24	48.63	30.52

MODE - RUN : RD-4

TABLE A3.22

BATCH	WEIGHT LOSS		CORRECTED DATA		WEIGHT LOSS	
	BASIS : W_v L_v (%)	BASIS : W_2 L_w (%)	WET PAPER WEIGHT W_{2c} (g)	VARNISH WEIGHT W_{vc} (g)	BASIS : W_{vc} L_{vc} (%)	BASIS : W_{2c} L_{wc} (%)
A_1	47.83	30.65	16.41	10.21	43.49	27.06
A_2	47.71	30.58	16.56	10.34	43.81	27.36
A_3	47.91	30.83	16.76	10.54	44.50	27.98
A_4	48.02	30.80	16.73	10.51	45.01	28.27
A_5	48.10	31.05	17.00	10.78	45.46	28.82
B_6	49.13	31.23	16.68	10.49	46.90	29.50
B_7	49.73	32.03	16.95	10.77	47.82	30.38
B_8	50.09	32.18	17.00	10.80	48.52	30.82
B_9	49.24	31.61	17.14	10.90	47.89	30.46
B_{10}	48.92	31.90	17.44	11.29	47.83	30.96
C_{11}	49.65	32.02	17.31	11.10	48.83	31.31
C_{12}	49.56	32.12	17.49	11.29	48.98	31.62
C_{13}	50.09	32.51	17.41	11.28	49.65	32.17
C_{14}	49.60	32.10	17.25	11.15	49.42	31.94
C_{15}	49.86	31.90	16.96	10.85	49.86	31.90

TABLE A3.23

Drying time t (min)	Basis : Varnish I β_1		Basis : Varnish I, II, III. β_2	
3	0.988	0.834	0.988	0.856
5	0.996	0.819	0.996	0.819
8	0.980	0.810	0.980	0.810
10	0.966	0.804	0.992	0.804
12	0.955	–	0.955	–
13	0.927	0.784	0.926	0.805
15	0.925	0.780	0.925	0.780
18	0.900	0.781	0.900	0.781
20	0.887	0.772	0.911	0.772
23	0.859	0.769	0.859	0.789
25	0.842	0.756	0.842	0.756
28	0.833	0.760	0.833	0.760
30	0.829	0.753	0.851	0.753
32	0.820	–	0.820	–
42	0.798	–	0.798	–
Drying mode →	SD	RD	SD	RD

APPENDIX A4

A4.1 Preliminary work

A4.1.1 Temperature distribution in electric press

The electric press platens measured 43.2 x 35.6 cm and they were heated by four elements as shown in figure A4.1(a). Each platen was independantly controlled by an on/off controller via a Ni-Cr/Ni-Al thermocouple acting as the temperature sensor.

Several Chromel/Alumel thermocouples (previously calibrated) were attached over the surface of the platen (figure A4.1 (b)) covering an area of approximately 625 cm^2, since only this part was utilised in the lamination experiments.

The lower platen was raised until it was within about 1 cm of the upper platen. Heating was applied and the temperature was measured at different settings of the controller. The results (for the lower platen) are shown in table A4.1. (Similar variation was observed with the upper platen temperature).

The temperature distribution in each platen was also measured by means of a small digital thermometer employing a thermocouple probe suitable for surface temperature determinations. The variation between the two sets of results was less than 2% over the temperature range considered. Figure A4.2 shows the electric press calibration chart.

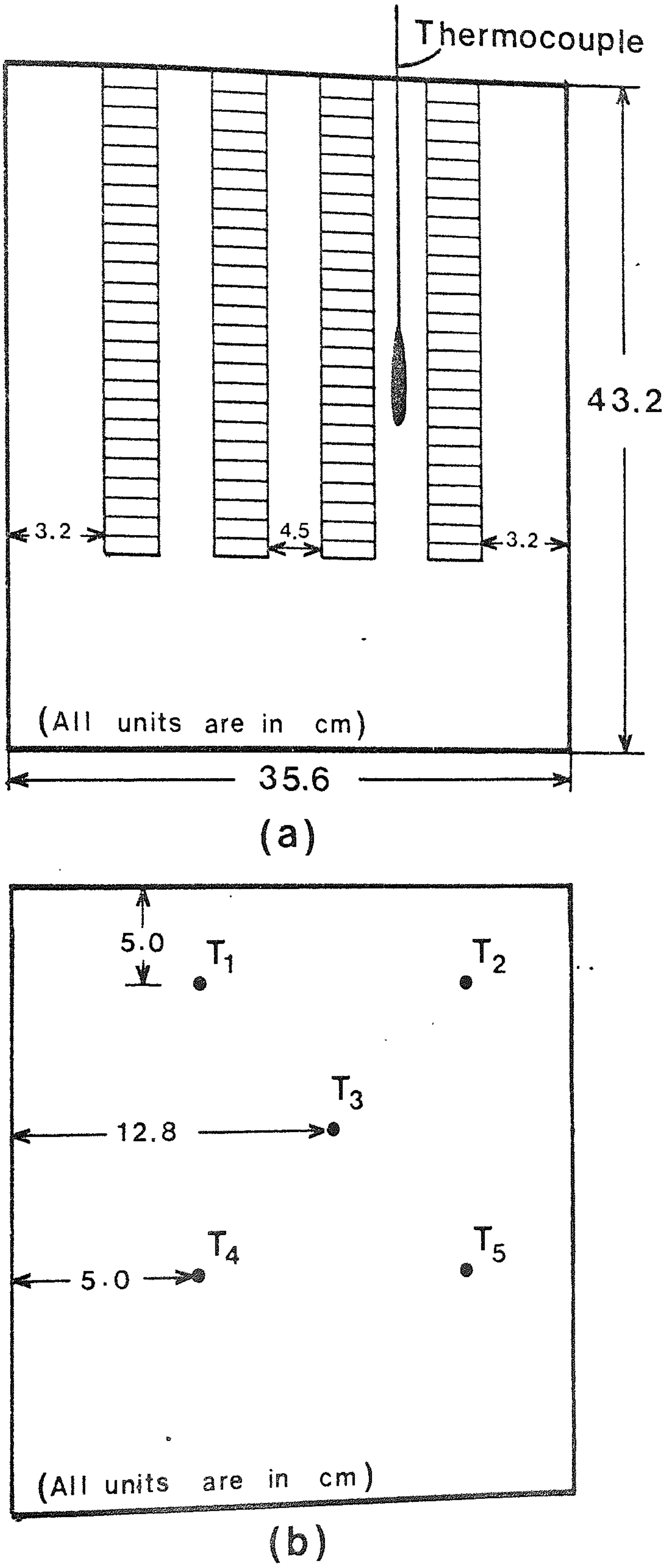


Figure A4.1 (a) Lower platen showing electric elements; (b) location of thermocouples.

Controller Setting (^{o}C)	Thermocouple Readings (^{o}C)				
	T_1	T_2	T_3	T_4	T_5
50	48.0	48.5	50.0	48.5	49.0
75	73.0	73.5	74.0	73.0	73.5
100	97.0	97.5	98.5	97.5	98.0
125	121.0	121.5	123.5	122.0	122.5
150	145.0	146.0	148.0	146.5	147.0
175	167.0	168.5	172.0	169.5	170.5

Table A4.1 Electric press temperature distribution.

