STUDIES OF THE EVALUATION OF SOLID PHASE DISPERSANTS IN POLYMER BLENDS

by

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SUMMARY

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The present study is concerned with the problem of recycling of mixtures of the thermoplastic polymers. Low-density polyethylene(LDPE) and polystyrene(PS) were chosen for this study,because of the mechanical properties of these blends. To improve performance ,block and graft copolymers of ethylene-styrene as solid phase dispersants(SPD's) were added to blends containing equal proportions of LDPE and PS. Since this composition represents the poorest balance of properties in this system.

It has been found that,the addition of SPD's generally increases yield strength,impact strength and elongation at break of the blends. The desired SPD's were prepared by four major procedures:

1 Grafting of styrene onto processed LDPE in which the preformed hydroperoxide acts as a free radical initiator for the graft copolymerization.
2 By grafting of styrene into LDPE in the presence of free radical generators such as benzoyl peroxide (BPO) and cumene hydroperoxide(CHP).
3 By mechano-chemical syntheses ,involving polymer-monomer interaction in the RAPRA Torque Rheometer in the absence and presence of BPO and CHP.
4 By polymer-polymer block interchange in the Torque Rheometer in the absence and presence of the initiators and also in the Brabender(Plasticorder) without initiator.

In order to measure yields of block and graft copolymers,the homopolymer (PS) was first extracted by toluene or methyl-ethyl-ketone(MEK) at 40-50°C and then the amount of the copolymer in the remaining fractions was determined by IR-spectroscopic method.

The highest yields of copolymers were obtained by mechano-chemical method (polymer-polymer interaction) at 170°C. Under these conditions. favourable reactions and unfavourable degradation reactions appear to be balanced.

Crystallinity,dynamic mechanical properties,morphology and stress-strain behavior of the blends in the absence and presence of the corresponding SPD's were examined before and after thermal and ultraviolet (UV) irradiation.

Key words:
Polyblends
Solid phase dispersants(SPD's)
Mechano-chemical synthesis
Rheovibron.

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The work described herein was carried out at the University of Aston in Birmingham between October 1977 and September 1980.

It has been done independently and has not been submitted for any other degree.

M.Hajian

To my father and mother,my first teachers

CONTENTS

CHAPTER ONE

1 Concepts of Solid Phase Dispersants (SPD's)

Due to the escallation in oil prices in recent years and because of increasing pollution problems by polymer wastes obtained from industrial and municipal uses,many polymer fabricating industries are paying increasing attention to the possibility of recycling of polymer wastes such as high and low-density polyethylene,polypropylene,polystyrene, polyvinyl chloride etc.

Two fundamental problems need to be solved before economic processes can be produced for the recycling process. The first problem is degradation of the polymeric materials during recycling which causes the subsequent environmental instability of the recycled products and the second is the inferior mechanical properties of the incompatible products.(1)

The first problem can be overcome by the use of stabilizers (ultra-violet and thermal stabilizers) such as benzophenone,substitued benzophenones .metals,especially transitional metal complexes etc(5,6) The second problem can be resolved by addition of compatibilizers or impact modifiers in the form of block and graft copolymers as solid phase dispersants "SPDs" to their corresponding blends.(5,6)

Usually,materials like plastics,papers,glass and metals once they have fulfilled their primary functions lose their value and are discarded.(9,10) Practical **work** has persuaded researchers to develop improved methods to reuse the waste materials, and in the case of paper and metals some success has been achieved.

The disposal of plastic wastes both industrial and municipal has proved to be more difficult problem. Special attention has been focussed upon plastics because of their omnipresence as packaging wastes and their indestructible nature. Such factors promoted a number of research programmes to investigate this problem from different points of view. Examples include segragation of plastic wastes into individual components followed by decomposition of the generic types into monomers (11,12) or chemicals which can be reconverted to virgin materials.

Conversion of the waste plastic into thermal energy by combustion or using them to make new products with desired properties for different purposes was also an attractive possibility.

Generally, recycling of both industrial and municipal waste is potentially important if marketable products can be made because it reduces the volume of the refuse that has been disposed of by conventional techniques.

The simplest form of recycling of plastics has proved particularly productive is the case of returnable bottles and cartons which may be reused in the same form.(5) Although this method is of considerable economic benefit, contamination and consequent cleansing sometimes does not permit reuse.

In the present project, reuse will not be considered and only methods of modification of polyblends by different SPDs will be considered.

1-1 Problems Arising in Polymer Recycling

In recent years in the United States, the Environmental protection Agency (EPA) has positively promoted the recycling of town refuse, and in February 1973 in a report presented to Congress(18), EPA stressed the necessity for recycling of polymer wates for the following reasons:

1 -Recycling is greatly influenced by the economics ofcollection and cleansing. The cost of producing articles from recycled materials may in some cases be greater than that of manufacture from virgin materials. Therefore, at present, recycling is important when the polymer wastes is at high quality and readily obtainable.

2-Today it is technically possible to obtain material for recycling from mixed town refuse. In some case where, the cost of collection is high, recycling is only economically attractive when the alternative waste disposal cost is also high and where, a market for recycled products is close to the recycling plant.

3-In manufacturing processes using materials obtained by recycling as the "raw material" it is a concern that, compared to the use of virgin raw materials, there will be a decrease in environmental pollution.

4- However, in general it is necessary to minimize manufacturing cost and to improve the quality of recycled products if recycling to be accepted.

A report about industrial and domestic polymer waste revealed that, five major thermoplastics make up 75 % of the total the United States plastic out put.(19) These are:

Low-density polyethylene (LDPE)	20 %
High-density polyethylene (HDPE)	9.5 %
Polystyrene (PS)	18.3 %
Polyvinyl chloride (PVC)	16.5 %
Polypropylene (PP)	7.4 %

It is clear that, any large scale attempts to recycle of polymer wastes will have to deal mainly with the polymers mentioned above.

Unfortunately, the hetero polymeric incompatibility of these polymers, which arises from their different chemical structures, results in very poor mechanical properties compared to the virgin materials.(20) This problem will be discussed in the following sections.

1-2 Incompatibility Problems in Polymers

In principle, two or more polymers may be blended together to form a wide variety of polyblends with random morphological structures to give products that offer desireable properties. In practice it may be difficult or in some cases it is impossible to achieve these potential combination through recycling, because of inherent and fundamental problems.

In general, polymers are thermodynamically immiscible preventing the formation of homogeneous products. This situation leads to the presence of at least two different phases with high interfacial tension and poor adhesion between the two phases.(21) This interfacial tension prevents the desired degree of dispersion in random mixtures and subsequent lack of stability due to gross phase separation or stratification during processing or use.This incompatibility of chemically different polymers makes the recycled artifacts weak and brittle(cheesy) with poor mechanical properties.

In the scientific literature the term compatibility in a thermodynamic sense,is synonymous with miscibility and in the technological literature it is used to characterize the properties of the two polymers in a blend .(22,23) Components that resist separation or phase segragation and give a degree of"compatibility" even through in a thermodynamic sence,they are not quite miscible. So ,incompatibility in a general sense is a problem in polymer blends.

It has been found that,the presence of certain polymeric species, usually block or graft copolymers can reduce the problem mentioned above.(24,25) Lundstedt and Bevilaqua(26) were the first to show that addition of a styrene-rubber graft copolymer to a polystyrene-rubber blend gave impact strength which was greater than that of either polystyrene or polystyrene-rubber blend. Generally,it is believed that,this is a result of the ability of the graft or block copolymer to alter the interfacial situation.(23,28) Such species are often termed "compatibilizers" or solid phase dispersants(SPD's).(30) The general view is that,a properly chosen block or graft copolymer can preferentially locate at the interface between the two phases, as shown in Fig 1-1.(25)

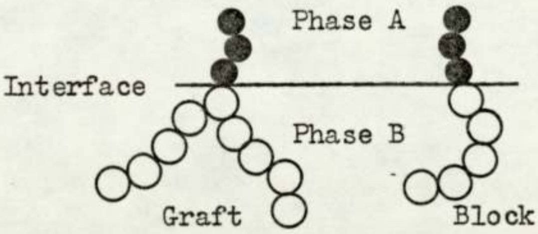


Fig 1-1 Ideal location of block and graft copolymers at the interface between polymer phases A and B.

Ideally, a compatibilizer should be a block or graft copolymer with different segments that are chemically identical to those in the respective polymer phases. However,the desired effect may result if one of the segments of the block or graft copolymer were to be miscible with one of the phases. It has been found that, this type of surface activity causes the following effects.

1- It provides a measure of stability against separation or segregation of the phases.

2- It reduces the interfacial energy between the phases in polymer blend systems.

3- It permits a finer dispersion of dispersed particles in the continous phase.

4- It increases interfacial adhesion which results in improved mechanical properties of the polyblends.(31)

The term solid phase dispersants will be used to describe agents which bring about one or more of these improvements in the experimental sections.

1-3 Fundamental Consideration of Solid Phase Dispersants (SPD's) in Polyblends

The technological usefulness of a blend of incompatible polymers such PE/PS and PE/PVC is in general limited by their poor mechanical properties. It has been found that, some additives in the form of block or graft copolymers, cause a significant improvement in the mechanical properties (impact strength, tensile strength and elongation at break) of the blends. (see section 1-2) .

The effectiveness of copolymers or SPD's appears to depend on the nature of each component of the blend, and the extent of the improvements of the mechanical properties depends on the surface activity of the SPD's.(31)

If one considers SPDs based on graft and block copolymers, conformational restraints are very important(32), and on this basis, a block copolymer might be superior to a graft copolymer.(33) since, SPD's with multiple branches would be likely to restrict the opportunities for the backbone polymer to penetrate into its homopolymer phase. For this reason, diblock copolymers might be more effective than triblocks.(33)

Another ideal requirement of an SPD is that, a segment of the block copolymer should be chemically identical to the homopolymer phase in the polyblend system. That is in Fig 1-1, there would be either an AB block or a A-G-B copolymer. The block or graft should have a segment miscible with phase A.

For an SPD to locate at the blend interface, it should have the ability to portion into two phases and this tendency depends on the interactions between the two segments and on their molecular weight of the SPD. Furthermore, the SPD should not be miscible as a whole molecule in one of the homopolymer phases.

Because SPD's based on block and graft copolymers are likely to be expensive, it would of interest to maximize their efficiency, so that small amounts are required, How much SPD is required depends on many factors such as conformation of SPD at the interface and the overall molecular weight .(21)

It is possible to estimate the amountsof SPD's required for impact modification of polyblends by means of the following equation.(21)

Suppose that a blend contains a volume fraction Q of polymer A as spherical particles of radius R ,has an interfacial area S per unit. The valume of the SPD is equal to $\frac{3Q}{R}$. If each SPD molecule occupies $\propto$ volume at this interface, then the mass of the SPD required is

$$\frac{\text{Mass of SPD}}{Vp} = \frac{3Q\,M}{\propto RN} \qquad (1\text{-}1)$$

where, N = Avagadros Number,

M = molecular weight of SPD

Vp= original volume of polymer,

Q = volume fraction of polymer.

It might be expected that, conformational restrictions prohibit filling the interface with block copolymer and may reduce the amount of SPD calculated by the above equation, because of the large difference between cohesion and chemical bond energy. (21)

1-4 The Effect of SPD's on Mechanical properties of Polyblends

Blends of immiscible polymers may assume phase morphologies rangeing from random dispersion to laminate structure. Addition of a solid phase dispersant with interfacial activity can improve the mechanical properties of polyblends.(35)(see section 1-3). Since, mechanical properties of polyblends are very important, it is pertinent to consider some examples in this area. The first set of examples discusses dispersed polyblends and the second deals with laminates.

1-4-1 The Effect of SPD's in Dispersed Polymer Blends

In many cases, dispersed mixtures of two incompatible polymers are weak and brittle (cheesy). Blends of polyethylene and polystyrene are a good example of this.(37,38,39) The ultimate strength and elongation at break of some blends may be less than that of either the pure components in the mixture.(38) It is known that poor adhesion between the phases plays a significant role in dispersed polyblends.(37) Fracture may initiate at the interface of dispersed blends and in any case, the fracture path would be expected to follow the interface between the two homopolymers. These processes are reflected in the laminate polymer blends in a more comlex manner.

In the following examples the SPD's are added directly to the polymer blends or they are formed during a mechano-chemical process.

1-4-1-1 Polyethylene and Polystyrene Blends with SPD's

Polystyrene has very poor mechanical properties and consideration has been given to improve this situation.(39,38) For this purpose, styrene has been grafted onto LDPE film by radiation method,(38) and in another technique this graft copolymer has been prepared by Friedel-Crafts alkylation of PS with LDPE according to the method reported by Carrik.(40) The effects of addition of the graft prepared by this method have been reported by Brentsen and Heikens(39). These effects are reproduced in Figs 1-2, 1-3 and 1-4.

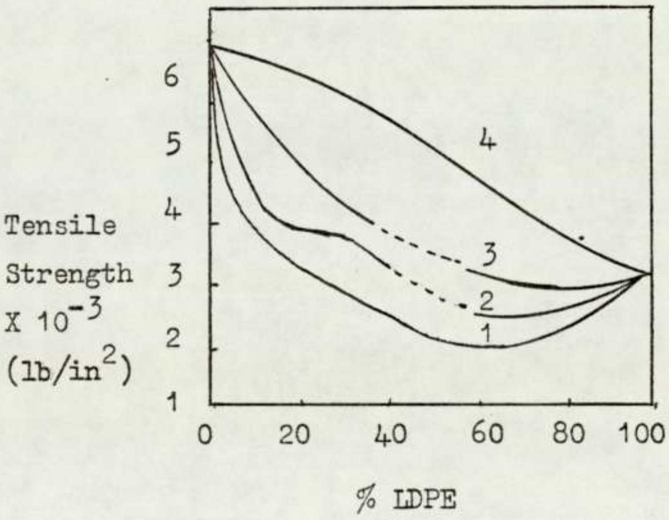


Fig 1-2 Tensile strength of LDPE-PS blends against ratio of LDPE.

1: Blends of LDPE/PS.

2: Blends with 5 % graft copolymer.

3: Blends with 30 % graft copolymer.

4: Graft copolymer.

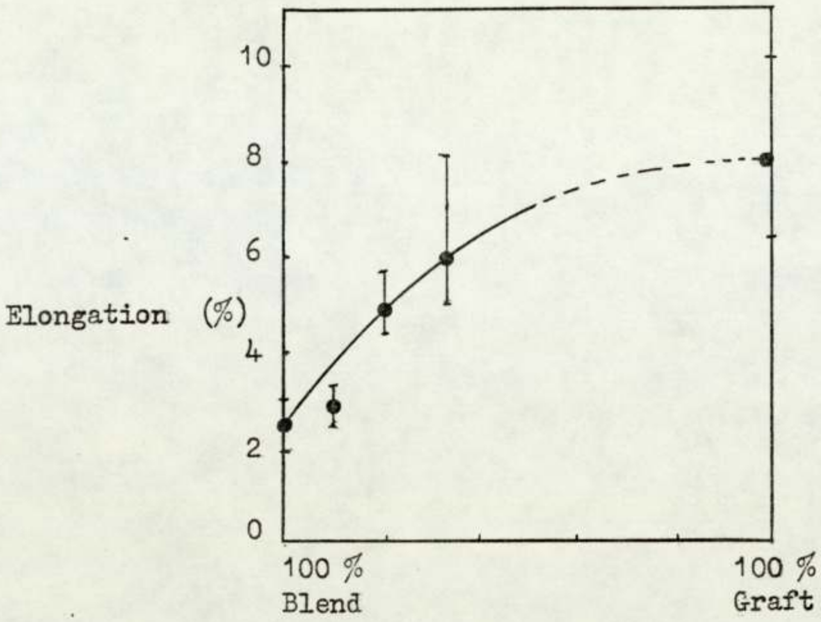


Fig 1-3 Effect of graft copolymer on elongation at break of LDPE-PS blends.The graft contains 50/50 % LDPE/PS.(Taken from Ref 39)

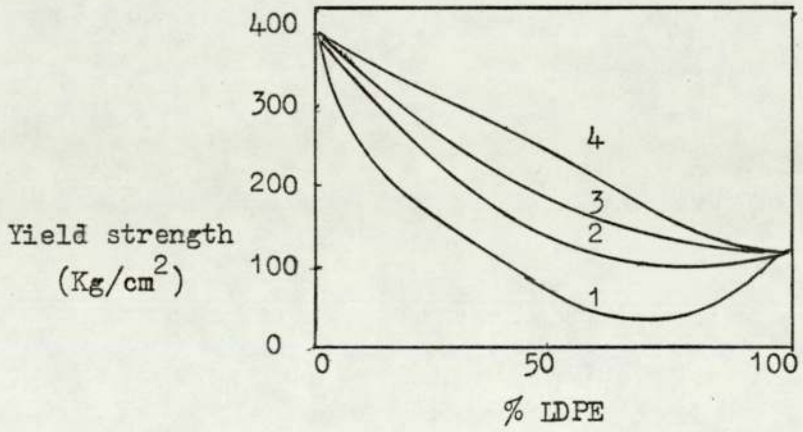


Fig 1-4 Yield strength of LDPE-PS blends against LDPE ratio.

1: Blends of LDPE and PS.
2: Blends with 5 % graft copolymer.
3: Blends with 30 % graft copolymer.
4: Graft copolymers of LDPE and PS.

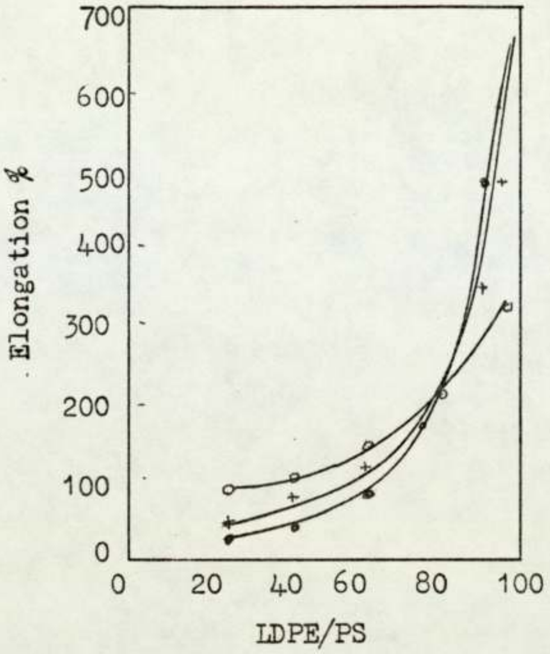


Fig 1-5: Effect of 5% graft copolymer on the elongation percent of PE/PSblends.•.blend,o=graft,+= +5%graft

In Figs 1-3and1-4,the lowest curves show the response for the binary PE-PS system, which displays a minimum in the mid-concentration range . The uppermost curve is for a series of grafts with different proportions of LDPEand PS, and it displays a more nearly additive response.The curves in between the lower and the uppermost display the effect of the graft as SPD's in the LDPE/PS blends.

Lock and Paul(36) simultaneously mixed equal parts of LDPE with PS with the corresponding graft copolymer prepared by irradiation grafting of styrene into LDPE. They found the elongation at break of the blends to be improved as the amount of the graft copolymer increased .This effect is shown in Figs1-4 and 1-5.

Improvement of mechanical properties of LDPE/PS blends was estabilished in the present work when the corresponding copolymer was prepared by solution polymerization and mechanochemical methods. (see chapter3).

1-4-1-2 Polyethelene- polyvinylchloride with Chlorinated Polyethylene as SPD's .

Athough blends of PE and PVC are not as immiscible as the previous system, many researchers have investigated suitable SPD's for this blend system. Schramm(42) has suggested that a useful "compatibilizer" for this polyblend is chlorinated polyethylene (CPE). Paul and his co-workers(43) also studied this polymer system extensively .

For prepration of these CPEs, chlorination of high density polyethene was carried out in the solid state rather than in solution (44) (see Fig 1-6). In solution all the hydrogens are equally accessible for replacement by chlorine leading to a random chlorine substitution. The resulting polymer is similar to a random copolymer of ethylene and polyvinylchloride and the crystallinity of the polymer decreases to zero at relatively low chlorine contents. In the solid state of chlorination however, only the carbon atoms in the amorphous phase can be chlorinated, since Cl_2 can not diffuse into the crystalline lattice. Consequently, the resulting polymer has a structure resembling a block copolymer in which the chlorinated parts are similar to PVC and the unreacted regions are similar to crystalline PE.

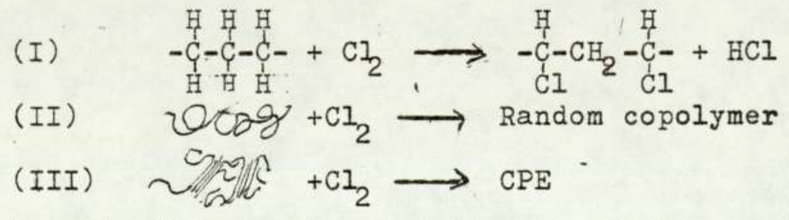


Fig1-6: Schematic illustriation of the chlorination of polyethylene

(I) chlorination of PE: (II) solution process:(III) solid state process.

As was mentioned before, chlorinated polyethylene can be used as an interfacial agent for incompatible polyblends(43) such as PVC/PE, PS/PE and PVC/PS. The effect of this compatibilizer on the strss-strain properties of PVC with high and low density polyethylene are shown in Fig 1-7.

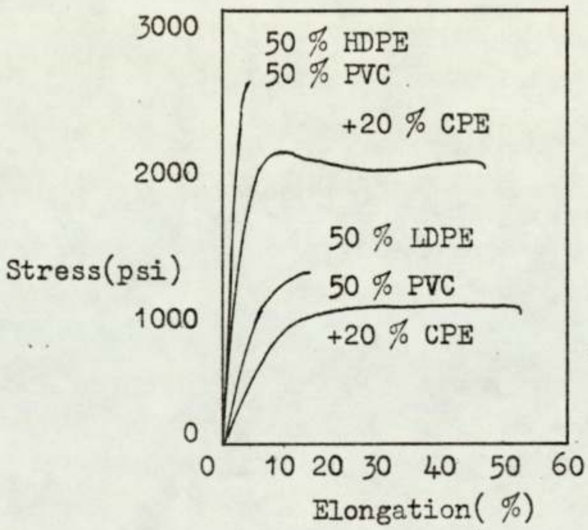


Fig 1-7: Effect of CPE(36 % chlorine) on stress- strain diagrams for PE/PVC blends(43)

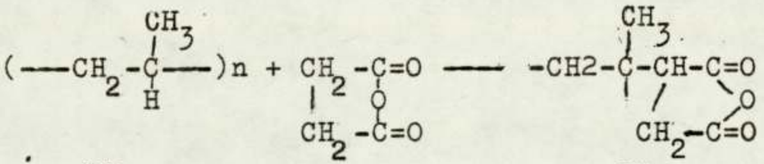
The upper curve in Fig1-7 shows that the unmodified blend is very brittle, but with 20% CPE, the blend becomes yielding and subsequent neck formation and the modulus and ultimate strength are reduced . Similar effect was shown for PE/PS blends.

Of the different compositions of CPE's (36 , 42 , and 48 %) the first was considered to be the most effective compatibilizer for PE/PVC blends, because of the lower content of unchlorinated chain segments.(43)

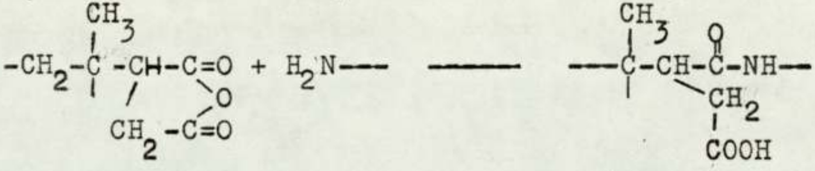
The morphological effect of CPE as a solid phase dispersant in PE/PVC blends is to reduce the domain size of PVC in the blend.(45)

1-4-1-3 Effect of SPD's in Nylon 6- Polypropylene Blends

Nylon 6 and polypropylene form an immiscible blend. Ide and Hasegawa(46) studied effects of addition of a graft copolymer (PP-g-MAH) in the blend. For this purpose they grafted maleic anhydride (MAH) into PP and then mixed the product with nylon 6. The reaction takes place as follows:



(1-1)



(1-2)

Loss of amine group provided evidence for the mechanical properties of a 80% PP and 20% nylon 6 blend is shown in Table1.(47)

PP %	Nylon 6	PP-gMAH	Yield strength lb/in^2	Elongation at break %
100	-	-	4600	30
-	100	-	10500	30
80	20	-	3300	5
80	20	1.8	5200	13
80	20	3.6	5500	28

Table1-1: Effect of PP-g-MAH as an interfacial agent in nylon 6 and PP blends.

As is shown in Table 1-1, the blend with no graft copolymer has a very low elongation at break ,weaker than the weakest component (PP).Addition of the graft increases yield strength, decreases greatly domain size and also makes the blends more ductile.

1-4-1-4 Effect of SPDs in Polystyrene- Rubber Blends.

As was mentioned earlier, polystyrene is a brittle material with poor energy absorbing ability and low impact strength. This problem can be overcome by polymerizing styrene in the presence of rubber(48-49) to produce a rubber modified blend. It was also found that simply blending polystyrene with rubber does not produce the same desired effect.

Lunstedt and Bevilacqua(50) showed that if a graft of styrene into rubber was added to the corresponding blend a significant increase in impact strength of the blend is obtained. This effect is shown in Fig1-8.(51)

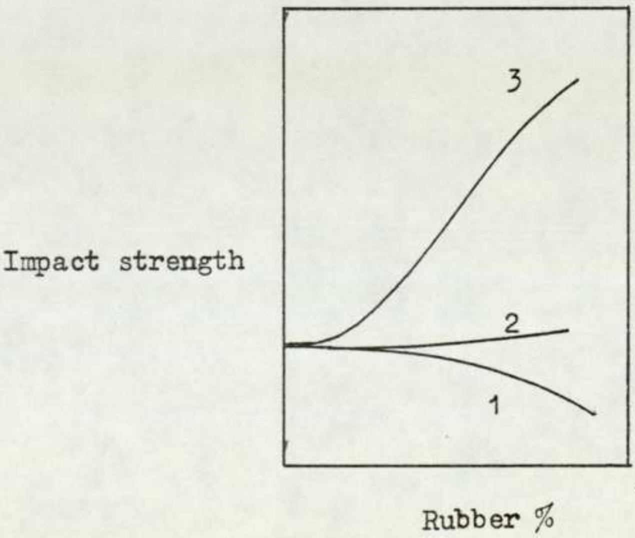


Fig1-8: Effect of addition of rubber to glassy polymers on impact strength.1: polystyrene- rubber blends,
2: polystyrene- rubber+graft,
3:rubber -g- polystyrene.

The lower curves in Fig1-8 (1and2) illustrate effect of blending of rubber with polystyrene and the upper curve (3) indicates the effect of grafting. It has been recognised(52) that during the polymerization of styrene in the presence of rubber the grafted segments which are formed act as an adhesive. However, it is believed that the graft copolymer provides improved adhesion between the glassy and rubbery phases which causes stress transfer between the phases.

1-4-2 Effect of SPD's in Laminate Polyblends.

In some cases in which direct stressing of the interface takes place in a polyblend, the polymers are arranged as laminates. In certain cases a homogeneous polymer may form a mutual adhesive between the polymer phases which acts as compatibilizer.(53) But it is clear that if the adhesives are in the form of block or graft copolymer, interfacial activity in the laminates blend can improve the desired mechanical properties. For this purpose the following example is considered.

Polyvinylchloride (PVC) and natural rubber (NR) are incompatible and a commercially used adhesive for these two polymers is a graft copolymer of methylmethacrylate (MMA) into NR.(54) The NR backbone of this graft adheres well to NR, while the PMMA graft chains adhere to PVC because of miscibility of PMMA with PVC.(55) The effect of this copolymer has been described by a 180-degree Peel Strength test.(53) (See Fig 1-9)

It has been found that where there is no PMMA, NR will adhere well to the NR sheet,but not to the PVC sheet,and the Peel Stength is zero. When a pure PMMA is used as adhesive,it will stick to the PVC sheet but not the NR sheet and the peel strngth is again zero. But when the (NR-PMMA) copolymer is used as interfacial agent the peel strength shows the highest value when PMMA and NR are present in nearly equal proportion in the graft.

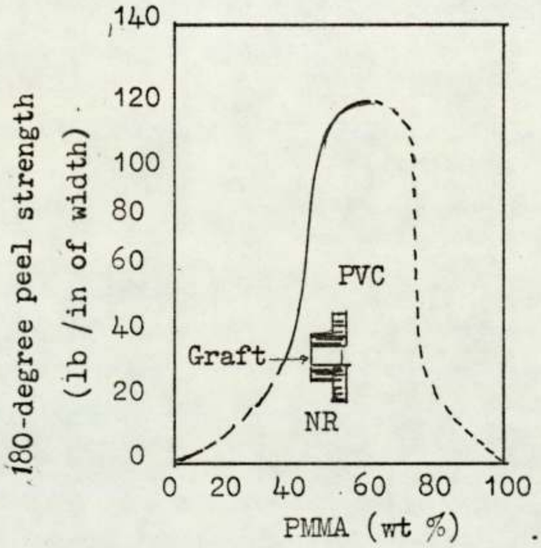


Fig1-9: Effect of (NR-g-PMMA) as a compatibilizer in (NR/PVC) laminate blend. (53)

In this example, the graft clearly does not form a monolayer at the interface, but rather exists as a third phase between the two sheets and adheres ,to both NR and PVC because its surface can present different kinds of segments to promote interpenetration of the chain segments between the two phases.

Other examples similar to the above,have been reported.For example in a patent(56) bonding of ethylene- propylene-diene terpolymer rubber (EPDM) with styrene-butadiene-rubber (SBN) by grafting of styrene into butadiene has been reported. Similarly butadiene styrene copolymer(SB) has been used to bond high impact polystyrene to acrylonitrile butadiene styrene (ABS) sheets.(57) It is believed that the styrene segments of the SB block, penetrates the styrene, while the butadiene segments of the SB pentrate or adhere to the rubber phase of the ABS.

1-5 General Aspects of Two-Phase Polymer Systems.

In general, there are two ways to make a polymeric material with new and useful properties. One is to develop new monomers and different methods of polymerization, the other is to mix existing polymers (prepared from recycling of wastes plastics) in such a way that the resulting materials have properties(especially mechanical properties) superior to those of the individual components. In the second method, compatibility is a considerable problem. If the two polymers are quite compatible due to their mutual solubility, they form a single phase and consequently give no improvement in mechanical properties. If two polymers are incompatible they form two different phases and such blends without a compatibilizer do not have improved mechanical properties. Therefore, an optimum compatibility between phases must be achieved, high enough to provide necssary adhesion between the phases. Two familiar examples are the rubber-reinforced polystyrenes and the ABS plastics. In both, a rubbery polymer is dispersed in glassy matrix. In these materials the valuable mechanical properties are due to the presence of two discrete polymeric phases.

Two-polymeric phases systems have achieved great commercial importance in the last decade. In the following sections some aspects of two-phase polymer system are mentioned.

1-5-1 Methods of Production of Two-Phase Polymer Systems.

The simplest and most direct methods of production of two-phase polymer systems is mechanical blending of polymers. This method may be accomplished on two-roll or in internal mixtures such as the RAPRA Torque Rheometer or Brabender (Plasti-Corder). The nature of the resulting dispersion depends on the time and temperature of mixing, and also depends on the shear intensity and rheological properties of the polymers.(58-59)

There is the possibility of chemical effects produced during blending operation such as chain scission and or crosslinking. These cases have be been studied during thermal processing of LDPE and PS. More details will be given in chapter3.

In the case of chain scission during two-phase formation, not only does this generally affect the molecular weight and hence the properties of the individual components, but it is possible that the free radicals produced by chain scisson can combine together to make block copolymers. More details about copolymer formation during thermal processing of LDPE and PS and also the significance of this copolymer as a compatibilizer will be discussed in (Chapters 3and4 respectively). If the components are in powdered form, they may be dry-blended with similar results.(60)

Another two-phase polymer production method involves the formation of a grafted chain on a backbone of an other polymer. This may be done by dissolving a rubbery polymer in a monomer of a glassy polymer and polymerizing the solution in bulk ., preferably by useing a suitable initiator and effective agitation. This method may be varied by adding an inert solvent to aid temperature control and minimize viscosity build-up.

Another alternative procedure is to suspend the rubber-monmer solution in a water phase followed by suspension polymerization.(61) Two-phase polymer production may also takes place by emulsion polymerization of a monomer of glassy polymer into an unsuturated rubbery polymer. It is however, doubtful whether complete grafting can be achieved by any of the standard two-phase polymer production techniques, because some homopolymer is always obtained in admixture with graft copolymer.

1-5-2 Physical Aspects of Incompatibility of Polymers

If in a polymer mixture consisting of two compatible polymers one phase is formed and as mentioned earlier, the mixture is transparent. In such polymer systems mechanical properties (tensile strength, impact strength and yield strength) are not improved. Therefore, to obtain a successful two-phase system with improved mechanical properties, an optimum compatibility between the components must be achieved. In other words, the compatibility between polymers should be great enough to provide the necessary interfacial adhesion at the glassy-rubbery interface.

Consider the process of mixing of two polymers at constant pressure and temprature, the change in free energy of mixing of the system (Gibbs energy) is given by this equation:(76)

$$\Delta G = \Delta H - T\Delta S \qquad (1\text{-}1)$$

Where, ΔH is the change in enthalpy, T, the absolute temperature and ΔS the change in the entropy of the system. When ΔG is positive, the two phase system which is formed is metastable,

,because of the lack of mobility of the polymeric chains. When ΔS increases the solution process is thermodynamically favoured and the two polymers show mutual solubility.(68) The important point is that the entropy change which occurs during mixing of polymers is quite small.(68) Because of the high molecular weight of polymers, their entropy changes are always less than for mixing of low molecular weight liquids.(69) Therefore, compatibility is a rare event for polymer mixtures.

The enthalpy of a mixture is a measure of the affinity of different molecules in a system, when it is negative, it indicates decrease in the energy of the system upon mixing (i,e. the molecules prefer self mixing rather than homogeneous phase formation). When there are strong interactions such as hydrogen bonding between substituent groups in the different molecules an exceptional case should be considered. (71)

A quantitative means of predicting the affinities of the polymer-pairs has been designed in the terms of easly measured properties of the compounds. One possibility is through the use of the solubility parameter(Q) which has proved useful in the study of the dissolution and swelling of polymers in low molecular weight liquids. The extent of swelling of a cross-linked polymer in a liquid indicates the tendency towards solution and can be calculated when the solubility parameters of solvent and liquid are the same(72), that is,

$$Q_1 = Q_2 \qquad (1\text{-}2)$$

For nonpolar liquids the internal energy of mixing(ΔE) upon mixing is given by :

$$\Delta E = V_1 V_2 \, (Q_1 - Q_2)^2 \text{ cal/cc of solution}$$

Where, the V_1 and V_2 are the volume fraction of the components (polymer and solvent respectively). Realising that amorphous polymers are essentially like liquids, and assuming that the volume change upon mixing is negligible at constant volume and pressure,(72-73) so $\Delta E = \Delta H$. Notice that this equation always results in positive ΔH for nonpolar high polymers. Therefore, since the ΔS term is small, true solution will not occur.

Although not too much work has been done on the compatibility of the polymer pairs alone, there has been extensive work on polymer solvent system in which the individual polymers are dissolved in a common solvent. In almost all cases, at polymer concentration of a few percent, initially homogeneous solutions and then a two-phase polymer system is formed; one liquid phase containing all of one polymer and the other phase containing all of the second polymer.(74) As predicted by the theory, as the molecular weight of polymers decreases and the ΔS increases, compatibility becomes greater.(74) Also as expected hydrogen bonding has a favorable influence on the compatibility of polymers. However, only a few completely soluble polymer-polymer solvent systems have been reported, and it is doubtful whether they can maintain their compatibility at higher concentrations.

Since true solubility will rarely be a problem, the design of successful two-phase impact systems by means of polymer blends, the greatest compatibility or adhesion between the phases can be achieved in the following ways.

(I) To match the solubility parameters of polymers as closely as possible. This may be done by varying the proportion of a common monomer to both phases, but this often presents drawbacks.

For example,a 60/40 butadiene-styrene-rubber is more compatilbe with polystyrene than a 75/25 copolymer,but it has a higher glass transition temperature (Tg) and low impact resistance.(77)

(II) To graft glassy monomers to the rubber backbone. The grafted material is quite compatible with the surrounding glassy phase and is chemically bonded to the rubber resulting in excellent adhesion and improved impact strength.This is the most successful method of improving phase adhesion in a two phase polymer systems.

1-5-3 Determination of Compatibility in Two-Phase Polymer Systems

The term compatibility as used for polymer- plsticizer system reflects the mutual solubility of polymer and plasticizers through the formation of a true solution.(62) Similarly ,thermodynamic compatibility of two polymers implies the formation of a true solution of one polymer in another. However, it is very difficult to estimate the mutual solubility of two solid phase polymers. Therefore, the compatibility of polymers has been estimated in solution by Dobry and Kavenoki.(63) They suggested that if solutions of two polymers in the same solvent remain clear, the polymers are compatible and if the solution becomes cloudy and separates into two layers ,they are incompatible.Separation does not occur in highly concentrated solutions owing to the high viscosity of the medium. Therefore,an average concentration range is selected,that is 5 to 10 percent.So the separation into two layers will not take too much time.Dobry and his co-worker used this method to study 78 pairs of polymers and discovered that only three of them were compatible ,they were:

(I) Celluluse nitrate (CN) and Polyvinyl acetate (PVA)

(II)Celluluse benzoate (CB) and Polystyrene (PS)

(III) (CB) and Polymethylmethacrylate (PMMA).

Other investigators have also shown that most polymer pairs are incompatible and separate into phases .The conclusion was drawn that polymer compatibility is an exception to the general rule, according to the thermodynamic reason which was discussed earlier.

1-5-4 Estimation of Mutual Solubility of Two- Phase Polymer Systems by Optical Density

The mutual solubility of polymers in the condensed state is determined by measuring the optical density of films obtained from a solution of two polymers in a common solvent.

As was mentioned earlier,if the polymers are mutually soluble their films are quite clear and transparent,and if they are insoluble, particles of the second phase act as light scattering centers. Optical densities of films containing different ratios of the two polymers, can be measured by Beer Lambert's equation (See section,3-11).

Usually, the addition of a small amount of a second polymer does not change the optical density of the polymeric system, but when the amount of the second polymer is increased the film becomes opaque and discontinuity appears on the curve (Fig1-10)

The concentration at which discontinuity is observed is known as the limit of solubility of one polymer in a second. Kuleznev(27) and co-workers have shown by this method, that the limit of solubility of PS in PMMA ,PMMA in PS and PS in polyisoprene (PIP) is 0.9 , 1.9 and 1.8(x) respectively .

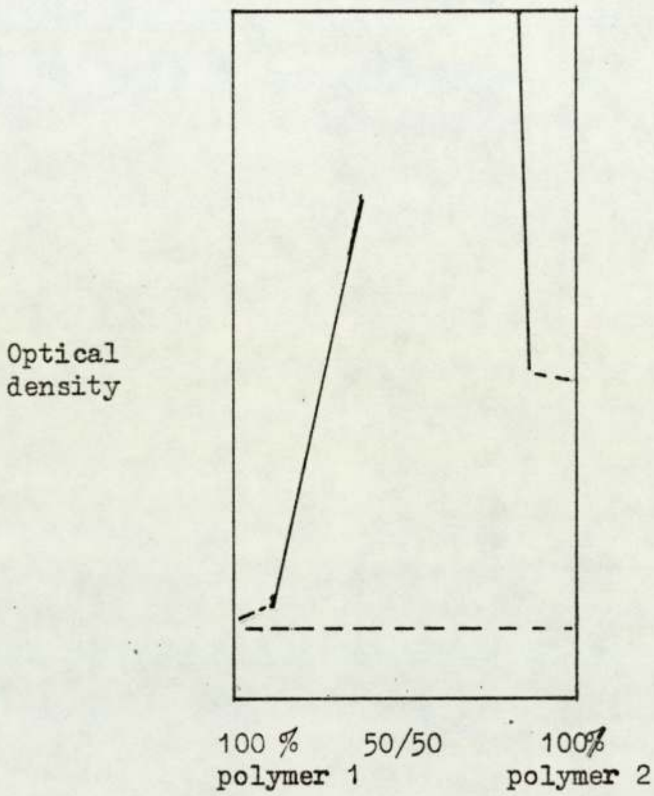


Fig1-10: Change in optical density of the films of polymer mixtures with the variation of the component ratios.

At the same time , the determination of the optical density of a mixture of (PVA) and (CN) has shown that they are clear in all proportions, that is they are mutually soluble and are compatible. (34)

1-5-5 Determination of Compatibility by Measuring of Dynamic Mechanical Properties of Two- Phase Polymer Systems.

Introduction: Dynamic mechanical methods,measure the ability of a material to store and to dissipate energy on mechanical deformation caused by shear, flexural or compression vibrations(169) and changes in frequency or in the amplitude of such vibrations is followed by using a suitable instrument named "Rheovibron", a viscoelastometer. Dynamic mechanical testing of polymeric materials is one of the useful mechanical test methods wich is capable of providing information both on chemical structure and physical properties of the materials. It is advantageous over many other mechanical methods because of its simplicity and non-destructive nature. The use of many destructive methods such as tensile stength, impact strength etc are known to give erroneous results and correlations are sometimes tedious because of duplication of test samples.

Dynamic-mechanical properties are very sensitive to crystallinity, moleclar weight distribution, crosslinking and various other molecular features of the polymeric chain.(172) All these factors are also greatly affected by temperature and frequency. Hence, changes produced in polymeric materials at varying temperatures and frequencies can be followed by corresponding changes in their modulus and damping values which will be described in the following sections.

(II) Theory and Deviation of Basic Dynamic Equation.

Generally, two quantities can be obtained from dynamic mechanical tests:

(a) Mechanical damping which is a measure of loss of energy and is defined as the ratio of the dissipated energy as heat to the energy stored as potential energy when the applied force is removed from a polymeric material.(171)

The mechanical damping can be calculated as logaritmic decrement (Δ) which is the logarithmic ratio of amplitudes of two successive damped oscillations. (See Fig 1-11)

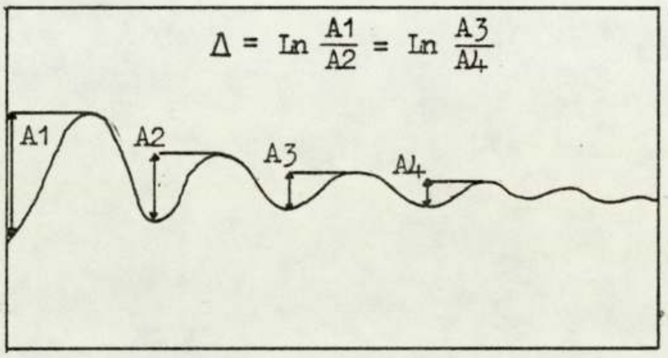


Fig 1-11: Schematic representation of typical damping oscillation curve.

(b) Modulus of elasticity which is a measure of recoverable energy when the applied force is removed from the sample. This modulus is defined as the ratio of stress to strain for the material which does not perfectly obey the Hook's law .In such materials the energy utilized in deforming a body is not recoverable,because a part is always lost as heat. However, the extent of the dissipation and recoverable energies vary from material to material.

As was mentioned earlier, perfectly elastic materials have no mechanical damping ie, they behave as a spring. In such materials the stress applied in deforming or stretching is stored as potential energy and is fully recoverable when the applied force or load is removed from the sample.

Viscous materials and liquids are examples of the other classification of materials where all the applied energy used in deforming is dissipated into heat.High polymers are the third classes of materials which have the characteristics of of both the viscous and elastic materials.So, in such materials if a stress is applied on the sample,the resulting strain reaches some value immediately ,and then decays or relaxes over a period of time. Thus sinusoidal experiments involving viscoelastic material appear to show two stress components,one in phase stress (a') which is parallel to the direction of strain,and the second is out of phase stress (a") which is perpendicular to the direction of stain. The magnitude of the two stresses is given by the following equations. (See Fig 1-12)

$$a' = E' \cdot \text{Strain} \qquad (1\text{-}3)$$

$$a'' = E'' \cdot \text{Strain} \qquad (1\text{-}4)$$

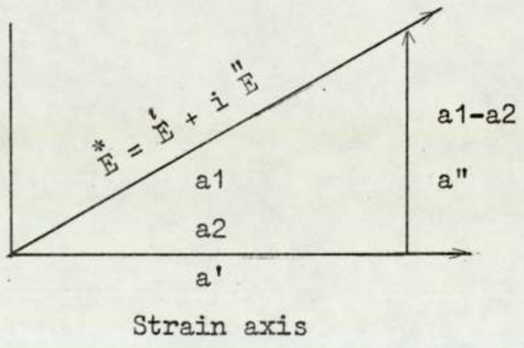


Fig 1-12: Vector diagram.

Where,E' and E" are real and imaginery parts of the complex modulus defined as :

$$E^* = E' + iE'' \qquad (1\text{-}5)$$

Where, i is an imaginary number.($\sqrt{-1}$)

The equation (1-5) can also be expressed in terms of the absolute value of complex modulus of elasticity I E* I and phase angle (δ) between stress and srtain.

$$E^* = E' + iE'' = (E')^2 + (E'')^2 = \frac{\sigma_{max}}{\varepsilon_{max}} \qquad (1\text{-}6)$$

$$I\,E^*\,I = I\,E^*\,I\,(\cos\delta + i\sin\delta) \qquad (1\text{-}7)$$

$$E' = I\,E^*\,I\,\cos\delta \qquad (1\text{-}8)$$

$$E'' = I\,E^*\,I\,\sin\delta \qquad (1\text{-}9)$$

In the case of very low damping i.e $\delta \longrightarrow 0$, $\cos\delta = 1$ and therefore, $E' = IE^*I$, and in this case $E' = E''$. From the Equations(1-8) and (1-9) the following Equation is obtained.

$$\tan\delta = \frac{E''}{E'} \qquad (1\text{-}10)$$

The term $\frac{E''}{E'}$ is called mechanical damping and is proportional to the ratio of the loss energy to the stored energy during a cycle of deformation.(171)

In the following section determination of compatibility of some samples containing two-phases is described .

As was mentioned earlier,compatibility of polymers can be determined by their glass transition tempratures(Tg),i.e, the point at which a polymer changes from a glassy solid state to an amorphous liquid of extremely high viscosity.This change can be clearly shown in its modulus temperature curve.

Copolymers and homogenous mixtures have modulus temperature curves lieing between those of the two homopolymers as shown in Fig 1-13 .(195)

Incompatible materials show multiple transitions and the shape of the curves are markedly altered as shown in Fig1-14.(195)

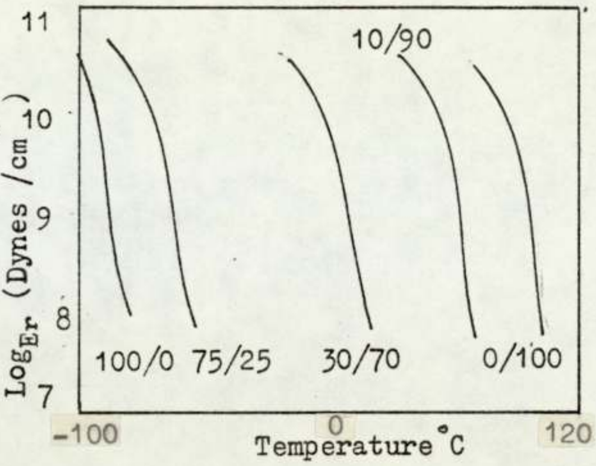


Fig1-13: Changes of modulus as a function of temperature for butadiene/ styrene copolymers.(Taken trom Ref 195).

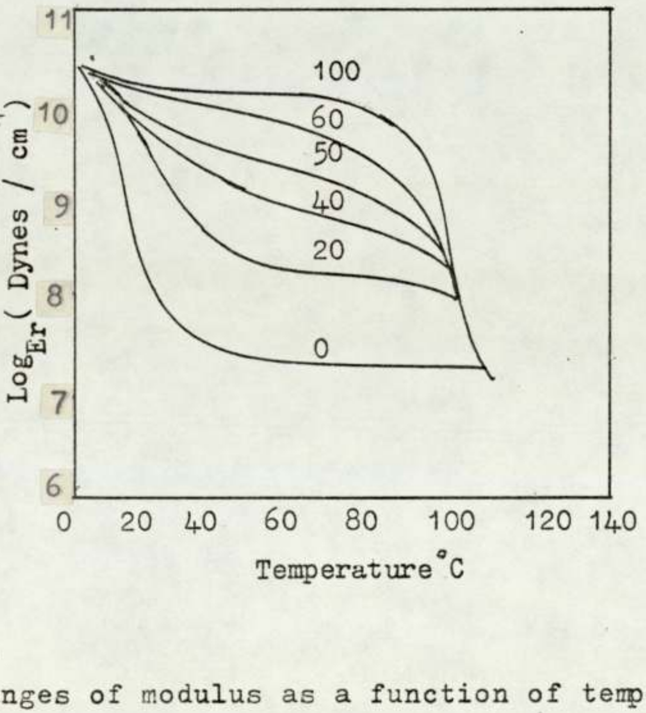


Fig1-14: Changes of modulus as a function of temperature for styrene and butadiene / styrene copolymers (30/70). Taken from Ref 195.

Measurement of the related dynamic loss also clearly shows multiple peaks,(196) that is, each polymeric constituent retains its characteristic glass transition temperature.

Measurement of glass transition can be also done by measuring of the volume of the polymers as a function of temperature.(197) Using this method, incompatible polymers show two changes of slope in a volume temperature plot.(198)

Measurement of heat capacity by differential thermal analysis (DTA) is also another method to show transition temperature, and incompatible mixtures have been distinguished by this technique.(197)

1-5-6 The effects of SPD's on Compatibility and transition Behaviour of Polyblends

It was mentioned earlier that true compatibility of polymers is rare, but by addition of graft and block copolymers, compatibility of polymer mixtures may be improved. A precise technique which has proved valuable in the study of the mechanical behavior of polymer systems with and without compatibilizer is dynamic mechanical testing. Basically, this technique consists of subjecting a sample to an oscillating stress or strain and measuring the resulted stress as a function of frequency and or temperature.

Typical dynamic properties of a glassy polymer, a rubber and a two-phase polymer dispersant are shown in Figs 1-15, 1-16 and 1-17.(68) The storage modulus and tan δ (damping) curves for the rubber and glassy polymers are a characteristic of those observed for amorphous polymers. At some temperatures, tan δ reaches a maximum value and at the same temperature the storage modulus drops to minimum value. This temperature is defined as (Tg). As is shown in Fig 1-15, SBR and PS show Tgs about -80 and +100°C' respectively and their mixtures show both Tgs . The magnitude of the damping curves depend on the ratio of the components in the mixture.Hence,in this case (copolymer) Tg is shifted a value intermediate between those observed for the pure rubber and glass.

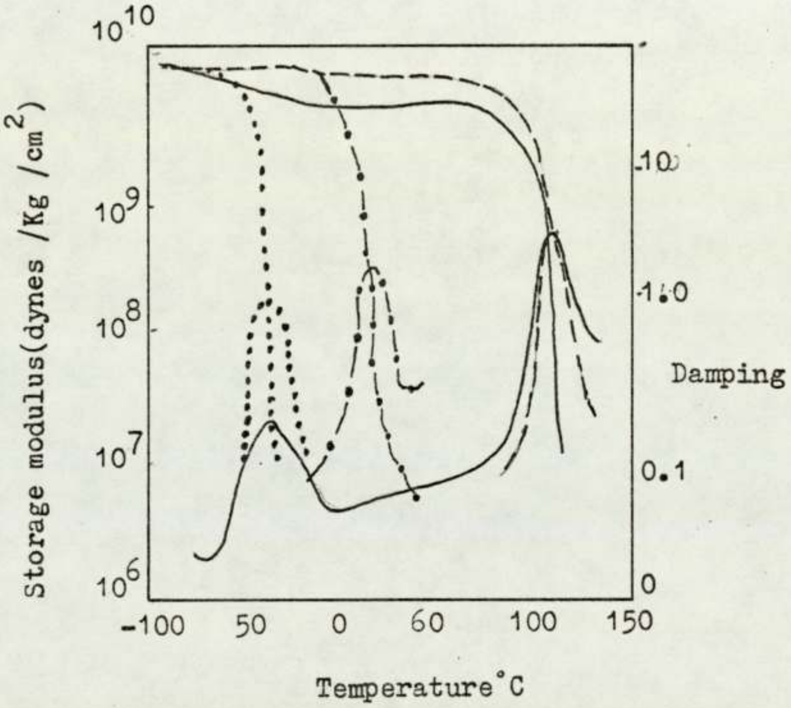


Fig1-15: Dynamic mechanical responses as a function of temperature. PS: (------), SBR: (......), PS/SBR:(-.-.-.-) and the mixture plus their copolymer: (———).(68)

Another example involves blends of polyvinyl chloride(PVC) and polybutadiene (PB). The Tg for the (PB)is observed at the range of -100°C' depending on the concentration of (PB) in the blend.

As is shown in Fig1-16, the value of the viscous modulus E" exhibits two distinct peaks which shift to higher temperature as the amount of (PB) is reduced.The E" curve shows the glass-transition of PVC at 80C' and this peak shifts to low temperature as the ratio of PVC in the blend is decreased. As shown by the storage modulus, at this temperature PVC softens from the glassy state to viscoelastic state.

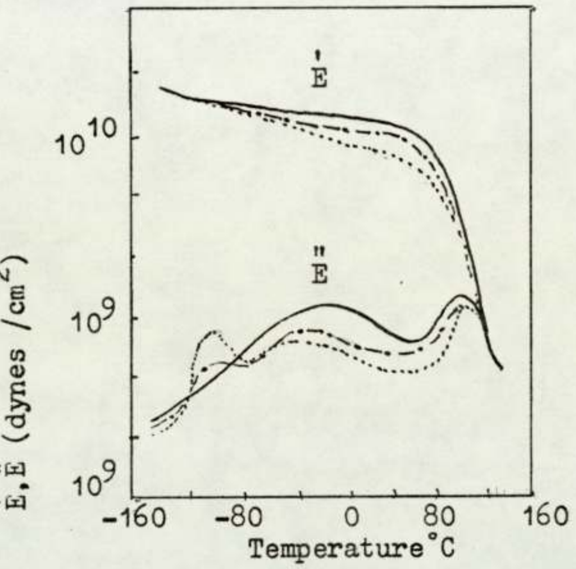


Fig1-16: Temperature dependence of dynamic modulus E' and dynamic loss modulus E" for PVC/PB blends. 100/0 (———), 100/5 (-.-.-.) and 100/15 (......).(79)

Another example which shows the behaviour of a random copolymer is a polymeric system containing PVC and nitrile butadiene rubber (NBR). The glass transition of BR and PVC alone are -80 and +80°C respectively.(79) As is shown in Fig1-17, values of storage modulus (E') exhibit only one transition which systematically moves down the temperature scale as the NBR content is increased.

Therefore, the PVC/NBR system is compatible. This copolymer can be used like many other SPD's as an impact modifier for polymeric materials having low impact strength.

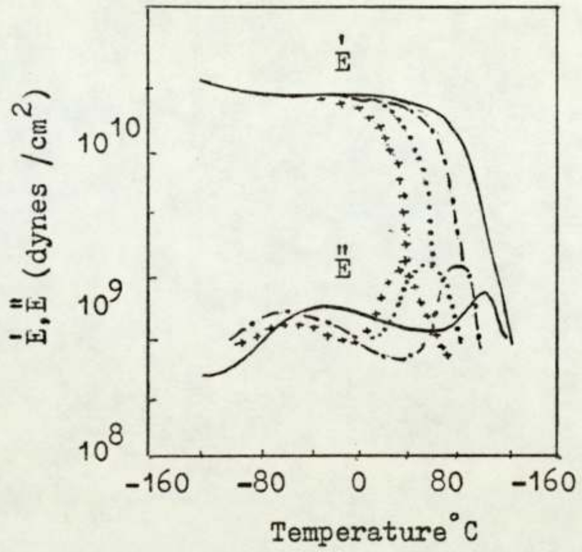


Fig1-17: Temperature dependence of dynamic modulus E' and dynamic loss modulus E" for PVC/NBR copolymers. 100/0: (———),100/10(-.-), 100/25: (....) and100/50:(+++++).(79)

Dynamic mechanical properties of LDPE/PS blends without and with the corresponding copolymers as impact modifiers have been studied in the present work.(See Chapter 4).

Several important pairs of polymers either compatible, semicompatible or incompatible are shown in Tables1-2 and1-3 respectively.(77)

Table1-2: Some compatible and semicompatible polymer pairs.

polymer 1	polymer 2	references
poly(vinylchloride)	poly(butadiene-co-acrylonitrile)	80
polyvinylactate	poly(methylacrylate)	81-82
poly(methylmethacrylate)	polymethylacrylate	82-83
polystyrene	poly(a-methylstyrene)	84
polystyrene	poly(2,6dimethylphenylene oxide)	85
polystyrene	Isotactic poly(vinylmethyl ether)	86
poly(vinylchloride)	poly(a-caprolactone)	87

Table1-3: Some incompatible polymers.(77)

polymer 1	polymer 2	Refs
polystyrene	poly isoprene	87
polymethylmethacrylate	poly(vinylchloride)	88
natural rubber	poly(styrene-co-butadiene)	89
polystyrene	polybutadiene	90
polystyrene	poly (vinyl chloride)	91
poly(methlmethacrylate)	polystyrene	84
poly(methylmethacrylate	cellulose triacetate	92
nylon 6	poly(methylmethacrylate)	93
nylon 6,6	poly(ethyl-terephthalate)	94
polystyrene	poly (ethylacrylate)	95-96
polystyrene	polyisoprene	97
polyurethane	poly(methylmethacrylate)	98

1-5-7 The Effect of SPD's on Optical Properties of Two- Phase Polymer Systems

Because light is scattered at the interfaces of polymer mixtures with different refractive index, the polymer mixtures lose their transparency. There appears to be two different ways to overcome this drawback.(99) The first way is to match the refractive indcies of the components by copolymerization of one or both of the phases .Therefore, the formed copolymers act as interfacial agents to reduce the scattered light in the system and to increase their transparencies. This method has an interesting limitation resulting from the great sensitivity of the refractive index to temperature. It will change as the temperature is raised or lowered. This senstivity is shown in Fig1-18.

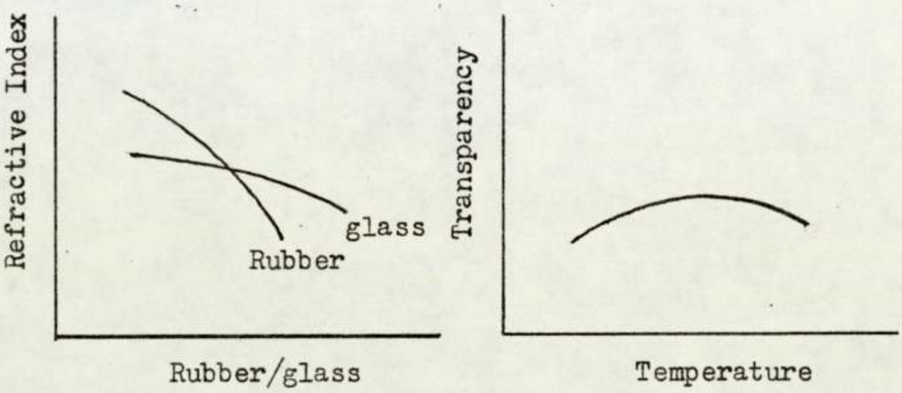


Fig 1-18: The effect of temperature on refractive index and transparency of a rubber-glass two-phase system.

The second way to increase transparency of polymer systems is to reduce the particle size of the dispersed phase. Since as the discontinuties become small in comparison with the wavelength of the light ,the amount of scattered light at the interfaces decreases.For visible light ,the particle sizes should be about 0.1μ or less.Recently, transparent ABS has been achieved in Japan based on this principle.(100)

CHAPTER TWO

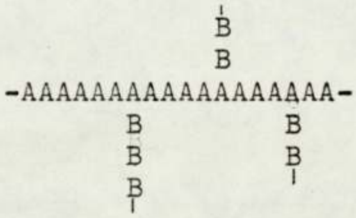
Preparation of Solid Phase Dispersants (SPDs)

As was mentioned in Chapter 1, both block and graft copolymers can be used as an interfacial agent or compatibilizer for impact modification of polyblend systems. In this chapter first, their nomenclature and structures will be discussed and then different methods used in their synthesis will be described.

2-1: Nomenclature and Structure

In the report on nomenclature in the field of macromolecules by the International Union of Pure and Applied Chemistry(101) graft and block copolymers are defined as follows.

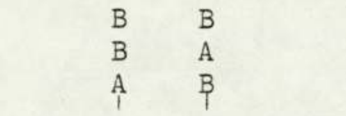
A graft copolymer is a high polymer, the molecules of which consist of two or more different compositions chemically joined together. A graft copolymer can be represent by:



$$\begin{array}{ccccccc} & & & | & & & \\ & & & \text{B} & & & \\ & & & \text{B} & & & \\ \text{-AAAAAA} & \text{A} & \text{AAA} & \text{A} & \text{AAA} & \text{A} & \text{AA-} \\ & \text{B} & & & & \text{B} & \\ & \text{B} & & & & \text{B} & \\ & \text{B} & & & & | & \\ & | & & & & & \end{array}$$

(2-1)

The sequence of A units in the graft copolymer is referred to as the backbone, and branch of B units as the graft. In graft copolymers the backbone and side chains may both be homopolymeric like (2-1) or backbone copolymeric (2-2) or vice versa (2-3).



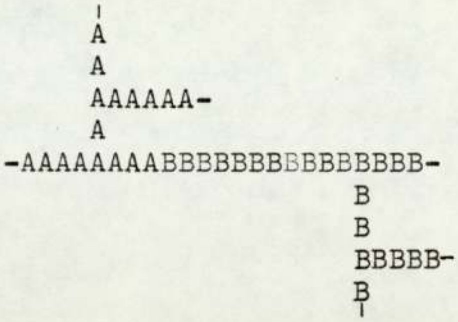
$$\begin{array}{ccccc} \text{-AAAAA} & \text{A} & \text{AAAA} & \text{A} & \text{AAAAA-} \\ & \text{B} & & \text{B} & \\ & \text{B} & & \text{A} & \\ & \text{A} & & \text{B} & \\ & | & & | & \end{array}$$

(2-2)

$$\begin{array}{ccccc} \text{-BABB} & \text{B} & \text{AABA} & \text{B} & \text{BAAB-} \\ & \text{A} & & \text{A} & \\ & \text{A} & & \text{A} & \\ & \text{A} & & \text{A} & \\ & | & & | & \end{array}$$

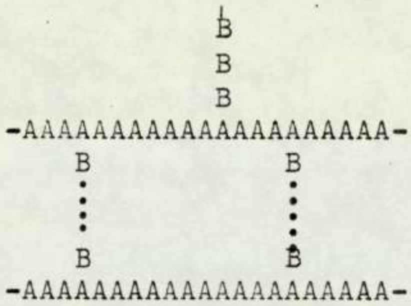
(2-3)

In another form, both backbone and side chains may be copolymer of different chemical compositions. (2-4)



(2-4)

Further complications are introduced if crosslinking takes place during the graft copolymerization. (2-5)



(2-5)

A block copolymer has been defined as a polymer composed of molecules in which two or more polymeric segments of different chemical composition are attached end to end.(102)

-AAAAAAAAAABBBBBBBBB-

-AAAAABBBBBBBBAAAAAA-

(2-6)

More sophisticated graft and block copolymers are discussed in Refs.(102-103-104)

In identifying segments, the term"-co" is interposed between the names of the constituent monomers ,like ethylene-styrene copolymer or poly(ethylene-co-styrene).The letter"-b-" is used to designate block and the letter"-g-" is used to indicate graft segments.i.e, poly(ethylene-b-styrene) and poly(ethylene-g-styrene).

2-2 :Synthesis of Solid Phase Dispersants (SPD's).

Introduction : The preparation procedures for graft and block copolymers used as SPD's are quite closely related.

Generally, graft copolymers involve the polymerization of monomers into a polymer backbone. Therefore, the various methods of accomplishing polymerization can be utilized. Thus addition polymerization of vinyl monomers initiated by free-radical or ionic means, polycondensation and ring-openg polymerization of cyclic monomers can be considered. The different methods of syntheses of block and graft copolymers are discussed in the following sections.

2-2-1: Transfer and Addition Syntheses.

During the free radical polymerization of a vinyl monomer, transfer reactions (transfer of a hydrogen or halogen atom from an inactive molecule to the growing chain) may take place. These are:(105)

(1) Transfer to polymer. $R^{\bullet} + P_s \longrightarrow P + P_s^{\bullet}$

(2) Transfer to the initiator. $R^{\bullet} + I \longrightarrow P + I^{\bullet}$

(3) Transfer to monomer. $R^{\bullet} + M \longrightarrow P + M^{\bullet}$

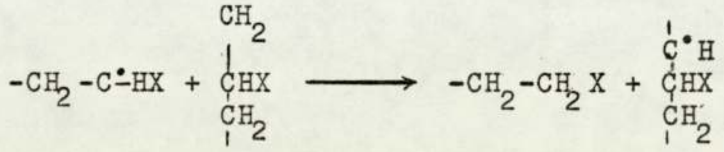
(4) Transfer to solvent. $R^{\bullet} + S \longrightarrow P + S^{\bullet}$

(5) Transfer with added mercaptans $R^{\bullet} + RSH \longrightarrow P + RS^{\bullet}$

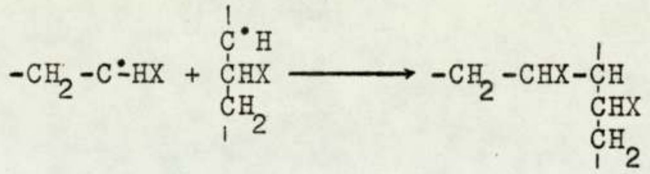
In any kind of chain transfer reaction, the growing chain is terminated and the free radical activity is transfered to the halogen or hydrogen donor. Since the reaction (1) is important in the syntheses of block and graft copolymers, this kind of reaction will be considered in greater details.

2- 1-1: Chain Transfer Reaction to Polymer.

In this kind of reaction a growing radical randomly abstracts a labile atom such as hydrogen or chlorine from an inactive chain or from another chain.



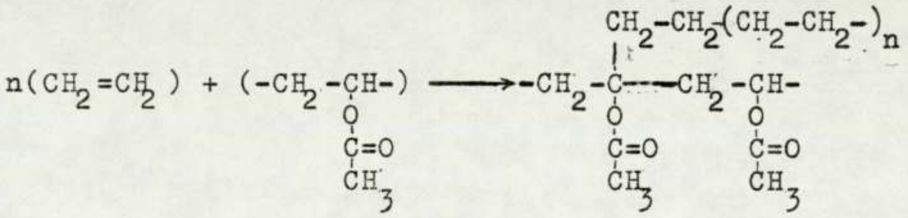
$$-CH_2-C^{\bullet}HX + \overset{CH_2}{\underset{CH_2}{CHX}} \longrightarrow -CH_2-CH_2X + \overset{C^{\bullet}H}{\underset{CH_2}{CHX}} \qquad (2\text{-}1)$$



$$-CH_2-C^{\bullet}HX + \overset{C^{\bullet}H}{\underset{CH_2}{CHX}} \longrightarrow -CH_2-CHX-\underset{\underset{CH_2}{CHX}}{CH} \qquad (2\text{-}2)$$

This mode of synthesis of copolymers was first suggested by Flory in 1937.(106)

Roland and Richard(107) prepared poly(vinyl acetate-g-ethylene) by polymerization of ethylene in benzene solution with diethylperoxide in the presence of preformed poly(vinyl acetate), according to the following reaction.



$$n(CH_2=CH_2) + (-CH_2-\underset{\underset{\underset{CH_3}{C=O}}{O}}{CH}-) \longrightarrow -CH_2-\overset{CH_2-CH_2(CH_2-CH_2-)_n}{\underset{\underset{\underset{CH_3}{C=O}}{O}}{C}}-CH_2-\underset{\underset{\underset{CH_3}{C=O}}{O}}{CH}- \qquad (2\text{-}3)$$

In 1952 Smets and Claesen(108) published their results on the grafting by transfer reaction of vinyl acetate, vinyl chloride styrene and methyl methacrylate with polyvinyl chloride, polystyrene, polyvinyl acetate and polymethyl methacrylate. In Table 2-1 the conditions of the grafting reactions are shown.

Table 2-1: Typical examples of copolymerization by transfer reaction to polymer.

copolymer	polymer (gm)	Monomer (gm)	solvent (cc)	Temp (C)	Time (hr)	Initiator (mg)
P(MMA-g-VAC)	2.5	10	benzene	700	5	50 BPO
P(MMA-g-VC)	1.5	5.37	benzene	100	3	50 BPO
P(VC-g-MMA)	1	2	B.Ph	118	4	10 BPO
P(S-g-VAC)	2	2.5	B.Ph	85,100	5	25 BPO
P(S-g-MMA)	2	6	B.Ph	85,115	5	30 BPO
P(MMA-g-S)	2	6	B.Ph	85,115	5	30 BPO
P(VC-g-S)	100	100	B.Ph	60	16	5 PPS
P(VC-g-VAC)	100	100	200 H20	60	16	5 PPS

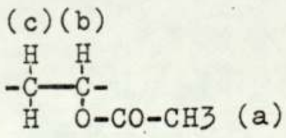
BPO = Benzoyl peroxide.

PPS = Potassium persulphate.

BPh = Butyl phthalate.

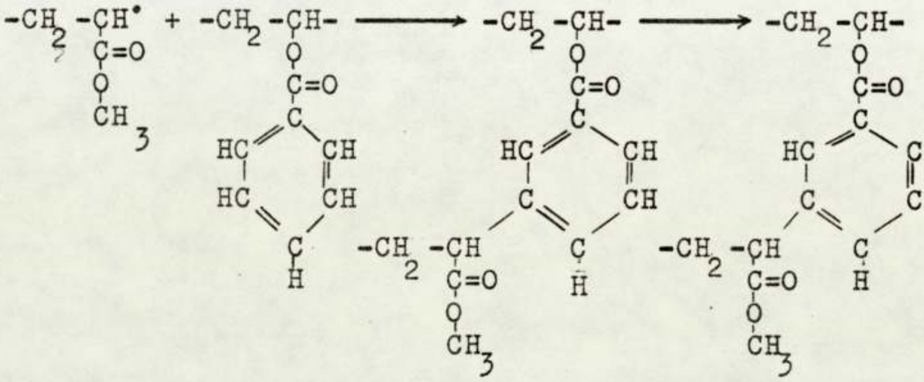
Also the grafting of different monomers to natural rubber has been reviewed by many researchers, notably Bateman(109) and Bevilaqua.(110)

When the reactive sites are present as side groups in the polymer, copolymerization leads to grafted structure. This point has already illustrated in the polymerization of ethylene in the presence of poly(vinylacetate) in benzen solution. (Reaction2-3) With diethylperoxide as an initiator, the grafting reaction takes place at the sites of (b) and (c) depending to the pressure of the reaction, and if the reaction initiated with alkaline methanol the grafting takes place at site (a).(107)



$$\overset{(c)}{}\overset{(b)}{}\quad -\underset{H}{\overset{H}{C}}-\underset{O-CO-CH3\ (a)}{\overset{H}{C}}-$$

A similar example is the grafting of methyl methacrylate onto poly(vinyl benzoate) with benzoyl peroxide.(111) In this case, the grafting takes place at the reactive sites on the aromatic nuclei, according to the following reactions.


(2-4)

Preformed polymers may have side groups containing chain transfer agents such as mercaptan groups. In this case, when the concentration of such groups is high the graft copolymer so formed are usually crosslinked.

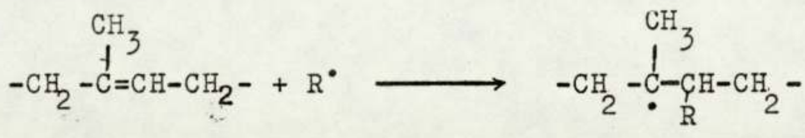
The chemical nature of the backbone polymer is not important, provided that the polymer does not contain groups which inhibit polymerization.(112) However, polymers without reactive groups such as polyethylene generally, form low yields of graft copolymers. In Chapter 3 more details will be given about graft copolymerization of styrene into processed and unprocessed LDPE.

2- 1-2: The effect of Initiator in Transfer reaction to Polymer

From the early studies of vinyl grafting into polyisoprene, it was noted that while good yields of grafted copolymer were obtained by the use of benzoyl peroxide as the initiator, asobisisobutyronitryl (AZBN) gave only a mixture of a homopolymers.(113)

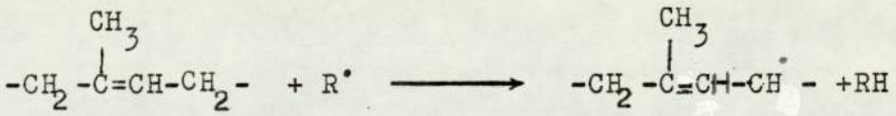
The "initiator effect " led to four alternative possibility of grafting reactions,namely,

(1) Addition of an initiator to the polyisoprene double bond to give a free radical site on the rubber molecule.



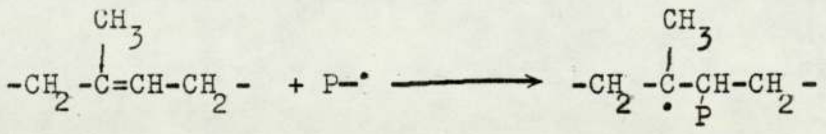
$$-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH}-\mathrm{CH_2}- + \mathrm{R}^{\bullet} \longrightarrow -\mathrm{CH_2}-\underset{\bullet}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}-\underset{\mathrm{R}}{\mathrm{CH}}-\mathrm{CH_2}- \qquad (2\text{-}5)$$

(2) Abstraction of a hydrogen atom from the rubber chain at the(α) position by the radical initiator to give a macromolecular free radical site for the subsequent grafting.



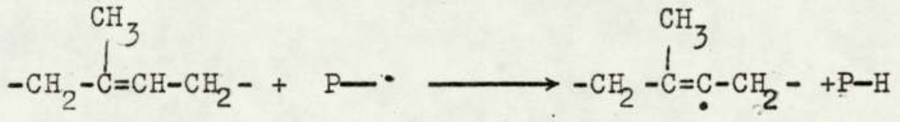
$$-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH}-\mathrm{CH_2}- + \mathrm{R}^{\bullet} \longrightarrow -\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH}-\dot{\mathrm{C}}\mathrm{H}- + \mathrm{RH} \qquad (2\text{-}6)$$

(3) Addition of a polymeric radical to the polyisoprene double bond.



$$-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH}-\mathrm{CH_2}- + \mathrm{P}-^{\bullet} \longrightarrow -\mathrm{CH_2}-\underset{\bullet}{\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}}-\underset{\mathrm{P}}{\mathrm{CH}}-\mathrm{CH_2}- \qquad (2\text{-}7)$$

(4)Abstraction of a hydrogen atom from the rubber chain by a growing polymeric radical to give a grafting site at (a) methylenic carbon atom.



$$-\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\mathrm{CH}-\mathrm{CH_2}- + \mathrm{P}-^{\bullet} \longrightarrow -\mathrm{CH_2}-\overset{\mathrm{CH_3}}{\overset{|}{\mathrm{C}}}=\underset{\bullet}{\mathrm{C}}-\mathrm{CH_2}- + \mathrm{P}-\mathrm{H} \qquad (2\text{-}8)$$

A group of researchers from the Natural Rubber Producers Research Association (NRAPRA)(114) used benzoyl peroxide containing C^{14} labelled initiators. They found the distribution of labelled phenyl and benzoyl fragments were such that only reactions(2-5) and (2-6) took place.

The inability of AZBN to initiate graft copolymerization was believed to be due to the inferior capacity of the resonance stabilized 2-cyano-2-propyl radical $(CH_3)_2C^\bullet-CN$ relative to phenyl and benzoyloxy radicals to engage in reactions(2-5) and (2-6).

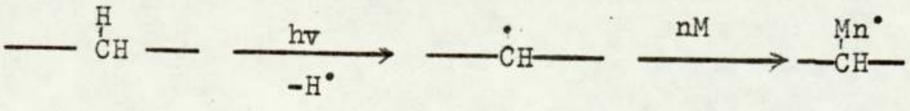
Another example of the effect of different initiators was mentioned earlier for the graft polymerization of ethylene into poly(vinyl acetate) (See section,2-2-1-1). In the present study the "effect of initiator" for these two different initiators has been investigated for polymerization of styrene into LDPE.(See Chapter 3).

2-2: Photochemical Syntheses of SPD's.

If a molecule absorbs electromagnetic radiation in the visible and ultraviolet regions,(200 - 700 m) its energy momentarily increased and the molecule is said to be in an exited state.This energy-rich molecule can either dissociate into reactive free radicals or dissipate its energy by fluorescence or phosphorescence (115-116)

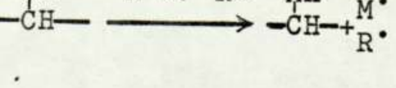
For a molecule, the former process can lead to the formation of free radical sites on the backbone of polymer to initiate graft polymerization.

If irradiation is carried out in the absence of oxygen and in the presence of monomer,the following reactions can be considered.



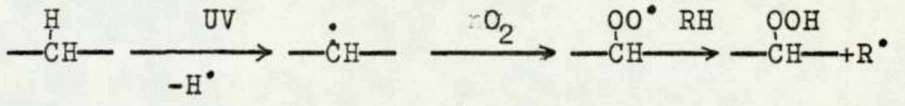
$$-\overset{H}{CH}- \xrightarrow[-H^\bullet]{h\nu} -\overset{\bullet}{CH}- \xrightarrow{nM} -\overset{Mn^\bullet}{CH}- \qquad (2\text{-}9)$$

Chain transfer to monomer or to polymer

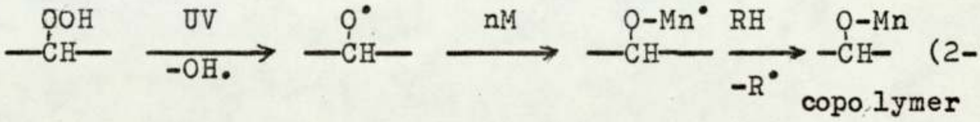


$$-\overset{Mn^\bullet}{CH}- \xrightarrow{M \text{ or } RH} -\overset{Mn}{CH}- + \overset{M^\bullet}{R^\bullet} \qquad (2\text{-}10)$$

But if irradiation is carried out in the presence of both oxygen and monomer, the following reactions take place.



$$\text{—}\overset{H}{C}H\text{—} \xrightarrow[-H^\bullet]{UV} \text{—}\dot{C}H\text{—} \xrightarrow{O_2} \text{—}\overset{OO^\bullet}{C}H\text{—} \xrightarrow{RH} \text{—}\overset{OOH}{C}H\text{—}+R^\bullet \quad (2\text{-}11)$$



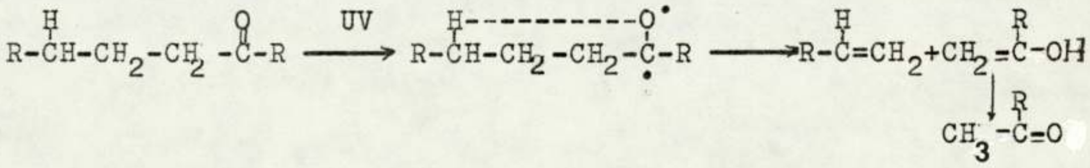
$$\text{—}\overset{OOH}{C}H\text{—} \xrightarrow[-OH.]{UV} \text{—}\overset{O^\bullet}{C}H\text{—} \xrightarrow{nM} \text{—}\overset{O-Mn^\bullet}{C}H\text{—} \xrightarrow[-R^\bullet]{RH} -\underset{\text{copo lymer}}{\overset{O-Mn}{C}H}- \quad (2\text{-}12)$$

Upon absorption of visible light or UV energy, a photosensitizer can itself decompose into active radicals or transfer its energy to another molecule(116) promoting copolymerization. Aliphatic ketones are useful photosensitizers, their photolysis both in solution and in the gas phase has been shown to occur by two simultaneous reactions.(117) One is Norrish type I reaction in which two free radicals are formed.

$$R\text{-}CH_2\text{-}CH_2\text{-}CO\text{-}R' \xrightarrow{UV} R\text{-}\dot{C}{=}O+\dot{R}' \longrightarrow R^\bullet+CO+\dot{R}' \quad (2\text{-}13)$$

and the other reaction is Norrish type II in which the molecule can split at the α-β position to the carbonyl group to give an olefin and a lower ketone without formation of free radicals.

(2-14)



$$R\text{-}\overset{H}{C}H\text{-}CH_2\text{-}CH_2\text{-}\overset{O}{\overset{\|}{C}}\text{-}R \xrightarrow{UV} R\text{-}\overset{H}{C}H\text{-}CH_2\text{-}CH_2\text{-}\underset{\bullet}{\overset{O^\bullet}{C}}\text{-}R \longrightarrow R\text{-}\overset{H}{C}{=}CH_2+CH_2{=}\overset{R}{C}\text{-}OH$$

$$\downarrow$$

$$CH_3\text{-}\overset{R}{C}{=}O$$

Therefore, vinyl polymers containing carbonyl groups may undergo similar reactions upon irradition.

Styrene has been grafted into LDPE by radiation technique and it has been found that the rate of grafting depends on the density of the polymer, thickness of the polymer film, concentration of the monomer and also on the intensity of the radiation.(118-119)

2- 3: Preparation of SPD's by Ionic Initiation

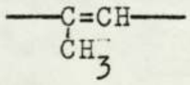
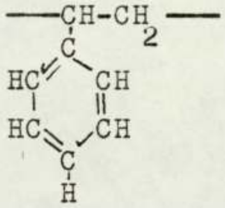
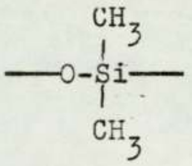
In addition to graft copolymerization initiated by free radical processes, SPD's can be prepared by cationic or by anionic initiators. In the anionic mechanism, copolymerization is initiated by carbanion $(-\overset{-}{C}-)$(122) and in cationic copolymerization, it is initiated by carbonium ion $(-\overset{+}{C}-)$.(118-119) For more details the reader is referred to the Refs of this section.

2 -4: Mechano-chemical Synthesis of SPD's.

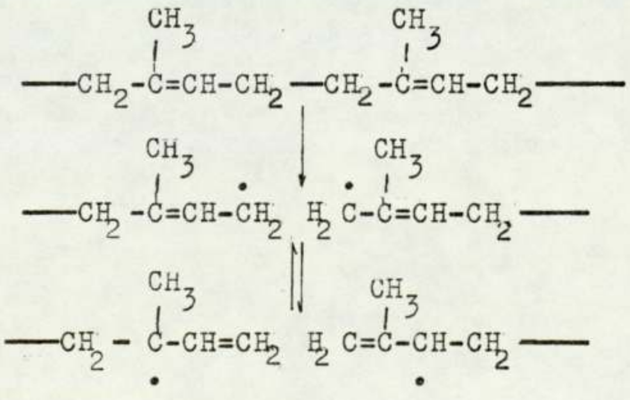
Introduction: The basic principle in the mechano-chemical synthesis of SPD's is the scission of carbon-carbon or other chemical bonds between atoms when the polymer is under the influence of an applied stress. Cottrell(123) has calculated the chemical energies required to break bonds between atoms. Some of them are shown in Table 2-2. It should be noted that these values have been calculated from small molecules and energy contributions from resonance structures, which are possible for the polymeric radicals resulting from chain scission of polymers have not been calculated yet.(124)

A second point is that the calculated bond energies are

Table 2-2:Bond energies for some molecules.

bond		energy K $\frac{Cal}{mole}$
$—CH_2-CH_2—$	C-C	82.6
$—CH_2-CH=$	C-C	-
 $—\underset{CH_3}{C}=CH—$	C=C	145.8
	C-C	-
$—CH_2-O-$	C-O	85.5
 $—O-\overset{CH_3}{\underset{CH_3}{Si}}—$	O-Si	106
$—CH_2-S—$	C-S	65
—O-O—	O-O	47

for molecules which undergo homolytic chain scission with formation of free radicals,i,e,chain scission of polyisoprene.

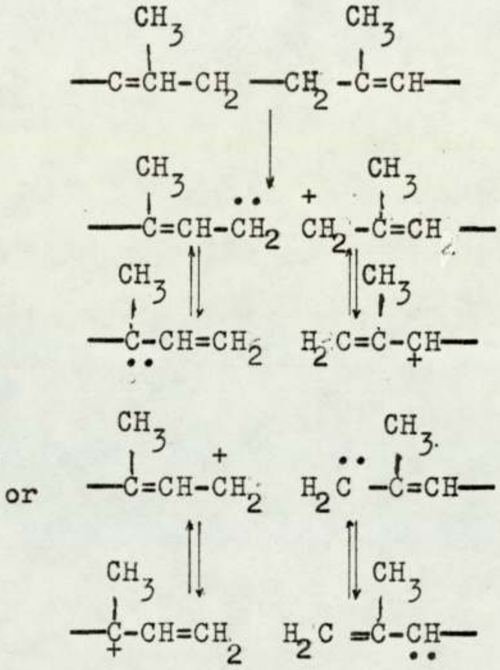


(2-15)

(2-16)

(2-17)

Some polymeric compounds undergo heterolytic chain scisson, when they are subjected to mechanical shear.(125) This kind of chain scission leads to the formation of macromolecular carbonium ions and carbanions. The energy required for heterolytic scission is greater than that required for homolytic scission. Heterolytic chain scission of natural rubber is shown in the following scheme.


(2-18)
(2-19)
(2-20)
(2-21)
(2-22)

Generally, the mechano-chemical methods for the syntheses of SPD's can be classified as follows:

(I) Subjecting a mixture of two or more polymers to mechanical degradation.

(II) Subjecting a polymer to degradation in the presence of a polymerizable monomer. These systems will be described in the next sections.

2- 4-1: Physical States in mechano-chemical Syntheses of SPD's

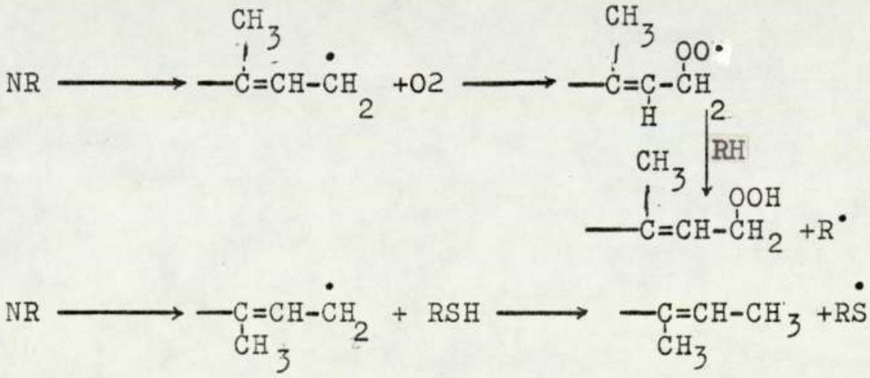
Mechano-chemical reactions can be performed in either the solid state, the rubbery state, the molten state, or the solution state.

2- 4-2 : Mechano-chemical synthesis of SPD's in Solid State

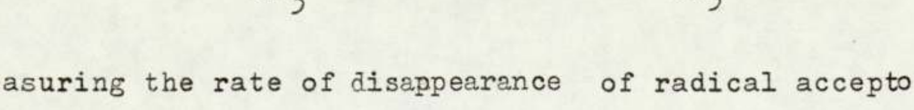
SPD's can be made by grinding or comminuting polymers at temperatures lower than their Tgs.Practically,the only equipment used for mechano-chemical reactions in solid state is an internal mixer such as Torque Rheometer.(See section 3-5) .

In the solid state (phase), blending and comminution is carried out to reduce heterogenity of the system by reduction of particles size.So, particle size can influence the mechano-chemical reactions.For example, in the grafting of polyvinyl - chloride on caprolactam,the chlorine content of the resultant polymer was 2.16 and 3.71 % ,when the preformed polymer had particle sizes of 0.4-0.6 and 0.05-0.09 mm diameter respectively.(127)

Generally, mechano-chemical reactions are effected by the presence of radical accepters such as thiophenol or oxygen.(128-129) In the case of natural rubber during cold mastication in the presence of the above radical accepters ,the following reactions take place.(130)



$$NR \longrightarrow -\overset{CH_3}{\overset{|}{C}}=CH-\dot{C}H_2 \;+02 \longrightarrow -\overset{CH_3}{\overset{|}{C}}=\underset{H}{C}-\overset{OO\cdot}{\overset{|}{C}}H_2 \xrightarrow{RH} -\overset{CH_3}{\overset{|}{C}}=CH-\overset{OOH}{\overset{|}{C}}H_2 + R^{\cdot} \qquad (2-23)$$

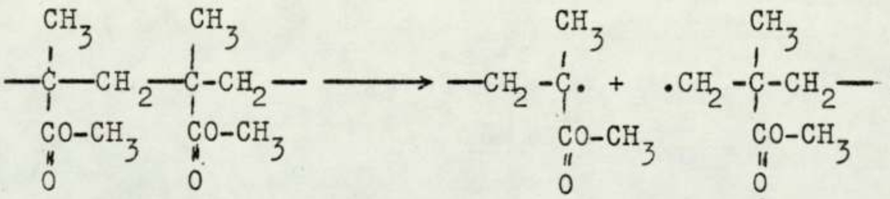


$$NR \longrightarrow -\underset{CH_3}{\underset{|}{C}}=CH-\dot{C}H_2 + RSH \longrightarrow -\underset{CH_3}{\underset{|}{C}}=CH-CH_3 + R\dot{S} \qquad (2-24)$$

By measuring the rate of disappearance of radical acceptors by Electron Magnetic Resonance (ESR) technique the rate of degradation of the polymer can be obtained.

In this method of preparation of SPD's, the yield of favourable reactions are increased with duration of mechanical stress, but if the milling time is too long, the properties of the products may detoriorate by degradation of the initial products. This effect has been studied in the case of LDPE and PS. (See section 3-14)

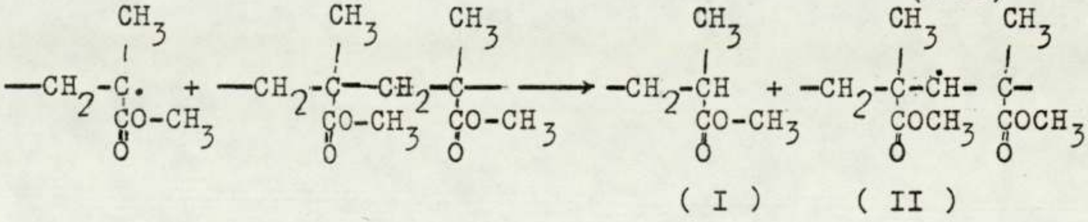
As was mentioned earlier, mechano-chemical synthesis in the solid state can be performed in both polymer-polymer and polymer monomer systems. A typical example of a polymer-monomer system is the grafting of vinyl chloride into poly(methyl methacrylate) by vibromilling, at 25°C and 12 hours.$^{(131)}$



$$-\underset{\substack{|\\CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-CH_2-\underset{\substack{|\\CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-CH_2- \longrightarrow -CH_2-\underset{\substack{|\\CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}\cdot \;+\; \cdot CH_2-\underset{\substack{|\\CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-CH_2- \qquad (2\text{-}25)$$

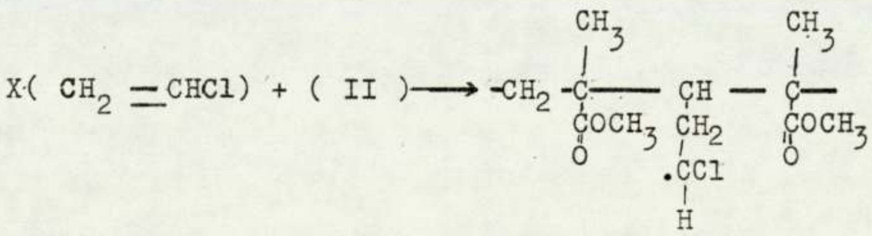
In the presence of the monomer (vinyl chloride), the following reactions take place.