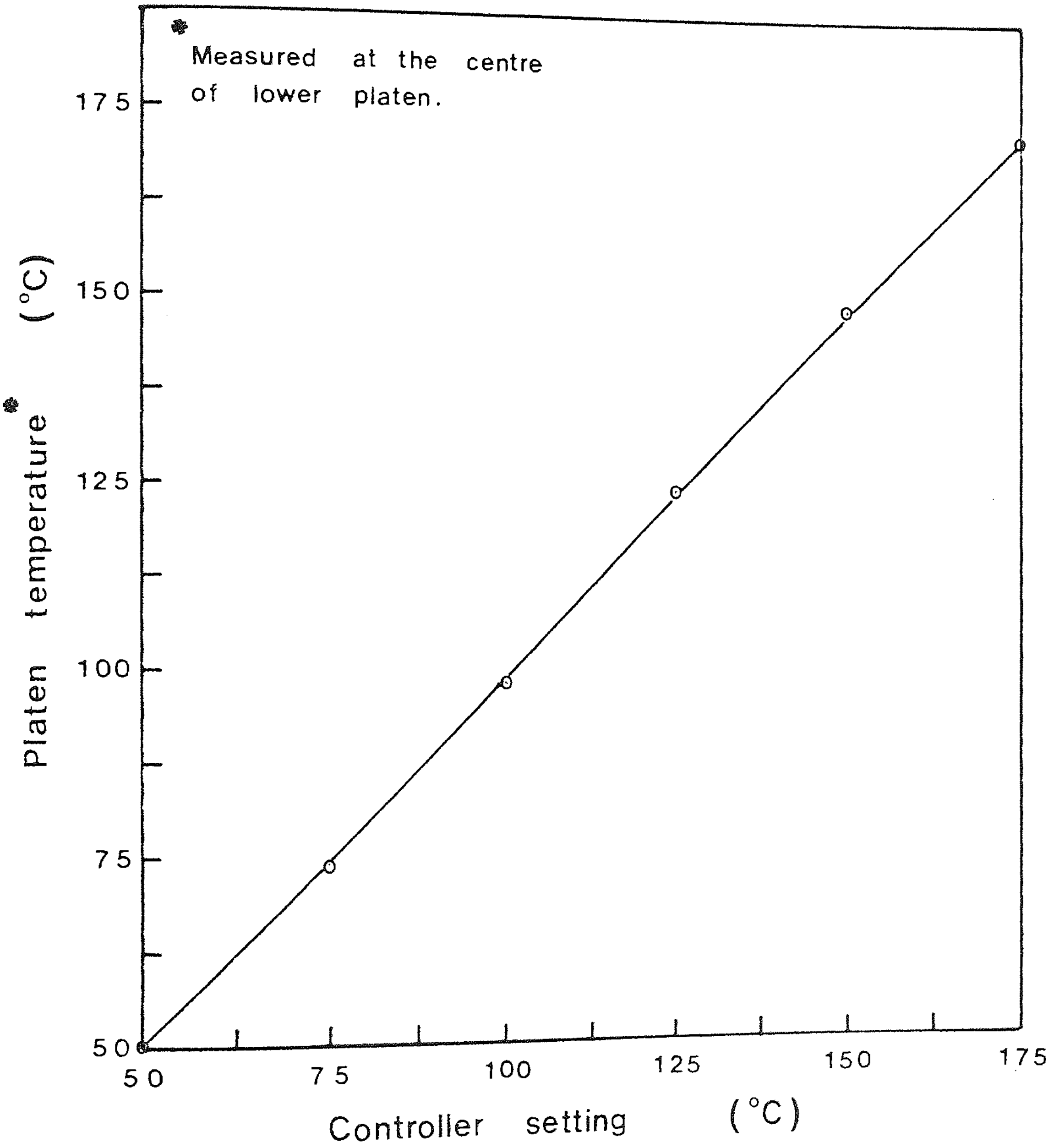


Figure A4.2 Electric press calibration chart.

A4.1.2 Thermocouple positions within the lay-ups

It was important that the thermocouples' position within each lay-up remained unaltered throughout the lamination stage.

In order to examine whether the form of attachment used was adequate for this purpose, two different types of tests were conducted. The first test involved repeated pressing at (150°C), cooling, withdrawing, and re-inserting into the press a lay-up consisting of several unimpregnated layers of kraft paper with thermocouples attached at various marked locations. At the end of these cyclic operations the position of each thermocouple was checked.

The second test involved laminating a series of sheets approximately 0.6 mm thick using production prepregs cut to the appropriate size. The thermocouples were placed between the first and second prepreg of each lay-up so that their position could be visually assessed after completion of pressing.

In both tests it was found that all thermocouples remained in their pre-determined locations, and the method of attachment employed was therefore satisfactory and it was used subsequently in all lamination experiments.

A4.2 Work on the steam-heated press

A4.2.1 Temperature distribution in press

The temperature distribution in the steam-heated press was determined according to a similar procedure as that for the electric press. The thermocouple location and temperature distribution are shown in figure A4.3 and table A4.2 respectively. The calibration chart is shown in figure A4.4. (It should be noted that when referring to press temperature, this is taken to mean the temperature in the centre of the platens - T_3 in figure A4.3.

A4.2.2 'Leaching' experiments

Fresh specimens from both the S- and M-series laminates were used to determine whether resin leaching occurs during repeated immersion in water at ambient conditions.

All specimens were firstly conditioned at 50 ± 2°C and 50 ± 5% relative humidity for two weeks. They were then dried at 50°C under vacuum (660 mbar), cooled in a dessicator (also under vacuum) and weighed. This was repeated until the difference in weight between successive measurements was less than 5 mg. At the end of the drying period each specimen was immersed in distilled water maintained at 23 ± 0.5°C for 24 hours, re-weighed and dried under vacuum to approximately constant weight. This procedure was repeated.

Table A4.3 shows the results obtained.

A4.2.3 Fabric-phenolic laminates

The lamination work on paper-phenolic resin was extended to fabric-based laminates in order to assess the suitability of the modified cycle. It must be emphasized that this was only a preliminary investigation and should be treated as such.

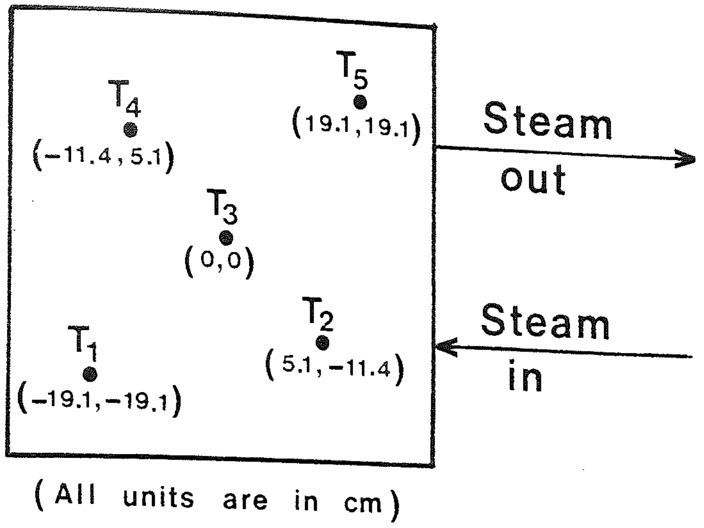


Figure A4.3 Location of thermocouples.