(2-26)



$$-CH_2-\underset{\substack{CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}\cdot \;+\; -CH_2-\underset{\substack{CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-CH_2-\underset{\substack{CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}- \longrightarrow -CH_2-\underset{\substack{CO-CH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{CH}} \;+\; -CH_2-\underset{\substack{COCH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-\dot{C}H-\underset{\substack{COCH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-$$

(I) (II)



$$X(CH_2=CHCl) + (\ II\ ) \longrightarrow -CH_2-\underset{\substack{COCH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}-\underset{\substack{CH_2\\|\\\cdot CCl\\|\\H}}{CH}-\underset{\substack{COCH_3\\\|\\O}}{\overset{\substack{CH_3\\|}}{C}}- \qquad (2\text{-}27)$$

2- 4-3 Mechano -chemical Syntheses in the Rubbery State

Mastication of polymers in the rubbery state is one of the most important methods of preparation of copolymers for use as SPD's.

Mastication of polymeric materials has been carried out on polymer-polymer,polymer-monomer and polymer-filler systems. It has been found that the properties of the products can vary widely according to the polymer structure and conditions of mastication such as temperature, mixing intensity,presence and nature of radical accepters,ratio of the components and time of mastication. The most important equipments used for mastication of polymers are,roll mills, internal mixer and extruders.

2- 4-4: Mechano-chemical Synthese of SPD's in the Molten State

A definition of a boundary between a rubbery and a molten state is arbitrary. Above the glass trasition temperature(Tg) amorphous polymers are in the rubbery state and increase of temperture changes the viscoelastic state of the polymers.That means the balance between elastic and viscous behavior is changed. Before reaching the purly viscous state,thermal oxidation has been shown to occur in many high polymers.So, in the preparation of SPD's by this method,oxidation can be accomplished by thermal oxidative reactions which becomes more important with increaing temperature.

Akutin and co-workers(135) extruded high density polyethylene with polyisobutylene at 200-300°C and obtained block and graft copolymers.Akutin also studied the influence of processing of nitryl rubber and poly(vinyl chloride) in a Brabender (plastograph) at 160-180°C,rotor spead 5-10 RMP. He found that the addition of nitryl rubber increased the impact strength of the composition. It was reported that ,addition of the rubber up to 10 % leads to a reduction in torque which indicates a plasticizing action by the rubber. By increasing the content of the rubber to 50 % the torque increases sharply due to the formation of gel. In the present study,LDPE and PS were processed in the torque rheometer (See section 3-14) and in a Brabender(See section 3-15) to make LDPE/PS copolymer as an impact modifiers for the corresponding polyblends.

2- 4-5: Mechano-chemical Synthesis of SPD's in Solution

The preparation of SPD's by this method is not so important as in the undiluted states.This is because the conversion of mechanical energy to free radical formation is much less efficient in solution. Another disadvantage of this method is the limitation imposed by combining polymers and monomers initially soluble in the same solvent.This method will not be dealt with in the present work,but information in the procedure is found in Refs.(136-137)

2-5 Modification of Elastomers.

It has been found that the intrinsic viscosity of rubber decreases during mastication in nitrogen.It is believed that the mastication process leads to the formation of branching without gel formation.(132)

Branching can be explained by a transfer reaction between molecules and polymeric radicals resulting from the mechanical scission.In some cases when there is labile hydrogen,unsaturated groups or double bond in the backbone of the polymers, cross-linking takes place.(133) Therefore, gel formation is a common side reaction in the modification of elastomers. In the case of mastication of natural rubber with neoprene, the electron withdrawing chlorine in the neoprene molecule enhances the reactivity of the double bond to radical attack causing gel formation.(See Fig2-1).

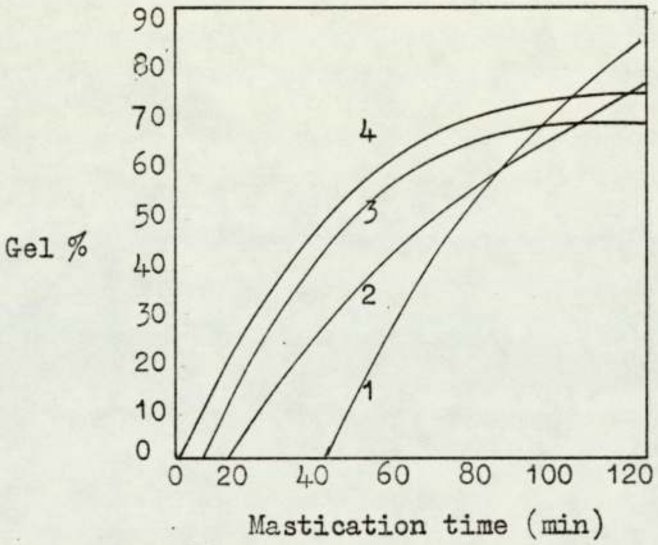


Fig 2-1: Effects of mastication time and neoprene ratio on the gel formation of natural rubber. Curves Nos 1,2,3,and 4 are related to 100,75,50 and 25 % neoprene respectively.(133)

2-6 Modification of Plastomers.

The production of resins poly(styrene-co-acrylonitrile) and polystyrene with relatively high toughness has been one of the most important objective of the polymer industry in recent years. This can be achieved by modifying a rigid polymer with small amounts of elastomers.

Berlin and co-workers(134) carried out plasticization of polystyrene with polyisoprene,butyl rubber,polychloroprene,polybutadiene,styrene rubber and nitrile rubber.The best result was obtained with the blends of polystyrene with styrene natural rubber and polystyrene with nitrile rubber.It was found that increasing of rubber content above 20-25 % was not useful,since the strength of the product was decreased.(Fig 2-2)

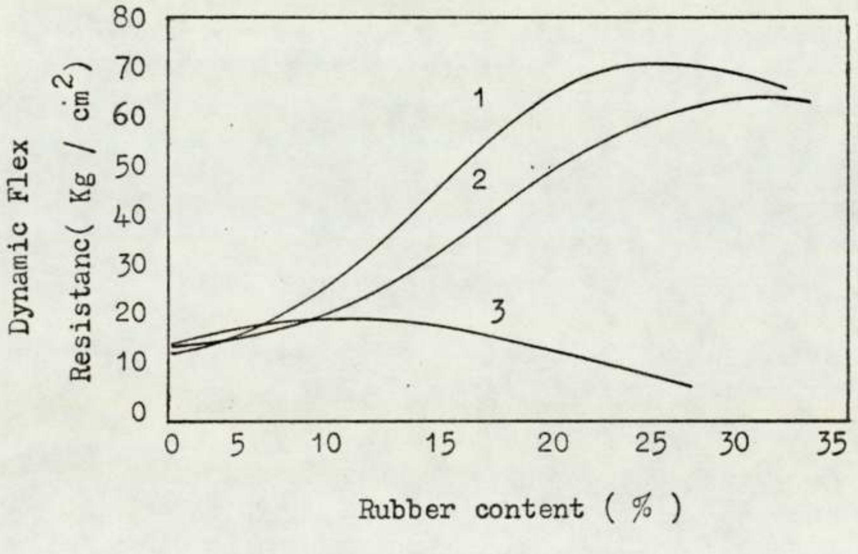


Fig 2-2: Effect of the amount and type of rubber on dynamic flex resistance of polystyrene.Curves 1,2 and3 styrene rubber nitrile rubber(SKN 18) and nitrile rubber(SKN 40) respectively.(134)

2-7 : Effects of Conditions on mechano-chemical Reactions

Generally, monomer concentration has a considerable effect on reactions resulting from mechanical shearing. This effect is shown in Fig 2-3 for the polymerization of methyl methacrylate with natural rubber.(138)

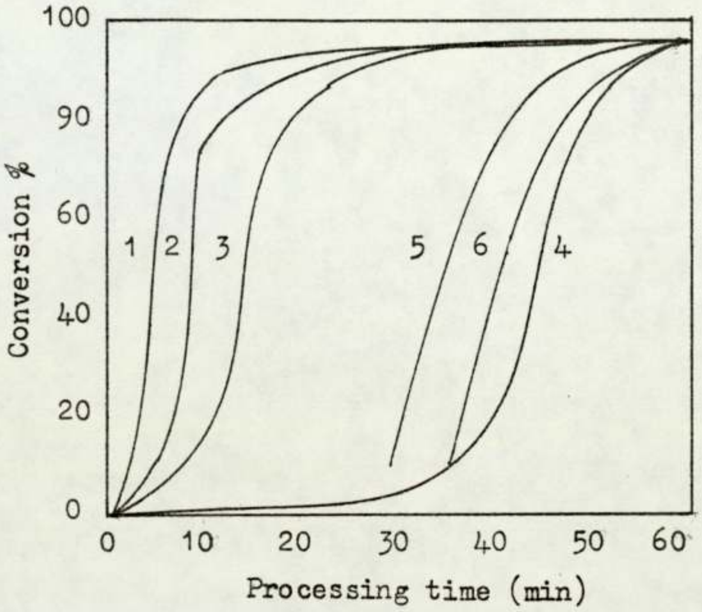


Fig 2-3: Effect of monomer concentration(methyl methacrylate) on mastication of natural rubber .Curves 1:23% monomer,2:38%, 3:48%,4:55%, 5:55%+1% BPO and 6: 55%+1%AZBN.(138)

It has been reported that although small amounts of the monomer had little effect on the viscosity of the product ,the ratios of initiator can also change the rate of mechano -chemical reactions and of side reactions such as gel formation. In the case of mastication of methyl methacrylate with natural rubber (Fig 2-3), at higher concentrations of the monomer and the initiators,the rate of the initiation and conversion of the reaction is considerably affected by termination and disproportionation and subsequently ,long induction periods appear through the reaction ,but the rate of the polymerization was nearly the same in all cases.(138) This behavior could be believed to be due to the autocatalytic nature of the polymerization and is directly related to the first increase in bulk viscosity of the copolymer during of consumption of the monomer with formation of the more rigid plastomer chain . So, as the reaction proceeds the bulk viscosity of the system increases rapidly and at constant shear rate ,the concentration of polymeric free radicals formed by mechanical shearing also increased .

Temperature has also a considerable effect on the rate of polymerization . This effect is shown in Fig2-4 for methyl methacrylate and natural rubber.(138)

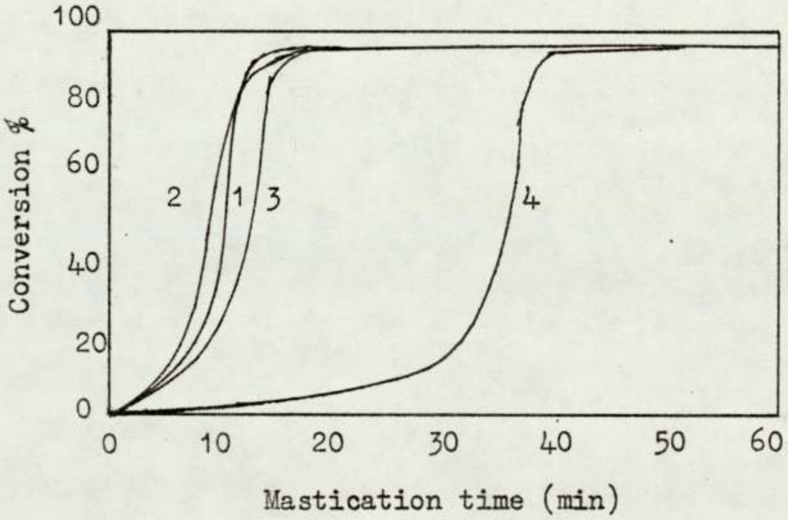


Fig 2-4: The effect of temperature and processing time on the monomer conversion at 76RPM. (methyl methacrylate concentration 38.5 %). Curves 1:15°C, 2:12°C at 360 RPM, 3: 25°C,and 4:35°C.

2-8 : Influence of Preformed Rubbery Polymer and Inter-Polymer Properties in Mechano-chemical Syntheses of SPDs.

The physical and chemical properties of initial polymer (rubbery polymer) and the inter-polymer which is formed should be considered together. Usually, the chemical nature of the rubber determines which bond is the weakest and is more likely to be ruptured during the mastication process.An increase in the degree of asymetry causes an increase in the stiffness and also the increased viscosity of inter-polymer facilates mechanical chain scission of the polymers.Resonance stability will also influence the activity of polymeric free radicals formed during mastication .This effect also prevents the tendency to disproportionation.Therefore, in this case termination is favoured. The presence of higher concentration of active groups will favour the formation of graft copolymer.(139)

As stated earlier, the physical and chemical properties of inter-polymers markedly influence the rate of mechan -chemical reactions after the inducton period. If the monomer present in the system forms a polymer stiffer than the original polymer,the rate of reaction will be increased during mastication.For example,in the polymerization of styrene and methylmethacrylate onto natural rubber this effect has been reported.But if the monomer present in the system causes formation of a polymer softer than the original polymer, the rate of reaction is not accelerated as in the case of terpolymers.The effect of inter-polymer formation during mastication of some copolymers are shown in Fig 2-5.(138)

The data in Fig 2-5 also show the effect of temperature and monomer concentration in mechan -chemical syntheses of SPD's.

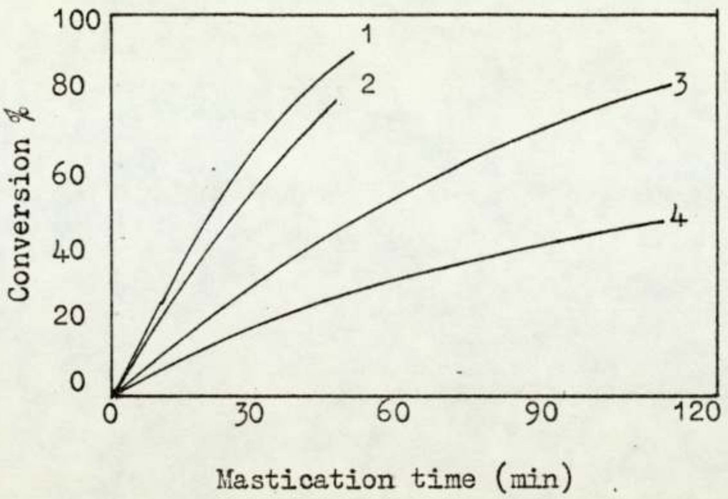


Fig 2-5: The influence of temperature, monomer concentration, mastication time and inter-polymer on the polymerization of chloroprene and natural rubber.(139)

Curves 1: 24.2 % chloroprene at 15°C

2: 24.2 % chloroprene at 25°C

3: 39 % chloroprene at 15°C

4: 49 % chloroprene at 25°C

CHAPTER THREE

3-Experimental Work

Introduction : In this chapter different methods of preparing poly(ethylene-g-styrene)are described in detail.These are as follows:

(I) Chemical Methods.In these methods styrene has been grafted into processed and unprocessed LDPE. In the case of the processed polyethylene,free radical initiator was not used but in the case of the unprocessed polyethylene,free radical initiators such as benzoyl peroxide and cumene hydroperoxide were used.

(II) Mechano-chemical Methods. In these methods the copolymer was made by separately processing both styrene and polystyrene with LDPE,without and with free radical initiators (benzoyl peroxide and cumene hydroperoxide).

3-1 Materials and Purification of Chemicals.

The materials used in the present study were,

(I) Low-density polyethylene. A low-density polyethylene in granular(bead) form,containing no antioxidant and identified by name"Alkathene" polymer WJG 47 supplied from Imperial Chemical Indusries Limited (ICI) was used throughout this study. The polymer had melt flow index (MFI) and density of 2 and 0.913 g/cm^3 respectively.

(II) Polystyrene.Supplied by Shell Chemical Company and named Garinex Polystyrene.This polymer grade was in crystal form as granules measuring approximately 3X2X2 mm in unlubricated form.Its general properties will be given in the appendix.

(III) Styrene. This is a toxic chemical and has the following physical properties.(140)

Density=.909 g/cm^3, Molecular Weight=104.15, Melting Point= -31 °C, and Boiling Point=145-146 °C.It was inhibited with 10-15ppm p-tert-butylcatechol.It was supplied by BDH Chemicals. Before using it was washed with 10 % of sodium hydroxide,followed by washing with distilled water until PH=7.Then it was dried with magnesium sulphate and sodium bicarbonate.It was distilled under vacum(0.01mm-Hg) at 50to60 °C,and then it was stored in a refregerator. 142)

(IV) Solvents. Commercial toluene,ethyl- methyl - ketone (MEK), tetralin,cyclohexane and acetone were supplied by BDH Chemicals. Only toluene was purified,first over sodium and then by distillation at normal presure.

(V) Initiators. Benzoyl peroxide(BPO) and cumene hydroperoxide (CHP) were supplied by BDH Chemicals Ltd and they were purified by the following procedures.

(a) Purification of benzoyl peroxide.

10g of benzoyl peroxide was disolved in 25ml of chloroform.The water layer was separated and then the rest was heated at about 40 °C to evaporate the solvent.Then 75ml of methanol was added to it and was allowed to cool. The benzoyl peroxide was filtered and washed with few ml of methanol and it was dried in vacuum at room temperature and then it was kept at 0 °C.

(b) Purification of cumene hydroperoxide .(141,142)

Cumene hydroperoxide,stabilized with 6 % of a 15 % W/W slurry of sodium bicarbonate and water,was purified by Karasch,s (215) method. For this purpose 50g(1.25mole) of caustic soda in 100ml of water was added to 152g(1mole) of cumene hydroperoxide at 0 °C.The sodium salt was filtered and washed with 25 % NaOH solution, then with petroleum ether and suspended in 500ml of water. Carbon dioxide gas was bubbled through the suspension and when all the hydroperoxide has been liberated, the solution became opaque and separated into two layers. The lower aqueous layer was extracted with ether. The combined ethereal fraction was washed with dilute sodium carbonate solution and dried with anhydrous sodium carbonate. After removal of the solvent, the product was distilled at 52-55 °C/0.01mmHg. The purified cumene hydroperoxide (colourless) was stored at 0 °C.

3-2 Processing of Low-Density Polyethylene.

It was mentioned in the first method, styrene was grafted into the processed LDPE and the hydroperoxide formed during the processing will act as an initiator. So, by processing of the polymer, optimum conditions for formation of hydroperoxide were determined. For this purpose, different amounts of the polymer (35 and20g) were processed at different temperatures at the range 150 to 180 °C and at different conditions as follows;

(I) Full and closed chambr(35g),

(II)Full and open chamber (35g),

(III) Half full and open chamber (20g) and

(IV) Full and closed chamber under nitrogen gas (35g).

The samples were processed in a RAPRA Torque Rheometer[143]. which is principally a small mixing chamber, containing mixing screws contrarotating at different speeds, low, medium and high speed. Throughout the processing, high shear rate (72rmp) was used. After predetermined processing time from 5 to 60mins the samples were removed from the Torque into cold water to prevent uncontrolled thermal oxidation.

3-3 Preparation of Films by Compression Moulding.

The film samples were prepared by compression moulding to study their Infra-red Spectroscopic and mechanical properties. In this method the samples were compression moulded by using two stainless steel glazing plates. The plates were carefully cleaned before use to ensure a smooth surface and to prevent the films from sticking. A special grade of cellophane paper was used as a mould releasing agent between the plates. Control of film thickness was achieved by using a definite amount of samples. About 4g of sample was used to obtain thickness 0.01-0.012 cm. The weighed samples were placed in cellophane sheets between the glazing plates and they were inserted into a hydrostatic press.

Pressing of the films involved three stages;

(I) Preprocessing of the sample for one minute.In this stage the glazing plates and the sample were preheated to desired temperature (170°C) with ram pressure 0-10 Tons/in^2.

(II) Pressing of sample.In this stage the plates and sample were pressed for two minutes with maximum ram pressure 30 Tons/in^2.

(III) Cooling of sample. In this step the plates and the sample were coled to 50-60°C by cooling the press with water and the plates were removed from the press.The sample films were stored at 0°C

3-4 Determination of Hydroperoxide

The hydroperoxide formed during processing of the LDPE was determined by the following methods.

(I) Infra-red spectroscopic method.

As was mentioned earlier, to obtain optimum conditions for hydroperoxide formation in LDPE, the polymer was processed in the torque rheometer under different conditions (section 3-2). Then film with exactly the same thickness were examined in the infra-red Spectrophotometer Perkin Elmer Model 457. For the samples processed at 150 °C for about 30 minutes in open chamber a maximum sharp band in the IR-spectra appeared at 3555 cm^{-1} which is due to O-H stretching of free hydroperoxide.(144-145) This band was measured for hydroperoxide index which is defined as (A3555/A'1895) cm^{-1} (Figs 3-1 and 3-2).

$$\text{Index} = \frac{\text{Absorbance of the functional group}}{\text{Absorbance of a standard peak}}$$

(II) Iodometric method.

This method is one of the most widely used techniques for the determination of hydroperoxides. In this method iodide is oxidized quantitatively to iodine by the hydroperoxide in an acetic medium according to the following equation.(146-147)

$$ROOH + 2I^- + 2H^+ \rightleftharpoons I_2 + ROH + H_2O \qquad (3\text{-}1)$$

If the polymer is processed in the present of air the dialkyl peroxide formed also can oxidize the iodide to iodine, but this reaction is slower than the former reaction.

$$2\,ROOH + 2I^- \xrightarrow{2H^+} 2ROH + I_2 \qquad (3\text{-}2)$$

$$2I^- \longrightarrow I_2 + 2e^-$$

therefore: $2I^- = 2e^- = ROOH = I_2$

The liberated iodine was determined by titration with solution of 0.01N sodium thiosulphate. The conditions used in this

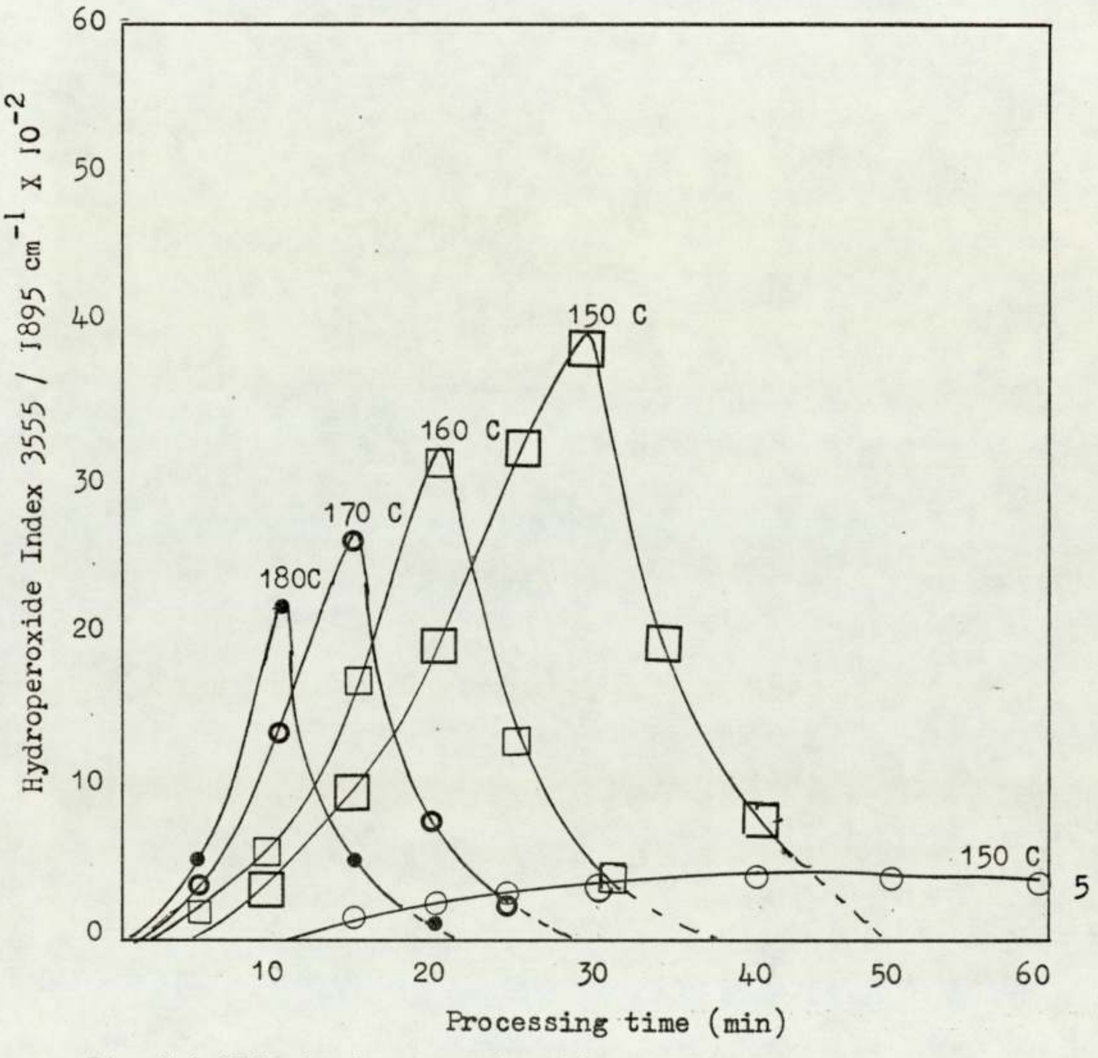


Fig 3-1 Effect of processing time on the formation and decomposition of hydroperoxide in LDPE.

Curve No 5=closed and full chamber under N2.

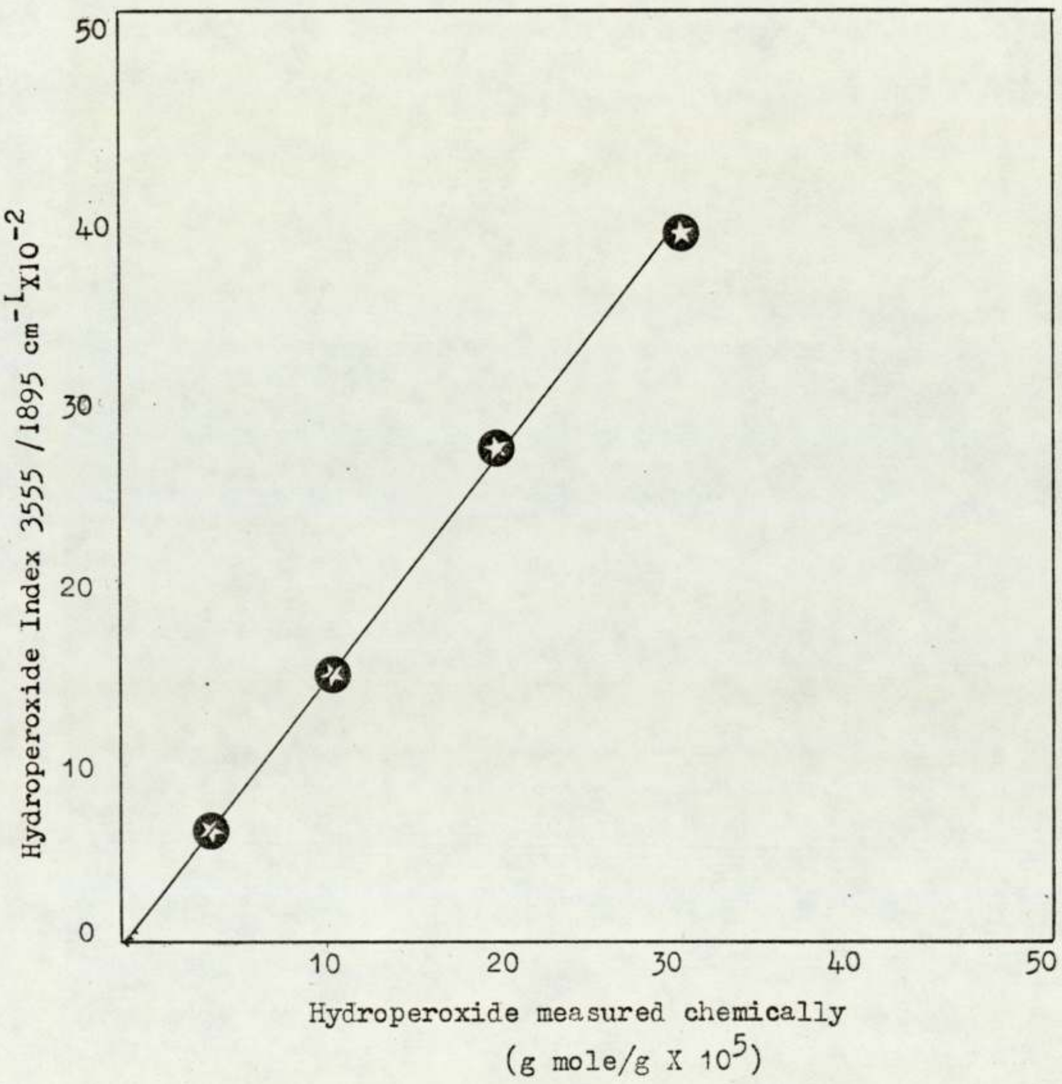


Fig 3-2 Correlation between chemical and IR methods of hydroperoxide measurements formed during processing of LDPE inTorque Rheometer at 150 C,half-full and open chamber, from 5 to 60 mins.

technique are important and many modifications of this procedure have been published.(147) In the present study the hydroperoxide formed during thermal processing of the polymer was determined by the procedure used by Smith and co-workers.(196)

3-4-1 Reagents required for determination of hydroperoxide

(I) 10 % (V/V) acetic acid in isopropanol,

(II) 20 %(W/V) sodium iodide in isopropanol,

(III) Chloroform and methanol,

(IV) 0.01N sodium thiosulphate.It was prepared with boiled water and was stabilized with a few drops of chloroform and stored in a flask covered with aluminium foil. The exact strength of the thiosulphate was determined by a standard solution of sodium iodide.

3-4-2 Procedure

1g of the processed LDPE film in small pieces was introduced into 21.7 ml of chloroform in a flask and N_2 gas was passed through it for about 30 mins.Then the sample was allowed to swell for 18hrs (this time has been determined to a maximum hydroperoxide concentration)(147).Then 3.3 ml of glacial acetic acid and 2 ml of freshly prepared 5 % solution of sodium iodine in methanol were subsequently added to the sample.All these steps were carried out under N_2 gas and the vessel was sealed with a rubber stopper. After adding the solvents ,the sample was kept in a dark place for 4 mins to complete the reaction(reaction 3-1).Then as mentioned earlier, the liberated iodine was titrated by the solution of sodium thiosulphate.A good correlation was obtained between hydroperoxide measured by this method and the IR technique (Fig3-2)

3-5 Evalution of Torque as a Function of Processing Time.

When a polymer is processed in the torque rheometer the torque rises sharply and then decreases to its minimum value and the subsequent changes depend on the mechano-chemical reactions which take place during the processing. An idealized torque vs processing time curve is illustrated in figure 3-3 .(148)

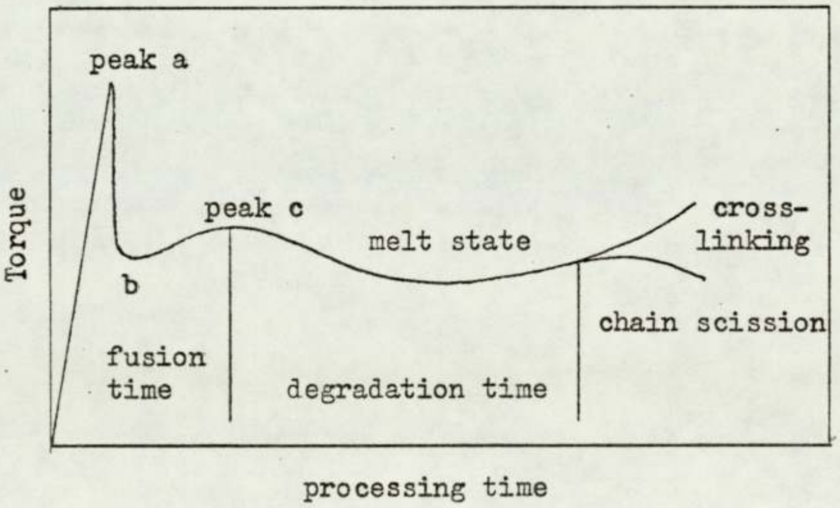


Fig 3-3: Idealized shape of torque versus processing time curve

When the ploymer is heated and it reaches its glass transition (Tg),the polymer becomes rubbery and torque decreases from point 'a',then the torque reaches to minimum value'b' and when the melting is completed the torque increases slightly to peak'c'. The time to reach the peak'c' is called the fusion or flux time. The fusion time for a particular polymer depends on temperature, mechanical stress and also on the presence of additives. However, when the melt state is completed chain scission takes place. At this stage the molecular weight of the polymer decreases and subsequently the Torque decreases. In some cases a side reaction, (crosslinking) takes place which depends mainly on the structure of the polymer and presence of oxygen. In this case the value of the torque increases slightly.

Changes in molecular weight (chain scission and crosslinking) were studied during thermal processing of LDPE. (see section 3-6 and 3-7). In the case of LDPE, changes of torque as a function of processing time are shown in Fig3-4.

3-6 Determination of Gel Content in Processed LDPE.

During processing of LDPE, chain scission occurs. When hydrogen transfer takes place from the polymer to the free radical polymer segment resulting from mechanical shearing, the polymer free radicals will react together to form insoluble materials (gel), provided the processing takes in the absence of oxygen. In the case of LDPE, gel formation is a side reaction which affect the melt viscosity of the resulting products.(149)

Gel content in the processed LDPE was determined in two different solvets as follows;

(I) Gel determination in p-xylene at 90°C. For this purpose 0.5g of the processed polymerfilm in small pieces was placed in a flask containing 50 ml of p-xylene. After heating the sample for 30 mins at 90°C under N_2 gas, the solution was filtered hot on a filter paper which had been dried at 90°C and weighed. The undisolved fraction (gel) was collected and dried in vacuum at 90°C to cnstant weight.

(II) Gel determination in tetralin at 125°C. 1 g of the sample film in small pieces was placed in a preheated and weighed thimble and it was put in a reaction flask containing tetralin. The reaction flask was equipped with a condenser and a thermometer. It was heated in an oil bath for 30 mins and the thimble was pulled up to to filter the insoluble fraction from the solution. Then the insoluble fraction was dried in a vacuum oven about 30 mm Hg at 100°C, and the residue was weighed as percentage of gel content in the polymer. The results are shown in Fig 3-5 curve 1 .

3-7 Measurement of Melt Flow Index (MFI)

Melt flow index is a measure of the melt viscosity of a polymer which is related to the molecular weight, it is defined as the amount of polymer in grammes extruded through a standard die in a given time (e.g. 10 mins). The melt flow index decreases as the molecular weight of the polymer increases. The approximate relationship of MFI with molecular weight ($\bar{Mn}$) and melt viscosity (η) are given by the following two equations respectively (in the case of LDPE).(152)

$$\bar{Mn} = 188-30 \log MFI \qquad (3-1)$$

$$\eta \text{ (poise)} = 7.5 \times 10^4 \times 1/MFI \qquad (3-2)$$

Since thermal processing of polymers cause changes in the molecular weight of the sample by virtue of such reactions as chain scission and crosslinking. Such changes are expected to be reflected in the melt flow index values. Hence, melt flow

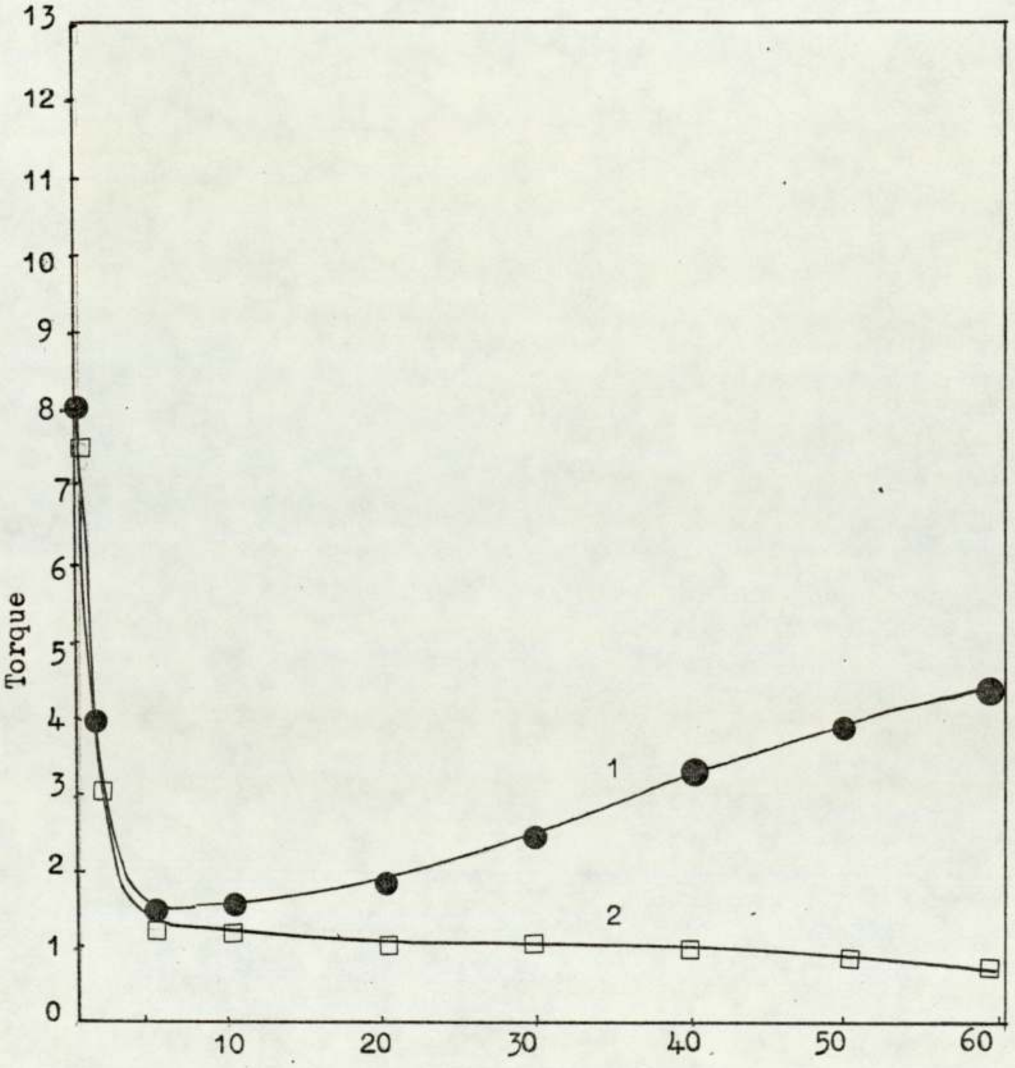


Fig 3-4 Changes in torque against processing time.

Curve No 1=closed,full chamber and under N_2 gas

Curve No 2=half full and open chamber.

Temperature of processing 150°C

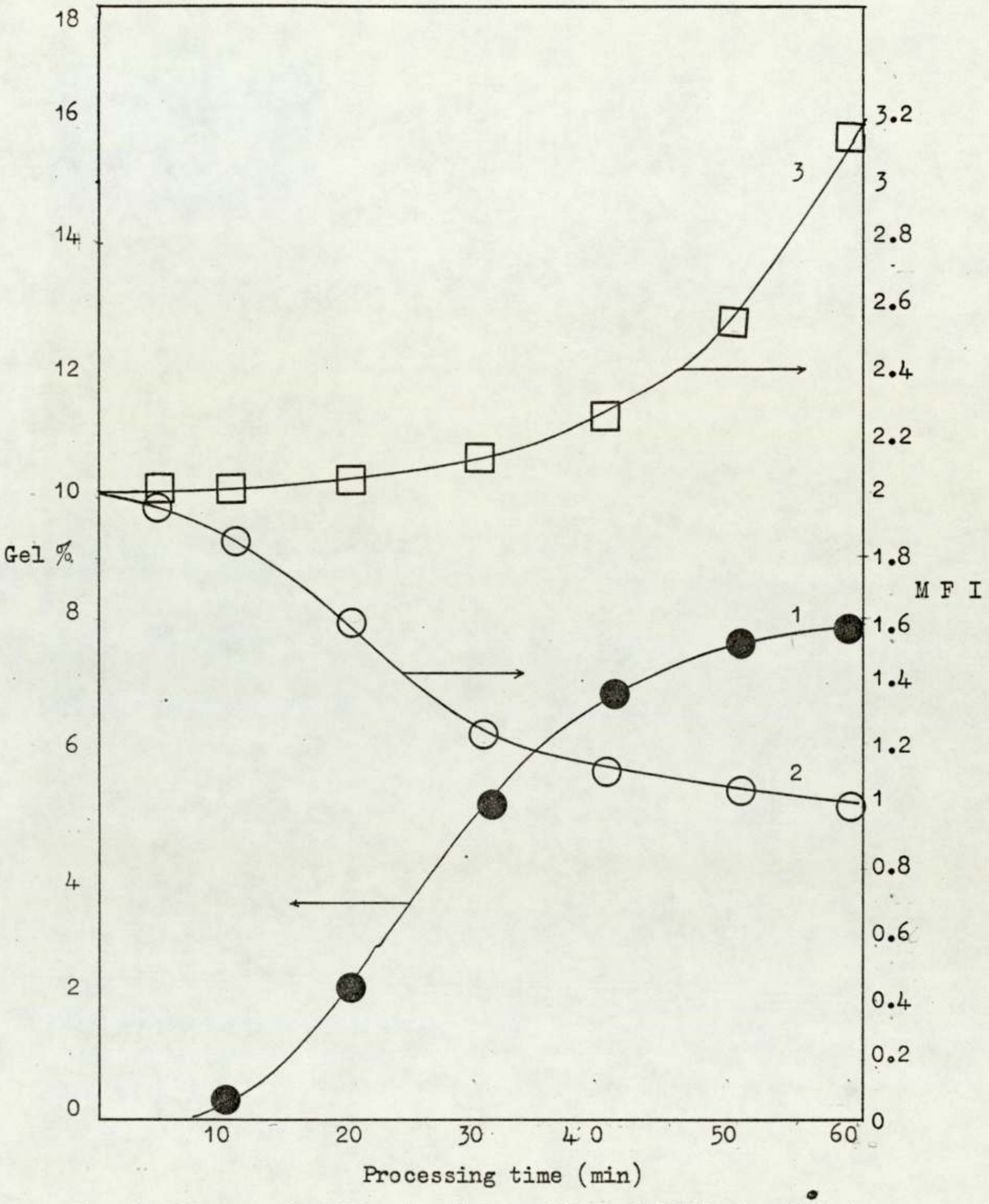


Fig 3-5 Changes in MFI and gel formation of LDPE at 150 °C in Torque Rheometer. Curves No 1 and 2 full and closed chamber under N_2. Curve No 3 half-full and open chamber.

index measurements may reflect any oxidation occuring during thermal oxidation of the sample.

Melt flow index was determined on processed and processed LDPE, LDPE/PS without and with the corresponding copolymers by Davenport Polyethylene Grader (see the following section).

3-7-1 The Davenport Polyethylene Grader

The apparatus is basically a plastimeter. Its general design is shown in Fig 3-6*.

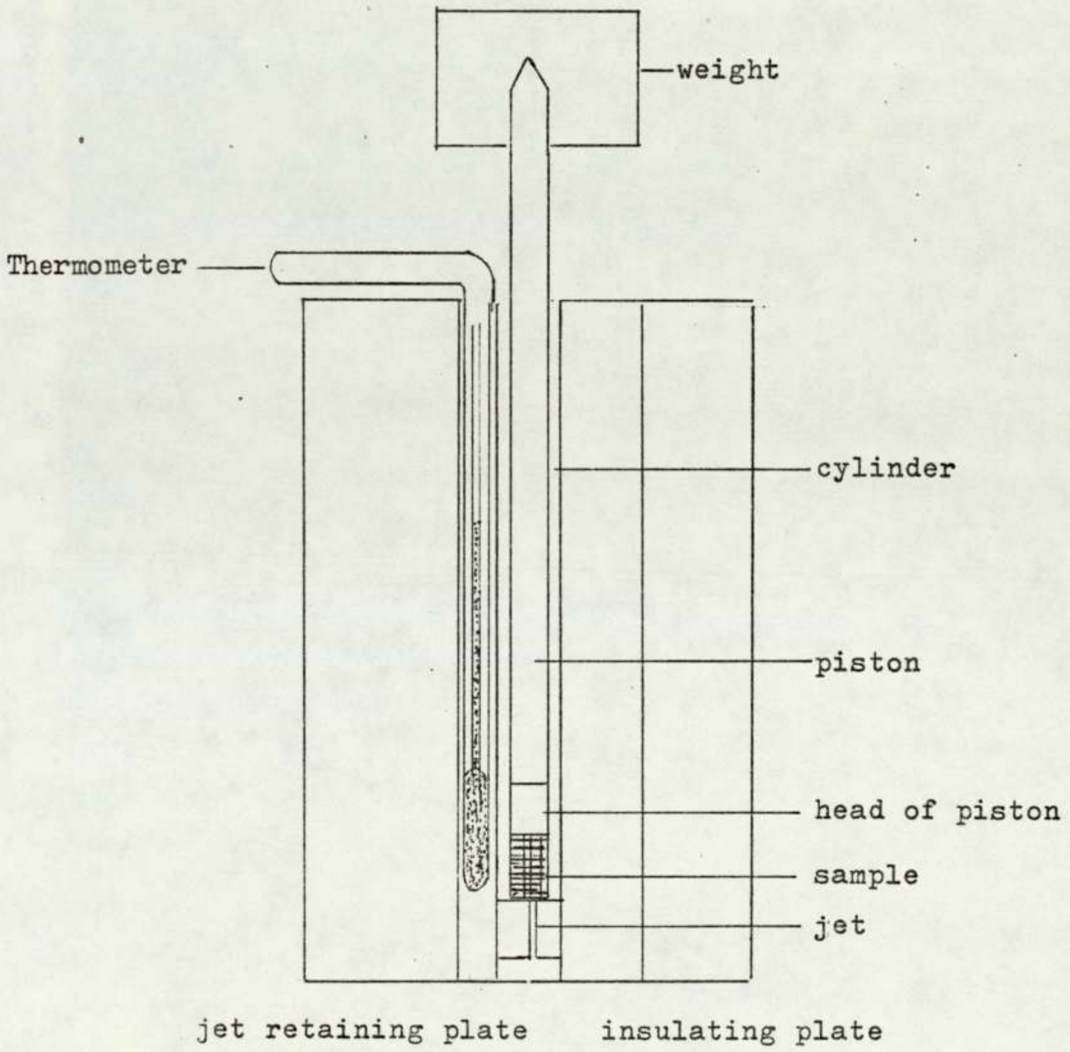


Fig 3-6* General design of the Davenport Polyethylene Grader.