STEAM TEMPERATURE* (°C)	THERMOCOUPLE READINGS (°C)				
	T_1	T_2	T_3	T_4	T_5
130	129	129	130	130	130
140	139	140	140	140	140
150	148	148	149	150	150
160	157	157	158	158	159
170	166	166	167	167	168
180	175	175	177	177	178

*Measured by inserting a thermocouple into a steam passage.

Table A4.2 Steam-heated press temperature distribution (lower platen).

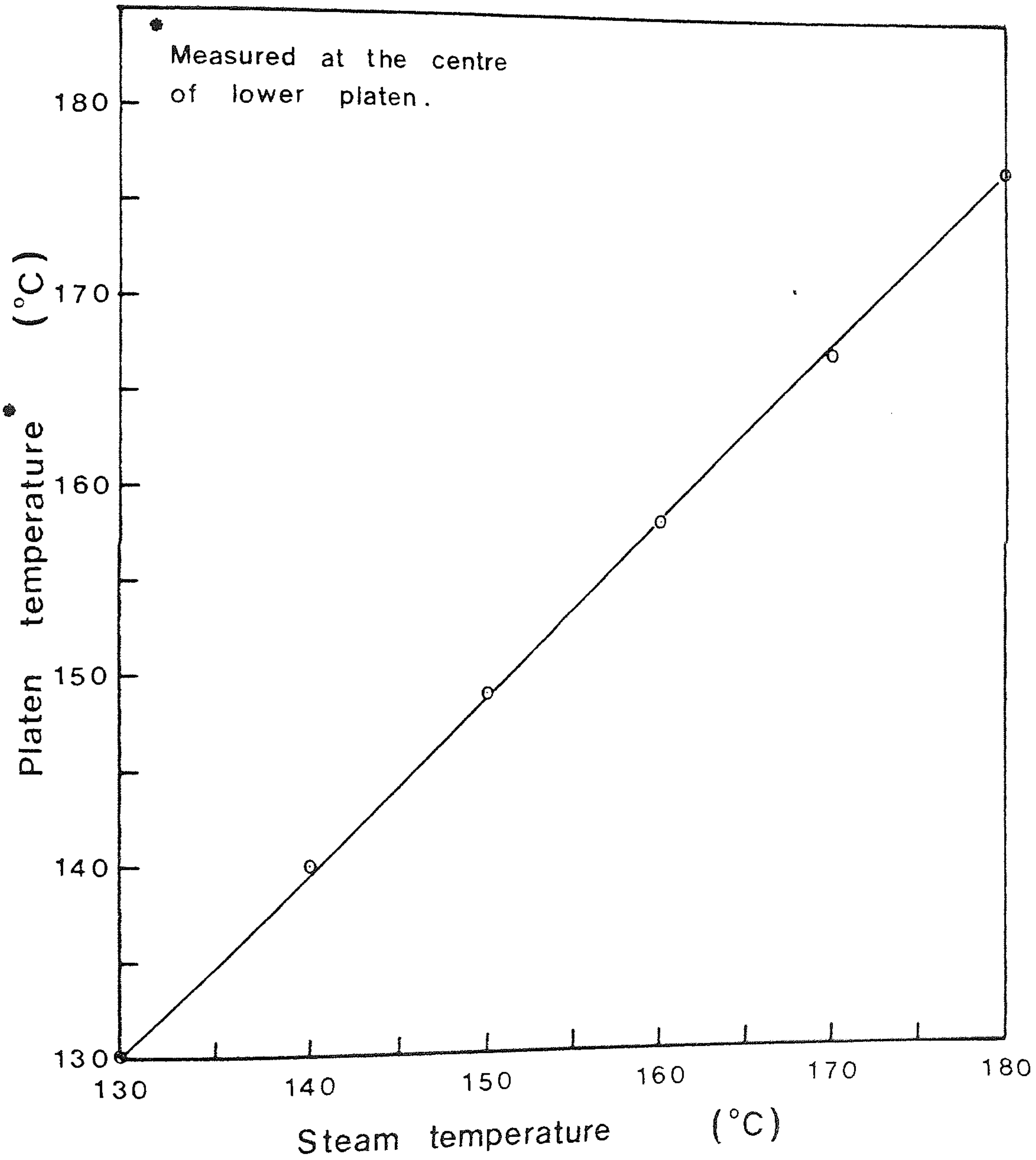


Figure A4.4 Steam-heated press calibration chart.

SERIES	SAMPLE	WEIGHT MEASUREMENTS (g)				
		DRYING	IMMERSION IN WATER	DRYING	IMMERSION IN WATER	DRYING
S	1	86.752	86.961	86.754	86.969	86.759
	2	87.063	87.283	87.070	87.275	87.072
M	3	87.036	87.164	87.044	87.161	87.046
	4	87.751	87.867	87.758	87.880	87.762

Table A4.3 Water absorption and de-sorption of various specimens (S- and M-series).

The work involved pressing two lay-ups (45.7 x 45.7 cm) using production prepregs. One of the lay-ups (SF1) was pressed under standard conditions; the other (MF1) was pressed using the shorter cycle.

The results of the temperature measurements during laminations are shown in tables A4.4 and A4.5. Table A4.6 summarises the results of the physical property tests.

A4.2.4 Results

The results of the temperature determinations for both S and M mode can be found in tables A4.7 to A4.14 at the end of the appendix.

Run:SF1

Table A4.4

TIME (min)	THERMOCOUPLE READINGS (°C)				
	T_1	T_2	T_3	T_4	T_5
0	18.5	18.5	18.5	18.5	18.5
2	71.0	19.0	18.5	18.5	18.5
4	98.5	34.0	19.5	19.5	19.5
6	108.0	55.5	25.5	25.5	25.5
8	115.0	69.5	38.0	37.5	36.0
10	119.0	78.0	54.5	55.5	53.5
12	122.5	86.5	71.5	71.5	67.5
14	125.5	94.5	84.0	84.5	80.5
16	129.0	102.0	92.5	92.5	87.5
18	131.5	109.0	101.0	101.5	96.0
20	134.0	116.0	108.5	108.5	101.5
25	139.5	128.0	124.0	124.0	116.5
30	144.0	138.5	136.0	135.5	126.0
35	147.0	146.5	146.5	145.5	134.5
40	150.5	154.0	155.0	154.0	141.0
45	152.5	159.0	161.0	160.0	146.0
50	154.0	161.5	164.5	163.0	148.5
55	154.5	162.0	165.0	163.5	150.5
60	154.0	161.0	163.5	162.5	151.0
65	153.5	159.5	161.5	160.5	150.5
70	152.5	157.5	159.0	158.5	150.0
75	152.0	156.0	157.5	157.0	149.0
80	152.0	155.0	156.0	155.5	148.0
85	151.5	154.0	155.0	154.0	147.0
COOLING PERIOD					
87	135.0	152.5	154.0	153.5	146.5
90	89.0	136.5	146.5	144.5	141.5
92	70.0	119.0	133.5	132.0	133.5
95	56.5	95.5	108.5	106.0	112.0
97	49.0	81.5	92.5	91.5	99.0
100	42.0	66.0	73.5	72.0	79.0
102	37.5	57.0	64.0	63.0	70.0
105	33.0	47.0	51.5	51.0	57.0
107	30.0	41.5	45.5	45.0	51.5
110	27.0	35.5	38.0	38.0	43.0