The apparatus consisted of the following essential parts.

1. A cylinder of mild steel, fixed in a vertical position. The cylinder was 115 mmlong and 9.550±0.025 mm internal diameter.

2. A piston of hardened steel, its length being as great as that of the cylinder. It was uniform along its length .

3. A recoverable load (A) that could be placed on top of the piston, the combined weight of load and piston being 2160∓ 10 g.

4. An automatic heating device to maintain the polyethylene in cylinder at a temperature of 190∓0.5 °C.

5. A die (jetA) of 2.095∓0.005mm internal diameter, made of hardened steel.

3-7-2 Test Procedure

Before starting an accurate measurement the apparatus was brought to a steady extrusion temperature 190∓ 0.5 °C. The barrel (cylinder) was charged with the correct amount of the polymer(4g) in the form of film(small pieces), tamping down with the charging tool to exclude air. The time taken to charge the barrel was not more than 1minute. The unloaded piston was then inserted into the barrel and 4 minutes time was allowed for the polymer to reach an equilibrium temperature. A load (weighing 2.16 kg) was then placed on the top of the piston and the polymer was allowed to extrude through the 0.209cm diameter die. The extrudate was cut with a suitable sharp-edged instrument. The time interval for the first extrudate or cut-off was 1minute and was discarded, then 4 cut-offs were taken each at the end of 30 seconds, any cut-off that contained air bubbles was rejected. The cut-offs were weighed separately and their average weight was determined. The melt flow index was calculated from the following equation.

$$\mathrm{MFI} = \frac{600 \text{ X average weight of cut-off in g}}{60 \text{ (interval of time in second)}} \qquad (3\text{-}3)$$

$$= \text{amount of polymer in g extruded in 10 mins}$$

Melt flow index calculated on LDPE processed at different conditions are shown in Fig3-5, curves 2 and 3.

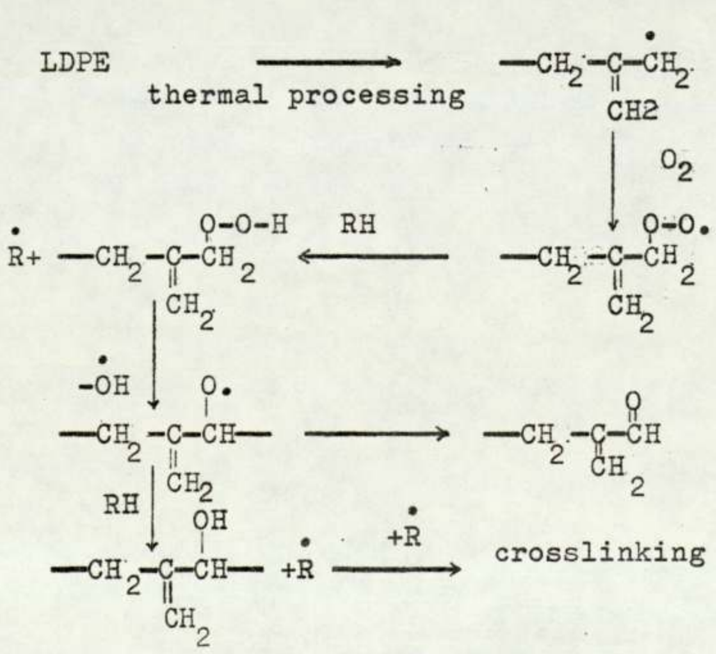
3-8 Results and Discussions

The formation of hydroperoxides measured chemically and by IR-spectroscopy in the processed LDPE at temperatures between 150 to 180 °C are shown in Figs 3-1 and 3-2 . At each temperature (processed in the open chamber) peroxide content increases rapidly to a very sharp maximum and then declines. As the temperature is increased the formation of hydroperoxide starts earlier and the time taken to reach maximum and the maximum concentration are both reduced (Fig 3-1) Less hydroperoxide is formed in the closed chamber in which there was limited air. No hydroperoxide was detected in the polymer processed in the absence of oxygen.

Another functional group which changes during thermal processing of LDPE in the open chamber is carbonyl indicated in the range of 1720 cm^{-1} to 1720 cm^{-1} and vinylidene groups with absorbing at 888 cm^{-1} which is initially present in the polymer remains almost constant up to 30 mins and then declines . More details about the changes of the functional groups in the LDPE during UV and thermal oxidation will be given in chapter 5.

The results showing marked changes in the torque, melt flow index and gel formation are given in Fig 3-4 and 3-5 respectively. These results indicate a delicate balance between the crosslinking and chain scission reactions during thermal processing of LDPE which have been previously observed in the polymer by Scott and co-workers.(159) They observed a significant increase in average molecular weight even at 20 minutes of processing time in a closed chamber under argon (Fig 3-6). This increase in molecular weight and the formation of the solvent insoluble gel under the conditions of limited air can be related to the similar crosslinking reactions observed in the photo-oxidation of the polymer at room temperature.(204) Decrease of molecular weight distribution of LDPE which results from chain scission of the polymer during thermal processing in the presence of air is shown in(Fig 3-7).(159)

The main reactions taking place during thermal processing of LDPE and chain scission and or crosslinking are as follows.



$$\text{LDPE} \xrightarrow[\text{thermal processing}]{} -CH_2-\underset{\underset{CH2}{\|}}{\overset{\bullet}{C}}-CH_2 \quad (3\text{-}3)$$

$$-CH_2-\underset{\underset{CH_2}{\|}}{\overset{O-O\bullet}{C}}-CH_2 \xrightarrow{RH} \overset{\bullet}{R}+ -CH_2-\underset{\underset{CH_2}{\|}}{\overset{O-O-H}{C}}-CH_2 \quad (3\text{-}4)$$

$$\xrightarrow{-\overset{\bullet}{O}H} -CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{O\bullet}{CH}- \longrightarrow -CH_2-\underset{CH_2}{C}-\overset{O}{\overset{\|}{C}}H \quad (3\text{-}5)$$

$$\xrightarrow{RH} -CH_2-\underset{\underset{CH_2}{\|}}{C}-\overset{OH}{CH}- +\overset{\bullet}{R} \xrightarrow{+\overset{\bullet}{R}} \text{crosslinking} \quad (3\text{-}6)$$

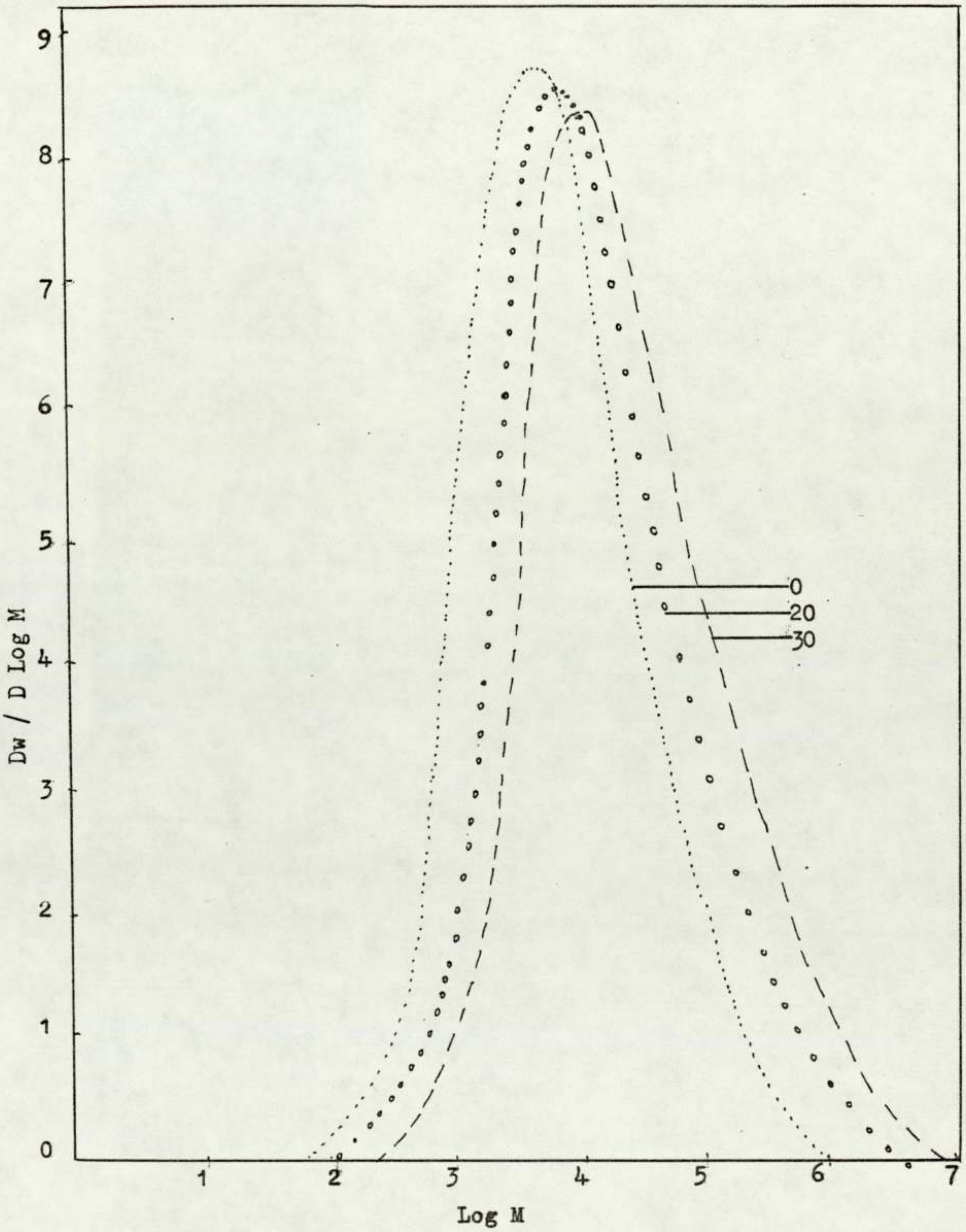


Fig 3-6 Effect of processing time on the molecular weight of LDPE in a limited amount of oxygen at 150°C .Nos indicate processing time in mins. (Taken from Ref 159)

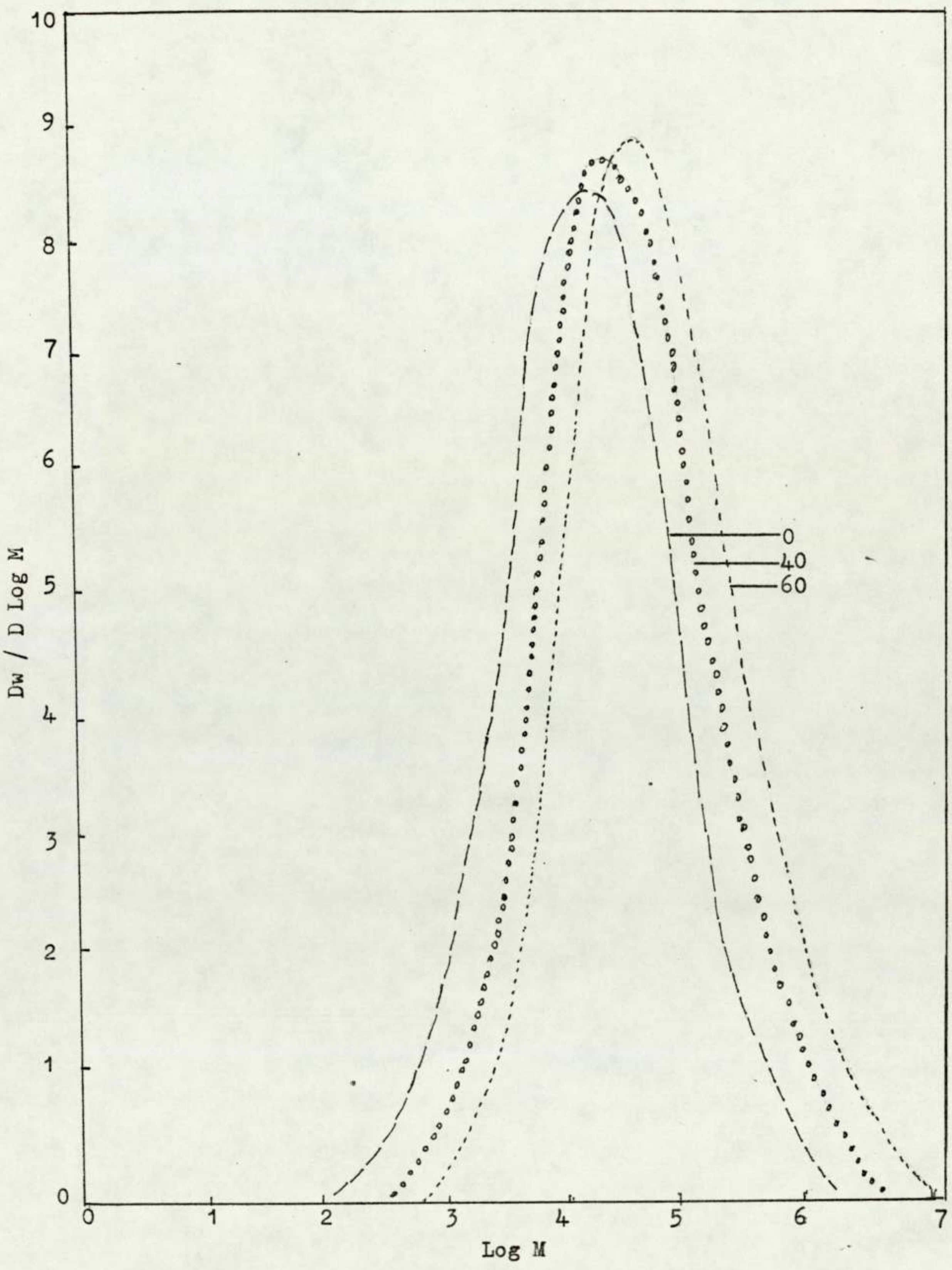


Fig 3-7 Effect of thermal processing on the molecular weight distribution of LDPE in the presence of oxygen. Nos of curves indicate processing time. (Taken from Ref 159).

From Fig 3-5(curves 2 and 3)it is shown that the changes of MFI occuring during thermal processing LDPE at 150°C which depend markedly on the oxygen present in the processing chamber. Curve 2 corresponds to the processing of the polymer in a full and closed chamber under N_2 gas. It shows an induction period of about 5 mins before a significant change in MFI occurs. After this induction period the MFI decreases due to the crosslinking reactions(reaction 3-6) and increase of molecular weight(Fig3-6). Conversely, the MFI of the sample processed in open chamber increases due to the presence of oxygen(reactions 3-4 and 3-5). In the case of chain scission molecular weight of the polymer decreases(Fig 3-7).

3-9 Grafting of Styrene onto the Processed LDPE

A five-necked reaction flask was equipped with a condenser, thermometer, an electric stirrer, N_2 gas inlet, and syringe to inject the monomer and or initiator. 5 gramme of the processed LDPE(processed in an open chamber at 150°C for 30 mins) and 100cc of toluene free from water (see section 3-1(IV) were placed in the flask. It was heated in an oil bath at different temperatures from 80 to 110°C and different amounts of styrene (1,2.5,5 and 10 g) were added to the polymer solution, for different periods of time, from 2 to 8 hours. In order to obtain the optimum conditions of grafting, after a period of time, the reaction flask was taken out from the oil bath and about 400cc methanol was added to the flask to precipitate the polymer containing unreacted LDPE, PS and poly(ethylene-g-styrene). The precipitates were filtered on a filter paper (No1) and dried in a vacuum oven at 50°C for 24 hours .The samples were then compression moulded to make films with the same thickness about 0.01-0.012 cm^{-1}(see section 3-3) for IR tests to measure the amount of styrene converted into PS and PE-g-PS ,using the aromatic absorption peak at 1595 to 1600 cm^{-1}(see section 3-11).The results are shown in Fig3-13,No1.

3-10 Extraction of Polystyrene

To calculate the amount of styrene grafted onto the LDPE, the ungrafted PS was extracted from the samples . For this purpose the films in small pieces(1 X 2 ins) were put in a marked thimble in a Soxhlet extractor (Fig 3-9) equipped with a condenser containing about 500 cc of solvent (methyl ethyl ketone or toluene). The extractor flask connected to an inlet N_2 gas and was heated by an isomantle electric heater at 50 °C from 5 to 70 hrs to extract the ungrafted PS from the rest of the sample. The extracted fractions were dried in a vacuum oven for 24 hrs to evaporate the solvent. The samples were compression moulded to make films with thickness about 0.01-0.012 cm^{-1},and the IR tests were conducted to measure the absorption peak at 1600 cm^{-1},which corresponds to the amount of styrene grafted onto the LDPE. (see Fig3-13,Nos 2,3,4,and 5).

The amount of styrene converted to the homopolymer and grafted onto the LDPE were also calculated as the total conversion of styrene into polystyrene and percentage of grafting respectively by the following equation.(153)

$$\text{Grafting}(\%) = \frac{m-\overset{*}{m}}{\overset{*}{m}} \times 100$$

Where,m and $\overset{*}{m}$ are weights of the polymer after and before grafting

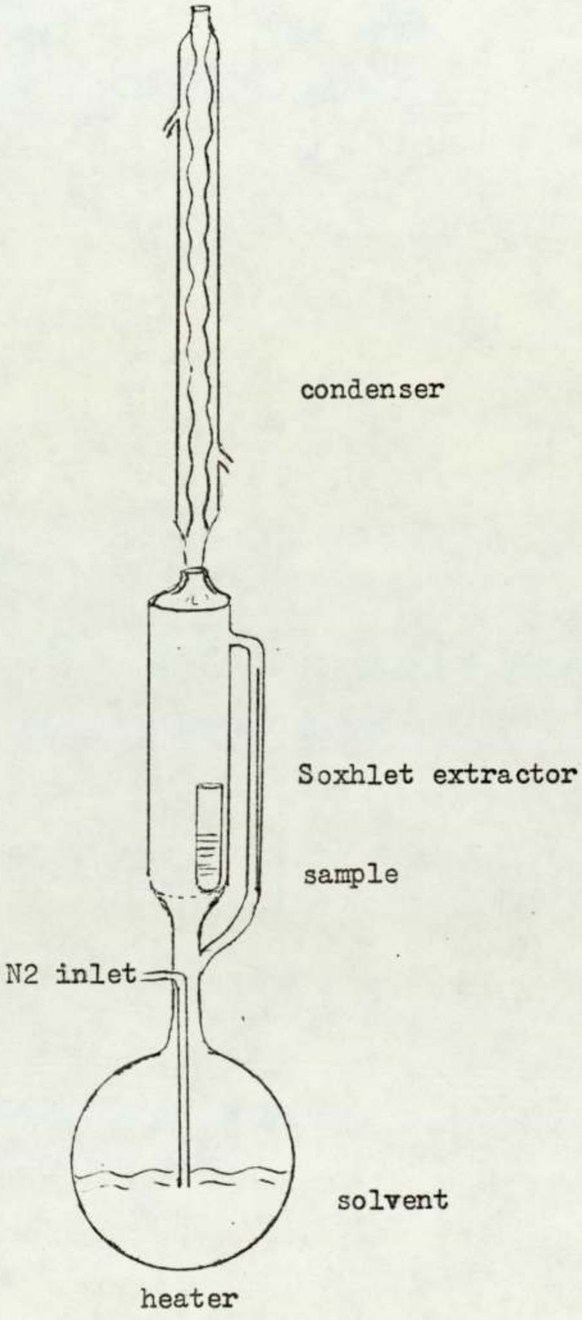
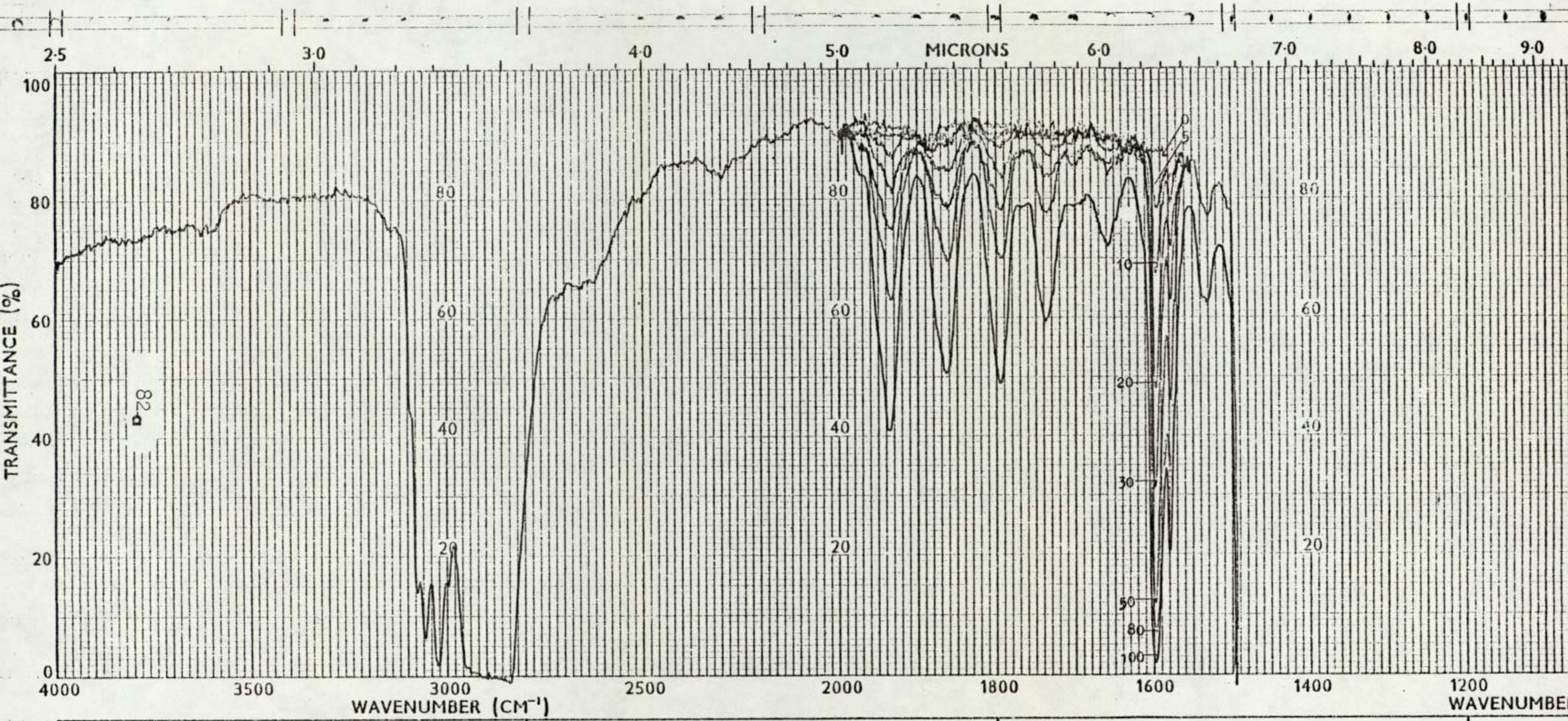


Fig 3 -9 : Hot extractor equipment

Fig 3-10a Changes in aromatic absorption (1600 cm^{-1}) of LDPE/PS blends film.



SAMPLE : LDPE/PS Nos on curves indicate percent of PS in the samples.

ORIGIN

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

REMARKS

Composition = LDPE/PS blends
Speed =M
Thickness = 0.01 cm
IR = Model 475

SCAN TIME

SLIT

OPERATOR

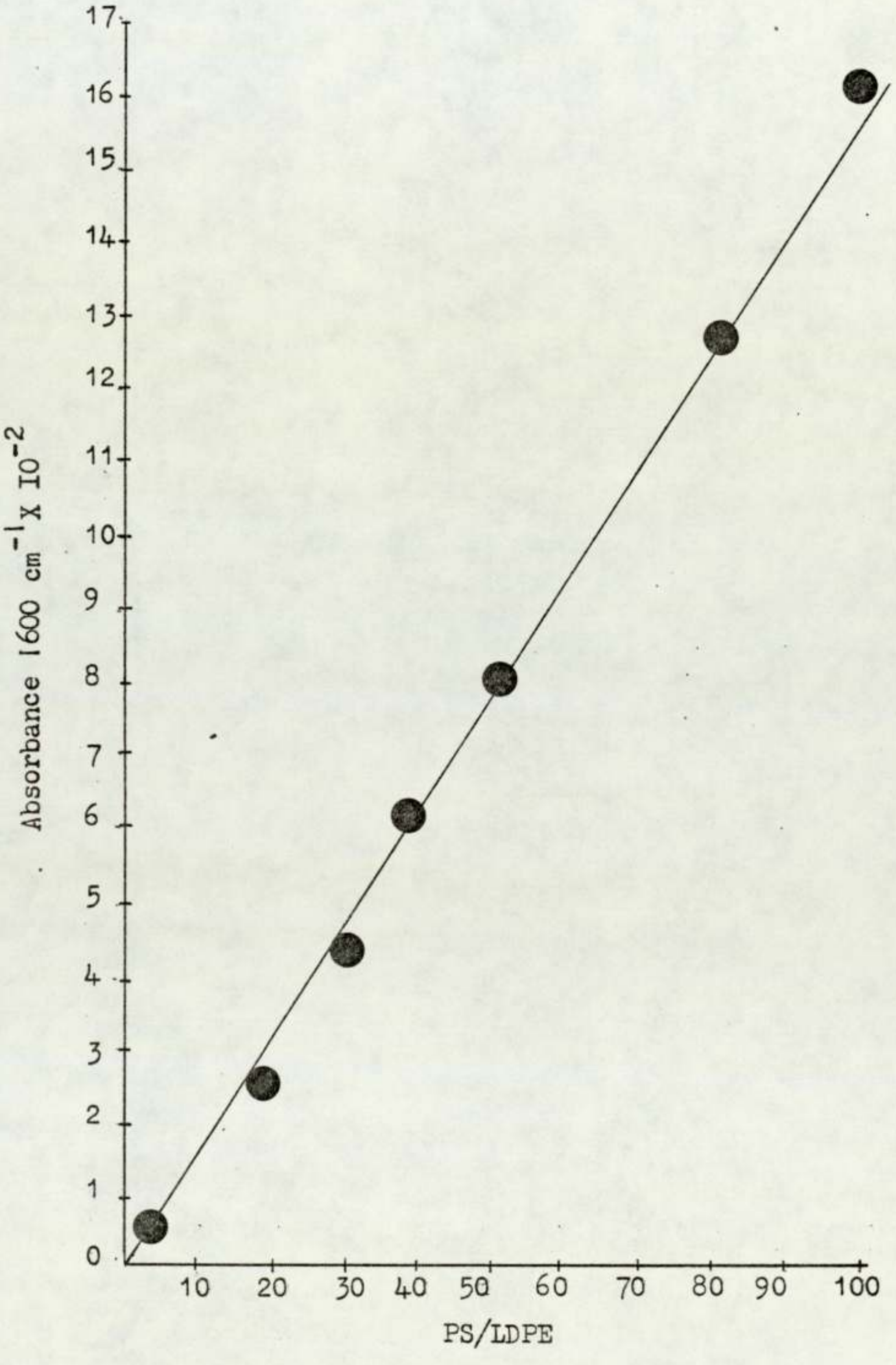


Fig 3-10 Calibration curve.

respectively. A definite correlation was obtained between percentages of the grafting measured by this method and by the IR technique.(Fig 3-10).

A calibration curve was made in order to calculate the percentage of grafting. For this purpose different ratios of LDPE/PS were blended in the Torque Rheometer (see section 3-2) at 170°C for 5 mins and the samples were compression moulded to make films with thickness about 0.01-0.012 cm^{-1} and the IR tests were conducted to calculate their absorbance by the following method.

3-11 Calculation of Absorbance

For this purpose the base line technique(154) was used to calculate the optical density or absorbance at 1600 cm^{-1} which corresponds to the aromatic absorption of the samples. This technique was done as shown in Fig 3-11 by drawing a straight line (base line) tangentical to adjacent the maximum absorption or shoulders of the peak, then by erecting a prependicular through the analytical wave length until it intercepts the base line.

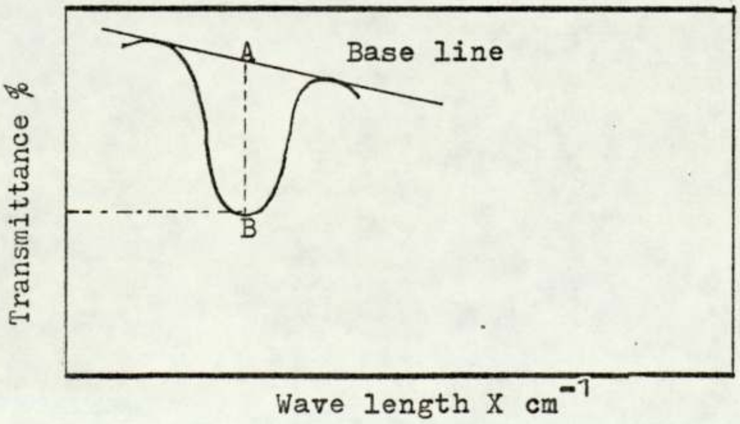


Fig 3-11

At point "A", the concentration of the particular functional group is zero, and at point "B", the absorption peak is a maximum and its height indicates concentration of the functional group.

If a functional group gives an absorption peak with small and different shoulders, the proper location of the base line is less obvious, in this case several base line can be considered such as a, b, or c, depending on the width of the shoulders B, C and D (Fig 3-12).(156,155) If all these shoulders are narrow, line "a" is used as the base line.

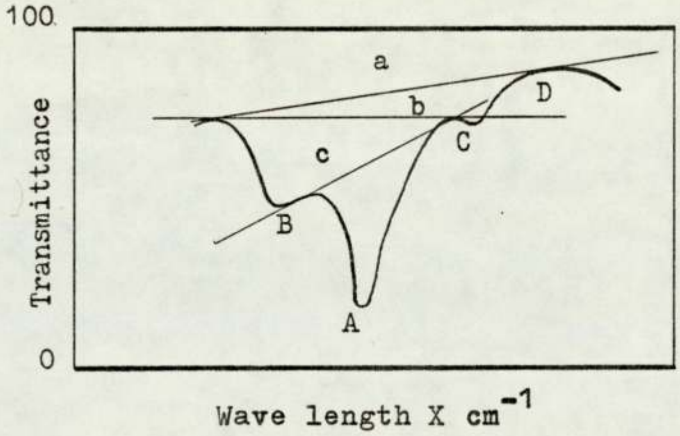


Fig 3-12

However, by measuring percentage of transmittance at the points "A" and "B" (Fig 3-11) and converting them to absorbance, the percentage of the functional group was obtained.

In the case of using a chemical liquid (i.e, styrene monomer, solution of styrene in a solvent such as acetone, toluene or MEK), or films of different thicknesses, the Beer Lamberts equation was used.(164)

$$A = \log_{10}\frac{\overset{*}{I}}{I} = E\ C\ L \qquad (3\text{-}8)$$

Where, A= Absorbance or optical density

I= Intensity of radiation emerging from the sample.

$\overset{*}{I}$= Intensity of radiation effecting from the sample.

E= Extinction coefficient expressed in litres $mol^{-1} cm^{-1}$

C= Concentration of absorbing group in the sample in mole/litre.

L= Path length of radiation in the sample in cm.

To minimize errors due to variation of the thickness of the films as well as the equipment errors, a standard absorbance peak was used as a reference to calculate any particular functional group. For example, in LDPE, the absorption peak was selected 1895 cm^{-1} to calculate changes of different functional groups during thermal and UV oxidation of the polymer. (see chapter 5).

The functional group index is defined as the ratio of the absorbance of the functional group peak to the reference peak.

3-12 Grafting of Styrene onto LDPE by Free Radical Initiators

(I) By benzoyl peroxide(BPO). For this purpose different concentrations of BPO in toluene (5 ml), were added to the reaction flsk (Sec 3-9), at different time intervals from 2 to 6 hours at 90 C. After the predetermined reaction times, the fractions were precipitated(by methanol) filtered, dried and compression moulded (see sections 3-9 and 3-3) to make films with thickness 0.01to 0.012 cm^{-1} for the IR (Perkin Elmer 457) tests to measure the amount of styrene converted into polystyrene and

PE-g-PS (Fig 3-14,No 1).Then percentage of the grafting was obtained after extraction of the ungrafted PS from the sample (see section 3-10)by MEK.The extracted fractions were dried at 50°C in a vacuum oven for 24 hours and compression moulded to make films same as the above thickness for the IR tests.The results are shown in(Fig 3-14,Nos 2 and 3) .

The effect of swelling of the preformed polymer (LDPE)in the monomer was examined under N_2 gas at different temperatures (from room temperature to 50°C for 2 hrs to 24 hrs. The optimum conditions of swelling of the polymer were obtained at 50°C and 16to 20 hrs(see Fig 3-14,No 3).

The effects of different concentrations of the monomer and initiator are shown in Figs3-15 and 3-17 respectively.

(II) By cumene hydroperoxide. In this case CHP was used instead of BPO at the same conditions which mentioned earlier.For this purpose the reactions were carried out at 90 ,100 and 110°C.The results obtained are shown in Fig 3-17. As it will be mentioned later ,at higher temperatures CHP is more active than BPO.

3-13 Graft Copolymerization of Styrene onto LDPE by Mechano- chemical Method

(I) Without using free radical initiator.

In this method,styrene was grafted onto LDPE in the Torque Rheometer(see section 3-2).For this purpose 25 g of the polymer was processed in the Torque Rheometer under N_2 gas passed through

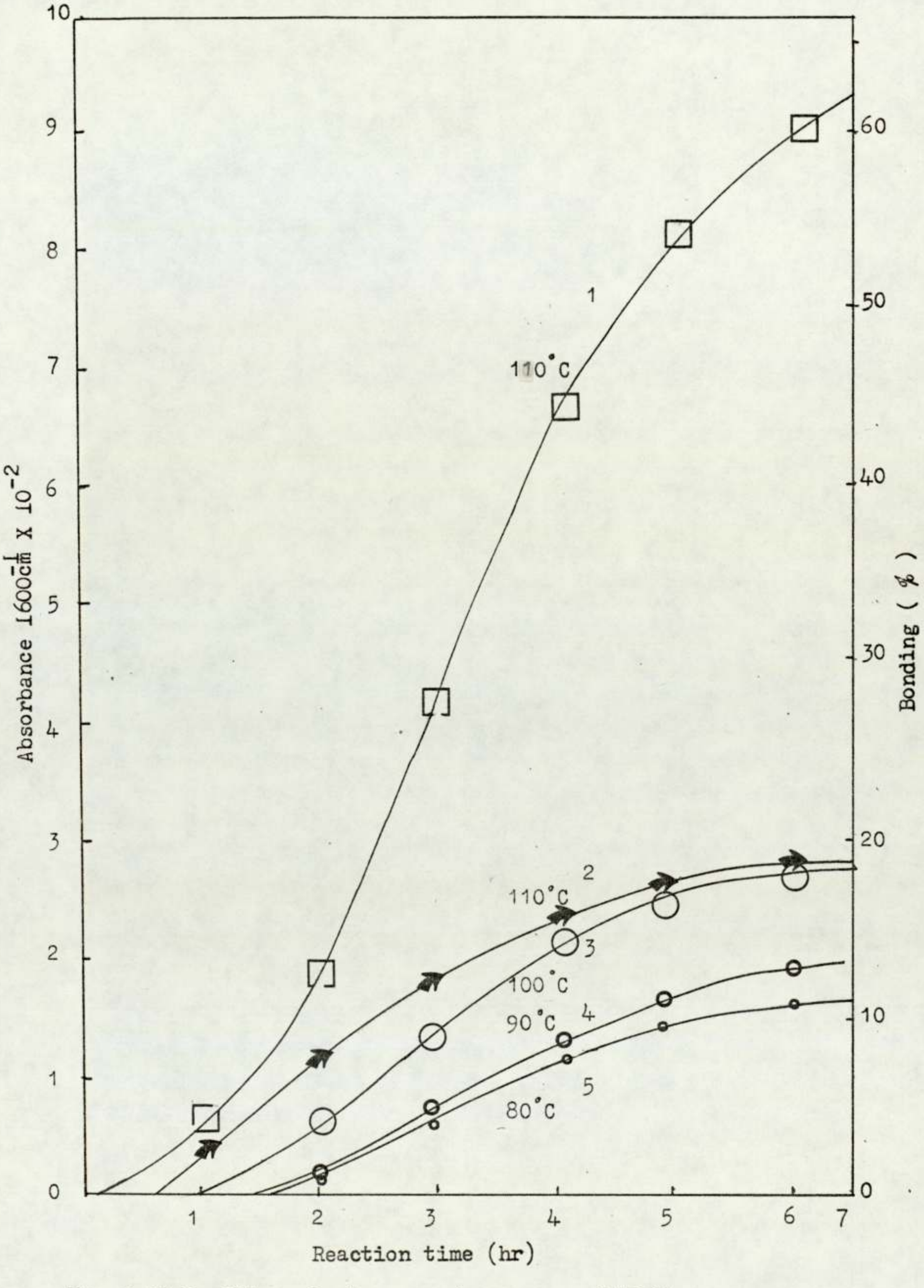


Fig 3-13 Grafting of styrene onto processed LDPE.

LDPE= 5g , styrene = 5ml, extraction =48 hrs, curve No 1=unextracted related to No 2. Curves Nos 3,4 and 5 after extraction.

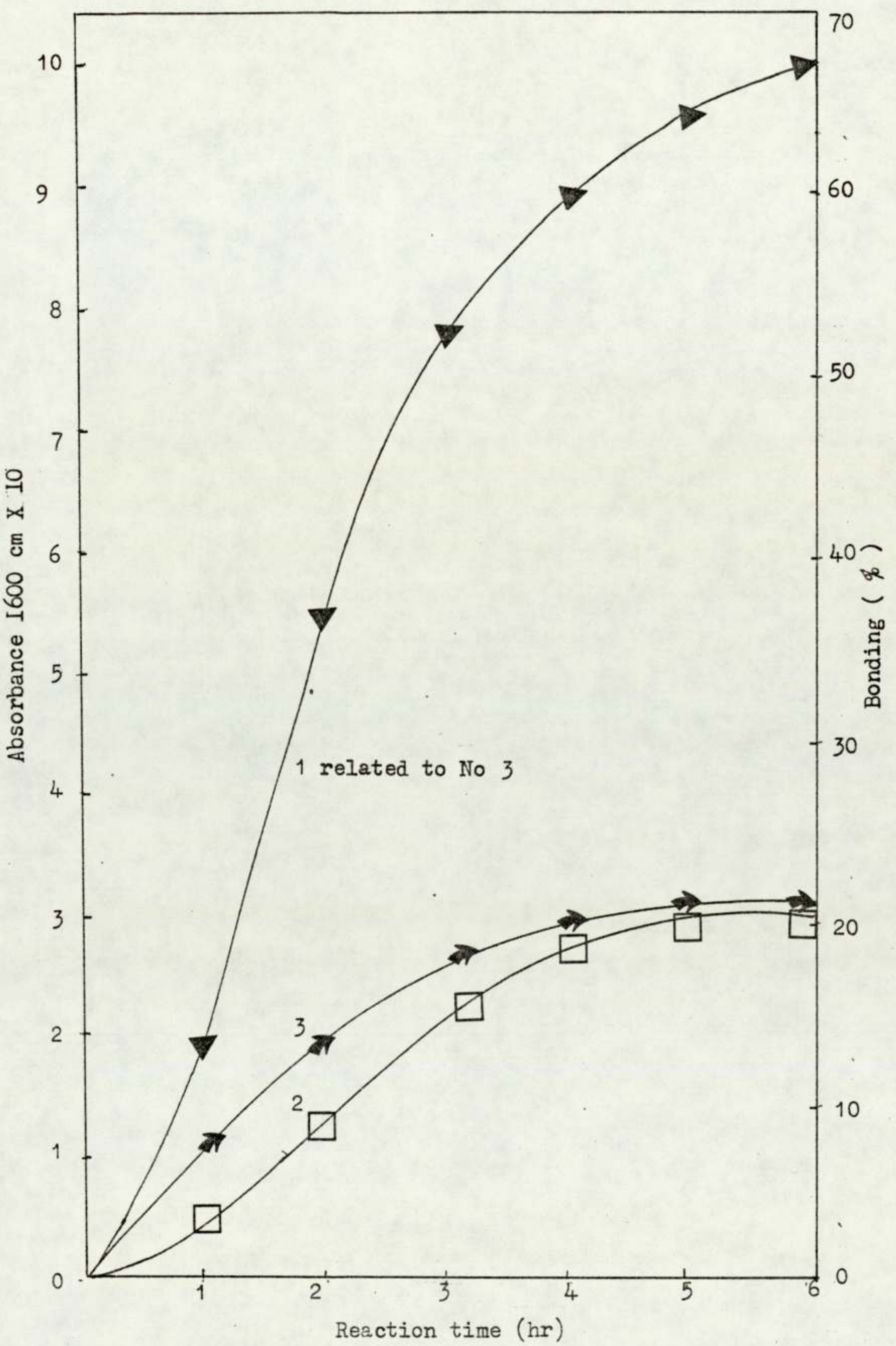


Fig 3-14 Grafting of styrene onto LDPE (5g).BPO =1/100 g,temperature= 100°C,swelling time=16 hrs at 50°C(No 3)and extraction time =48 hrs. No 1 before extraction and Nos 2 and 3 after extraction.

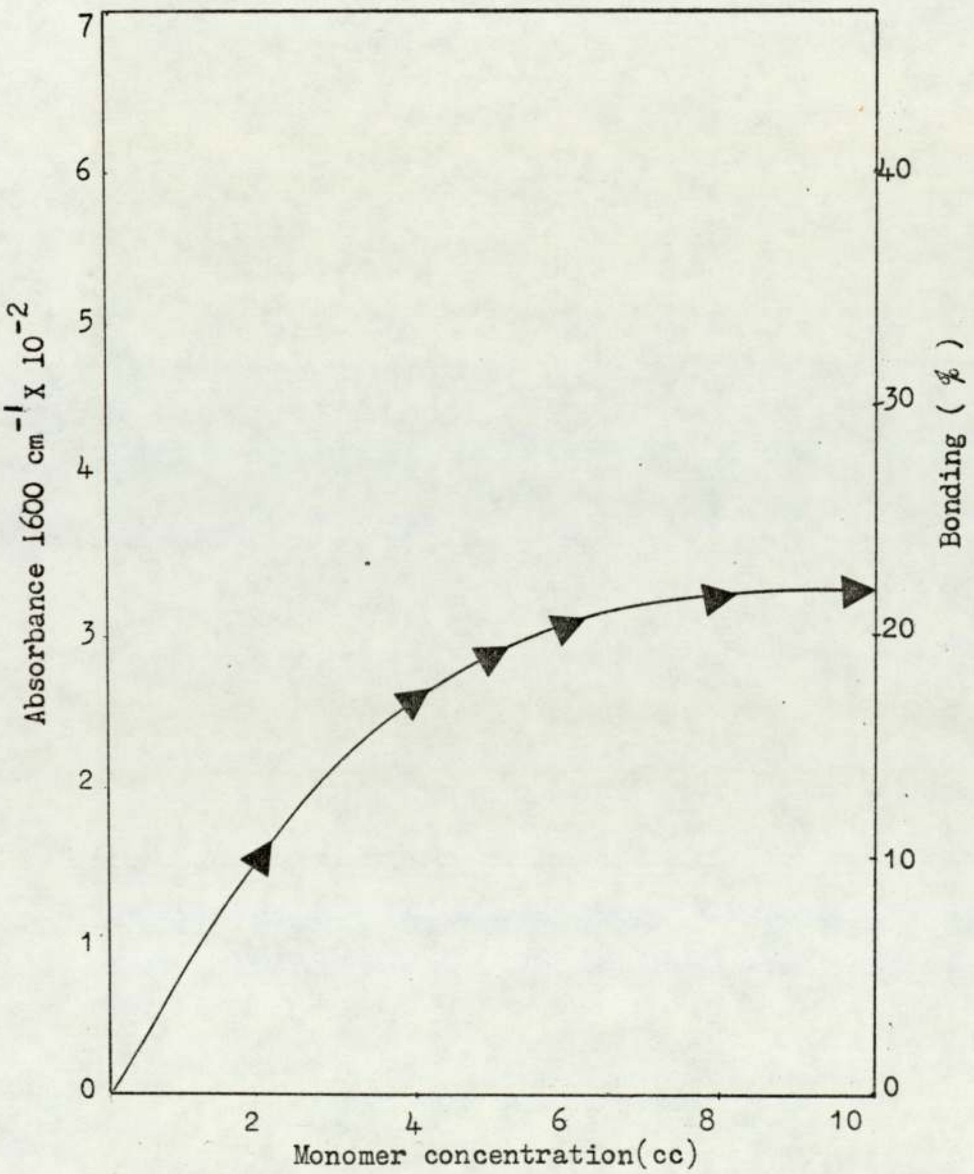


Fig 3-15 Grafting of styrene onto LDPE .
Initiator = BPO 1/100 g, temperature =100°C,
LDPE =5 g, swelling time =16 hrs and extraction
time =48 hrs.