Run: MF1

Table A4.5

TIME (mim)	THERMOCOUPLE READINGS (°C)				
	T_1	T_2	T_3	T_4	T_5
0	17.0	17.0	17.0	17.0	17.0
2	73.0	18.0	17.0	17.0	19.5
4	98.0	35.0	18.0	18.5	21.0
6	108.0	56.0	25.0	25.5	27.5
8	115.0	69.0	37.5	37.5	37.5
10	118.5	78.0	56.0	56.5	54.5
12	122.5	87.0	73.0	72.5	68.0
14	125.5	95.0	84.5	85.0	79.5
16	129.0	103.0	93.0	92.5	86.0
18	132.0	110.0	102.0	102.0	94.0
20	135.0	116.5	109.0	109.0	99.0
25	140.0	129.0	124.5	124.0	113.0
30	144.5	139.5	136.5	136.0	121.5
35	148.0	147.5	147.0	146.0	129.0
40	151.0	154.5	155.5	154.0	133.5
STEAM TURNED OFF					
45	148.5	159.0	162.0	160.5	138.0
48	143.5	158.0	162.5	161.0	139.0
50	141.0	156.0	161.0	159.5	138.5
55	133.5	149.0	154.5	153.0	135.0
COOLING PERIOD					
57	122.0	145.0	151.0	149.0	132.5
60	80.0	128.0	140.5	139.0	127.0
62	68.0	113.5	127.0	125.0	118.5
65	54.5	91.5	106.0	104.5	104.5
67	49.0	80.0	90.5	88.5	91.0
70	40.0	64.0	72.5	72.0	77.5
72	36.0	56.0	62.5	61.5	67.5
75	30.5	45.5	51.0	50.5	57.5
77	28.0	40.0	44.5	44.0	50.5
80	24.0	33.0	36.5	36.5	43.5

LAMINATE[a]	FLEXURAL STRENGTH[b] (MPa)	WATER ABSORPTION[c] (mg)	INSULATION RESISTANCE[d] (10^8 ohms)
SF1	141	245	3.1
MF1	145	212	3.0

[a] Thickness: 24.9 ± 0.3 mm.

[b] Mean of six determinations.

[c] Mean of three determinations.

[d] Mean of four determinations.

Table A4.6 Results of physical property tests for fabric-based phenolic laminates.

Run:S1

TIME	THERMOCOUPLE READINGS (°C)									
(min)	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	26.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0
2	77.0	27.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0	26.0
4	107.0	43.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0	27.0
6	114.0	58.5	31.5	32.0	32.5	33.0	33.0	33.5	33.5	33.5
8	121.0	72.5	42.0	42.0	42.0	41.6	40.5	41.0	41.0	40.5
10	124.0	80.0	55.0	54.0	56.5	56.5	55.5	58.5	58.5	58.0
12	128.0	87.5	70.0	68.0	70.0	69.0	67.0	69.0	69.0	66.0
14	130.0	92.5	79.5	77.0	80.0	80.0	78.0	81.5	81.5	79.0
16	133.0	100.5	88.5	85.0	88.5	88.0	84.5	88.0	87.5	84.0
18	134.5	105.5	94.5	91.0	95.5	95.5	92.0	97.0	97.0	93.0
20	137.5	113.0	102.5	98.0	102.0	102.0	97.0	102.0	102.0	97.0
22	138.5	117.5	109.0	105.0	110.0	110.0	105.5	111.0	111.0	106.0
24	140.5	122.5	115.0	109.5	115.0	115.0	109.0	115.0	115.0	109.0
26	141.5	125.0	119.0	113.5	119.5	119.5	114.0	120.0	120.0	114.5
28	143.5	130.5	125.0	118.0	124.0	124.0	118.0	124.0	124.0	117.5
30	144.0	133.0	128.0	122.0	128.5	128.5	122.0	129.0	129.0	123.0
35	147.5	142.5	139.0	131.0	139.0	139.0	130.5	139.0	139.0	130.0
40	150.0	149.5	148.5	139.0	149.0	149.0	139.0	149.0	150.0	139.5
45	153.0	159.0	160.5	146.0	159.0	159.0	146.0	159.0	159.0	146.5
50	155.5	166.5	170.0	152.0	169.0	169.0	152.5	169.5	169.5	153.0
55	159.0	175.0	181.0	159.0	178.0	178.0	158.0	178.0	179.5	158.0
60	160.5	177.5	184.0	164.0	184.0	183.0	163.5	182.0	183.5	163.5
65	160.5	175.5	182.0	167.0	180.5	181.0	166.0	181.0	182.0	165.5
70	159.5	173.0	177.5	167.0	176.5	176.5	166.0	176.0	176.5	165.5
75	157.5	168.0	172.0	165.5	171.5	172.0	164.5	172.0	172.5	164.5
80	156.5	165.0	168.0	163.0	167.5	167.5	162.0	167.5	168.0	161.0
85	155.0	162.5	165.0	160.5	165.0	165.0	159.5	165.0	165.0	159.0
COOLING PERIOD										
87	151.5	161.0	163.0	159.0	163.0	163.0	158.0	163.0	163.0	157.5
90	90.5	147.5	158.0	156.5	158.0	158.5	155.0	159.0	159.5	155.5
92	80.0	135.5	150.5	150.0	149.0	149.0	148.0	148.5	148.0	147.0
95	63.0	111.5	130.5	134.0	130.5	131.0	134.0	132.0	132.0	134.0
97	59.0	102.5	119.0	123.0	117.5	117.0	121.0	116.5	116.0	118.0
100	51.0	86.5	97.5	103.5	98.5	100.0	105.5	101.5	101.5	105.0
102	48.5	82.0	90.0	95.0	88.5	88.0	92.5	88.0	87.0	89.5
105	43.5	68.0	75.5	81.0	75.5	76.0	81.0	77.0	76.5	79.5
107	42.0	64.5	70.0	75.0	69.0	69.0	73.0	68.5	68.0	70.0
110	38.0	53.5	59.5	64.5	59.5	59.5	64.0	60.0	60.0	62.5
112	36.5	51.0	55.5	60.0	55.0	55.0	58.0	54.5	54.0	56.0
115	34.0	45.0	49.0	53.0	49.0	49.0	52.5	49.5	49.0	51.5