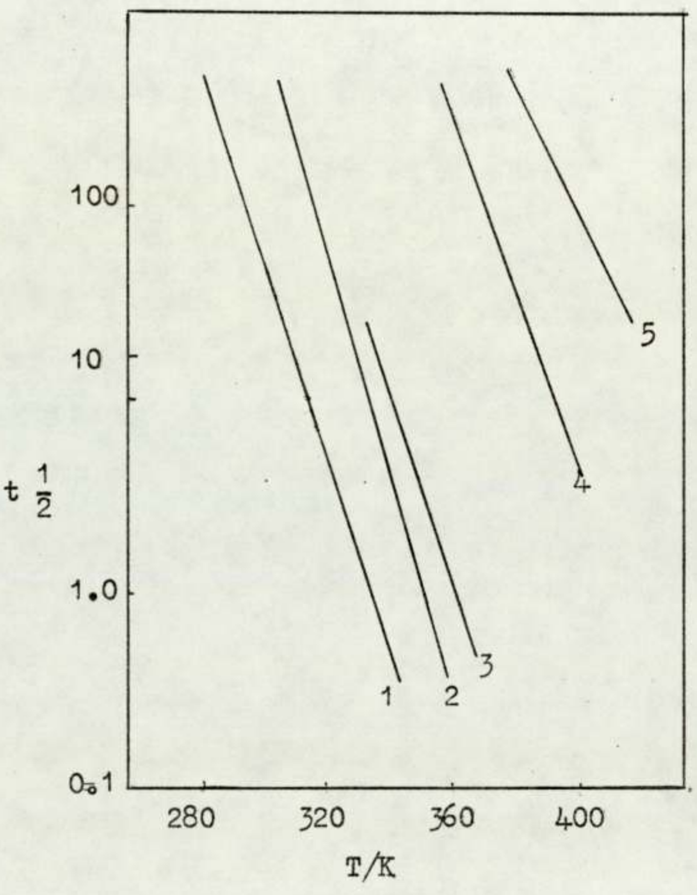


Fig 3-16 Half-lives of selected peroxide initiators. Curve 1, isopropyl percarbonate, curve 2,2,2 azo-bis-isobutyronitrile, curve 3, benzol peroxide, 4, di-tertiary butyl peroxide and 5, cumene hydroperoxide . Taken from Ref78.

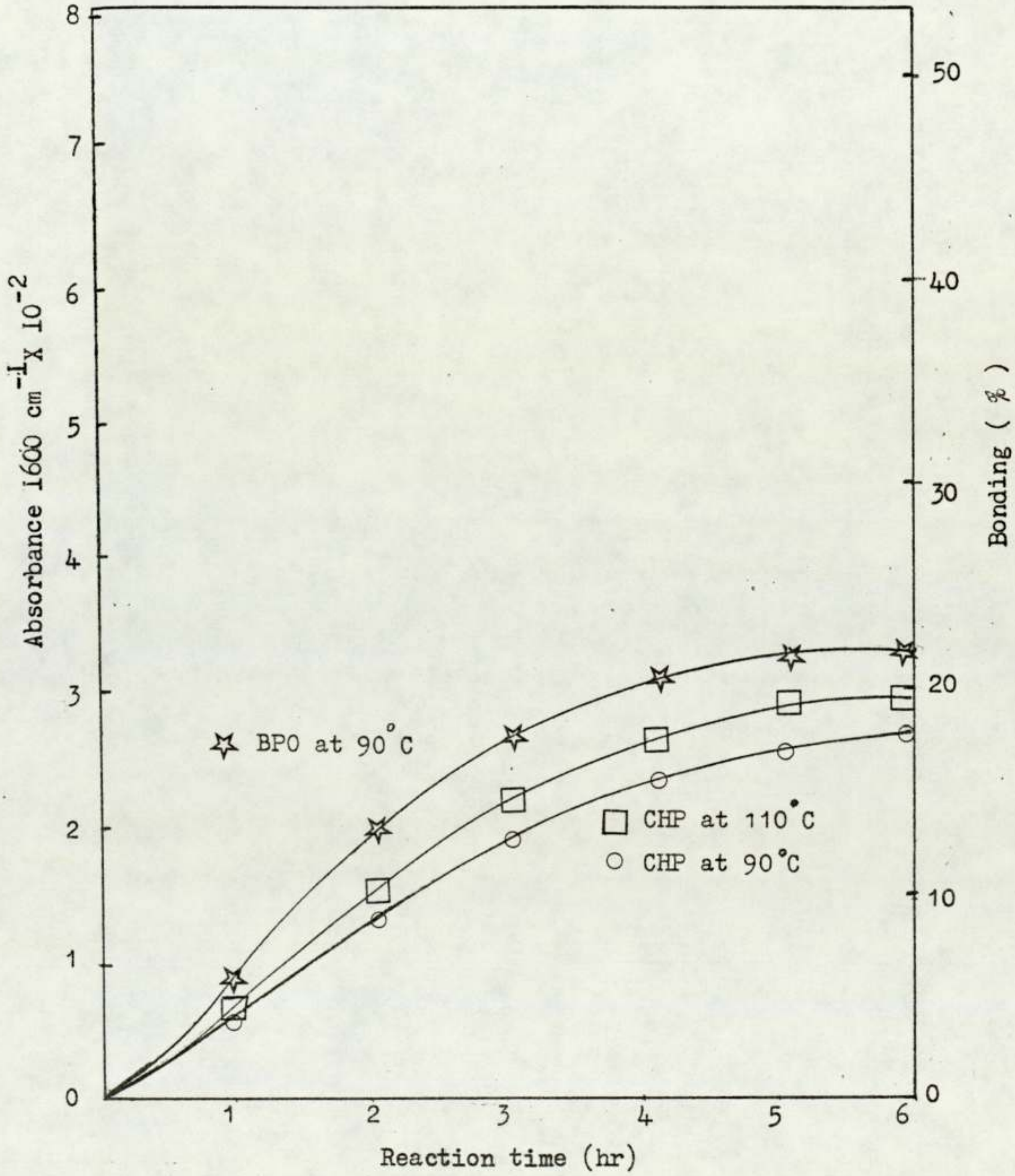


Fig 3-17 Grafting of styrene onto LDPE at 90°C. LDPE =5 g, CHP= BPO =1/100g ,styrene =10ml, swelling time =16 hrs at 50°C and extraction time =48 hrs.

solution of pyrogallol in water (5 %W/V) to exclude the air present in the chamber.This was done to minimize the effect of the radical scavenger(oxygen),see section 2-2-4-2 .The processes were carried out at different temperatures from 120-160°C. After 5 mins processing time(minimum time to reach melt state), different amounts of the purified styrene were injected into the Torque Rheometer,for differnt periods of time from 10-60mins.

As was mentioned (section 3-1,(III) ,styrene is a toxic material ,so,special care was taken during its handling.After the monomer injection,the chamber of the mixer was immediately closed.

However, after predetermined processing times,the samples were quickly discharged into chilled water and then compression moulded to make films of thickness 0.01-0.012 cm^{-1}. The films were extracted with hot actone (Fig3-9) to separate the unreacted styrene.The end of the extraction was identified by IR test of the sample .When there was no peak at the aromatic absorption (1600 cm^{-1}),(Optimum extraction time was obtained 10-12 hours),the samples were dried in a vacuum oven at about 50°C for 24 hours to evaporate the solvent,and then they were compression moulded to make films (0.01-0.012 cm^{-1}tkickness) for the IR tests were carried out to determine the amounts of styrene converted into grafted and ungrafted polystyrene(see Fig 3-18, No 1).

To determine percentage of the grafting,the homopolystyrene was extracted from the samples by toluene(see section 3-10). The extracted films were compression moulded(see section 3-3) to make films of thickness (0.01-0.012 cm^{-1}) for the IR tests to determine the percentage of styrene grafted onto the LDPE. The obtained results are shown in(Fig 3-18,No 2).

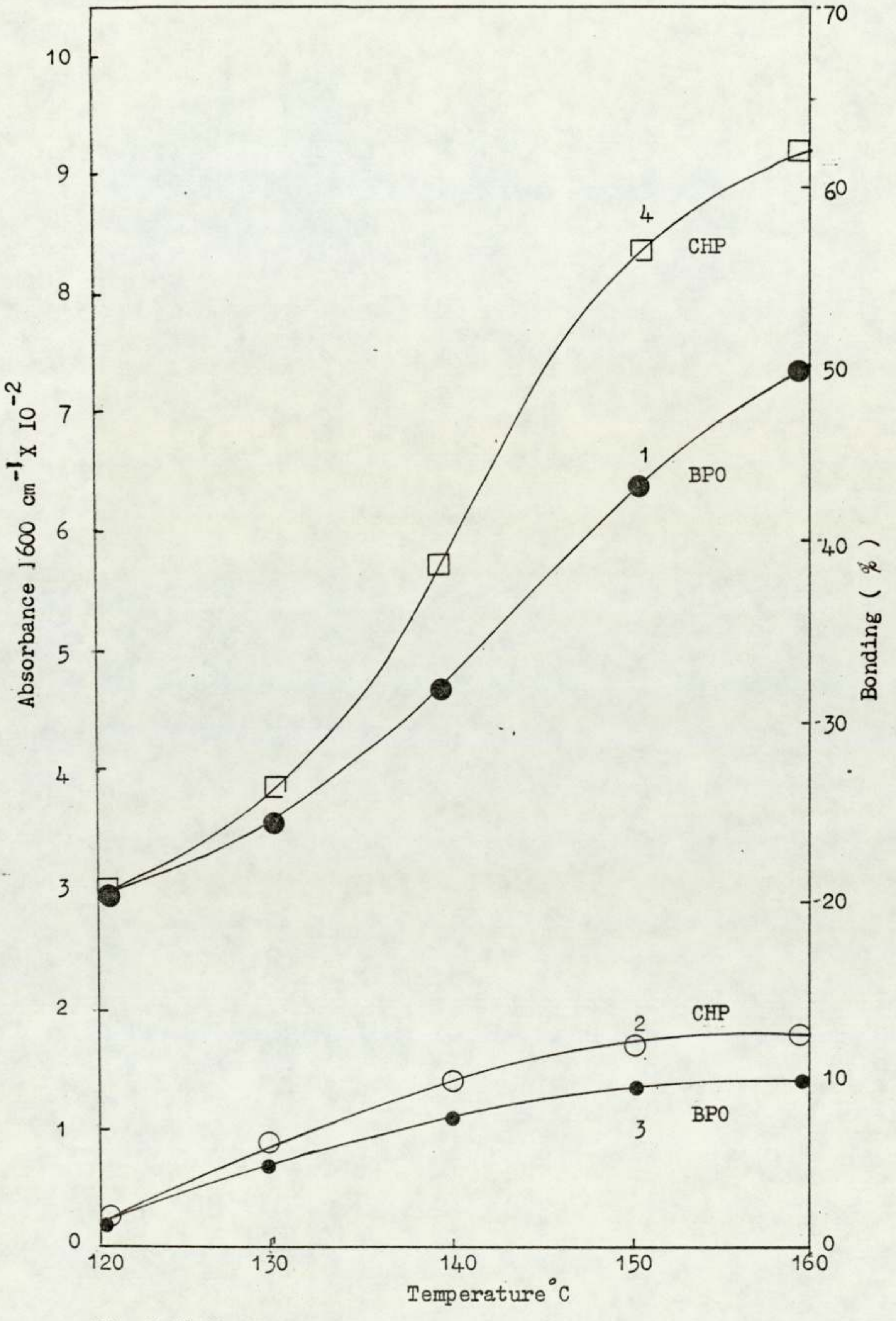


Fig 3-18 Mechano-chemical grafting of styrene onto LDPE. CHP = BPO = 1/100g/5ml styrene, reaction time=20 mins, Curves Nos 1 and 4 before extraction, Nos 2 and 3 after extraction.

(II) By using free radical initiators.

The same concentration of BPO and CHP in toluene (1 X 100^{-1}g in 5 cc of toluene)separately were added with the monomer to the torque rheometer under the same conditinns which were described earlier at 140°C for 60 mins. The unreacted styrene and also the ungrafted polystyrene were extracted by acetone and toluene respectively (see section I). The extracted samples were compression moulded to make films with thickness of 0.01-0.012 cm^{-1} for the IR tests to measure the percentage of the grafting .The obtained results are shown in(Figs 3-19 and 3-20). The maximum grafting was obtained at about 15-17% at 140 C for 40 mins.

The effect of swelling of the polymer in the monomer(10 ml) is shown in(Fig 3-20,No 2).For this purpose 25gs of LDPE is swelled in 5 cc of the monomer under N_2 gas at 50°C for 16 hours. After the swelling time,the monomer was filtered and the it was injected into the torque rheometer during processing of the polymer under the same conditions which were described earlier.As it is shown in Fig 3-20,No 2), in the case of the swelling,at each processing temperature ,the percentage of the grafting is increased to about 25 % .

However, in the case of using the free radical initiators, at higher temperatures, CHP was more active than BPO(Figs3-18, No 3and 3-20,No 1 and 2).

3-14 Mechano-chemical Synthesis of LDPE-PS Copolymers by Polymer-Polymer Interaction

---

(I) Without using free radical initiator.

35 gs of 50/50 LDPE-PS were processed in the torque rheometer at different temperatures (100-180°C) for different periods of time from 5 - 60 mins in the open and closed chamber under N_2 gas passed through 5 % solution of pyrogallol in water.Then the samples were inserted into cold water,cut into small pieces and compression moulded to make films with thicknesses of 0.01-0.012 cm^{-1}. The films were extracted by toluene (see section 3-10)to separate the unbound polystyrene from the LDPE. After the extraction,the smaples were dried and compression moulded like the previous procedures to make films with thicknesses of 0.01-0.012 cm^{-1}for the IR tests to obtain the amounts of the PS bounded with the LDPE (Figs 3-22 and3-23).

However, in this method,the maximum percentage of PS bounded with the LDPE was obtained about 38-40 % at 170 C,30 mins of processing time and in the closed chamber under N_2 gas(Fig3-23).

(II) By addition of free radical initiators.

In this method, same concentration of BPO and CHP (1X100^{-1} g in 2 ml of toluene) were injected to the Torque Rheometer during processing of LDPE with PS at the same conditions which were mentioned above,and percentage of the PS bound to the LDPE was obtained by the previous procedure(section I).In this method,the percentage of the bounding was increased to 43 % by using 1/100 g of CHP.(Fig 3-25,No1).

The amounts the unreacted PS and also the percentage of the gel formation (cross-linked LDPE) are shown in (Fig3-25,Nos 3 and 2 respectively.

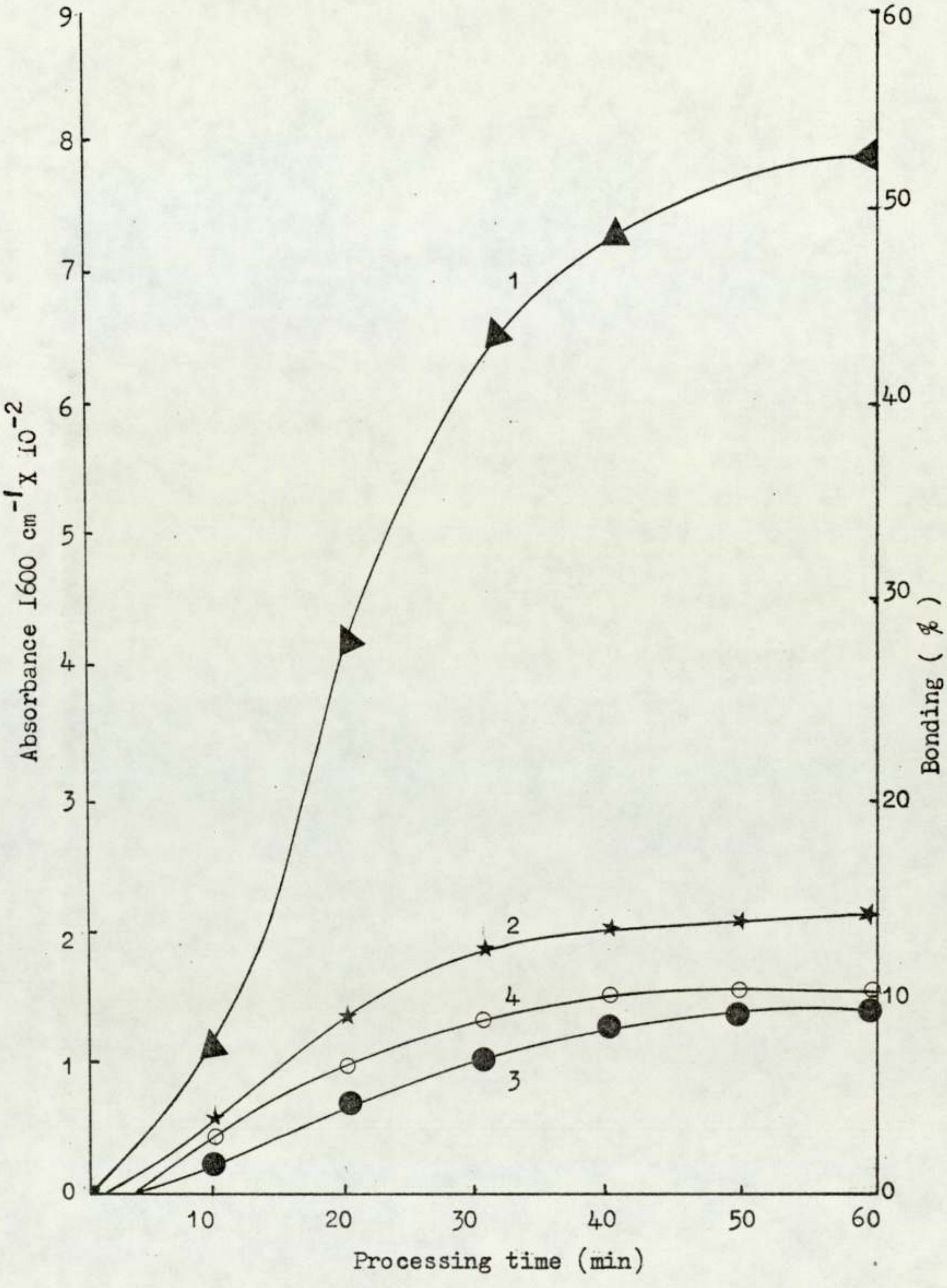


Fig 3-19 Mechano-chemical grafting of styrene onto LDPE.
Temperature =140°C,
No 1=before extraction,Nos2,3 and 4 after 48 hrs extraction.No3=no initiator,No2=CHP(1/100g),No4=BPO (1/100g),LDPE =25g ,styrene =10ml and processing in closed chamber under N_2.

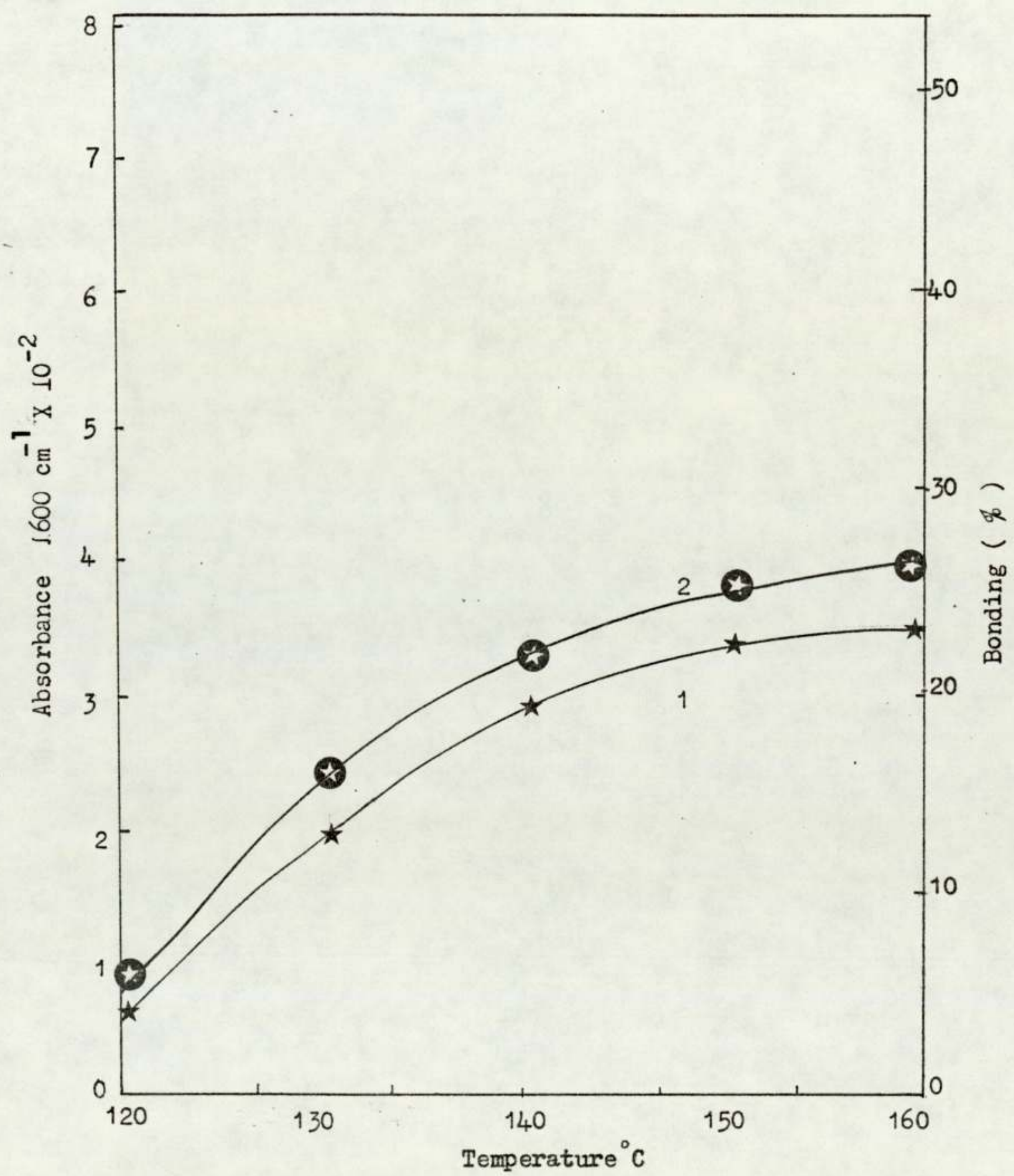


Fig 3-20 Mechano-chemical grafting of styrene onto LDPE under N_2. Initiator =1/100g CHP , styrene = 10ml. No 1 =without swelling,No 2 = 16 hr , LDPE =25 g,extraction =48 hr.

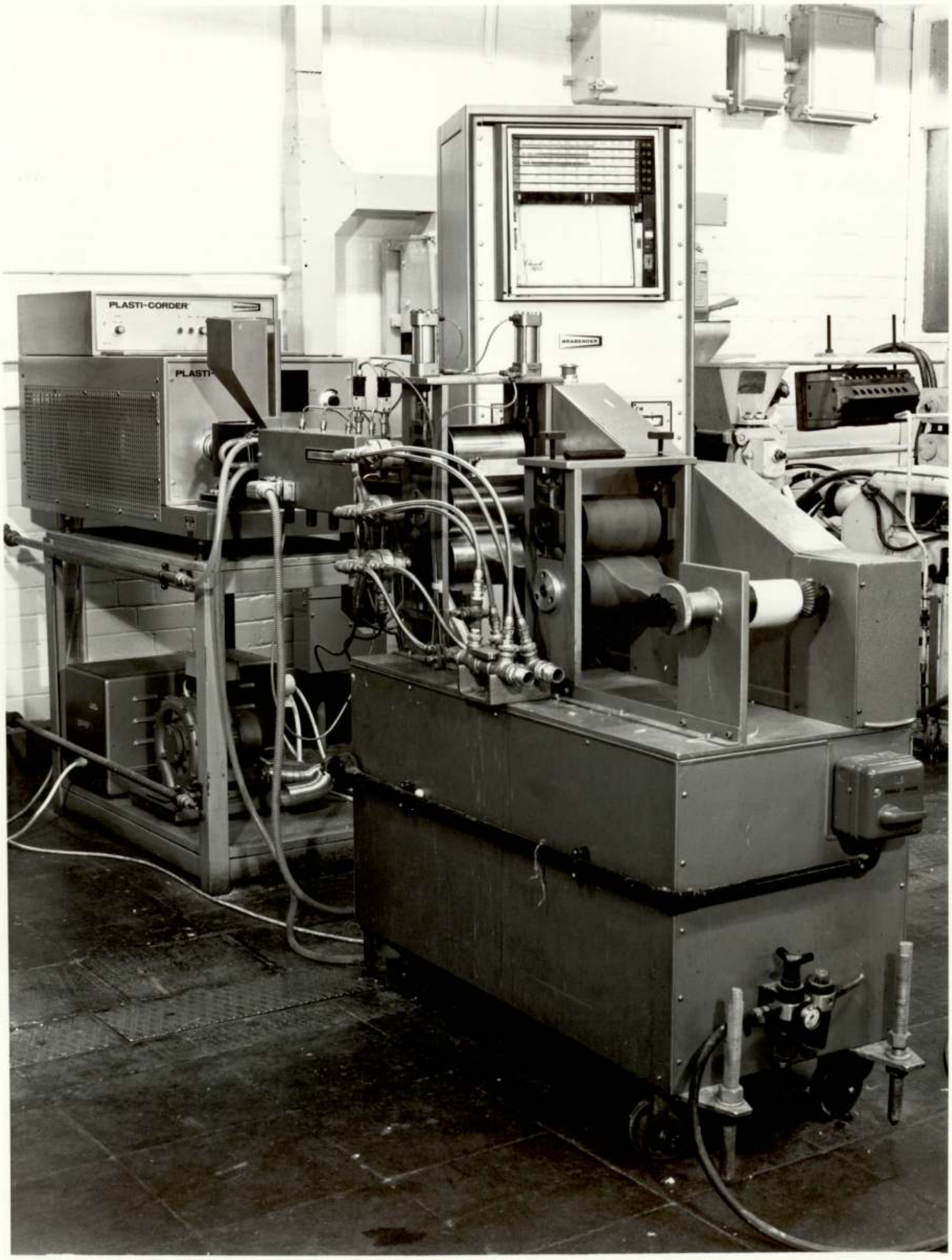
3-15 Mechano-chemical Synthesis of LDPE-PS Copolymers in a Plasti-Corder (Brabender)

(I) General Description: The Brabender Plasti-Corder PLE 330, PLE 650 or PLE 651 is torque rheometer which simulates the processing of elastomers and many other plastics materials. Production processes such as blending,mixing,extruding calendering,grinding etc can be precisely simulated by the Brabender.(photograph No 3-1).

(II) Procedure. Different ratios of LDPE/PS (5to50%) were processed in the Brabender at 200° C.The processing time was 1 minute.To obtain the amount of the PS bounded with LDPE, the samples were extracted to separate the unreacted PS(see 3-10),then the extracted samples were dried and compression moulded to make films with thicknesses 0.01-0.012 $cm^{-1}$for the IR tests and like the previous methods,percentage of the grafting was calculated by absorbance peak at 1600 cm^{-1}(see section 3-11).The results are shown in (Fig3-26).

3-16 Chemical Reactions Involved in The Mechano-chemical Methods

In the mechano-chemical synthesis without using free radical initiator, the polymeric radical formed during the chain scission acts as an initiator to form graft copolymer(in the case of the polymer-monomer system) , block copolymer (in the case of the polymer-polymer interaction)and gel formation .These reactions can be represented as follows.



Photograph No 3 - 1

(Brabender)

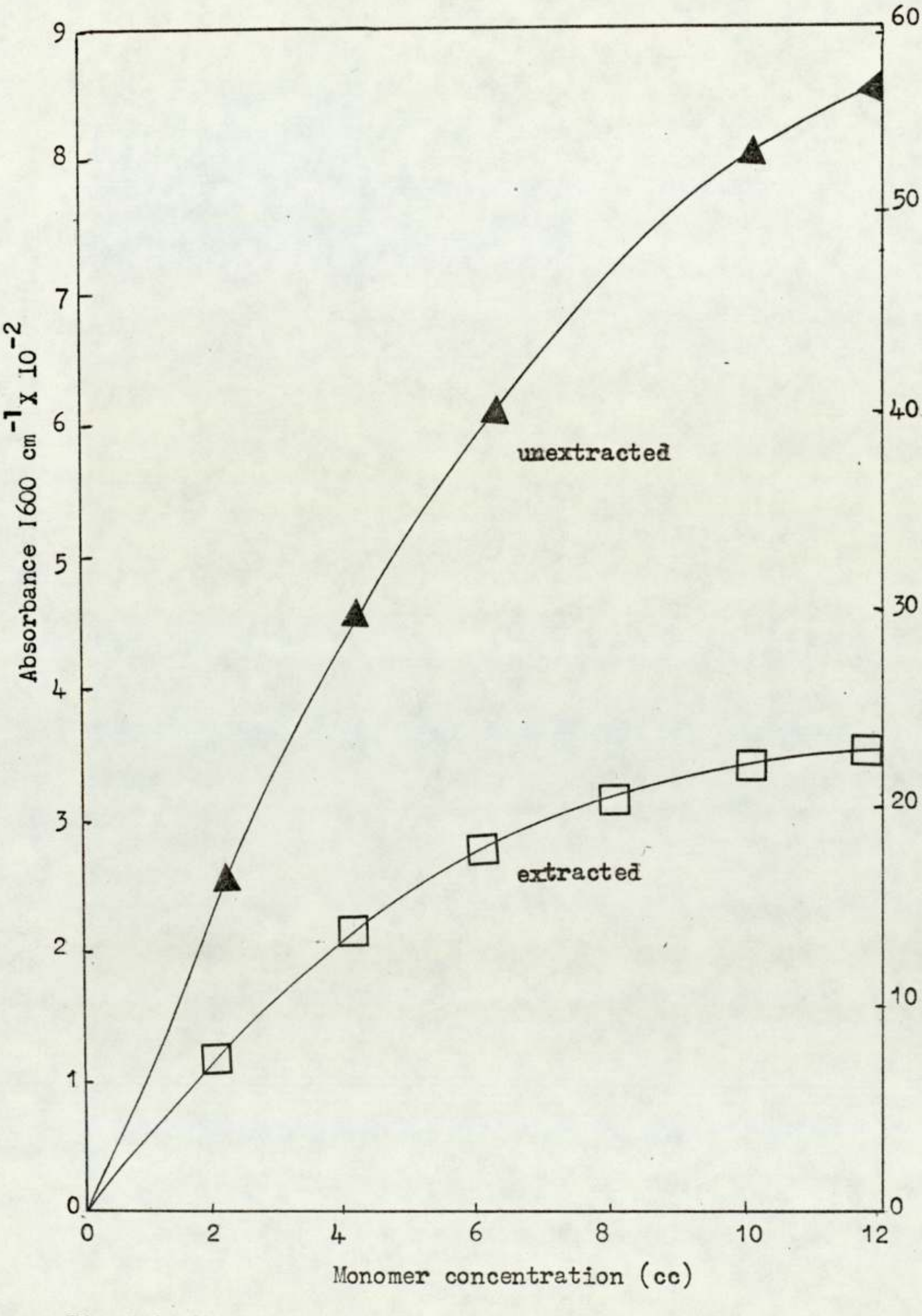


Fig 3-21 Mechano-chemical grafting of styrene onto LDPE under N_2 Reaction time =40 mins, initiator =1/100g CHP, LDPE =25 g, swelling time =16 hrs at 50 °C and extraction time =48 hrs.

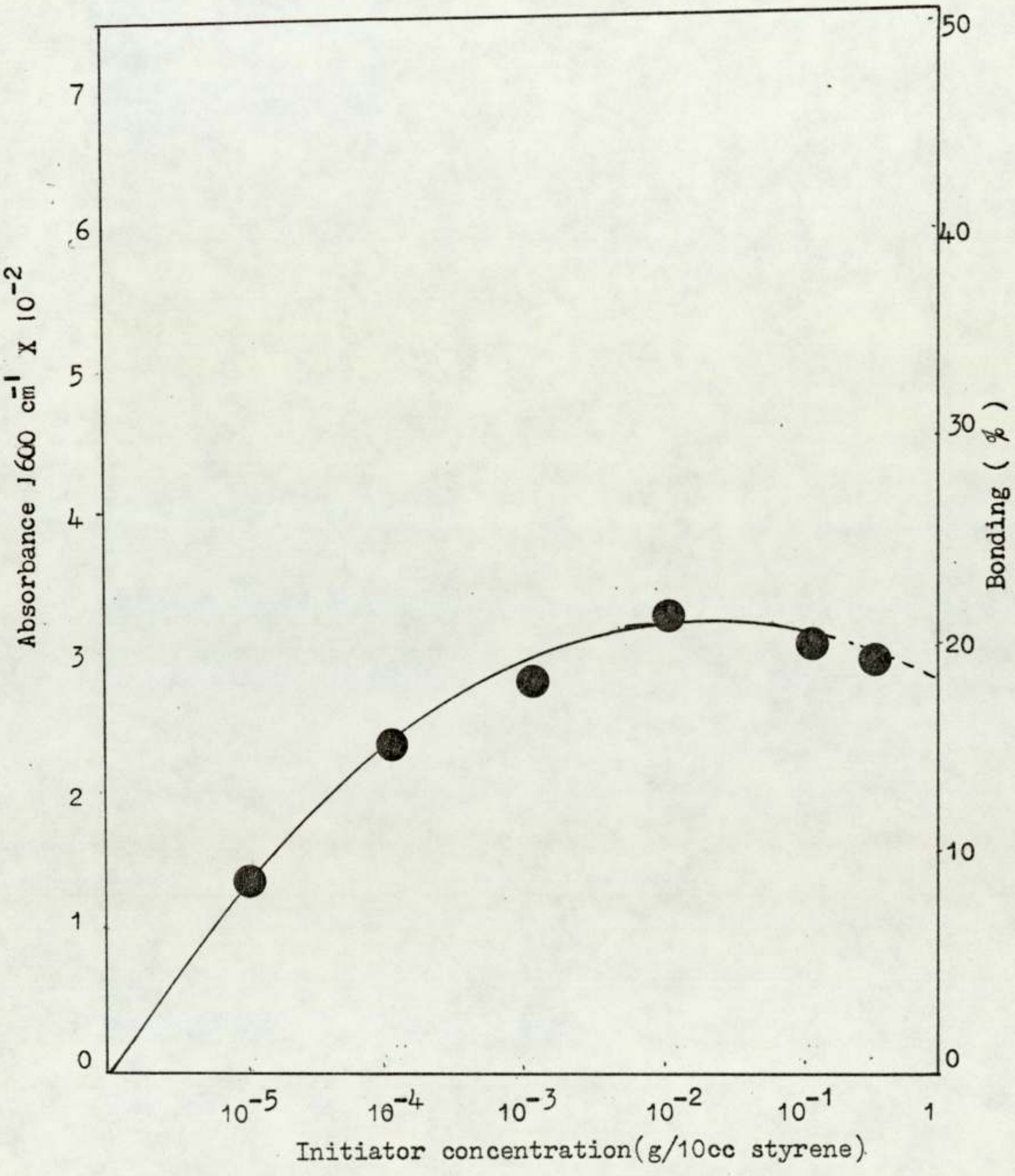


Fig 3-22 Grafting of styrene onto LDPE at 90°C for 6 hrs. LDPE = 5 g ,styrene = 10cc, swelling time =16 hrs and extraction time = 48 hrs.

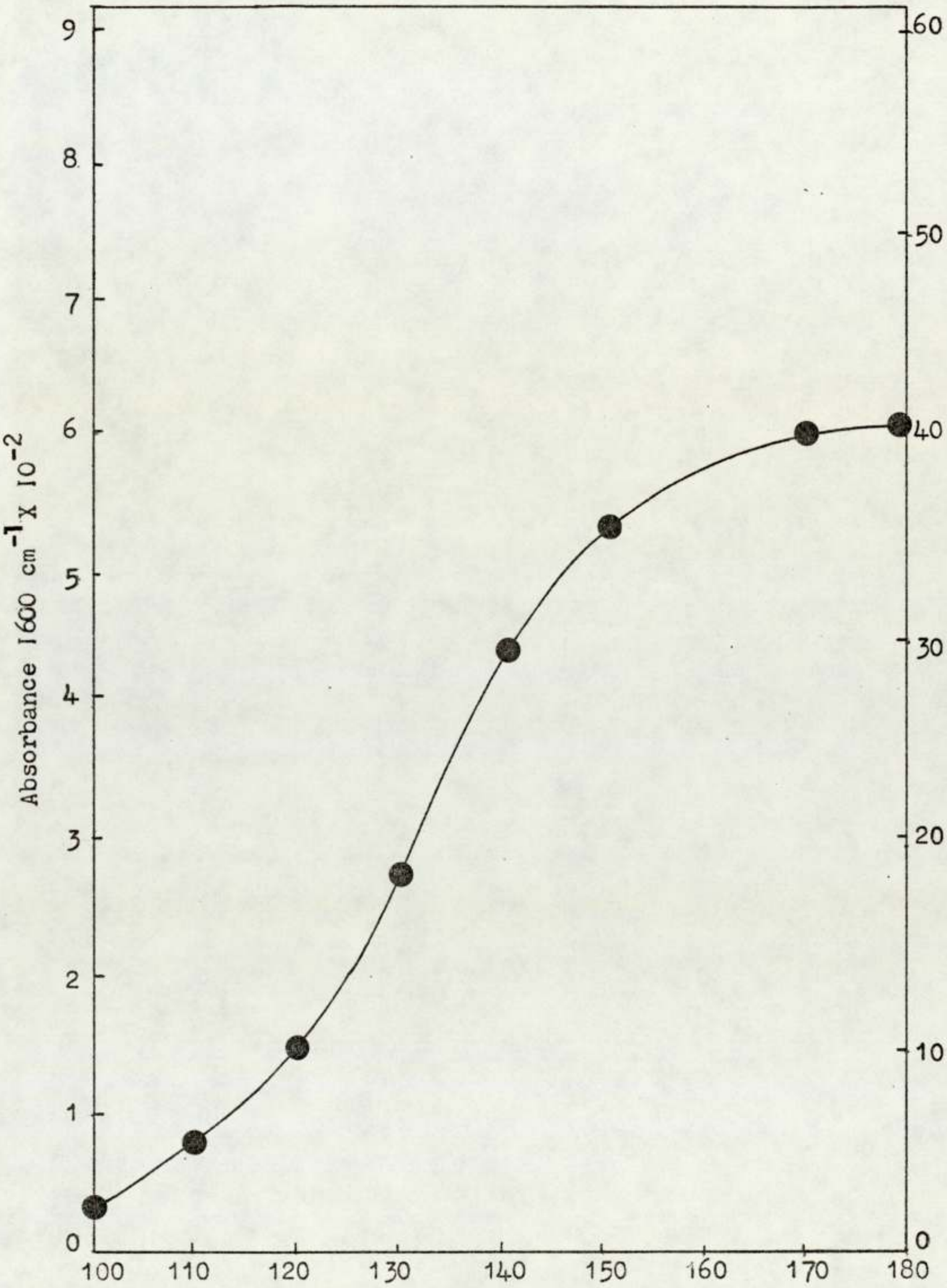


Fig 3-23 Thermo-mechanical processing ofLDPE and PS(50/50) under N_2.
Processing time = 30 mins , initiator =CHP (1/100g).
Extraction = 48 hrs.

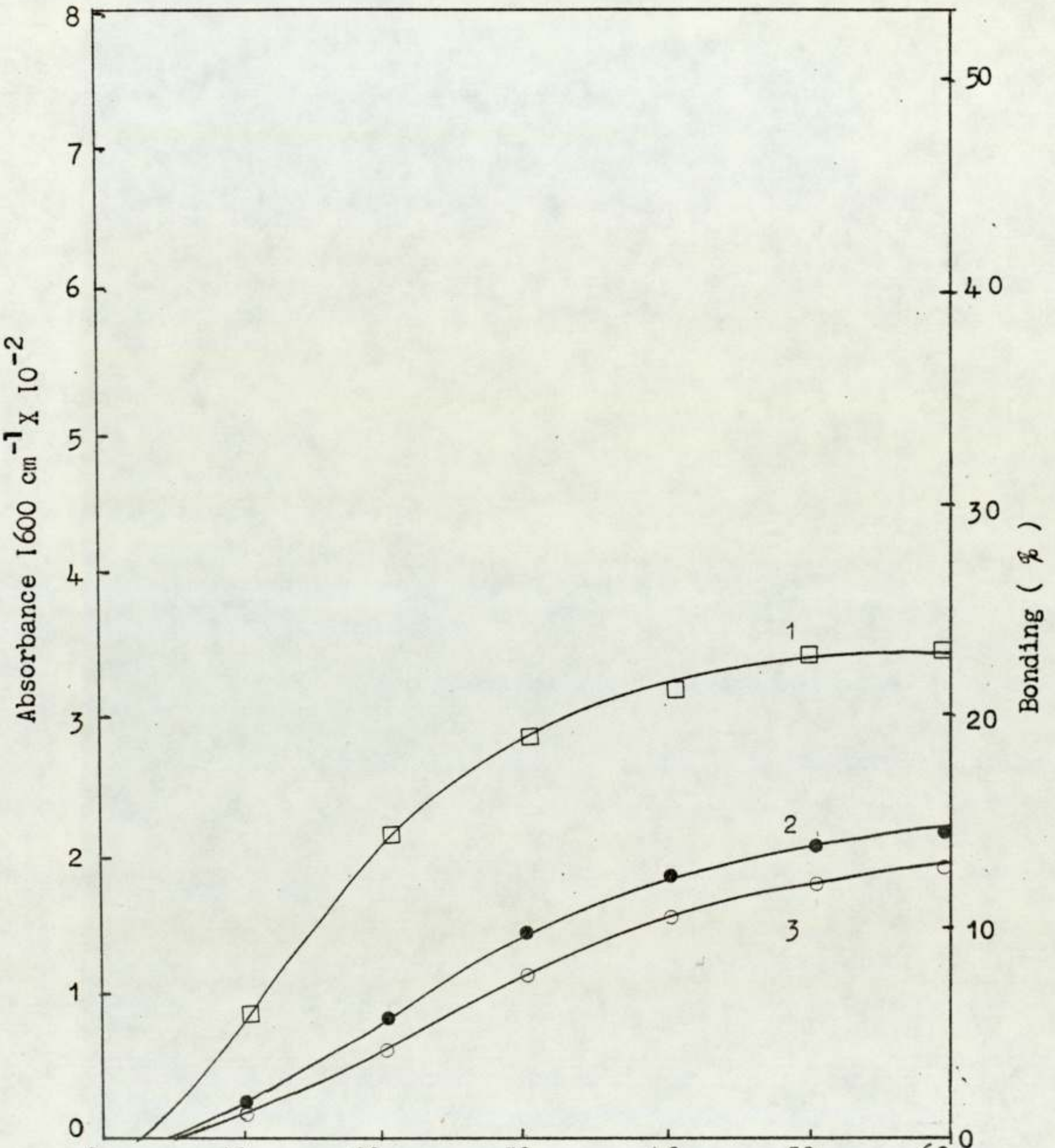


Fig 3-24 Mechano-chemical synthesis of LDPE-PS copolymer at 170°C in Torque Rheometer under N .
No 1 =1/100g CHP, No 2 =1/100g BPO and No 3=no initiator.