Table A4.7

Run:S2

TIME (min)	THERMOCOUPLE READINGS (°C)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
2	80.0	23.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
4	111.0	41.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0	23.0
6	117.0	56.0	28.0	28.0	29.0	29.0	29.0	30.0	30.0	30.0
8	124.5	71.5	40.5	39.0	40.0	39.0	38.0	38.0	38.0	37.0
10	127.0	77.0	51.5	50.0	53.0	53.0	51.5	55.0	55.0	55.0
12	130.5	86.0	68.5	65.0	68.0	67.5	64.0	67.5	67.0	65.0
14	132.0	92.0	78.0	74.5	79.5	79.0	75.5	81.0	81.0	79.0
16	135.0	100.5	87.5	82.5	87.0	87.0	82.0	87.0	87.0	83.5
18	136.5	106.0	94.0	89.0	95.0	95.0	90.0	96.0	96.5	93.0
20	139.0	113.0	102.0	96.0	102.0	101.5	95.5	102.0	102.0	97.5
22	140.5	117.0	108.0	102.0	108.5	108.5	102.5	110.0	110.0	106.0
24	142.5	123.0	115.0	107.5	115.0	114.0	107.5	114.5	115.0	110.0
26	143.5	126.5	119.5	112.0	119.5	119.5	112.5	120.5	120.5	116.0
28	145.0	131.0	125.0	117.0	125.0	124.0	117.0	124.5	125.0	119.0
30	146.0	134.0	129.0	120.5	129.0	129.0	121.0	130.0	130.0	124.5
35	149.5	144.0	140.5	130.5	140.5	140.0	130.0	140.5	141.0	133.0
40	152.0	151.5	150.5	138.5	150.5	150.5	139.0	151.0	152.0	143.0
45	155.0	160.5	162.0	146.0	161.5	161.0	146.0	161.0	162.0	150.0
50	157.5	168.5	173.0	153.0	173.0	172.0	153.0	173.0	174.5	158.5
55	160.5	177.5	183.5	160.0	182.5	181.0	159.5	181.5	183.0	164.0
60	162.0	180.0	186.0	165.0	184.5	184.0	165.0	184.5	185.0	169.5
65	161.5	177.5	183.0	168.0	182.0	181.0	167.0	181.5	182.0	170.0
70	160.0	174.0	178.0	168.0	177.0	176.5	167.0	176.5	176.5	168.5
75	158.5	169.0	173.0	166.0	172.0	172.0	165.0	172.0	172.0	166.5
80	157.0	165.5	168.5	162.5	167.5	167.5	162.0	167.5	167.5	162.5
85	155.5	162.5	165.0	160.0	164.5	164.0	159.0	164.5	164.5	160.0
COOLING PERIOD										
87	151.0	161.6	161.5	159.0	163.0	163.0	158.0	163.0	163.0	158.5
90	85.0	147.0	158.5	155.5	158.5	158.5	155.0	159.0	159.0	156.0
92	72.5	135.0	150.5	150.5	149.0	148.5	148.5	148.0	147.5	147.0
95	56.0	111.0	130.0	134.5	129.5	130.0	134.0	134.0	130.5	130.0
97	52.0	100.0	116.5	122.0	114.0	114.0	119.0	113.0	112.0	116.0
100	45.0	82.0	96.0	103.0	95.0	96.0	103.0	96.5	96.0	102.5
102	42.5	75.5	87.0	93.0	85.5	85.5	91.0	84.5	83.5	87.5
105	37.0	63.0	72.5	80.0	72.0	72.5	79.0	72.5	72.0	77.0
107	35.5	58.0	66.0	73.0	65.0	65.0	70.5	64.0	63.0	67.0
110	31.5	48.5	55.0	62.0	55.0	55.0	61.0	55.0	54.5	59.0
112	30.0	45.0	50.5	57.0	49.5	49.5	55.0	49.0	48.0	52.0
115	27.5	39.0	43.0	49.0	43.0	43.0	48.5	43.5	43.0	46.5

Table A4.8

Run: S3

TIME (min)	THERMOCOUPLE READINGS (^oC)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
2	75.0	22.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
4	105.0	36.5	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
6	112.0	52.0	26.0	25.5	26.5	26.5	26.0	27.5	27.5	27.5
8	120.0	67.0	37.0	36.5	36.5	36.0	35.0	36.0	36.0	35.0
10	123.0	73.5	49.0	46.5	50.0	50.0	49.0	52.5	52.5	52.5
12	126.5	82.5	65.0	61.5	64.5	64.0	61.0	64.5	64.0	62.0
14	128.0	88.0	75.0	71.0	75.5	75.5	72.5	77.0	77.0	74.5
16	131.0	96.5	85.0	79.0	85.0	84.5	79.5	84.5	84.5	80.0
18	132.5	102.0	91.0	85.5	91.5	91.5	86.5	93.0	93.0	89.0
20	136.0	110.0	99.5	92.5	99.0	98.5	92.0	99.0	99.0	93.5
22	137.0	114.0	105.5	98.5	106.0	106.0	99.5	107.5	107.5	102.5
24	139.5	119.5	112.0	104.0	112.0	111.0	104.5	112.0	112.0	107.0
26	140.5	123.0	116.5	108.5	117.0	116.5	109.0	118.0	118.0	112.0
28	142.0	128.0	122.0	114.0	121.5	121.0	114.0	122.0	122.0	116.0
30	143.0	131.0	126.0	117.0	126.0	126.0	117.0	127.0	127.5	121.0
35	146.0	140.5	137.0	127.0	137.0	136.0	126.5	137.0	137.5	129.0
40	148.5	147.5	146.5	135.0	147.0	146.0	135.5	148.0	148.0	138.5
45	151.5	156.5	158.0	142.0	157.0	156.0	142.5	157.5	158.0	145.0
50	154.5	165.0	168.5	149.0	167.5	167.0	149.5	169.0	170.0	153.5
55	157.0	173.0	179.0	156.0	176.5	175.0	156.0	177.5	179.0	159.5
60	158.5	176.0	182.5	161.0	180.0	179.0	160.5	181.0	182.0	164.5
65	159.0	175.0	180.5	164.0	178.5	178.0	164.0	179.0	180.0	167.0
70	158.0	172.0	176.0	164.0	175.0	174.5	164.0	174.5	175.0	165.5
75	157.0	167.5	171.5	162.0	170.5	170.0	162.0	170.5	171.0	163.5
80	156.0	164.5	167.5	158.5	167.0	166.5	159.0	166.5	166.5	160.5
85	154.5	161.5	164.0	157.5	163.5	163.5	157.5	163.5	154.0	159.0
COOLING PERIOD										
87	150.0	160.5	162.5	156.5	162.0	162.0	156.5	162.0	162.0	158.0
90	86.0	146.5	158.0	154.0	157.5	157.5	154.0	158.0	158.0	155.0
92	74.0	135.0	149.5	149.5	148.0	148.0	148.0	147.0	147.0	146.5
95	56.5	110.5	128.5	135.0	128.0	129.0	134.0	129.0	129.0	132.0
97	52.5	100.0	115.0	124.0	114.0	114.0	120.5	112.0	111.5	115.5
100	44.5	81.5	94.0	104.5	94.0	95.0	103.0	95.0	95.0	101.0
102	41.5	74.0	85.0	95.0	84.0	84.0	91.5	82.0	82.0	86.0
105	36.0	61.5	70.5	80.5	70.0	71.0	79.0	70.5	70.5	75.0
107	34.0	56.0	63.5	73.0	62.5	62.5	70.0	61.5	61.5	65.0
110	29.0	46.5	52.5	61.5	52.5	53.0	60.0	52.5	53.0	56.5
112	28.0	43.0	47.5	56.0	47.0	47.0	53.5	46.5	46.5	49.0
115	25.0	36.5	40.5	41.0	47.0	40.5	40.5	40.5	40.5	43.5