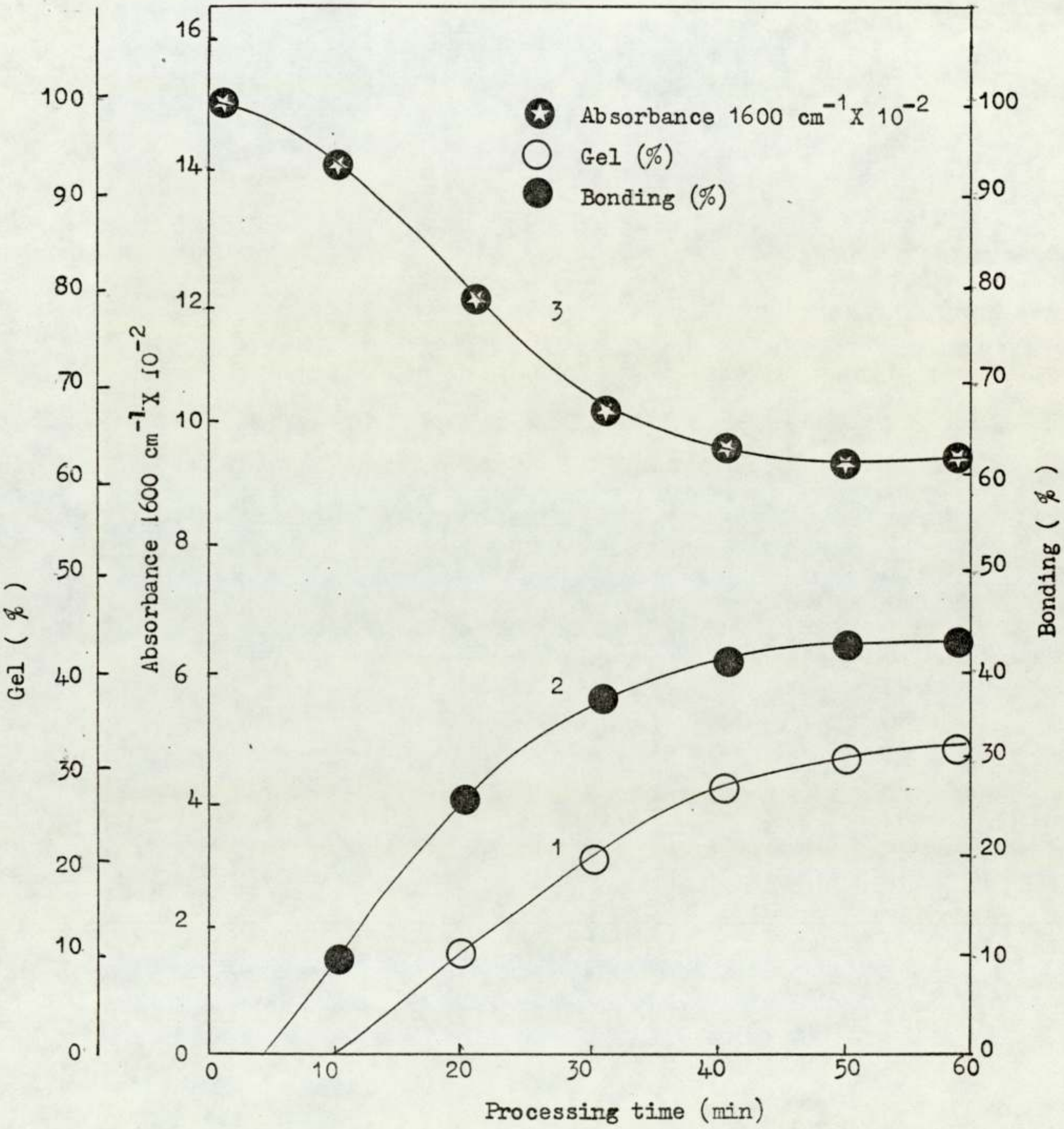


Fig 3-25 Gel formation of LDPE during mechanico-chemical synthesis of LDPE-PS copolymer.
Initiator = 1/100g CHP, processing temperature =170 C, closed, full-chamber and under N_2. Composition = 50/50 .

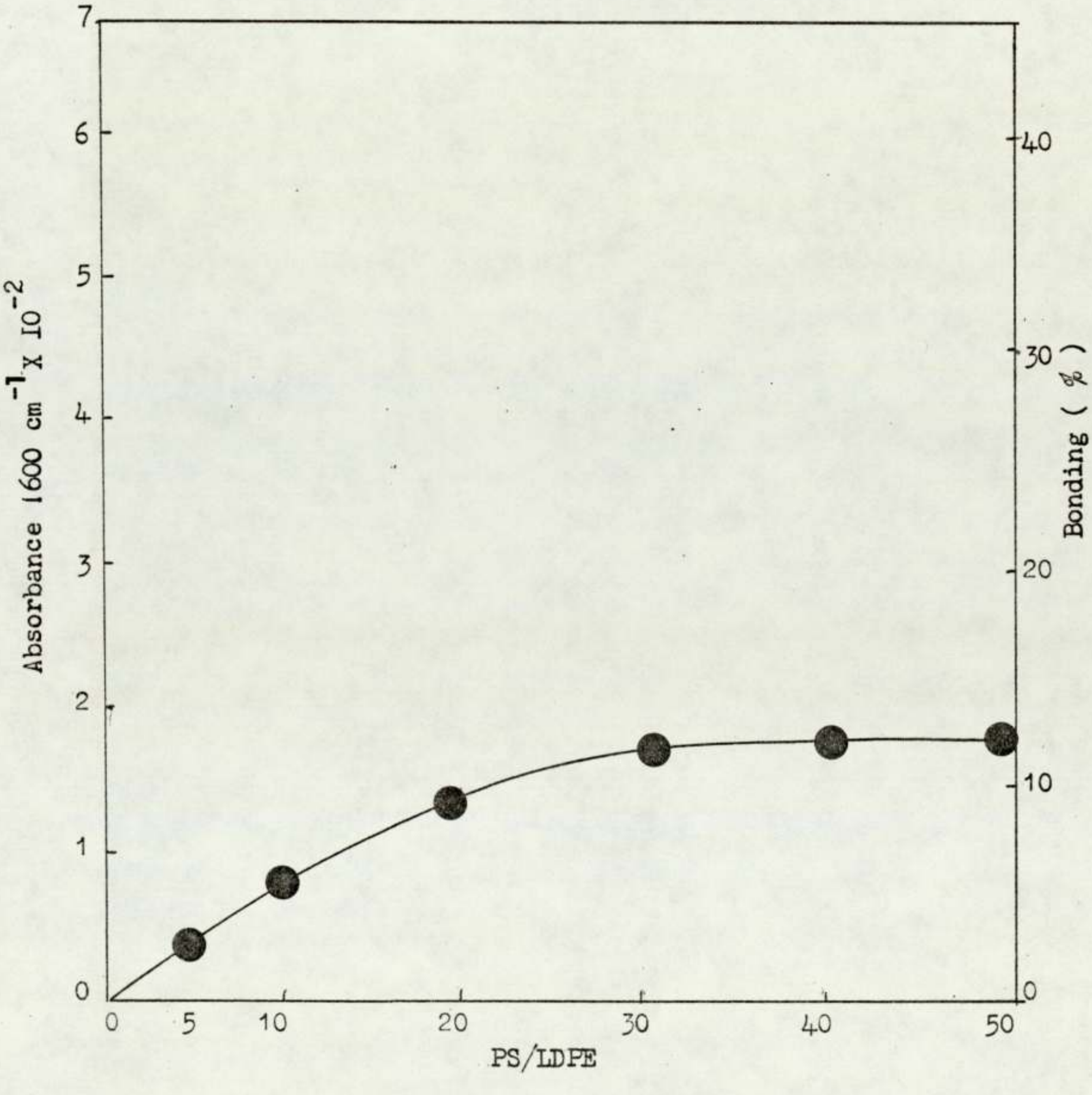
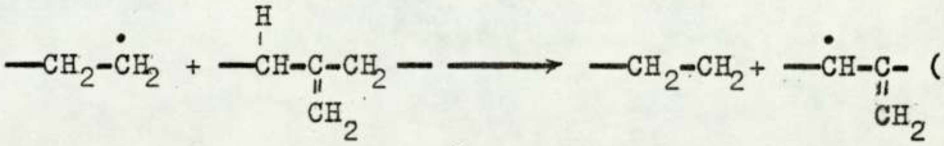


Fig 3-26 Mechano-chemical processing ofLDPE and PS in Brabender at 200 C.

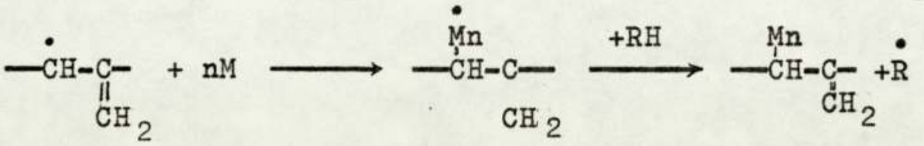
Extraction = 48 hrs.

(I) In the case of the polymer-monomer system.

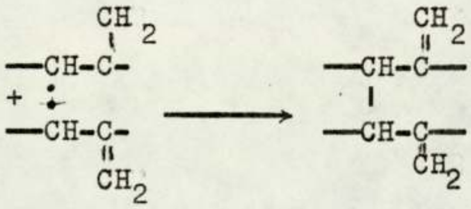
$$\text{LDPE} \longrightarrow -CH_2-\dot{C}H_2 + H_2\dot{C}-CH_2- \qquad (3\text{-}9)$$



$$-CH_2-\dot{C}H_2 + -\overset{H}{CH}-\underset{\overset{\|}{CH_2}}{C}-CH_2- \longrightarrow -CH_2-CH_2 + -\dot{C}H-\underset{\overset{\|}{CH_2}}{C}- \qquad (3\text{-}10)$$



$$-\dot{C}H-\underset{\overset{\|}{CH_2}}{C}- + nM \longrightarrow -\overset{\dot{M}n}{CH}-\underset{CH_2}{C}- \xrightarrow{+RH} -\overset{Mn}{CH}-\underset{\overset{\|}{CH_2}}{C}- + \dot{R} \qquad (3\text{-}11)$$



$$\begin{array}{l} -CH-\overset{CH_2}{C}- \\ +\ \dot{\cdot} \\ -CH-\underset{\overset{\|}{CH_2}}{C}- \end{array} \longrightarrow \begin{array}{l} -CH-\overset{\overset{CH_2}{\|}}{C}- \\ \quad\ | \\ -CH-\underset{\overset{\|}{CH_2}}{C}- \end{array} \qquad (3\text{-}12)$$

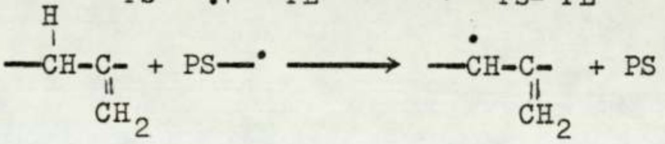
$$\dot{R} + nM \longrightarrow R-\dot{M}n \xrightarrow{M} \dot{M} + PS \qquad (3\text{-}13)$$

(II)In the case of the polymer-polymer interaction

$$\text{LDPE} \longrightarrow -CH_2-\dot{C}H_2 + H_2\dot{C}-CH_2- \qquad (3\text{-}9)$$

$$PS \longrightarrow PS-. + .-PS \qquad (3\text{-}14)$$

$$PS-. + -PE \longrightarrow PS-PE \qquad (3\text{-}15)$$



$$-\overset{H}{CH}-\underset{\overset{\|}{CH_2}}{C}- + PS-^{\bullet} \longrightarrow -\dot{C}H-\underset{\overset{\|}{CH_2}}{C}- + PS \qquad (3\text{-}16)$$

$$PS-^{\bullet} + {}^{\bullet}-PS \longrightarrow PS \qquad (3\text{-}17)$$

and also reaction No (3-12)can take place.

But in the case of addition of the free radical initiators (BPO andCHP), initiation is a two -step sequence,first decomposition of the initiators and addition of the initiator fragment radical to the vinyl monomer (styrene).In this stage an initiated monomer radical is formed and then the above reactions will take place provided in the absence of oxygen,otherwise the reactions (3-3 to 3-6) can be considered.

3-17 Results and Discussions

The results obtained in this study show the possibility of grafting of styrene into processed and unprocessed LDPE by chemical and mechnochemical methods at different temperatures under N_2 gas.

In the first method which the LDPE processed at 150°C(containing maximum hydroperoxide,Fig 3-1) was used ,the preformed hydroperoxide act as free radical initiator and percentage of the bonding was reached to 16-18 % after 6 hours reaction time at 110°C,Fig 3-13. It was found that reaction time, temperature,changes in monomer and initiator concentration had a considerable effect on the rate of conversion of styrene into polystyrene and percentage of the bonding according to the following equation.(78)

$$R_p = K_p\left(K_d f\left[I\right] / K_t \right)^{\frac{1}{2}} \left[M\right]$$

Where, R_p = the overall rate polymerization,

K_p = the rate constant of propagation,

K_p = the rate constant of initiation (initiator decomposition),

f = the initiator efficiency,

$\left[I\right]$ = the initiator concentration,

K_t = the rate constant of termination (termination by combination or/and by disproportionation and in the case of polystyrene experimental evidence suggests that the first kind of termination predominantly takes place).

and M = the monomer concentration.

In the second method in which BPO and CHP were used as initiators,the percentage of the bonding was raised to about 22%(Fig 3-17).It was found that at the optimum temperature for this method(90°C) BPO was more effective than CHP,but in the mechano-chemical methods,CHP was more effective at higher processing temperatures ,since the half-life of CHP is more than that of BPO (see Fig 3-16).

Swelling of LDPE in the monomer(styrene) had a considerable effect on the percentage of the bonding specially at the early stages of the reaction(Fig 3-14 Nos 2 and 3).It is believed that the swelling, specially at above room temperture ,causes penetration of the monomer in the amorphous region of the polymer and increases the extent of the bonding .This effect has been demonstrated during grafting of styrene into LDPE by photo-chemical method.(118,119)

In the mechano-chemical method (polymer-monomer system)the percentage of the bonding was increased to about 25 % (Fig 3-20,No 2) in the presence of CHP.However, the percentage of the grafting was raised to about 40-42 % by polymer -polymer interaction(Fig 3-23).In this method equal ratio of PS and LDPE (17.5 g PS and 17.5 g LDPE)were procssed in the Torque Rheometer from 100 -180°C under purified N_2 gas, from 10 to 60 mins.It was found that from 5mins to 30 mins the extent of bonding increased sharply and after 30 mins the amount of bonding increases only slightly .The optimum processing condition was obtained at 170 C Although above this temperature ,the percentage of the bonding could be increased slightly,the deterioration effects caused by the gel formation in the LDPE and by thermal degradation on the mechanical properties of the products will be considered later. The amount of the bonding formed in the Brabender was not considerable (12 %) due to the lower shearing effect and interaction time of the radical fragments compared to that of the torque rheometer.

CHAPTER FOUR

4 Experimental Techniques for Measurements of Extent of Bonding and Mechanical Properties of LDPE-PS Copolymers

In the previous sections (Chapter3),the different methods of preparation of polyethylene and polystyrene copolymers were discussed .In the following sections different techniques which strengthened the extent of bonding and dynamic mechanical behavior and morphology of the copolymers and their effects in the corresponding blends are described.

4-1 Infra-red Spectroscopy

The Perkin Elmer Model 457 was used to measure percentage of the grafting (section3-11) and to study changes of some functional groups during thermal and UV degradation (Chapter5)of LDPE/PS blends without and with the corresponding copolymers.

The wide application of Infra-red spectroscopy at the range 4000 cm^{-1}-200 cm^{-1} dependson the association of characteristic vibrational frequencies with particular groups.For example, a C-H group stretching vibration has a characteristic frequency approximately $9X10^{13}$HZ (3000 cm^{-1})(164). Some functional groups will be shown in chapter 5.

4-2 The Davenport Polymer Grader

As was mentioned before (section 3-7-1),this apparatus was used to determined the melt flow index of the unprocessed and processed LDPE at different conditions.

4-3 Tensile Strength Measurements

In order to obtain the effect of LDPE-PS copolymers as solid phase dispersants (SPD's)on the mechanical properties of the corresponding polyblends, the Instron Tensile Tester was used with cross-head speed and chart speed 2 and 5cm/min respectively(Photograph No 2).

Usually,four tests were carried out with the same thickness (0.01-0.012 cm^{-1}) for each sample to obtain an average .The samples used for the tensile tests were dumbell shape cut by steel cutter. The samples had the following dimensions.

breadth	0.35 cm
gauge length	3 cm
length	5 cm

From the stress-strain curves,modulus,tensile strength , yield strength and elongation at break were calculated from the following equations.(166)

$$\text{Tensile strength} = \frac{\text{force at break}}{\text{thickness} \times \text{width}} \qquad (4\text{-}1)$$

$$\text{Yield strength} = \frac{\text{force at yield}}{\text{thickness} \times \text{width}} \qquad (4\text{-}2)$$

$$\text{Elongation \%} = \frac{\text{chart length} \times \text{cross-head speed} \times 100}{\text{chart speed} \times \text{gauge length}} \qquad (4\text{-}3)$$

$$\text{Modulus} = \frac{\text{chart speed} \times \text{gauge length} \times \text{initial slope}}{\text{cross-head speed} \times \text{width} \times \text{gauge length}} \qquad (4\text{-}4)$$

Practically,tensile tests are made by stretching the samples at a constant rate of elongation until failure occurs.The stress is generally built up until the sample either breaks or yields. The stress-strain curves indicate whether a sample is brittle or ductile in nature.(167) The types of stress-strain curves obtained

by polymers with different mechanical behaviour are classified into five groups, they are illustrated in (Fig4-1 from I - V).

I soft and weak,

II hard and brittle,

III soft and tough,

IV hard and strongth,

V hard and tough.

If the rate of strain is very high, this type of test becomes similar to an impact test which measures toughness or energy required to break test sample. The area under a strain-stress is proportional to the energy absorbed in breaking of the sample .

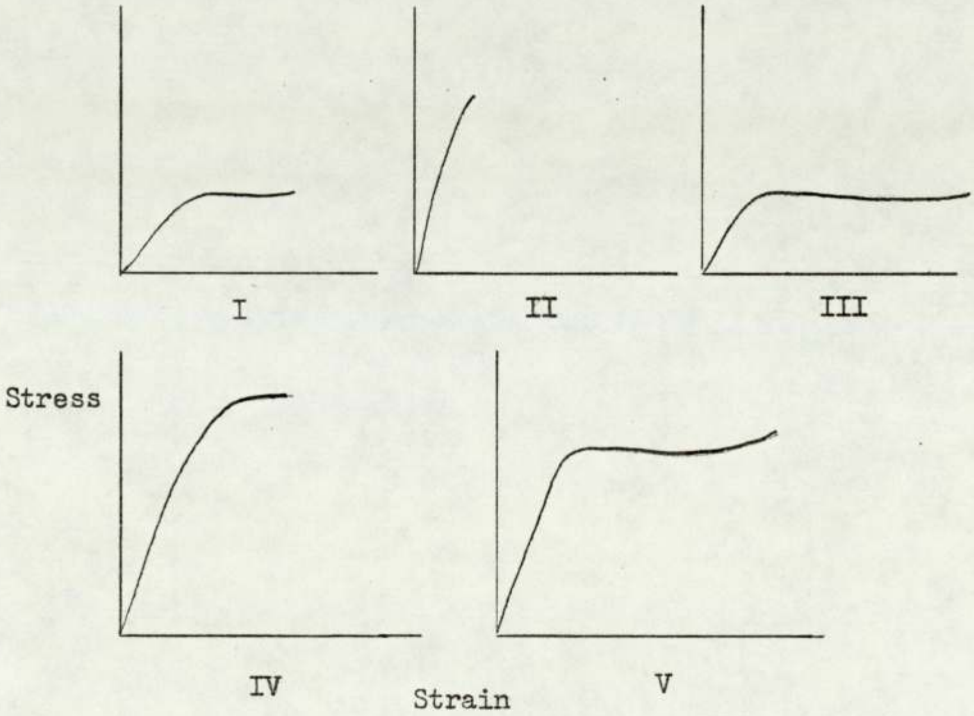


Fig 4-1 Tensile stress-strain curves for polymers having different mechanical properties.(168)

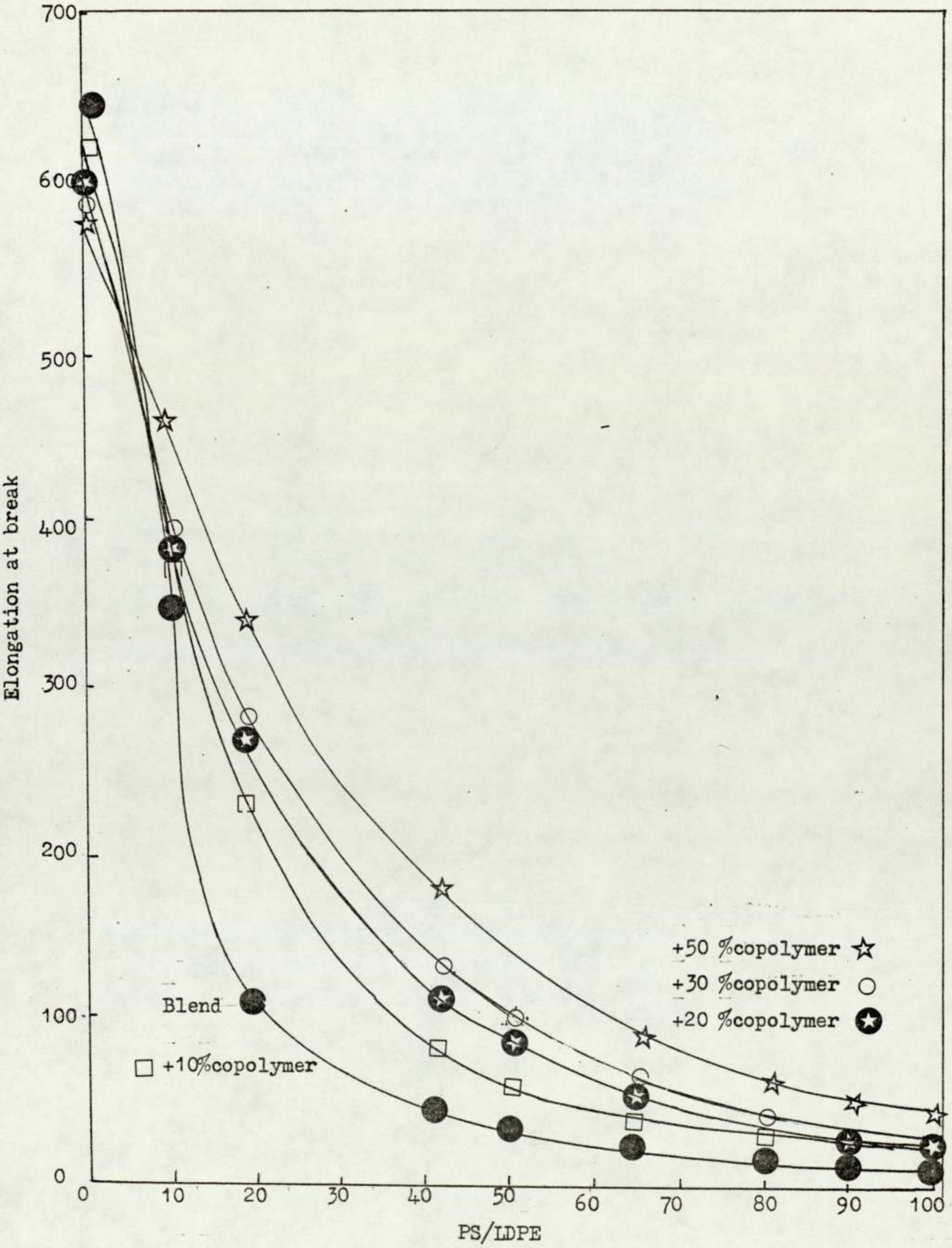


Fig4-2 Effect of LDPE-PS copolymer on elongation at break of LDPE/PS blends.

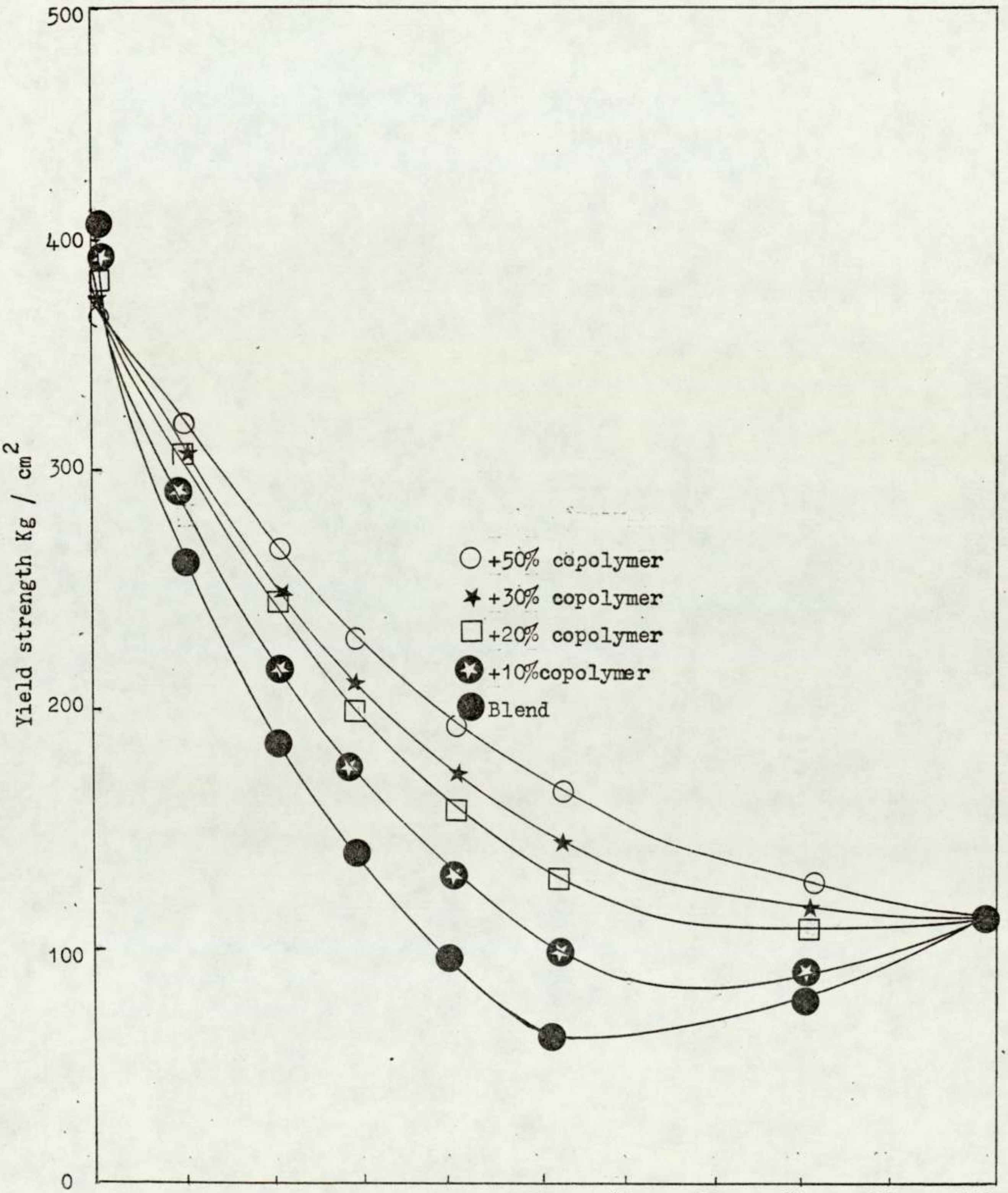


Fig 4-3 Effect of varying concentration of LDPE-PS copolymers on yield-strength of the corresponding blends.

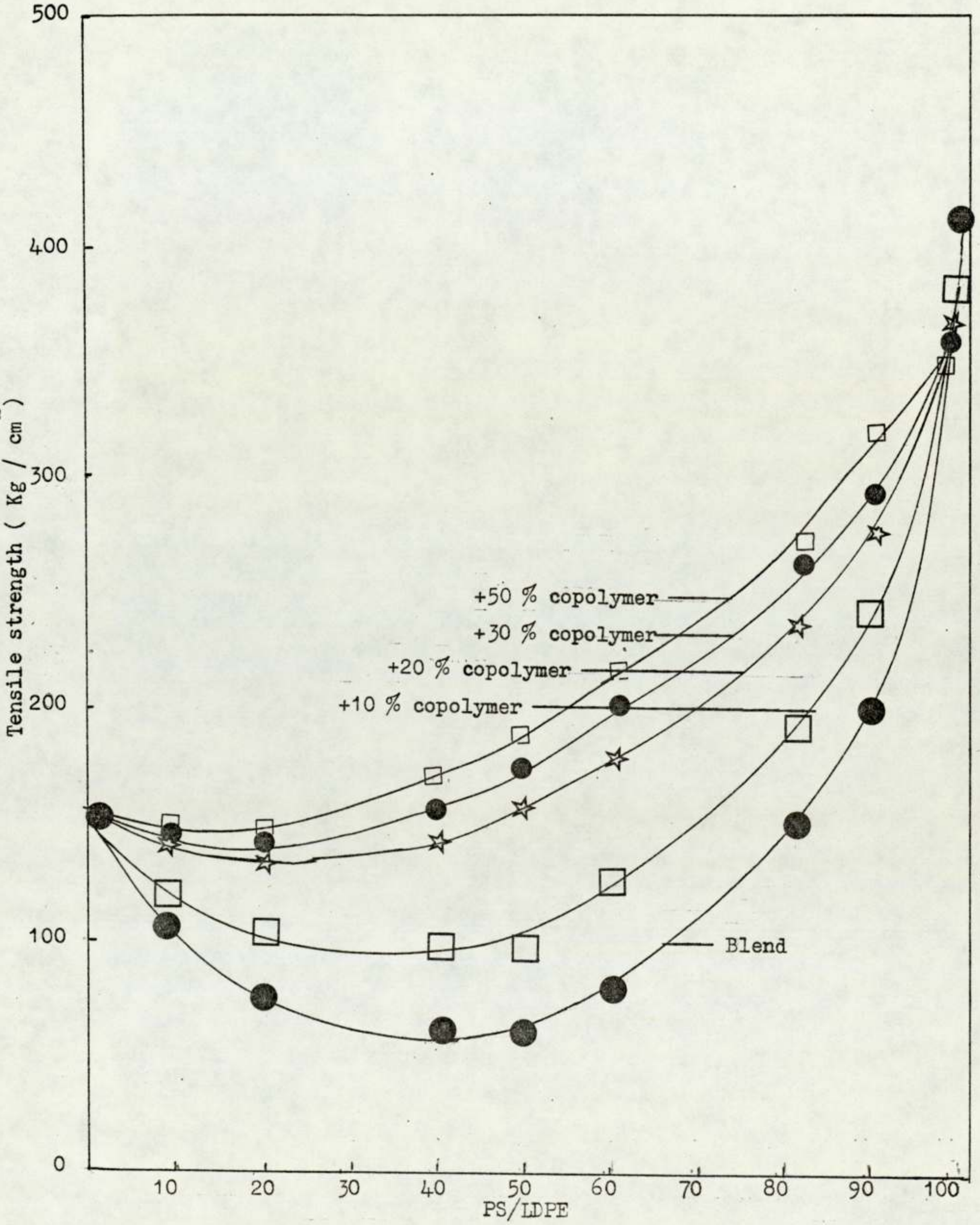


Fig 4-4 Effect of LDPE-PS copolymers on tensile strength of LDPE/PS blends.

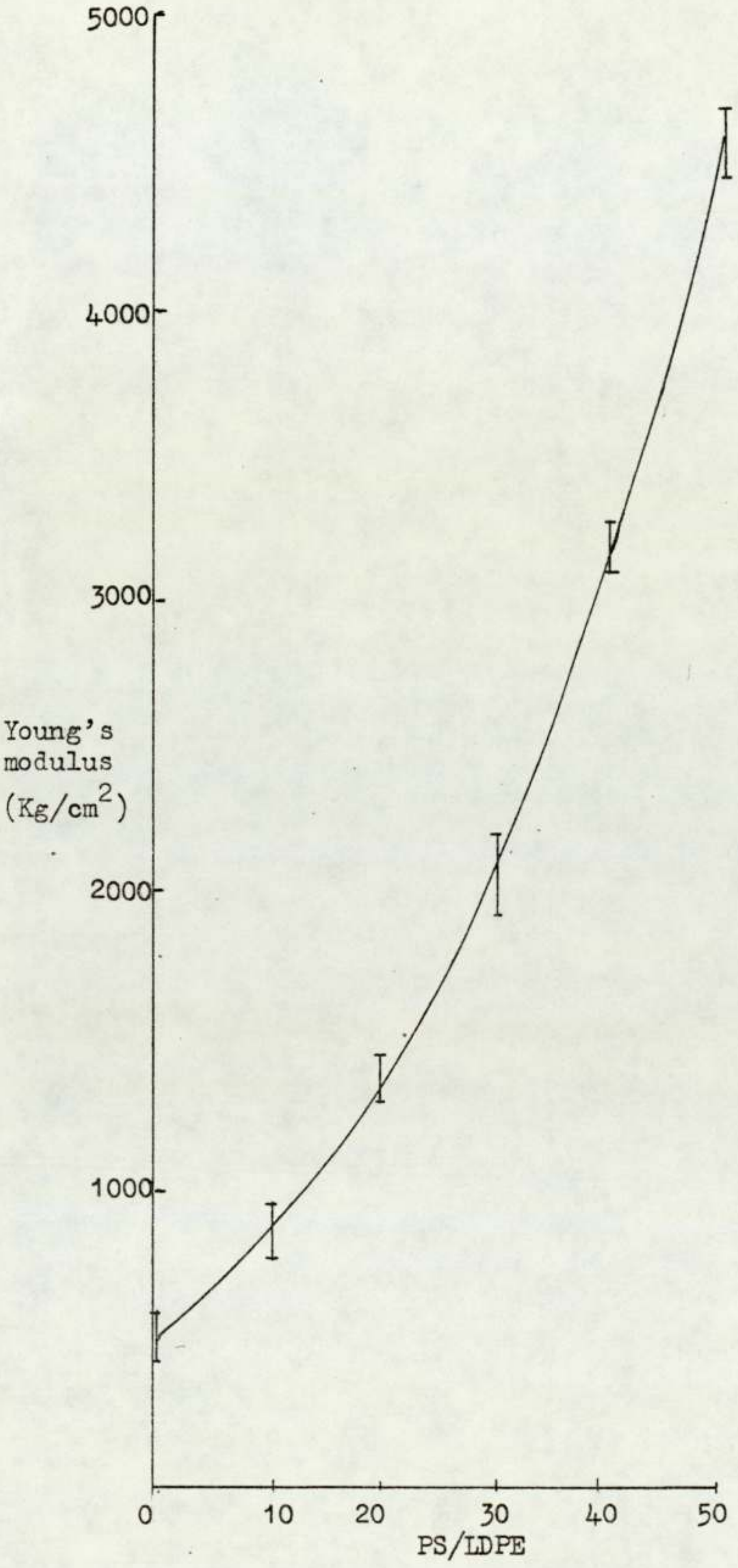


Fig 4-5 Effect of PS ratio on Young's modulus of LDPE/PS blends.

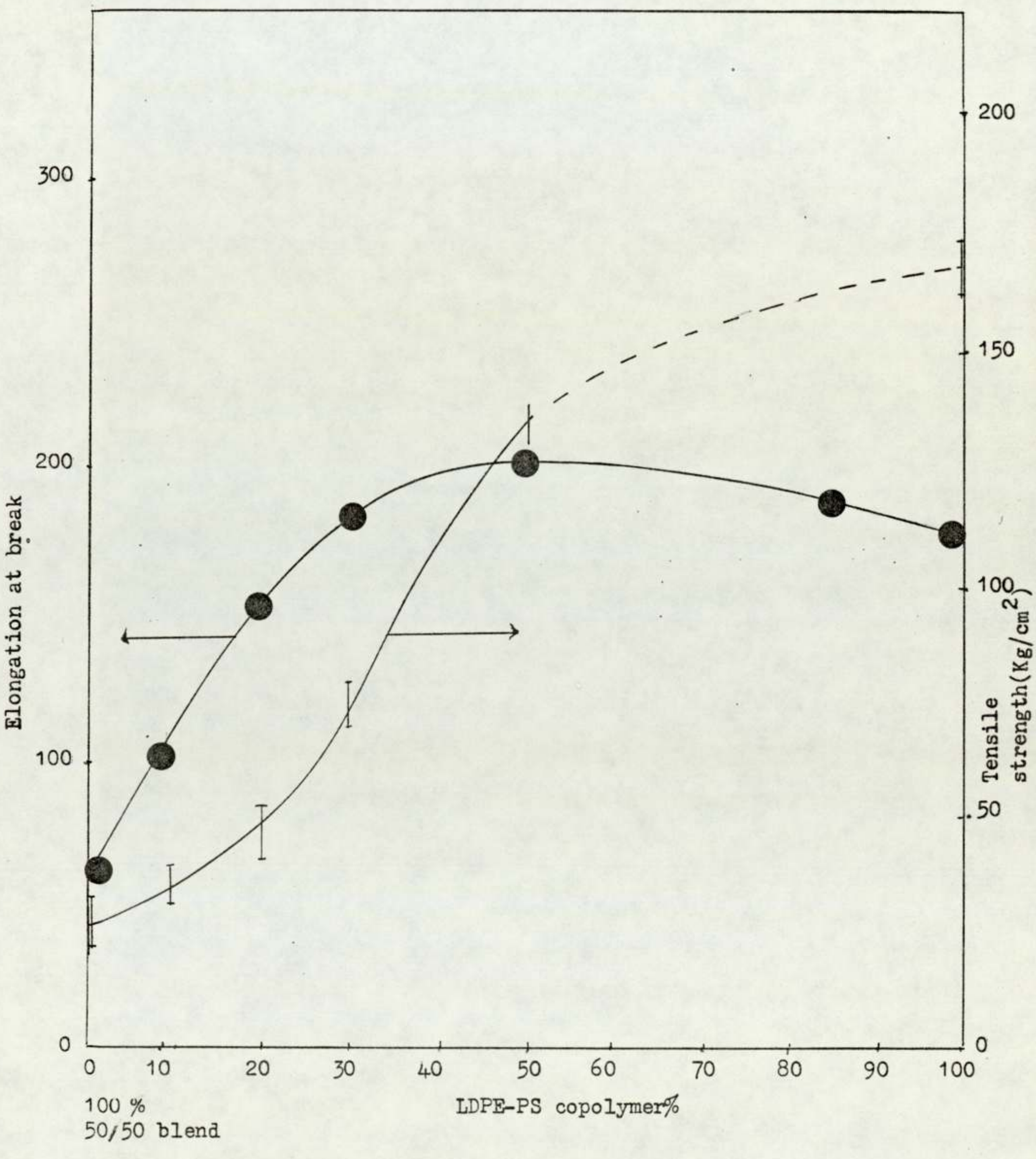


Fig 4-6 Effect of LDPE/PS copolymer ratio on the tensile strength and elongation at break of LDPE/PS blend.

Brittle materials such as PS and PVC have low toughness while,ductile materials such as HIPS and ABS which are subjected to cold drawing are very tough because of the high elongation to break value.

The speed at which the samples are stressed is important, since their mechanical properties are time dependent by virtue of their long chain structure.At very slow speed,molecules of the specimen tend to slip past each other (creep) and the applied force relatively is transferred between the molecules, but at high speeds,there will be no time for the molecules to move relative to each other and the specimen will break only when the individual molecular chains are broken. So, the tensile stress will generally be higher and the elongation at break is lower than the lower spead.

The results obtained for the mechanical properties of LDPE/PS without and with the corresponding copolymers are shown in(Figs 4-2 to 4-6).

4-4 Impact Strength Tests

Impact strength of a polymeric material is the amount of energy required to break the sample. The falling dart method was used to measure the impact strength of the samples. This method involves dropping a known weight onto the clamped film sample from a certain height. For this purpose a relatively simple labratory-made impact tester was used. As it is shown in Fig 4-7,it consists of two metal blocks with concentric drilled holes in the middle. A metal pipe with a narrow hole along its length is mounted directly above the hole of the upper metal block. A ruler is attched closely beside the pipe. Metal rods of different length (different weights) were used(depend on the thickness and impact strength of the samples.

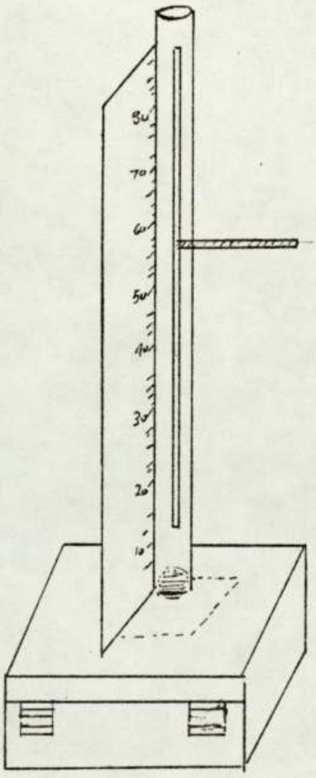


Fig 4-7 Falling dart impact tester

To use the impact tester, a ball bearing is initially dropped from the top of the pipe onto the film. Repeated tests on different samples were carried out to find the approximate energy to break the sampe by varying weight and height . The results were recorded as the minimum weight that can break the specimen.

The impact resistance of the film is the potential energy of the dart which could just break the film, according to the

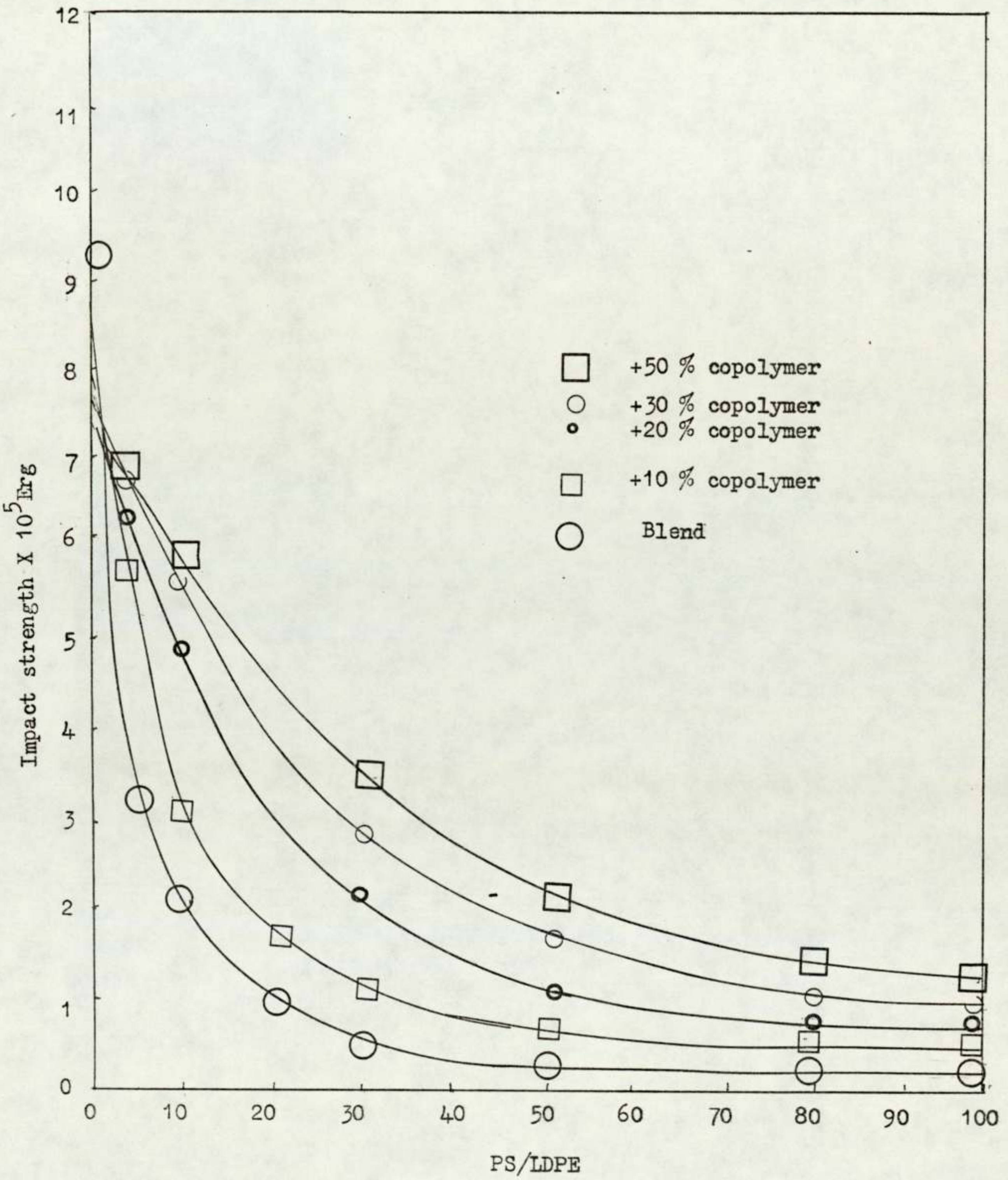


Fig 4-8 Effect of LDPE-PS copolymer on the impact strength of LDPE/PS blends.

following equation.(166)

$$\text{Impact resistanc} = E = m \times g \times h \qquad (4\text{-}5)$$

Where, m= mass of the dart in g

g= gravity force (981 cm/sec)

h= height of the dart from the sample in cm

To measure the impact strength of the samples due to the non-uniformity of the films, for each sample, four tests were carried out to obtain an average value. The results obtained on impact strength of LDPE/PS blend without and with the corresponding copolymers are shown in Fig 4-8.

4-5 Rheovibron (Viscoelastometer)

I- Principles involved in the Rheovibron. The Rheovibron used in the present study was Model DDVII, TOYO Measuring Instrument Company LTD (TMI) Tokyo,(173) (Photograph No 4-2 and 4-3).

As it is shown in Fig 4-9, Rheovibron consits of five main sections as follows.

1-Source

2-Amplifier

3-Oscillator

4-Furnace

5-Motor

The sample in the form of films having dimensions as follows,

length = 0.1-5 cm,

maximum breadth = 0.5 cm and

maximum thickness = 0.1 cm, is horizontally set in the furnace with both its ends attached to the two gauges (T-7 strain) by a chuck and connection. In the present studies, measuring low temperature tests with liquid nitrogen, to prevent the contraction of the sample , it was found necessary to reduce the distance between the clamps as the sample was cooled down to the desired temperature. The procedure ensured that the sample was straight between the clamps.

Of the two gauges, one is a transducer of displacement (Fig 4-9); as is shown by (T-7) it has a maximum force and displacement of 8 g 0.3 mm and an out put of 4000 X 6^{-6} strain. The other is a transducer of 550 g and approximtely 4000 X 10^{-6} strain (T-1). Both the amplitude of displacement and main magnitude of the load applied on the specimen is measured by the T-7 and T-1 gauges respectively and when they are adjusted to unity, their phase angle δ can be read directly from the main meter. To obtain the angle δ, both the magnitude of the oscillating displacement L and oscillating force F are measured by trnsducers T-7 and T-1 respectively. The calculation of these parameters are both described as follows.

I- Calculation of oscllating load ΔF.

This is obtained by this equation,

$$F = 10^4 \text{dynes} \frac{10^3}{D} N \qquad (4-6a)$$

Where, 10^4dynes = calibration value of T-1 gauge ($\simeq$ 10 g)

D = Value of the dynamic force dial (D.F) at the time of measuring tan δ

N = The value of the tan δ range at the time of measuring tan δ .These values are obtained from Table 4-1.

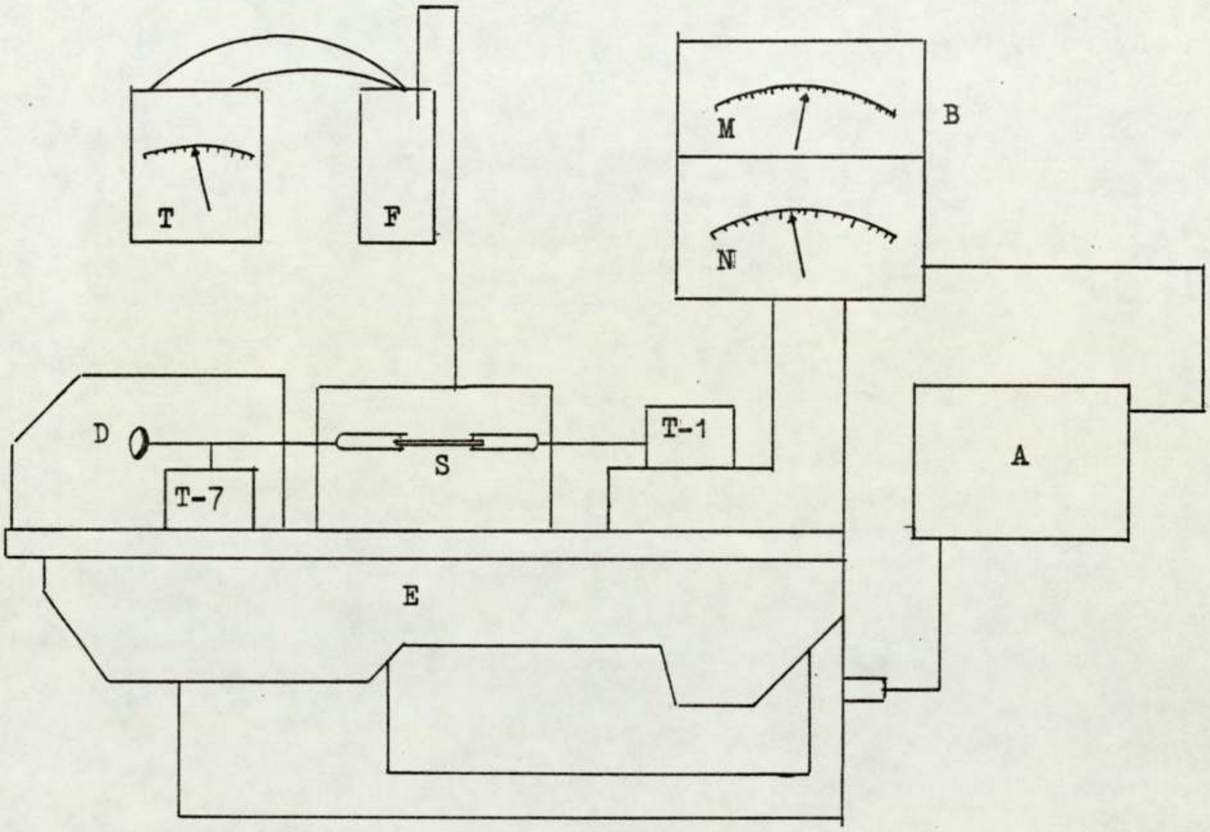


Fig 4-9 Sectional diagram of Rheovibron .

A = Energy source
B = Amplifier and oscillator
C = Furnace
D = Driving section
E = Base
F = Cold point thermos
T = Thermometer
S = Sample
M = Tan δ meter
N = Balance meter

Table 4-1

Tan δ range or amplitude factor	N or A
0	31.6
10	10
20	3.16
30	1.0
40	0.316
50	0.1
60	0.016

II- Calculation of oscillating displacement ΔL.

This parameter is obtained by this equation ,

$$\Delta L. = 5 \times 10^{-3} A.N \text{ cm} \qquad (4\text{-}6)$$

Where, 5×10^{-3}cm =Calibration value of T-7 gauge,

A = The value of the amplitude factor, when $\tan\delta$ is measured from Table 4-1.

III-Calculation of complex modulus.

It was mentioned earlier, (equation 3-4) that, $\overset{*}{E} = \frac{\sigma_{max}}{\varepsilon_{max}}$ and now, by substitution the values ΔF and ΔL in the following equation,

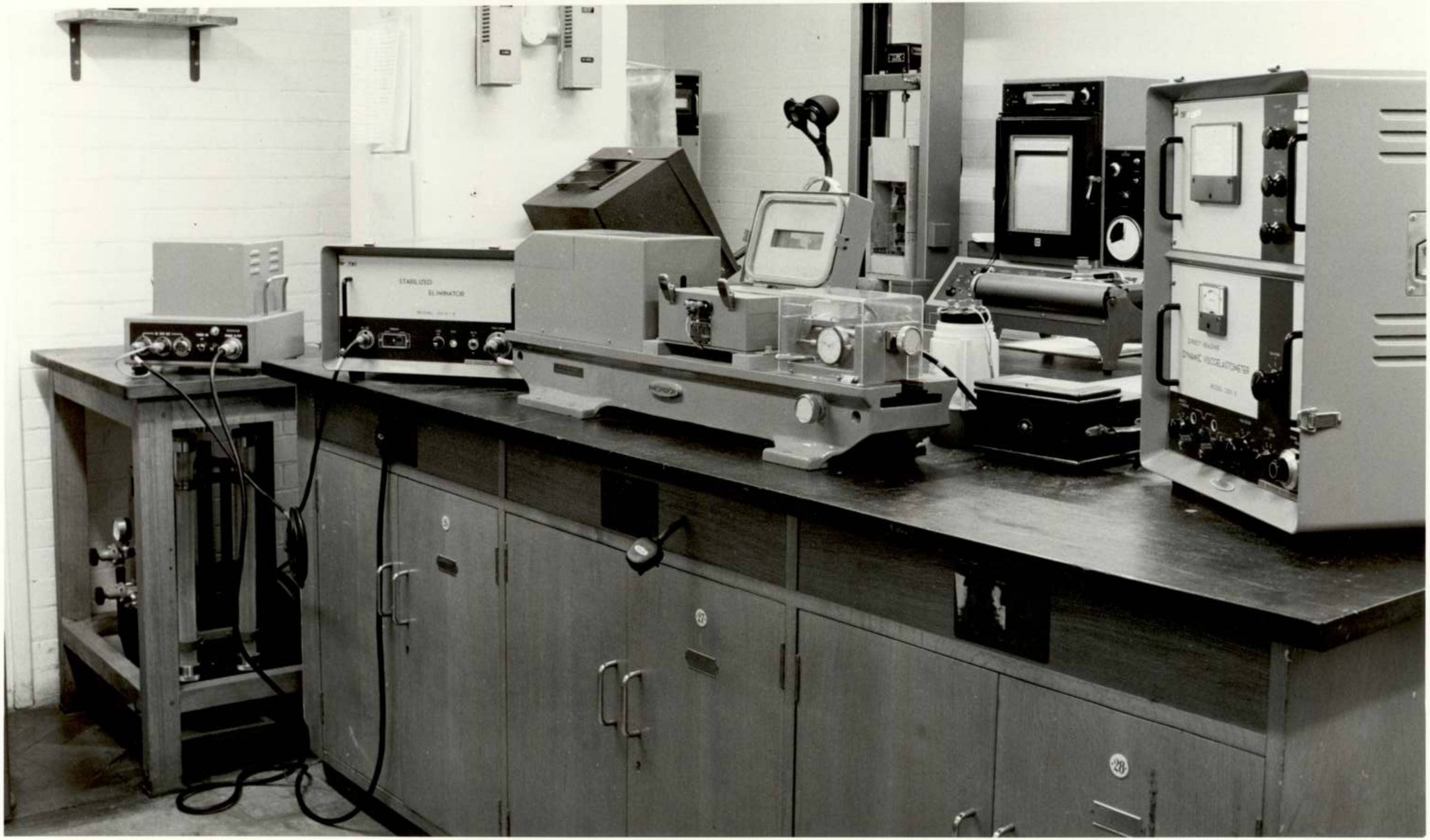
$$\left|\overset{*}{E}\right| = \frac{F}{S} \Big/ \frac{L}{L} = \frac{\text{Force}}{\text{Area}} \Big/ \frac{\text{Length}}{\text{Elongation}} \qquad (4\text{-}7)$$

complex modulus can be shown by this form.

$$\left|\overset{*}{E}\right| = \frac{10^{7}\ L}{5 \times 10^{-3} A \times S \times D} = \frac{2L}{A.S.D} \times 10^{9} \text{dynes/cm}^{2} \qquad (4\text{-}8)$$

Photograph No 4-2 Rheovibron with cold chamber

Photograph No 4-3 Rheovibron with hot chamber



Since during the displacement of the sample ,there is also a slight displacement in the chuck rod T-1 rod which gives an error in the final L values. To eliminate this ,an error constant "K" is introduced in the above equation .So the complex modulus of elasticity is as follows.

$$\left|\overset{*}{E}\right| = 2 \times \frac{L}{A(D-K)\ S} \times 10^9 \text{ dynes/cm}^2 \qquad (4\text{-}9)$$

Where, A = value corresponding to amplitude factor selected

D = dynamic force reading on dial,

K = error factor,

L = length of sample (cm)

S = cross sectional area (cm^2).

4-6 Ultraviolet Exposure Cabinet

Ultraviolet (UV) irradiation of the samples was carried out in an UV cabinet (Photograph No 4-4).This UV cabinet comprised a metal cylinder of about 110 cm in outer diameter and having a concentric circular rotating sample drum whose circumfrence was 15cm from the periphery of the metal cylinder. Thirty two fluorescent tube lamps were mounted on the inside of the cylinder. The rotating arrangement of the samples allows an identical amount of total radiation to fall on every sample. The cylindrical cabinet was opened to the atmosphere on both lower and upper sides, and the circulation of the air in the cabinet was ensured by the driven ventilator situated under the rotating frame.

The samples were attached separately to cardboard (window frame) and arranged vertically on a rotating cylinder. In this position the light beam fell perpendicularly on the surface of the film. The temperature recorded inside the cabinet with the lamps on was 30 ±1°C. The radiation source consisted of a cylindrical array of 20 W lamps mounted inside of the cabinet. 24 lamps, type C (Phillips actinic blue OS) and 8 lamps, type A1 (Westinghouse sunlamps FS20) were used and these were symmetrically distributed so that the combination was one lamp type A1 for every 3 lamps of type C. The spectral distribution of both types of lamps used is shown in Figs 4-10 and 4-11. The maximum in the relative intensity of the lamp A1 is at 317 nm and of lamp C is 374 nm. The available wavelength with the above combination of lamps was between 280nm-500 nm and the radiation intensity Io at the sample surface was, $I_o = 44.3\ W/m^2$.

To minimise the problem of decline in lamp output, the tubes were replaced every 2000 hours of exposure.

4-7 Wallace Oven

Thermal oxidation of LDPE/PS blends without and with the corresponding copolymers was carried out in a Wallace oven at 110 C±2°C. It comprised seven separated cells with a temperature control. There was an arrangement for controlling air flow through the cells. Each sample film was put in a separate cell during thermal oxidation. The

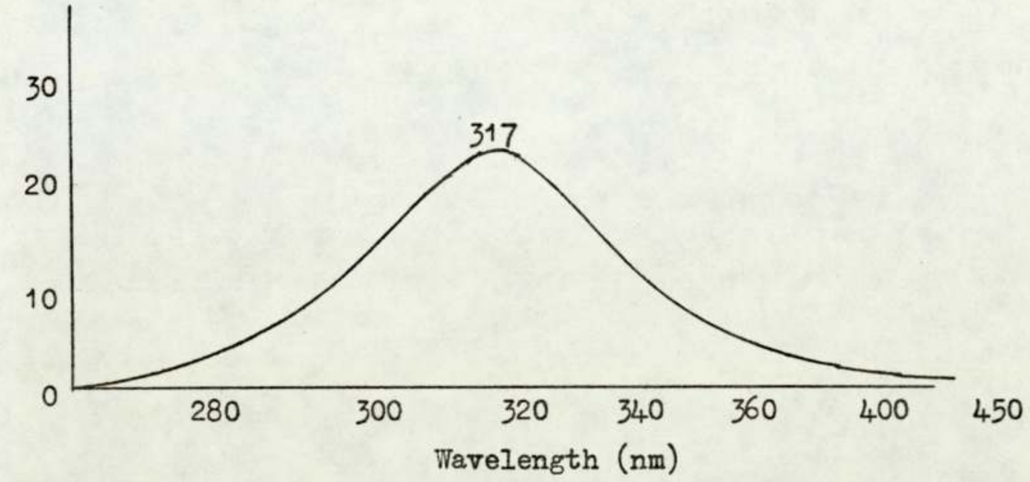


Fig 4-10 Spectral distribution of fluorescent lamp type A1 (Westinghouse Sunlamp FS20)

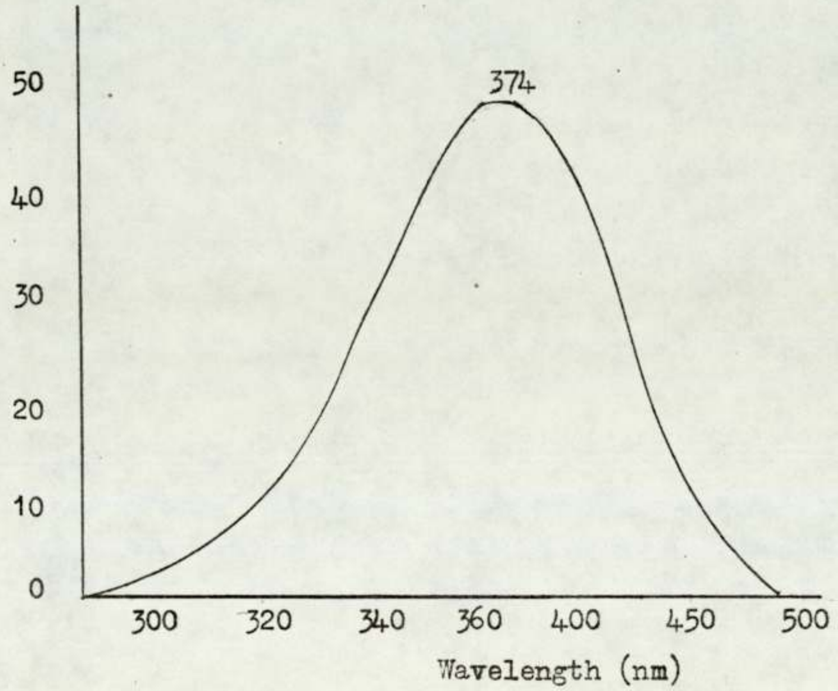


Fig 4-11 Spectral distribution of fluorescent lamp C (Phillips actinic Blue OS).

Photograph No 4-4, the Ultra Violet cabinet

UV and thermal oxidised samples were tested by the IR-spectroscopy (section 4-1). The results are shown in Chapter 5.

4-8 Optical Microscopy (phase contrast)

Morphology of LDPE/PS blends and the corresponding copolymers were studied by the Vicker's Photoplan Optical Microscope(Photograph No 4-5).

4-8-1 Principle

Phase contrast microscopy has been an available method of studying the nature and uniformity of a dispersed polymer in a continous phase polymer(morphology). It is based on the principle of magnifying the differences in the amplitude of waves which combine at the eye-piece of the microscope to form the image, with the effect of modifying the relative intensities of background and the object to increase the contrast. This is attained by illuminating the sample with a hollow cone of light from a substage condenser having a special annular lens. Light from the specimen passes through a special diffraction plate situated behind the focal plane of the objective and light unaffected by the specimen is advanced in phase by one quarter of the wavelength. The two waves fronts, diffracted and undiffracted, interfere at the final image plane to produce of enhanced contrast.

4-8-2 Procedure

Small pieces of the samples were melted between two glass slides

Photograph No 4-I (Tensile Instron)

Photograph No 4-5, Optical Microscope

on a hot plate to form a very thin film about 2 µ. The first slide (bottom one) acts as heat transfer and the second one (upper)prevents any dirt getting on the sample.A flat bottom metal is pressed gently on the sample for a short time (5-10seconds),the sample is firmly sandwhiched between the glass slides.

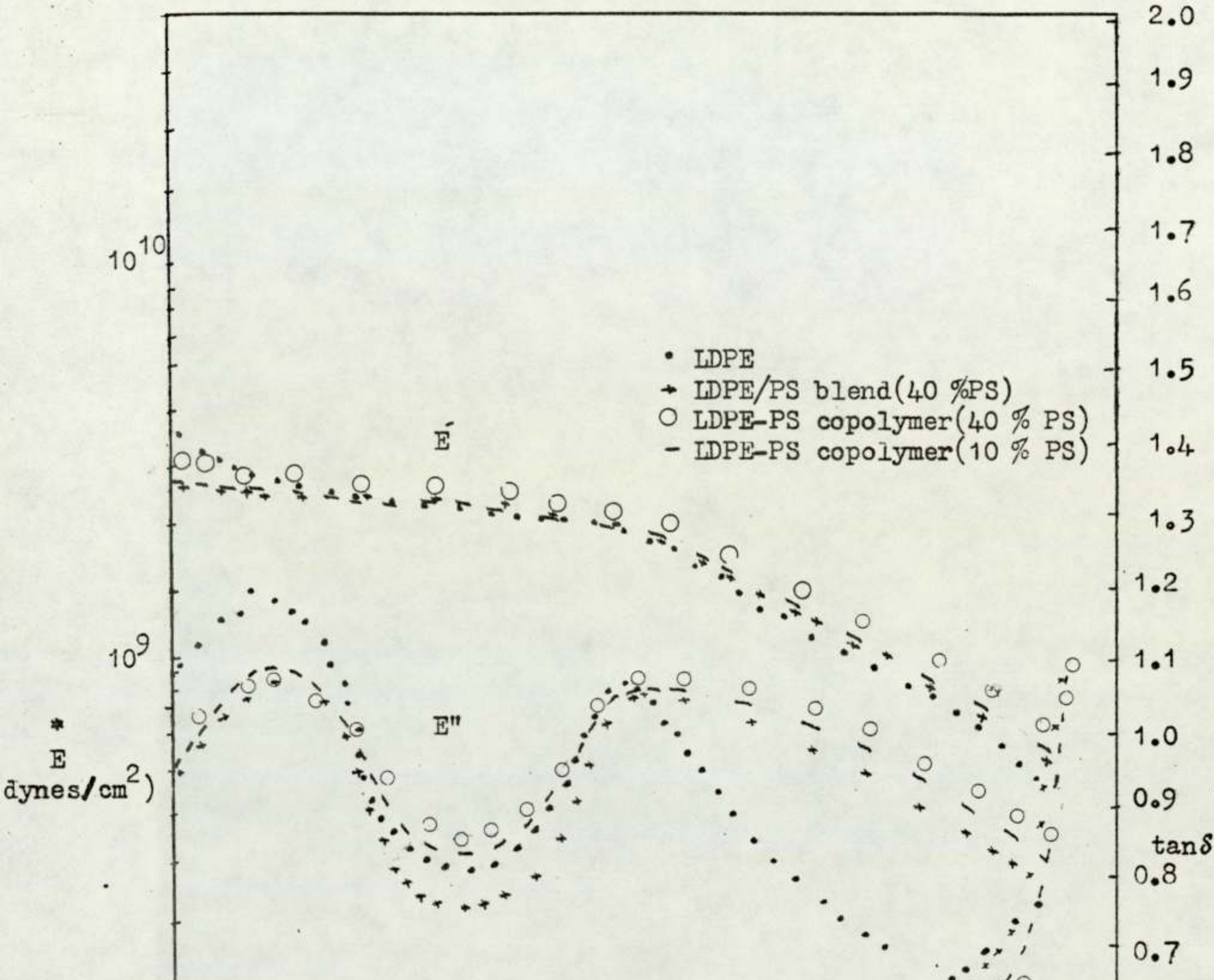


Fig 4-13 Changes of dynamic mechanical behavior of LDPE, LDPE/PS blends and LDPE-PS copolymer.

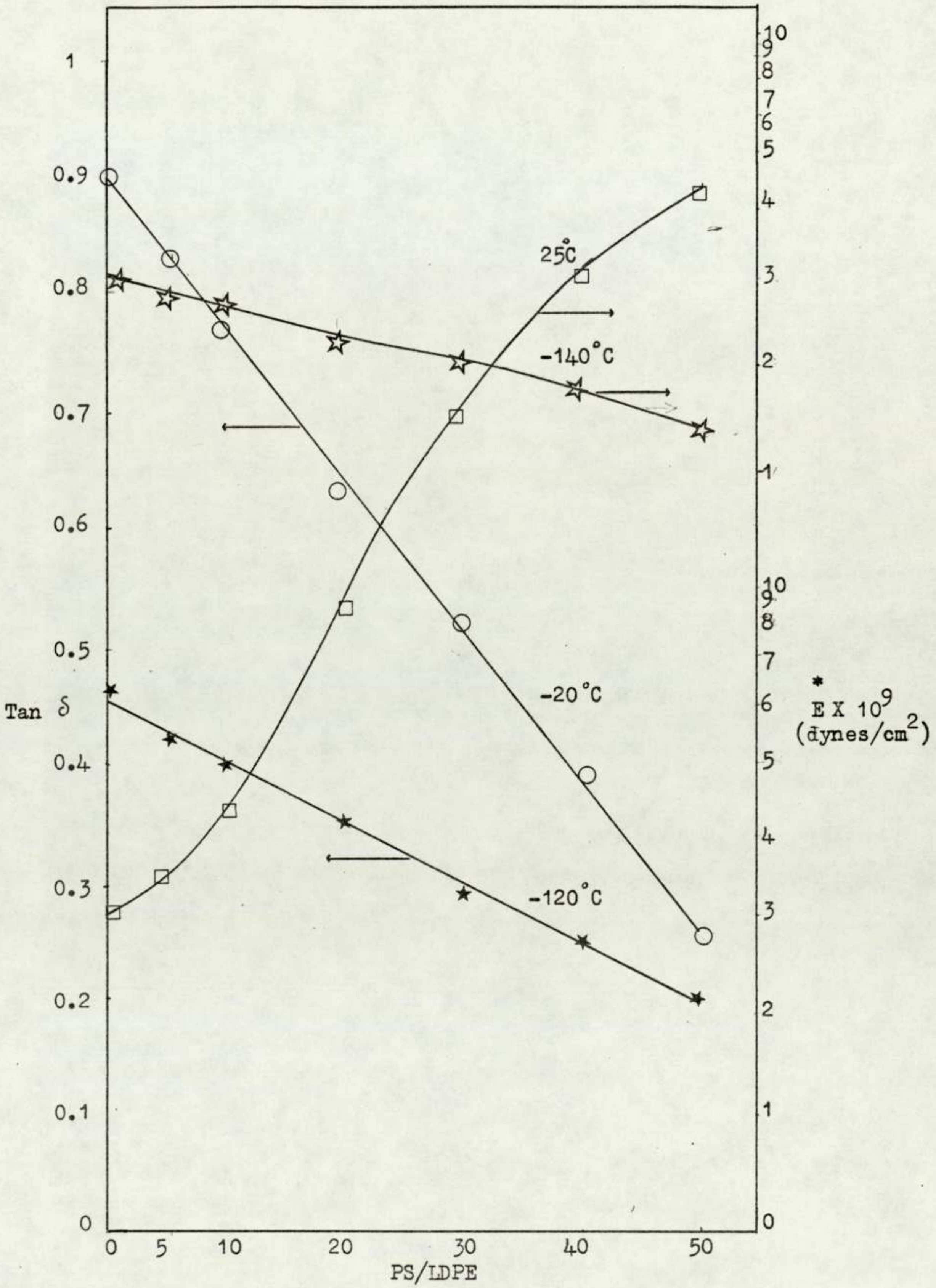


Fig 4-15 Effect of PS ratio on Tan δ and E* of LDPE/PS blends at -140 ,-120 , -20 and 25°C .

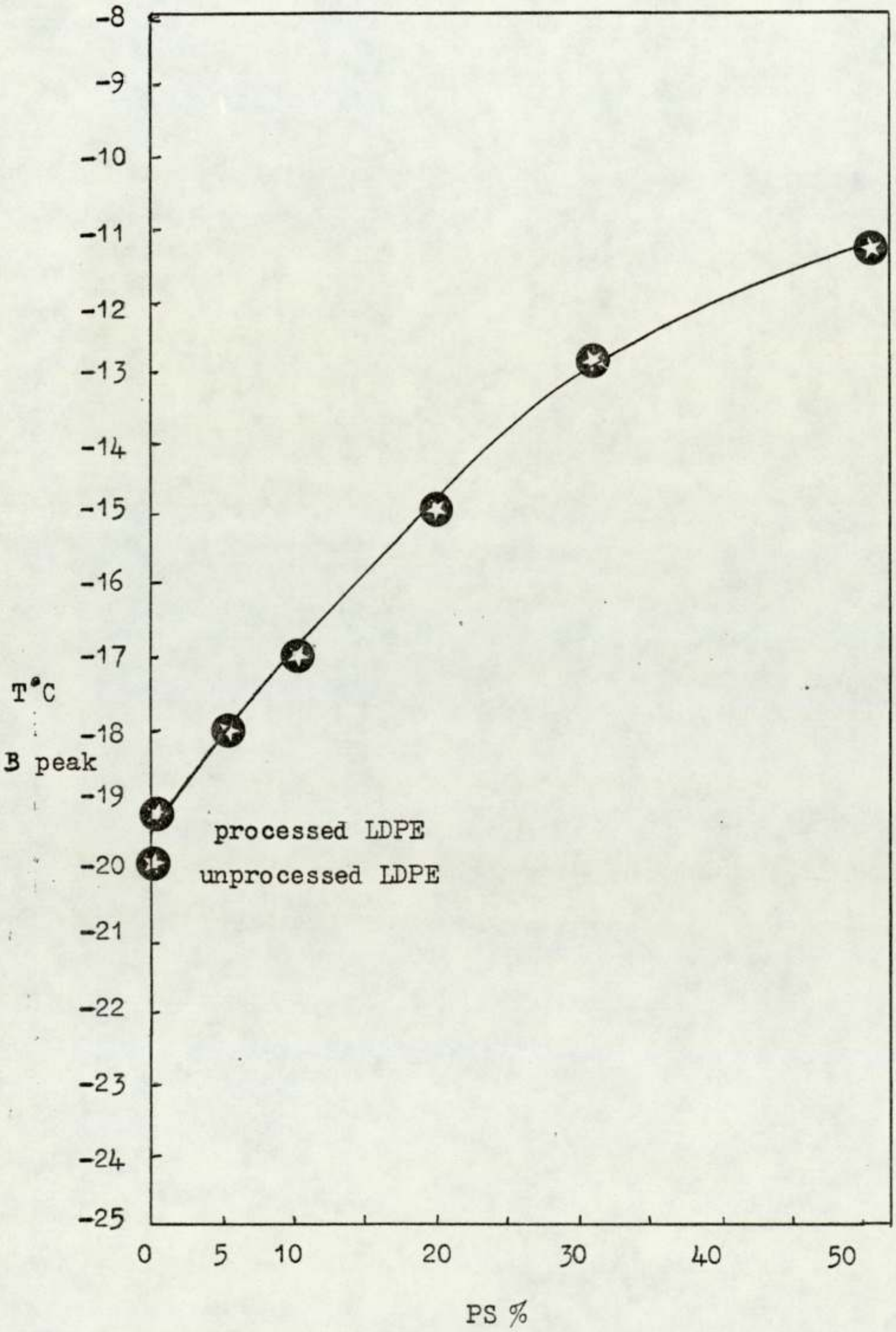


Fig 4-16 Effect of P S on the processed LDPE B-peak as a function of temperature.

4-9 Effect of LDPE-PS Copolymers on the Impact Strength, Stress-Strain Behavior, Dynamic Mechanical Properties and Morphology of LDPE -PS Blends

4-9-1 Results and discussions.

The average values for elongation at break (EB), ultimate tensile strength(UTS), impact strength and Young's modulus of the samples containing 10,20,30 and 50 % of the extracted (with 40 % of grafted polystyrene) are shown in Figs 4-(2,4,8,5) respectively. There is a sharp drop in the elongation at break and impact strength of the blends to 20 % of PS, then this value decreases up to 50 % PS which shows the poorest mechanical properties. For more than 50 % PS, elongation at break and impact strength decrease slightly to 100% PS which has the lowest value. Tensile strength increases as the ratio of PS increases(Fig 4-4). As the continous phase, which makes easy transition of the force between the dispersed particles(PS domains), is increased there is is a marked increase in Young's modulus(up to 5 % PS) suggesting that, although the PS particles weaken the structure of the blends, it makes them more rigid. These results are supported by conclusions of Scott and co-worker(66), even in the case of less compatible polymer blends such as LDPE/PP and LDPE/PVC.

Kerner (206) predicted an "S" shaped relationship between UTS and composition using PE/PS blends. The essential concept of his work is the mutual adhesion of the phases, with good adhesion the "S" shaped should be followed. It is therefore, reasonable to assume that in the present case, no significant adhesion exists between the unmodified blends. However, when different amounts of LDPE/PS copolymers were added to 50/50 % (LDPE/PS), all mechanical properties of the samples were improved because the copolymers act as interfacial agents, thus improving their mutual compatibility and this in turn reflects on their mechanical properties(see Chapter 1). It was concluded that addition of copolymers (up to 30%)to the blends sharply improved their tensile strength, elongation at break and impact strength . Addition of the copolymers up to 50 % followed by introducing small further improvement on their mechanical properties.

The results obtained by stress-strain studies are supported by an examination of the morphology(see Plates Nos 4-1 to 4-16).As is shown in Fig 4-1, up to 0.5 % PS, the samples seem to show one phase, but above this limited solubility, there are rather large domains suspended in the continous (rubbery) phase. These discrete domains are polystyrene and they generally increase in size as the PS ratio is increased. In addition to the shearing force ,processing time has a considerable effect on the size of the dispersed particles . As is shown , using the same composition, the PS domain sizes resulting from the Torque Rheometer processing are much smaller than those obtained with the Brabender. However, in all the samples, the PS particles are distributed in aggregated form but in the samples containing the copolymers the PS particles are distributed in a more homogeneous fashion. These results are supported by Lock(1) and Sadrmohaghegh.(2)

Dynamic mechanical tests on LDPE/PS blend (40 % PS) and LDPE-PS copolymers containing 10 and 40 % bonding were carried out in the temperature range from -140 to 120 °C. The loss modulus of the copolymers indicates transition in the range of -120 °C and -10 to 20 °C(Fig 4-13). LDPE has these same transitions, but the second transition is located at a slightly different temperature range depending on the degree of cross-linking of the polymer .These transitions have been also reported by Paul and co-workers(207). Another transition at 85°C has been reported by Amin(5). However,the loss modulus or Tan δ peak at -120°C has been labeled as "γ Transition " and is believed to be due to the motion of a limited number of (— CH_2—)groups in the LDPE main chain (208,209,210,211). The second transition has been labeled" β Transition" and is thought to be due to the movement of the polymer chain in the vicinity of branch points.(208)

The storage modulus (E') for the graft copolymer (calculated from Equation No 4- 9) is related to the recoverable energy and does not drop as rapidly with temperature as it does for the LDPE (Fig 4- 13). The loss modulus(E'') which is related to the amount of energy dissipated in the polymer and has a relatively constant value in the temperature 10° to 40°C for all the graft copolymers,and temperature range of this plateau increases with increase in grafting extent .Because the presence of the graft makes the samples more stiff in this temperature range,LDPE has no such plateau. The plateau was however observed slightly in the corresponding blends.

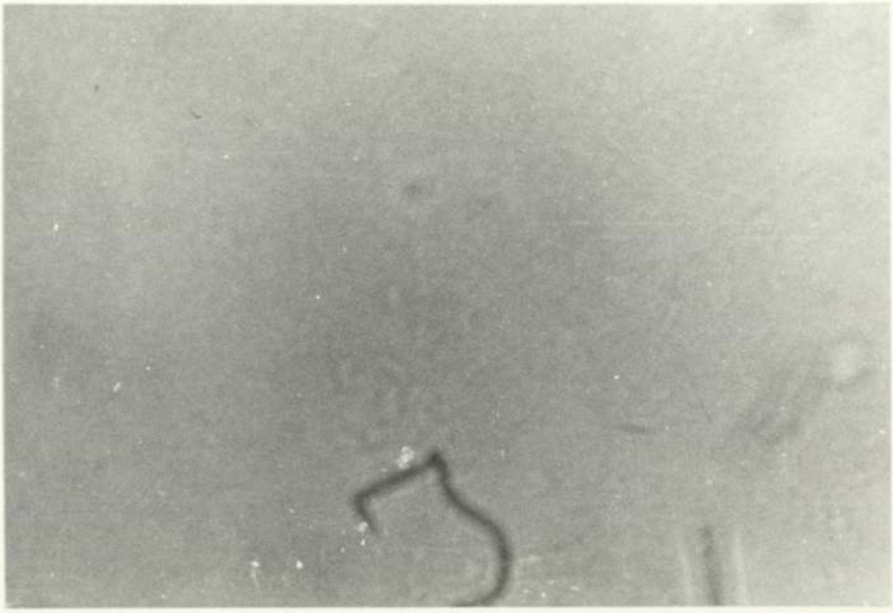
Another difference between LDPE and the graft copolymer is that the height of the loss modulus is smaller for the graft copolymers. The reason for this is that the amorphous regions present in LDPE are occupied by graft points.(structure of LDPE will be described in Chapter 5).

The data in Fig 4-13 also indicates that the storage modulus of the blends are lower than those of the graft at all temperatures. For example at -120°C ,the blend and graft copolymer with the same amount of PS (40 %),showed storage modulus 2.8 X10^9 and 3 X10^9 dynes/cm^2

respectively. The lower storage modulus of the blends is believed to be due to the lower degree of crystallinity of LDPE in the blends.(207) This effect is reflected in an improvement in their tensile strength.

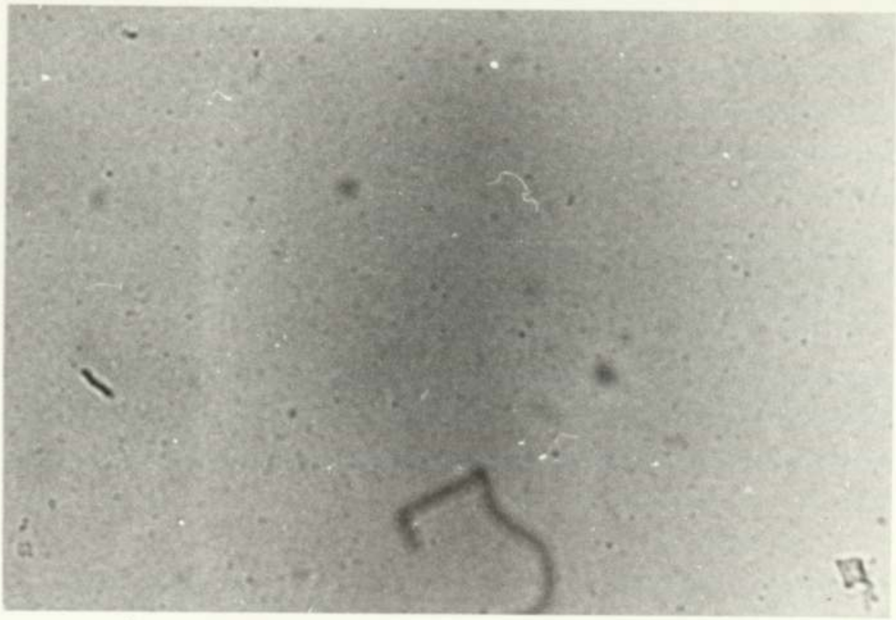
The loss moduli for the blends and grafts are similar for the γ and β transitions at -120 °C and -20 °C respectively. There is a plateau region for the transition range of the graft and even for the blends. This is found to depend on the ratio of PS to PE in the samples. This effect is greater for the graft copolymers than for the blends. Therefore, as the extent of the bonding increases, the β transition shifts to higher temperatures (Fig 4-13). This plateau is believed to be caused by direct chemical bonding of PS with the LDPE which increases the stiffening effect of the chain allowing better stress transfer between the phases.

Fig 4-15 shows the changes of the storage modulus and tan δ with increasing PS content of the grafts at -140, -120 and -20 °C. The data are seen to be quite linear at -120 °C and at -20 °C. This effect can be correlated with the more homogeneous distribution of PS particles in the graft samples compared to the corresponding blends. As was mentioned earlier, the temperature shift and magnitude of the β transition for the graft seems to differ slightly with the LDPE (Fig 4-13). In a further analysis, the slight shift in the transition was examined as a function of temperature and polystyrene content (Fig 4-16). As is shown, unprocessed LDPE has a β transition lower than in the case of processed LDPE (from -20 to -10 °C). This transition shifts to higher temperatures as the content of PS or extent of the grafting is increased.