Table A4.9

Run:S4

TIME (min)	THERMOCOUPLE READINGS (^{o}C)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
2	75.0	26.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0	25.0
4	105.0	42.5	26.0	27.5	25.5	25.5	26.5	25.5	25.5	26.0
6	112.5	56.0	30.5	33.5	31.5	31.5	33.0	32.0	32.0	32.5
8	121.0	70.0	45.0	47.0	44.5	43.5	43.5	43.0	42.0	40.0
10	124.0	77.0	58.0	59.5	59.0	59.0	59.0	60.0	60.0	57.5
12	128.0	86.5	71.0	71.0	70.0	69.5	68.0	69.0	69.0	65.0
14	130.0	92.0	79.5	79.5	80.0	79.5	78.0	80.0	80.5	76.0
16	133.5	101.0	89.0	88.0	88.0	87.0	85.0	87.0	87.0	82.0
18	135.0	106.5	95.0	94.0	95.5	95.0	92.5	95.5	96.0	91.5
20	137.5	114.0	103.0	101.5	102.0	101.0	98.0	101.0	101.0	94.0
22	139.0	118.0	109.5	107.5	109.5	109.0	105.5	109.0	109.5	102.0
24	141.0	123.0	115.5	113.0	115.0	114.0	110.0	114.0	114.0	105.0
26	142.0	126.5	120.0	117.5	120.0	119.5	115.0	119.5	120.0	111.0
28	143.5	131.5	126.0	122.5	124.5	124.0	119.0	124.0	124.0	114.0
30	144.5	134.5	130.0	126.0	129.5	129.0	123.5	129.0	130.0	119.0
35	147.5	144.0	141.0	136.0	141.0	140.0	132.0	139.0	140.0	126.0
40	150.0	151.5	151.0	144.0	151.0	150.0	140.0	150.0	151.0	134.0
45	153.5	161.0	163.0	152.0	162.5	160.5	146.0	160.0	161.5	140.0
50	156.0	168.5	173.5	159.0	173.0	171.0	152.5	171.0	173.5	146.0
55	158.5	175.5	182.0	165.0	181.0	178.0	157.0	178.0	180.0	149.5
60	159.5	176.5	182.5	168.0	181.5	179.0	160.5	180.0	181.0	154.0
65	159.0	173.5	179.0	168.0	178.0	176.5	161.5	177.5	178.5	155.5
70	158.0	170.0	174.0	166.0	173.5	172.5	160.5	173.0	173.5	156.5
75	156.0	166.0	169.0	162.5	169.0	168.0	158.0	169.0	169.0	155.5
80	155.0	163.0	165.5	159.5	165.0	164.5	156.0	165.0	165.0	154.0
85	154.0	160.0	162.5	157.0	162.5	162.0	154.0	162.5	162.5	152.5
COOLING PERIOD										
87	149.5	159.0	161.5	156.0	161.5	161.0	153.5	161.0	161.0	151.5
90	84.5	144.0	156.0	152.0	156.5	156.5	150.0	157.0	157.5	149.5
92	72.5	131.5	147.5	144.0	146.0	146.0	141.0	145.5	145.0	141.5
95	57.0	108.0	126.0	125.0	126.0	127.0	125.0	128.0	128.0	129.0
97	53.0	97.0	114.0	113.0	112.5	113.0	110.5	113.0	111.5	114.0
100	46.0	80.0	92.5	93.5	93.0	94.0	93.0	95.5	95.0	98.5
102	43.0	73.0	84.0	84.0	83.0	83.5	82.5	84.0	83.0	86.0
105	38.5	61.0	69.5	70.5	70.0	71.0	70.5	72.0	71.5	75.0
107	37.0	56.5	63.5	64.0	63.0	63.5	63.0	64.0	63.0	66.0
110	33.0	48.0	53.5	54.5	54.0	54.5	54.5	55.5	55.0	58.0
112	32.0	45.0	49.5	50.5	49.0	49.5	49.5	50.0	49.0	52.0
115	29.5	39.5	43.0	44.5	43.5	44.0	44.0	44.5	44.0	47.0

Table A4.10

Run:M1

TIME (min)	THERMOCOUPLE READINGS (°C)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
2	83.0	22.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
4	106.5	35.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
6	114.0	55.0	24.0	23.5	24.0	24.5	24.5	25.0	25.0	25.0
8	121.0	70.0	33.5	32.0	33.0	33.0	31.5	33.0	32.0	31.5
10	124.0	77.0	46.0	45.0	47.5	48.0	46.5	50.0	50.0	48.5
12	127.5	85.5	64.0	61.0	64.0	64.0	60.5	64.0	63.0	60.0
14	129.0	90.5	75.0	71.5	76.0	76.0	72.5	77.0	77.0	73.5
16	132.0	98.5	85.0	80.5	85.0	85.0	80.0	85.0	84.0	80.0
18	133.5	104.5	92.0	87.5	92.5	93.0	88.0	93.5	93.5	89.0
20	136.0	111.5	99.5	94.0	99.0	99.0	93.0	99.0	99.0	93.5
22	137.5	115.5	106.0	100.5	106.5	106.5	100.5	107.0	107.0	101.5
24	139.5	121.0	112.5	106.0	112.0	112.0	105.0	112.0	112.0	105.0
26	140.5	124.5	117.0	110.5	117.5	117.5	110.5	117.5	117.5	111.0
28	142.0	129.0	122.5	115.5	122.0	122.0	115.0	122.0	122.0	114.5
30	143.0	132.0	127.0	119.5	127.0	127.0	120.0	127.0	127.0	119.5
35	146.5	141.5	138.0	128.5	137.5	137.0	127.5	137.0	137.5	127.5
40	149.5	149.0	149.0	138.0	149.0	149.0	137.5	149.0	149.5	138.0
STEAM TURNED OFF										
42	149.0	154.0	155.0	141.5	154.5	153.5	140.5	153.0	154.0	140.0
45	146.5	157.0	160.0	145.0	160.0	159.0	144.0	159.0	160.0	144.0
50	138.0	159.0	166.5	149.0	166.0	164.5	147.5	164.0	166.0	147.5
55	132.0	156.0	165.5	148.5	164.0	163.0	147.0	162.0	164.0	147.0
COOLING PERIOD										
57	109.0	152.0	162.5	146.0	161.5	160.0	145.5	159.0	161.0	145.0
60	80.0	140.0	156.0	140.0	153.5	153.0	140.0	151.0	152.0	141.0
62	63.0	124.0	144.0	134.0	142.5	142.0	132.5	141.5	143.0	133.0
65	55.5	108.5	127.5	118.5	125.0	124.0	117.0	122.5	123.0	118.5
67	48.0	95.0	113.0	109.5	112.0	112.0	107.0	115.5	112.5	106.0
70	43.5	81.0	96.0	91.0	93.0	93.0	89.0	91.0	91.0	90.0
72	39.0	71.5	84.5	85.5	83.0	83.5	82.5	83.5	84.0	81.5
75	36.0	62.5	72.0	72.0	71.0	70.5	69.0	69.5	69.5	69.0
77	33.0	54.5	64.0	66.5	62.5	63.5	63.0	63.5	63.5	62.0
80	30.0	48.0	55.0	57.0	54.0	53.0	53.5	53.0	53.0	53.0
82	28.0	42.0	48.0	52.5	48.0	48.5	49.5	49.0	49.0	47.0
85	26.0	37.5	42.5	46.0	41.0	41.5	43.0	42.0	41.5	41.0

Table A4.11

Run : M2

TIME (min)	THERMOCOUPLE READINGS (°C)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0.	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
2	77.0	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
4	106.0	33.5	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
6	113.0	51.5	24.0	25.0	24.5	25.0	25.0	25.0	25.0	24.5
8	120.5	68.0	33.5	32.0	34.0	33.0	33.0	33.0	32.5	34.0
10	123.5	75.5	47.0	48.5	49.0	49.0	48.0	50.5	50.0	47.5
12	127.0	84.0	64.0	59.5	64.0	63.5	61.0	63.0	61.5	63.0
14	129.0	89.5	75.0	73.0	76.0	76.0	73.0	77.0	76.5	73.5
16	131.5	97.5	85.0	80.5	85.0	85.0	81.0	84.5	84.0	82.5
18	133.0	103.5	92.0	88.5	93.0	93.0	89.0	93.0	93.0	90.0
20	136.0	110.5	100.0	94.5	100.0	99.5	95.0	99.0	99.0	96.0
22	137.5	115.0	106.5	101.0	107.0	107.0	102.0	107.0	107.0	104.0
24	139.5	120.5	113.0	106.0	113.0	112.0	106.5	112.0	112.0	108.5
26	141.0	124.0	117.5	110.5	118.0	118.0	112.0	118.0	118.0	114.5
28	142.5	129.0	123.0	116.0	123.0	122.0	116.0	122.0	122.0	117.5
30	143.5	132.0	127.0	119.0	127.5	127.0	120.0	127.0	127.5	123.0
35	146.5	141.0	138.0	128.5	138.0	137.5	128.5	137.0	137.5	131.0
40	149.5	149.5	149.5	136.0	149.5	149.0	138.0	149.0	150.0	141.0
STEAM TURNED OFF										
42	149.0	154.0	155.0	138.0	154.0	153.0	140.5	153.0	153.5	143.0
45	147.0	157.0	160.0	143.0	159.5	158.5	144.5	158.5	160.0	146.5
50	139.5	160.0	167.0	145.5	165.5	164.0	147.5	163.5	165.5	150.0
55	134.0	157.5	166.0	144.0	164.5	163.0	146.5	162.0	163.5	149.5
COOLING PERIOD										
57	111.0	153.0	163.0	142.5	161.5	160.0	145.0	159.0	160.5	147.5
60	82.0	142.0	156.0	136.5	154.0	152.5	139.5	150.5	151.5	143.0
62	65.0	125.5	144.5	130.5	143.0	142.0	132.0	141.0	142.5	134.5
65	57.0	110.0	128.0	114.5	125.0	124.0	117.0	122.0	122.5	120.5
67	50.5	96.0	113.5	106.5	112.0	111.5	107.0	115.0	112.0	108.5
70	45.5	83.0	96.0	88.0	93.5	92.5	89.5	91.0	91.0	92.5
72	41.5	73.0	85.0	82.0	83.5	83.0	82.0	83.0	83.5	83.0
75	38.0	64.0	73.0	68.5	71.0	70.0	69.0	69.5	69.0	71.5
77	35.0	56.0	64.5	63.5	63.0	63.0	63.0	63.0	63.0	64.0
80	32.0	49.0	55.0	53.0	54.0	53.0	53.5	53.0	53.0	55.0
82	29.5	44.0	49.0	49.5	48.0	48.0	49.0	48.5	48.5	49.5
85	28.0	39.0	43.0	42.5	42.0	41.5	42.5	41.5	41.5	43.5

Table A4.12

Run: M3

TIME (min)	THERMOCOUPLE READINGS ($^{\circ}C$)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
2	79.0	22.0	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
4	107.0	34.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
6	114.0	52.0	23.5	28.0	24.5	24.0	26.0	23.0	23.0	23.0
8	120.5	68.5	33.0	35.5	34.0	32.0	33.5	31.0	30.5	31.0
10	124.0	76.0	47.0	51.0	49.0	48.5	49.0	49.5	48.5	44.5
12	127.5	84.0	63.5	63.0	63.5	63.0	61.5	61.5	60.0	60.0
14	129.5	89.5	75.0	76.5	75.5	75.5	74.0	75.5	75.0	70.0
16	132.0	98.0	84.0	83.5	85.0	84.0	82.0	83.0	82.5	79.5
18	133.0	104.0	91.5	92.0	92.5	92.0	89.5	91.5	91.5	87.0
20	136.5	111.0	100.0	97.5	99.5	99.0	96.5	97.5	97.5	92.5
22	137.5	115.5	106.0	104.5	106.0	106.0	103.0	106.0	105.5	100.5
24	140.0	121.0	112.5	109.5	112.0	111.5	107.0	111.5	111.0	104.5
26	141.5	124.0	117.0	114.0	117.0	117.0	113.0	117.0	116.5	110.5
28	142.5	129.0	122.5	120.0	122.5	121.0	117.0	122.0	121.0	114.0
30	144.0	132.0	127.0	123.0	127.0	126.0	121.0	126.0	127.0	120.0
35	147.0	141.5	137.5	132.0	137.0	137.0	129.5	136.5	137.5	129.5
40	150.0	149.5	149.0	140.0	148.5	148.0	139.0	147.0	148.0	137.0
STEAM TURNED OFF										
42	150.5	152.0	152.0	144.0	153.0	152.5	142.5	152.0	153.0	141.0
45	147.5	157.0	158.5	148.0	158.5	158.0	146.0	157.5	158.5	144.5
50	142.0	159.5	165.0	152.5	165.0	164.0	150.5	164.0	165.5	149.0
55	136.5	158.0	165.5	152.0	165.0	164.0	150.0	163.5	165.0	149.0
COOLING PERIOD										
57	128.5	156.0	163.5	151.0	163.0	161.5	148.0	161.0	162.0	147.0
60	77.5	140.0	155.0	144.5	154.5	153.5	142.5	153.5	155.0	142.0
62	69.0	130.0	146.5	137.5	144.5	143.0	134.0	142.5	143.0	133.0
65	55.0	108.5	126.0	120.0	125.0	124.0	119.0	125.0	126.0	120.0
67	51.0	98.0	114.0	109.0	112.0	111.0	107.5	110.5	110.5	106.5
70	42.5	80.0	92.5	90.5	91.5	91.5	90.0	92.5	92.5	92.0
72	40.0	73.0	84.0	82.0	82.0	81.5	80.0	81.5	81.0	81.0
75	34.5	60.0	69.0	69.0	68.0	68.0	68.0	69.0	69.0	70.0
77	32.0	54.5	62.0	62.0	60.5	60.0	60.0	60.5	60.0	61.0
80	28.0	45.0	51.0	51.5	50.0	50.0	51.0	51.0	50.5	53.0
82	26.5	41.5	46.0	46.5	45.0	44.5	45.0	45.0	44.5	46.5
85	23.5	35.0	39.0	40.0	38.5	38.5	39.5	39.5	39.0	41.5

Table A4.13

Run : M4

TIME (min)	THERMOCOUPLE READINGS (°C)									
	T_1	T_2	T_3	T_4	T_5	T_6	T_7	T_8	T_9	T_{10}
0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
2	76.0	23.0	22.0	23.0	22.0	22.0	22.0	22.0	22.0	22.0
4	105.0	39.5	23.0	25.5	22.5	22.5	24.0	22.5	22.5	23.5
6	113.0	56.0	27.0	31.5	27.0	27.5	29.0	28.0	28.0	29.0
8	121.0	69.5	40.0	42.5	38.5	38.5	38.0	38.5	37.5	35.5
10	123.0	76.0	53.0	55.0	53.5	53.5	51.5	55.5	55.5	53.0
12	127.0	85.0	68.0	68.0	67.0	66.5	62.5	66.5	66.0	61.5
14	129.5	91.0	76.5	76.5	77.0	76.5	72.5	78.0	78.0	74.0
16	132.5	99.5	86.0	85.0	85.0	84.5	79.5	85.0	84.5	79.0
18	134.0	105.0	93.0	91.0	93.0	92.5	87.0	94.0	94.0	88.0
20	137.0	112.0	101.0	98.0	100.0	99.0	92.0	100.0	99.5	92.0
22	138.0	116.5	107.0	104.0	107.0	106.5	98.5	108.0	108.0	100.0
24	140.0	122.0	113.5	109.0	112.5	112.0	103.0	112.0	112.0	103.0
26	141.0	125.5	118.5	113.5	118.0	117.5	108.0	118.5	119.0	108.5
28	143.0	130.0	124.0	118.5	123.0	122.0	112.0	123.0	122.5	111.5
30	144.0	133.0	128.0	121.5	127.0	126.5	116.0	128.0	128.0	116.0
35	147.0	142.0	139.5	131.0	137.5	137.0	124.0	138.5	138.5	123.5
40	150.0	150.0	150.0	138.5	149.5	148.0	132.0	150.0	150.0	131.5
STEAM TURNED OFF										
45	147.0	157.5	160.5	146.0	160.0	157.5	138.0	159.5	160.0	136.5
50	142.0	161.0	168.5	150.5	168.0	165.0	142.5	168.0	168.5	141.5
55	136.0	159.5	169.0	150.5	168.0	165.0	143.0	168.0	168.0	141.0
COOLING PERIOD										
57	131.5	158.0	167.0	149.5	166.0	163.0	142.0	165.5	166.0	140.0
60	81.0	144.0	160.0	145.0	159.0	157.0	138.5	159.5	160.0	137.0
62	71.5	133.0	152.0	139.0	150.0	147.5	131.5	148.5	148.0	129.0
65	56.5	111.5	132.5	123.5	132.0	131.0	119.0	132.5	132.5	118.0
67	53.0	101.5	121.5	113.5	119.0	118.0	108.0	118.0	117.0	105.5
70	45.0	84.5	100.0	96.0	100.0	99.0	93.5	100.5	100.5	93.0
72	42.5	77.0	90.0	87.0	89.0	88.0	84.0	87.5	86.5	81.5
75	37.0	64.0	75.0	74.5	75.5	75.0	73.5	75.5	75.0	72.0
77	35.0	58.5	68.0	67.5	67.5	66.5	66.0	66.0	65.5	64.0
80	31.5	49.5	57.0	58.0	57.0	57.0	58.0	57.0	56.5	56.5
82	30.0	45.5	52.0	53.0	51.5	51.0	52.5	51.0	50.0	51.0
85	27.5	39.5	44.0	46.0	44.5	44.5	46.5	44.5	44.0	45.5

Figure A4.14

NOMENCLATURE

A	Arrhenious frequency factor	(s^{-1})
A_L	Total surface area of lay-up	(cm^2)
a_L	Surface area of lay-up in contact with the press platen	(m^2)
B	Width of test piece	(mm)
D	Mass diffusivity	($mm^2\ s^{-1}$)
D_c	Degree of cure	(%)
d	Thickness of test piece	(mm)
ΔH_o	Overall heat of reaction	($J\ g^{-1}$)
E	Acetone soluble matter	(%)
E_a	Activation energy	($J\ mol^{-1}$)
e	Potential difference	(volts)
F	Resin flow	(%)
F_H	Force delivered by hydraulic ram	(N)
F_L	Load at fracture	(N)
f	Fractional extent of conversion	
G	Air mass velosity	($kg\ m^{-2}\ s^{-1}$)
H	Partial heat of reaction	($J\ g^{-1}$)
H_R	Residual heat of reaction	($J\ g^{-1}$)
h	Heat transfer coefficient	($Wm^{-2}\ K^{-1}$)

I	Direct current	(amps)
J	Parameter defined by equation 8.5	(dimensionless)
K	Dissociation constant	
k	Rate constant	(s^{-1})
L	Weight loss	(%)
L_v	Weight loss based on varnish weight	(%)
L_{vc}	Corrected weight loss based on varnish weight	(%)
L_w	Weight loss based on wet paper weight	(%)
L_{wc}	Corrected weight loss based on wet paper weight	(%)
l	Distance between supports in flexural strength tests	(mm)
M	Moisture fraction of untreated paper	
M_s	Moisture content of specimen	(%)
n	Reaction order	
P	Untreated (raw) paper weight	(g)
p_L	Pressure applied on lay-up	(Pa)
R	Resin content	(%)
RD	Rapid drying mode	
R_G	Gas constant	(J mol^{-1} K^{-1})
R_i	Insulation resistance	(ohms)

R'_1	Resin ratio	
r	Weight ratio as defined by equation A3.1	
S	Resin solids	(%)
SD	Slow drying mode	
S_F	Flexural strength	(Pa)
T	Temperature	(^{o}C)
T_{PL}	Platen temperature	(^{o}C)
t	Time	
$\tan\delta$	Power-factor	
V	Volatile content	(%)
V_L	Volume of lay-up	(cm^3)
W	Weight	
W_d	Weight of dry specimen	(g)
W_{ds}	Weight of resin solids in treated samples	(g)
W_F	Final weight of laminate after pressing and removal of bead	(g)
W_i	Initial weight of test pieces (equation 7.2)	(g)
W_s	Weight of specimen in water absorption tests	(mg)
W_{vc}	Corrected varnish weight	(g)
W_{vs}	Weight of varnish solids (initial)	(g)
W_1	Untreated paper weight	(g)

W_2	Wet impregnated weight	(g)
W_{2c}	Corrected wet paper weight	(g)
W_3	Treated paper weight	(g)
W_4	Treated paper weight after heating at 105°C (volatile content determinations)	(g)

GREEK LETTERS

α	Empirical constant (equation 7.19)	(J kg^{-1} K^{-1})
β	Solids weight ratio (equation A3.8)	
δ	Phase displacement angle	(rad)
θ	Absolute temperature (appendix A1)	(K)
κ'	Relative permittivity or dielectric constant	
κ''	Loss factor (loss index)	

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