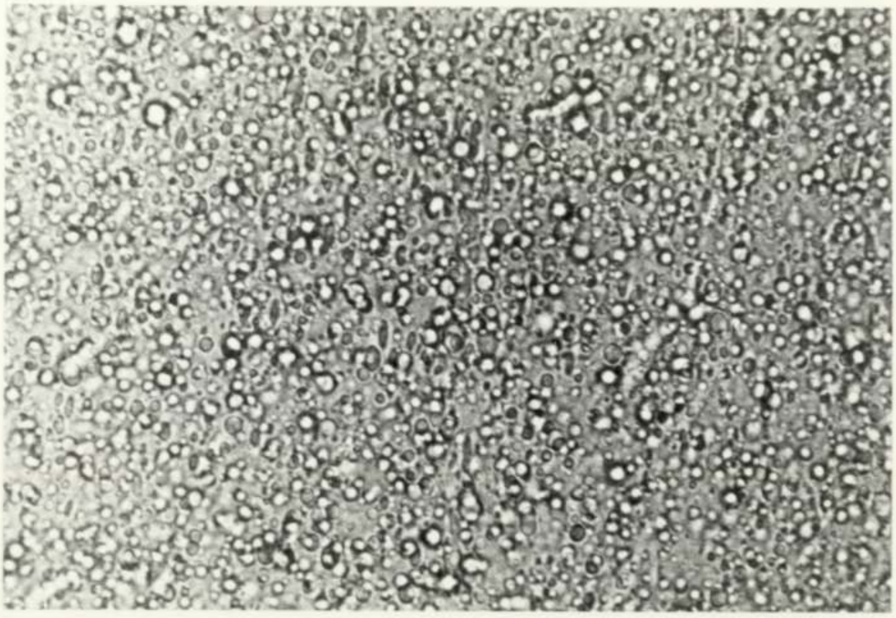
(X 200)   Plate No 1

100 % LDPE



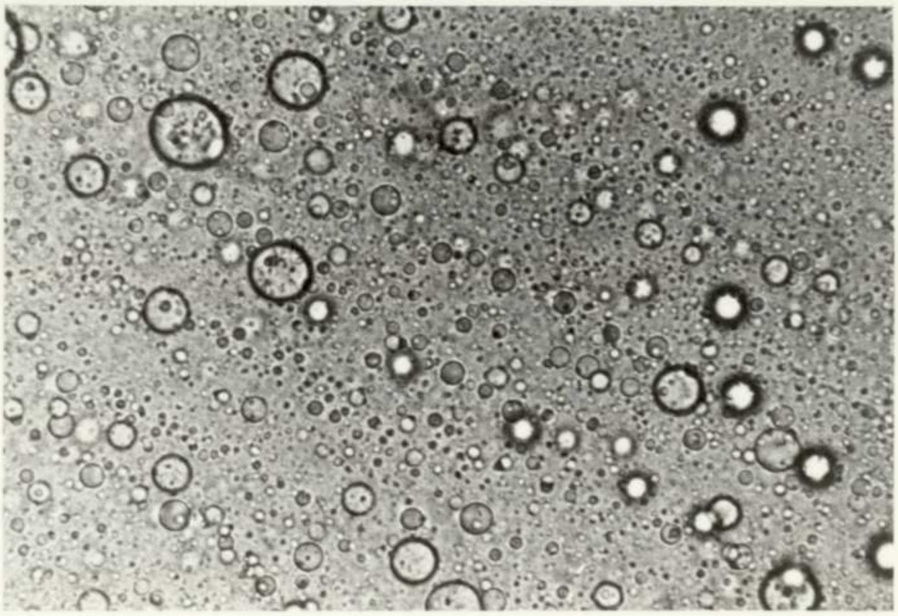
(X 200)   Plate No 2

LDPE + 0.5 % PS processed in Torque Rheometer



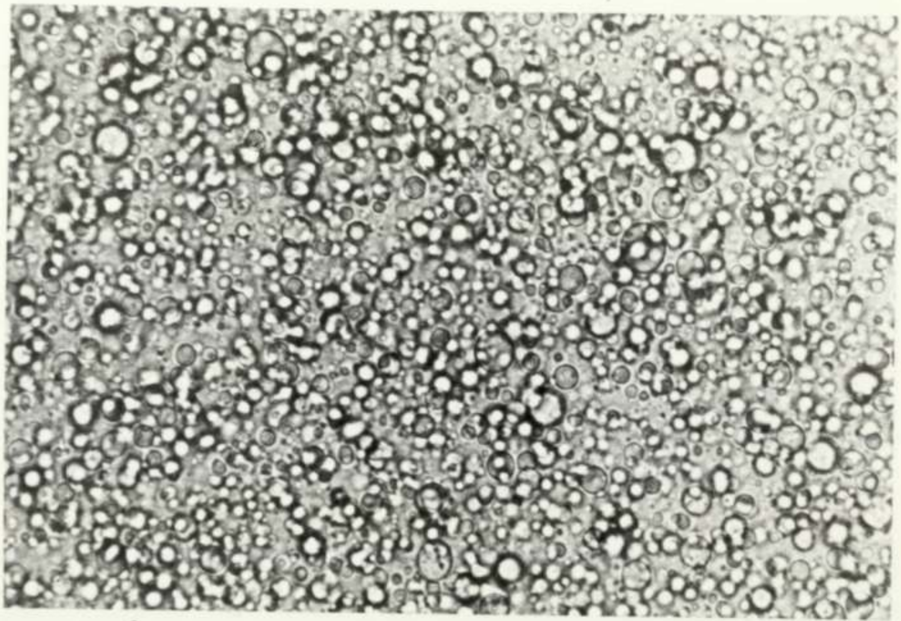
(X 200) Plate No 3

LDPE + 5 % PS processed in Torque Rheometer



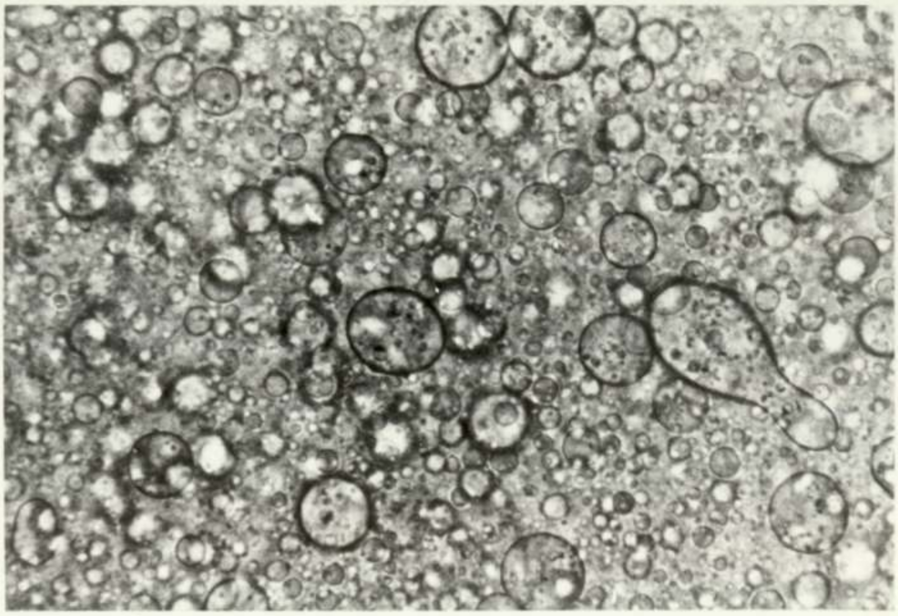
(X 200) Plate No 4

LDPE + 5 % PS processed in Brabender



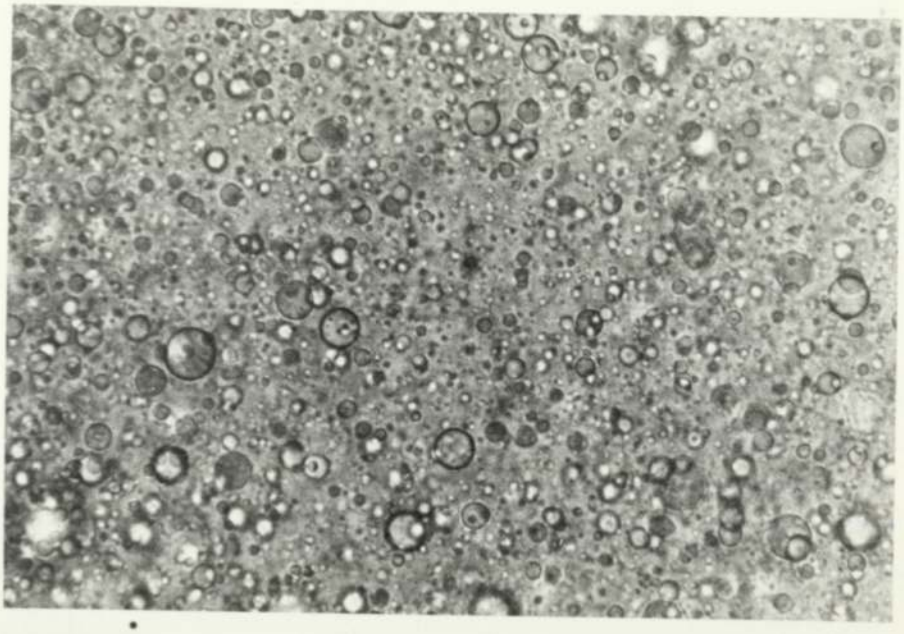
(X 200) Plate No 5

LDPE + 10 % PS processed in Torque Rheometer



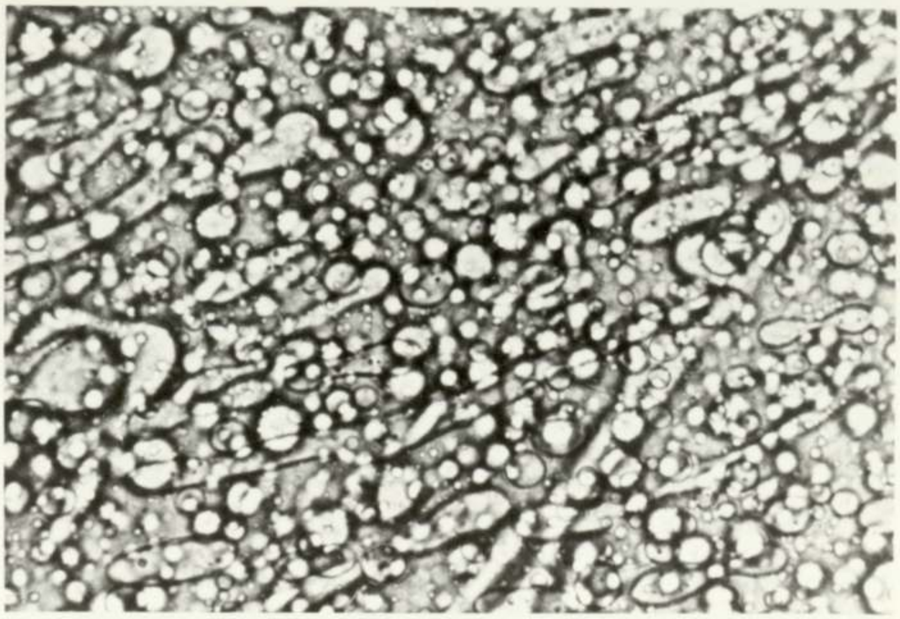
(X 200) Plate No6

LDPE + 10 % PS processed in Brabender



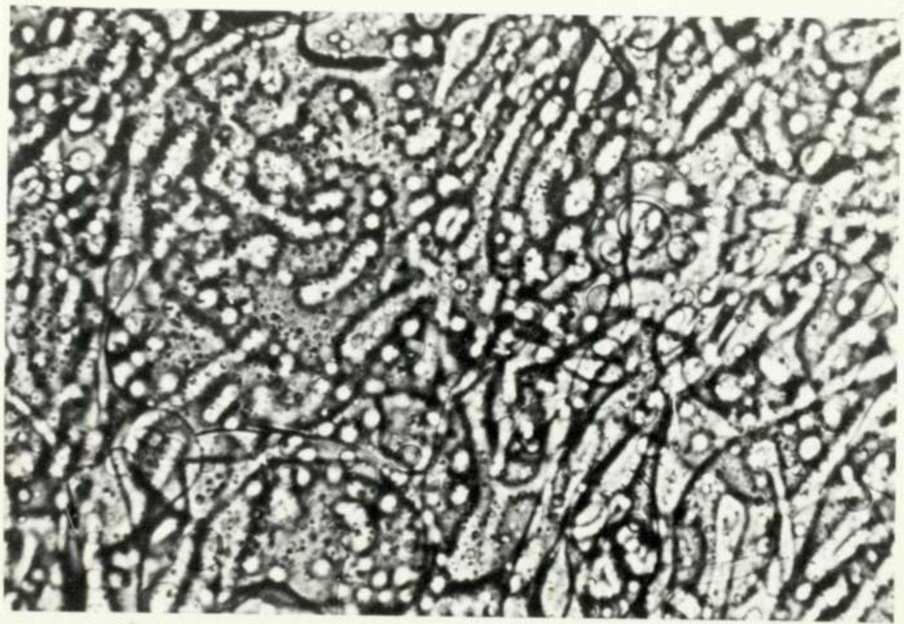
(X 200)   Plate No 7

LDPE + 30 % PS processed in Torque Rheometer



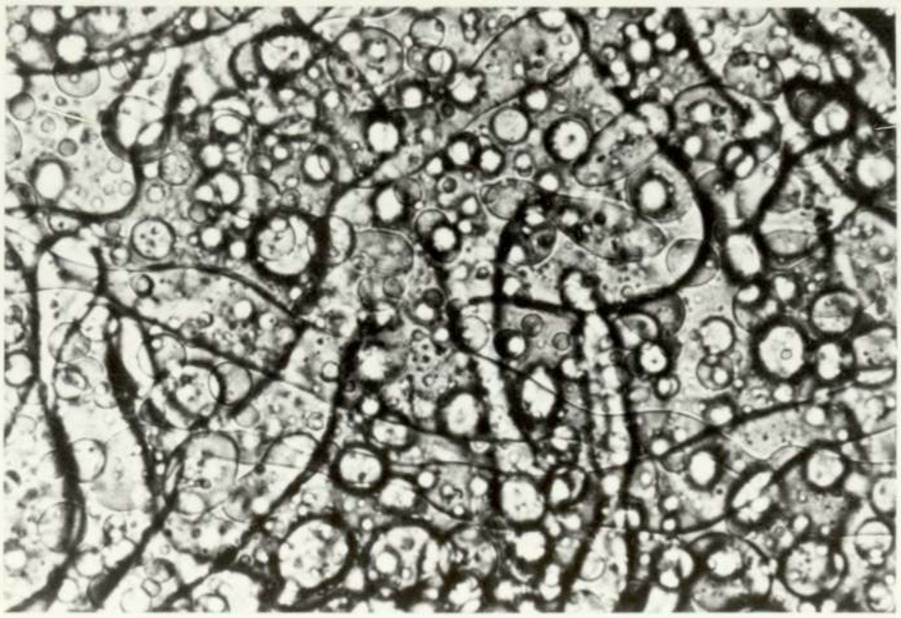
(X 200)   Plate No 8

LDPE + 30%PS processed in Brabender



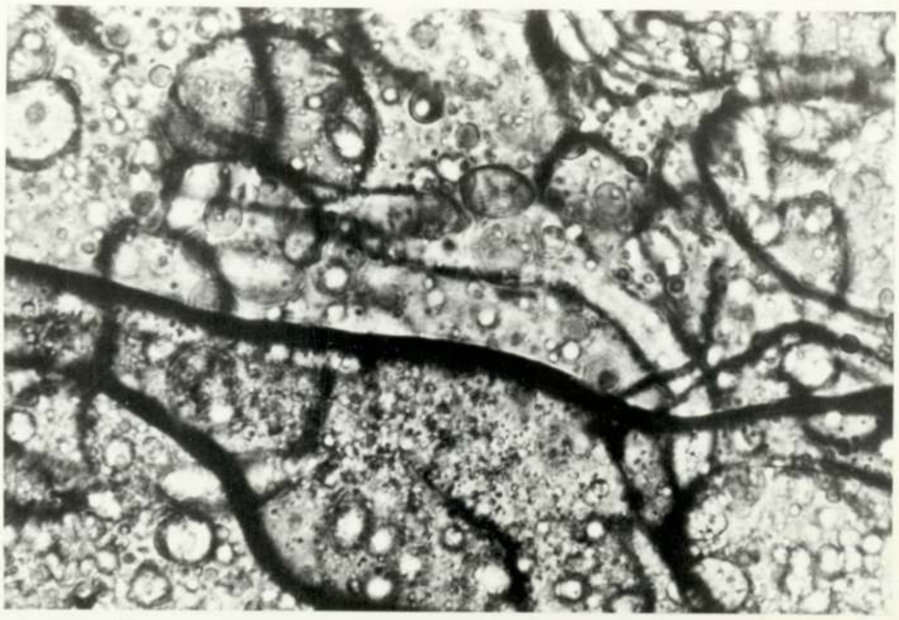
(X 200)   Plate No 9

LDPE + 40 % PS processed in Torque Rheometer



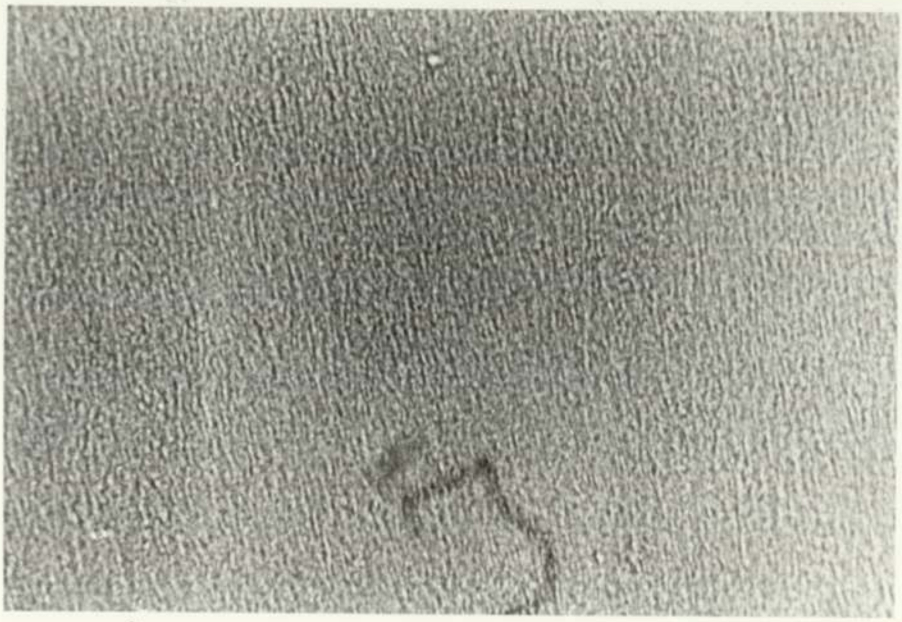
(X 200)   Plate No 10

LDPE + 50 % PS processed in Torque Rheometer



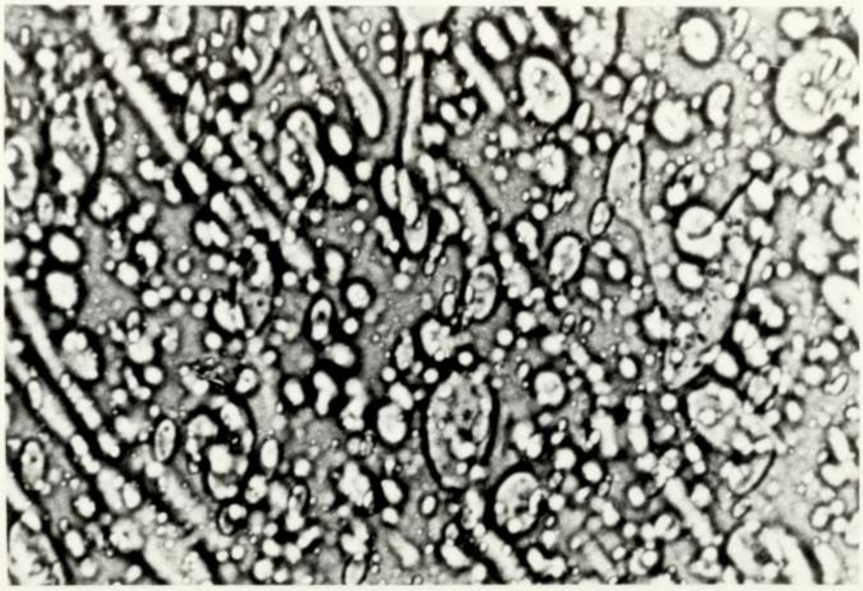
(X 100)   Plate No 11

LDPE + 80 % PS processed in Torque Rheometer



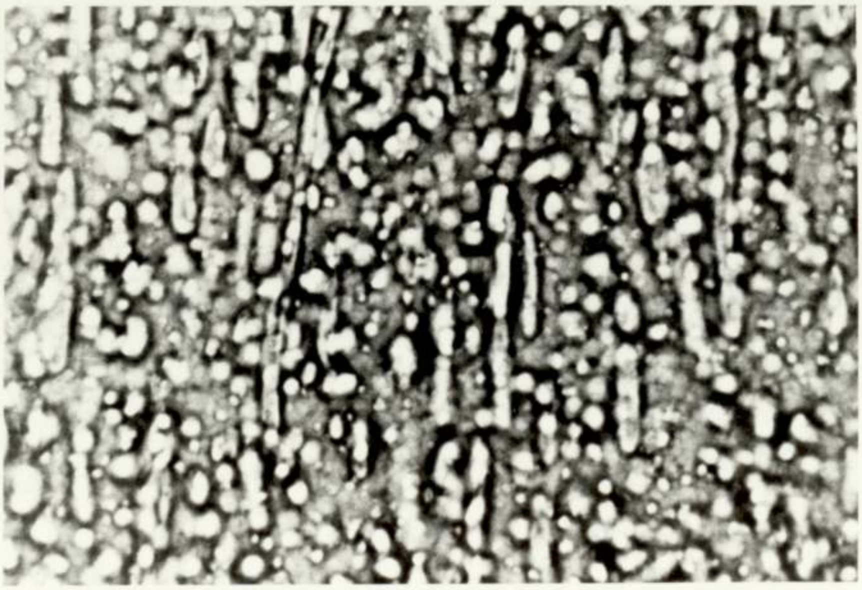
(X 200)   Plate No 12

LDPE-PS copolymer containing 42 % bounding



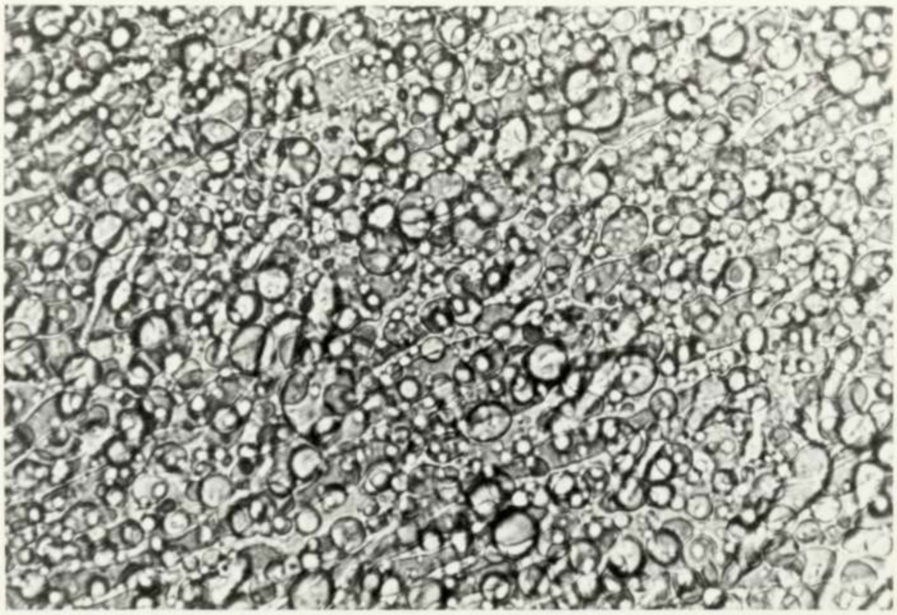
(X 200) Plate No 13

LDPE/PS (50/50) + 10 % copolymer processed in Torque Rheometer



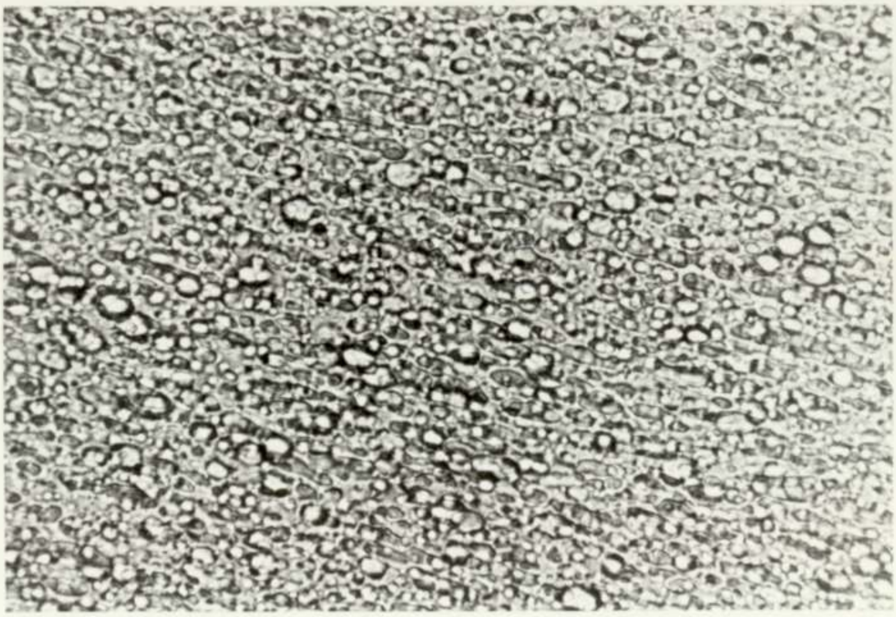
(X 200) Plate No 14

LDPE/PS (50/50) + 20 % copolymer processed in Torque Rheometer



(X 200)   Plate No 15

LDPE/PS (50/50) + 30 % copolymer processed in Torque Rheometer



(X 200)   Plate No 16

LDPE/PS (50/50) + 50 % copolymer processed in Torque Rheometer.

CHAPTER FIVE

Effect of SPD's on Thermal and Photo-degradation of Polyblends

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5-1 Introduction. Degradation involves rapture of chemical bonds in the main chain of the macromolecules. Depending on the type of chemical bond (σ or π bond), two mechanisms of polymer degradation are possible: radical and ionic-radical.(174) If the bond between the atoms of the main chain is covalent, rapture of the macromolecules will involve the formation of free macroradical which can be detected by electron spin resonance (ESR) .

Depending on the chain structure, it is possible to distinguish between physical and chemical degradation. Physical degradation involves degradation by heat, mechanical shear and phtochemical chain scission. Chemical degradation occurs under the action of various chemical agents. The most important types of chemical degradation are: oxidative degradation, hydrolysis, alcoholysis and aminolysis. However, during the degradation of polymers, such effects as discolouration, surface cracking and deterioration of mechanical properties are also manifested.(175) It has been found that surface cracking or embrittlement can lead to drastic reduction in toughness, tensile strength and elongation at break of the polymers.

Degradation of polymers can take place at two general stages. The first occurs during fabrication of the polymers, that is during different processes such as moulding or extruding into the form in which they are to be used. This stage is characterized by exposure to relatively high temperatures over short times. Degradation of some polymers can and probably does take place during preparation of SPD's by mechano -chemical methods(see Chapter 2).Protection of polymers in this stage is impractical, since stabilizers that inhibit deterioration usually retard polymerization. Extreme conditions such as high temperature and mechanical stress can itself cause deterioration. The presence of impurities introduced into a small fraction may act as simultaneous accelerating deterioration of the polymers during their service lives.

The second important period of exposure is long-term aging. During this stage,polymers are exposed in ultra-violet light, heat and/or affected by chemical agents and invironmental factors. Although temperature and mechanical stress are usually lower during aging than during fabrication,the time of exposure is much longer, under practical applications,degradation takes place during this period. Polymer stabilization should therefore take into account both types of exposure .

Macroradicals formed during degradation may enter into various reactions ,resulting in end products of linear,branched or cross-linked structure.This will be discussed in the following sections. However, in some cases mechanical degradation is used purposely to obtain products with lower molecular masses,e,g,mastication of natural rubber.Synthesis of solid phase dispersants by mechano - chemical methods is based on this advantage (see Chapter 2).

5-2 General Factors in Polymer Deterioration

The chemical composition of polymers change during ageing as a result of a complex sequence of reactions. The molecular weight of polymer is often changed considerably,but deterioration can occur with no significant change in the size of molecules.As was mentioned earlier,change in molecular weight can be related to the chain scisson and crosslinking(see section 3-6) and both reactions can take place simultaneously in many polymers.The rate of these two different kinds of reactions are dependent on the polymer structure and reaction conditions.

Chemical bonds in polymers are broken under a variety of conditions.For example, chemical reactions,ionizing radition, heat and mechanical stress.to form free radicals as the first products. These are relatively short-lived and react rapidly with other polymeric molecules or with available reactants.However,chain scission occurs, when chemical bonds of the backbone chain are broken irreversibly.

Recombinations of radicals can also occur to reverse the process of chain scission,because of the restricted motion in polymer matrix.

$$-CH_2-CH_2- \underset{\text{recombination}}{\overset{\text{chain scission}}{\rightleftarrows}} -\dot{C}H_2 + \dot{C}H_2- \quad (5\text{-}1)$$

However , it is important to note that in the presence of some chemical reactants such as oxygen, rapid addition to alkyl radicals occurs and the original molecules can not reform.

$$-\dot{C}H_2 + O_2 \longrightarrow -CH_2-O-O. \quad (5\text{-}2)$$

Peroxy radicals can react with alkyl radicals according to the following reaction.

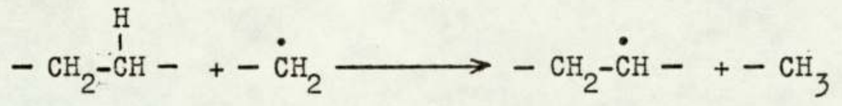
$$-CH_2-O-O^{\bullet}+{}^{\bullet}CH_2- \longrightarrow -CH_2-O-O-CH_2- \qquad (5\text{-}3)$$

Chain scission can be a random reaction ,occuring at any position along the backbone chain and resulting in a broad spectrum of molecular weight(see Fig 3 - 6). Polyethylene, polypropylene and many condensation polymers undergo random chain scission.(177) For some polymers such as poly(α-methyl styrene) and polytetrafluoro ethylene , chain scission leads to formation of their monomers (depolymerization) in the absence of oxygen.(177)

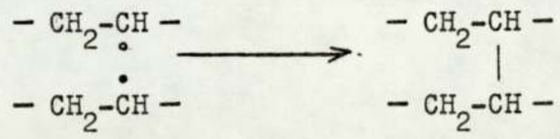
5 - 3 Crosslinking Reactions and Their Effects on The Mechanical Properties of Polymers

Radicals which are formed in polymers by cleavage of chemical bonds during degradation process may not be the backbone chain. A common example is cleavage of a carbon-hydrogen bond to form a polymer radical and a hydrogen atom. The latter may combine with another proton from a neighbouring molecule to form a second polymeric free radical. Combination of these free radical fragments leads to a crosslinked reaction. In the case of LDPE ,the following reactions might be considered.

$$\text{LDPE} \xrightarrow{\text{mechanical shear}} -\dot{C}H_2 \qquad (5\text{-}4)$$



$$-CH_2-\overset{\overset{H}{|}}{C}H- \;+\; -\dot{C}H_2 \longrightarrow -CH_2-\dot{C}H- \;+\; -CH_3 \quad (5\text{-}5)$$



$$\begin{array}{c}-CH_2-\underset{\circ}{C}H-\\ -CH_2-\dot{C}H-\end{array} \longrightarrow \begin{array}{c}-CH_2-CH-\\ |\\ -CH_2-CH-\end{array} \quad (5\text{-}6)$$

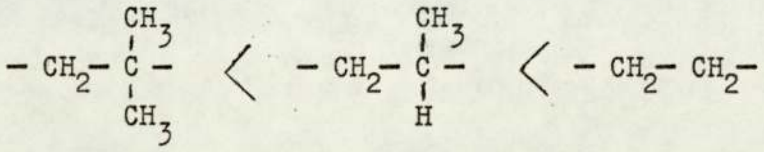
In the presence of oxygen ,the peroxy radicals which are formed can combine together.These crosslinks are less stable than those composed of carbon-carbon bonds and subsequently break to give two new free radicals.(176)

In contrast to chain scission , crosslinking reactions increase the molecular weight of polymers.However,both chain scission and crosslinking reactions have a considerable effect on mechanical properties of polymers. As will be shown latter, reduction of molecular weight through chain scission leads to decrease of Young's modulus,tensile strength and other related properties. As network structures develop through crosslinking polymers become brittle, elongation at break decreases and ultimately,insoluble gel structures are formed.(see section 3-4-2).

5-4 Effect of Chemical Structure on Degradation of Polymers

Generally,the rate at which the mechanical properties of a polymer deteriorates depends on the strength of chemical bonds in its structure.The energy required to cleave individual bonds can vary considerably, depending on the complexity and inhomogenety of the polymer.

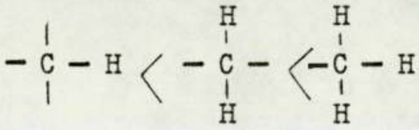
The presence of branching and certain side groups in polymer molecules, contribute to the lowering of bond strengths. In the following polymers, thermal stability decreases as branch groups are added to the basic polyethylene chain.(176)



$$-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}- \;<\; -CH_2-\underset{H}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}- \;<\; -CH_2-CH_2- \qquad (5\text{-}7)$$

polyisobutylene polypropylene polyethylene

The ease of hydrogen abstraction from a polymer molecule(carbon-carbon bond cleavage) usually indicates the ease of degradation by oxidation. The rate at which these reactions occur therefore, depends on the type of carbon- hydrogen bond(primary, secondary and tertiary)in the polymer. The strength of carbon-hydrogen bond decreases in the following order.(180)



$$-\overset{|}{\underset{|}{C}}-H \;<\; -\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}- \;<\; -\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}-H \qquad (5\text{-}8)$$

III II I

Consequently, at branch point in a polymer, (III) hydrogen is more readily abstracted than those of ethylene groups (II) or the hydrogens of methyl groups (I).

Another factor which influence the ease of hydrogen abstraction is the presence of aromatic groups in the polymer. For example, both polystyrene and polypropylene have only one labile hydrogen in each repeating unit. But in polystyrene there is a benzylic hydrogen,which should be more reactive than the labile hydrogen in polypropylene. Therefore, it is expected that the oxidation rate of polystyrene should be more rapid than that of polypropylene. In practice the oxidative stability of polystyrene is much greater than that of polypropylene and is even higher than that of polyethylene which has less labile hydrogens than polypropylene.

The unusual stability of polystyrene may result from shielding effect of the bulky phenyl group or from loss in resonance energy caused by unfavourable orientation of phenyl groups in the crowded structure.(178-179) Hansen and co-worker(179) have shown that,the effect oxidative stability decreases rapidly as methyl groups are introduced between the phenyl groups and the main chain.(see Table 5-1)

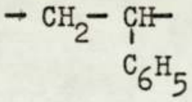
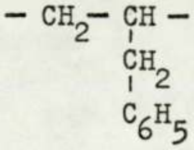
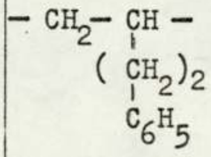
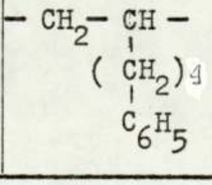
polymer	structure	induction period(hr) at 80°C	 at 110°C
polystyrene	 $-CH_2-CH(C_6H_5)-$	-	10000
poly(3-phenyl 1-propen)	 $-CH_2-CH(CH_2C_6H_5)-$	10000	1900
poly(4-phenyl 1-butene)	 $-CH_2-CH((CH_2)_2C_6H_5)-$	500	30
poly(6-phenyl 1-hexene)	 $-CH_2-CH((CH_2)_4C_6H_5)-$	200	13

Table 5-1 Oxidative stability of polystyrene and related polymers.

5-5 Effect of Physical Structure on Degradation of Polymers

Deterioration of mechanical properties of polymers not only depends on their chemical structure described earlier, physical structure or morphology of polymers are also important in this respect.

Usually, the effects of physical structure are related to the arrangement of molecules in ordered (crystalline) and disordered (amorphous) regions present in the polymer matrix. Many polymers are semicrystalline and have both oriented and unoriented regions and the rate of deterioration depends on the permeation of the reactants into the polymer matrix (amorphous region). Therefore, the factors influencing permeability have an important effect on polymer degradation.

Permeability of reactants into a polymer matrix is dependent on the density of the polymeric materials which vary with the degree of crystallinity and the compactness of amorphous and crystalline regions. Many studies have been carried out on the degradation of polyolefins and the effect of permeation and crystallinity have been extensively studied.(181,182)

Scott and co-workers(212) have investigated the effect of glass transition temperatures of polybutadiene,high impact polystyrene and crystal polystyrene on the photo-oxidation of these polymers.They found that rate of diffusion of oxygen in polybutadiene is higher than that in HIPS and PS,since polybutadiene has the lowest Tg.

5-6 Mechanical Aspects of Thermal and Photo-degradation of LDPE, PS and LDPE / PS Blends Containing Solid Phase Dispersants(SPDs)

In the following sections the molecular structure of LDPE and PS are first described and then the effect of thermal and photo - oxidation on the mechanical and dynamic mechanical properties of these polymers and their blends containing the corresponding copolymers will be described.

5-6-1 Molecular Structure of LDPE

Linear or unbranched polyethlene has the simple structural formula $CH_3-(CH_2-CH_2)_n-CH_3$, but this structure is not closely maintained by polyethylene prepared by commercial processes

High pressure polymerized polyethylene contains not only methylene groups, but also several methyl groups per molecule,depending on the molecular weight of the polymer. The methyl groups ($-CH_3$) are associated with branching in the molecule. Different polymerization conditions cause variation in branching and physical characteristics. Polyethylene is therefore,classified into two distinct types,low-density polyethylene (LDPE) and high density polyethylene (HDPE). The latter is characterized by a more linear structure and the former is identified as non-linear or branchd. The presence of some branching in LDPE allows less close packing of the molecules giving a lower density and crystallinity compared with HDPE.

Investigation of LDPE prepared by high pressure processes using infra-red spectroscopy indicates the presence of a bout 20 to 30 methyl groups per 1000 carbon atoms.(184,185) It appears from the above formula that, a completely linear polyethylene should have a maximum of two methyl groups per molecule(at the terminal positions) and any excess over this number must be related to branches.

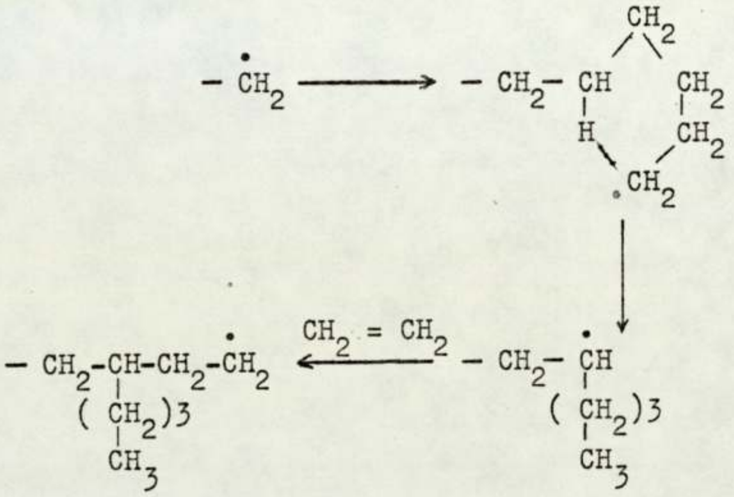
Cross and co-workers(186) reported that the content of methyl group can be quantitatively measured by the intensity of absorption bond at range 1378 cm^{-1}(7.26μ). From their results, it was found that a typical LDPE of molecular weight 32000 and M F I =1.8(the amount of polymer extruded through a standard die in a given time), contains 23 methyl groups per 1000 carbon atoms and 52 methyl groups per molecule. This indicated 50 branches points in the chain.

Although, the presence of branches in LDPE has been established, the length of such branches is still under debate, and it is assumed that, both short and long branches are present in the polymer. The first report by Elliot(187) and co-workers suggested the presence of methyl groups and butyl branches in the polymer by IR-spectroscopy. This was confirmed by Harlen(213) and Dole(214) on analysing the gaseous products obtained by high energy irradition of polyethylene. They concluded that, since the products obtained from irradiation of LDPE are mainly hydrocarbons containing 2 to 4 carbon atoms, the branches present in the polymer might have a similar carbon skeleton.

5-6-2 Formation of Branches in LDPE

5-6-2-1 Formation of Short Branches.

The branches with only 2 to 4 carbon atoms result from intramolecular chain transfer or " back-biting " of the growing radical involving formation of six member ring which can be shown as follows.

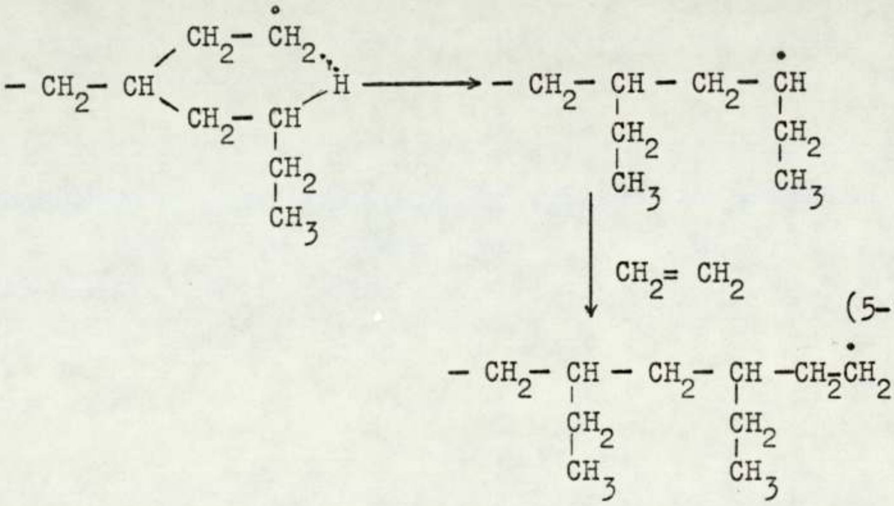


(5-9)

(5-10)

5-6-2-2 Formation of Ethyl Branch

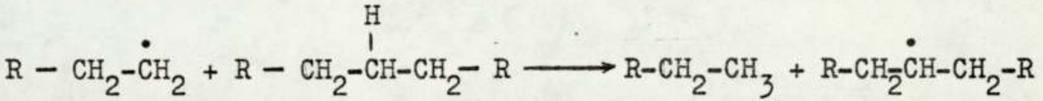
Ethyl branches in LDPE also are formed by intramolecular chain transfer according to the following reactions.(190)



(5-11)

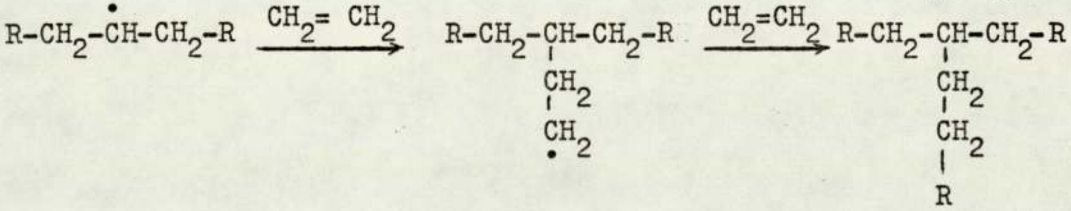
5-6-2-3 Formation of Long Chain Branches

Although, most of the branches in LDPE are short, there are a few long chain branches which could be produced by termination of a growing chain by hydrogen transfer from a dead polymer(190)(intermolecular hyrogen transfer).



$$R-CH_2-\overset{\bullet}{C}H_2 + R-CH_2-\overset{H}{\overset{|}{C}}H-CH_2-R \longrightarrow R-CH_2-CH_3 + R-CH_2-\overset{\bullet}{C}H-CH_2-R \qquad (5-12)$$

(5-13)



$$R-CH_2-\overset{\bullet}{C}H-CH_2-R \xrightarrow{CH_2=CH_2} R-CH_2-\underset{\underset{\overset{|}{\overset{\bullet}{C}H_2}}{\overset{|}{CH_2}}}{CH}-CH_2-R \xrightarrow{CH_2=CH_2} R-CH_2-\underset{\underset{\underset{R}{\overset{|}{\overset{|}{CH_2}}}}{\overset{|}{CH_2}}}{CH}-CH_2-R$$

5-7 Effects of Branching on the Properties of LDPE

There is no doubt that branching in LDPE or any polymer greatly effects its physical and chemical properties . The short branches have a considerable effect on the degree of crystallinity in the polymer.(191)Due to prevention of close packing of molecules in the unit cell. Other properties,like density,melting point,Young's modulus ,elongation at break, impact strength and tensile strength and also permeability to gases and vapours are effected by short branching. Chain branching mainly changes the rheological properties of the polymer,such as viscosity and melt flow index (MFI) and also is responsible for its molecular weigth distribution.

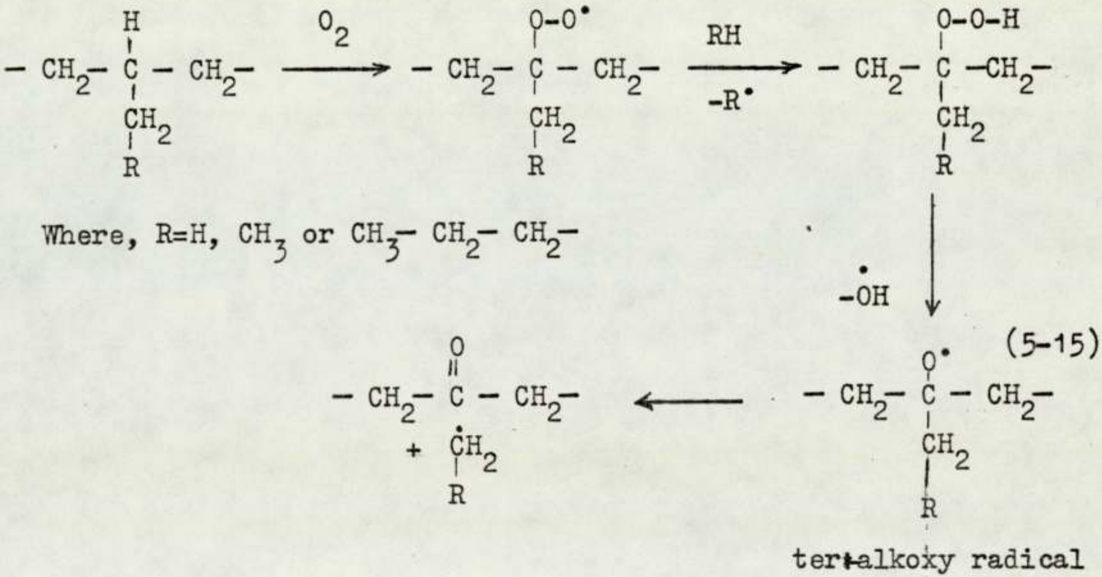
Besides the presence of short and long chain branching in commercial LDPE, this polymer may contains other structural units such as oxygen containg groups, unsaturated groups and transition metal ions. Formation of these structural units are discussed briefly in the following sections.

5-8 Formation of Carbonyl Group in LDPE

It is well known that oxygen containing groups such as carbonyl and peroxide are formed in commercial LDPE by thermal oxidation during polymerization(due to the presence of oxygen or peroxide) or during subsequent processing stages such as compounding ,film making etc.

Oxidation of LDPE takes place preferentially at branch points, (tertiary carbon atom) by the following mechanism.(192)

(5-14)



$$-CH_2-\overset{H}{\underset{\underset{R}{CH_2}}{C}}-CH_2- \xrightarrow{O_2} -CH_2-\overset{O-O^{\bullet}}{\underset{\underset{R}{CH_2}}{C}}-CH_2- \xrightarrow[-R^{\bullet}]{RH} -CH_2-\overset{O-O-H}{\underset{\underset{R}{CH_2}}{C}}-CH_2-$$

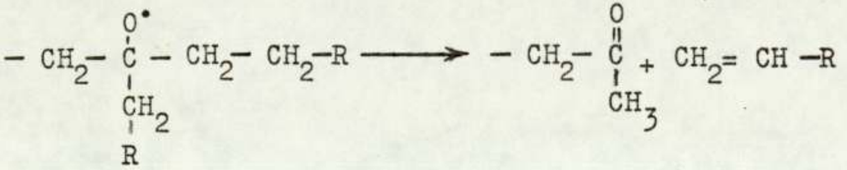
Where, R=H, CH_3 or $CH_3-CH_2-CH_2-$

(5-15)

$$-CH_2-\overset{O^{\bullet}}{\underset{\underset{R}{CH_2}}{C}}-CH_2- \longrightarrow -CH_2-\overset{O}{\overset{\|}{C}}-CH_2- + \underset{R}{\dot{C}H_2} \quad (-\dot{O}H)$$

$$\dot{O}H + R-\dot{C}H_2 \longrightarrow R-CH_2OH \qquad (5\text{-}16)$$

It is expected that β scission of tert-alkoxy radical(5-15) takes place.In this case,ketonic group at the chain end(methyl ketone) is formed.



$$-CH_2-\overset{O^{\bullet}}{\underset{\underset{R}{CH_2}}{C}}-CH_2-CH_2-R \longrightarrow -CH_2-\overset{O}{\overset{\|}{\underset{CH_3}{C}}} + CH_2=CH-R \qquad (5\text{-}17)$$

5-9 Formation of Unsaturation in LDPE

It has been found that LDPE contains three different olefinic double bonds,namely :

I-Vinyl group or terminal double bond : $R - CH = CH_2$

II-Internal or chain double bond : $R - CH = CHR$

III- Vinylidene or side chain methylene group: $CH_2 = \underset{R2}{\underset{|}{C}} - R_1$

Vinylidene groups or side chain methylene groups are predominant in LDPE comprising about 68 % of the total unsaturation present in LDPE,wheras ,high density polyethylene mainly contains terminal unsaturation(about 94 %).

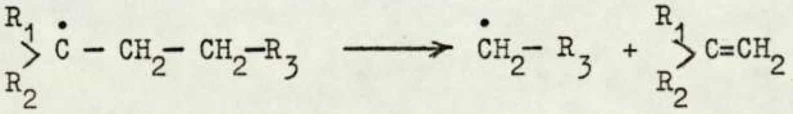
The presence of vinylidene groups in LDPE is confirmed by IR-spectroscopy(absorption peak at 888 cm^{-1}). IR absorption of some functional groups are shown in Table 5-2.(193)

Functional group	Absorption bond(cm^{-1})	Functional group	Absorption bond (cm^{-1})
terminal ketone	1725 ±	internal unsaturation	1645±1
internal ketone	1720 ±	aldehyde	1735
hydroxyl group	3400	ester group	1748
carboxilic acid	1710	butyl group or	984±1
vinylidene double bond	887 ±1	ethyl group	
terminal double bond	909	per acid or ester	1785

Table 5-2 Infra-red absorption of different functional groups present in LDPE.(193)

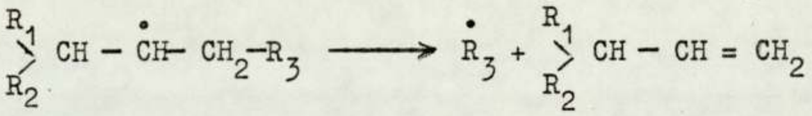
Unsaturation in commercial LDPE is believed to be formed by thermal degradation or depolymerization reaction at high polymerizing temperatures or at high temperaturesof processing of the polymer.Formation of the three different types of olefinic double bonds can be shown as follows.(194,195)

(5-18)



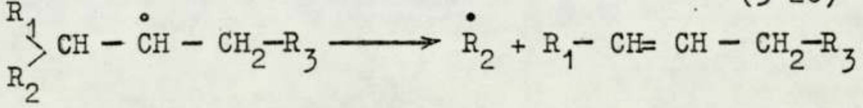
$$\begin{matrix}R_1\\R_2\end{matrix}\!>\dot{C}-CH_2-CH_2-R_3 \longrightarrow \dot{C}H_2-R_3+\begin{matrix}R_1\\R_2\end{matrix}\!>C{=}CH_2$$

(5-19)



$$\begin{matrix}R_1\\R_2\end{matrix}\!>CH-\dot{C}H-CH_2-R_3 \longrightarrow \dot{R}_3+\begin{matrix}R_1\\R_2\end{matrix}\!>CH-CH=CH_2$$

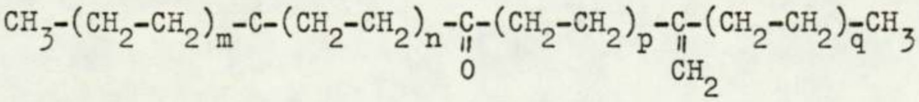
(5-20)



$$\begin{matrix}R_1\\R_2\end{matrix}\!>CH-\overset{\circ}{C}H-CH_2-R_3 \longrightarrow \dot{R}_2+R_1-CH{=}CH-CH_2-R_3$$

It also assumed that the primary radicals formed during degradation of LDPE can continue the chain reaction by removing a hydrogen atom from another molecule.

From the foregoing discussions it appears that the main structural features in LDPE which largely determines its reactivity towards,light,heat,oxygen and other chemical agents are main chain branching,carbonyl and vinylidene groups. So,the following generalized structural formula can be proposed for commercial LDPE.



(5-21)

$$CH_3-(CH_2-CH_2)_m-C-(CH_2-CH_2)_n-\underset{\underset{O}{\parallel}}{C}-(CH_2-CH_2)_p-\underset{\underset{CH_2}{\parallel}}{C}-(CH_2-CH_2)_q-CH_3$$

Where, R = H,CH_3 or C_3H_7

5-10 Structure of Polystyrene

There is experimental evidence that polystyrene has a head to tail structure.Since the arrangement of styrene skeltons in the compounds obtained by pyrolysis of this polymer in vacuo at 290 - 320 °C is head to tail,it is reasonable to conclude that the same arrangement predominates in polystyrene itself.(157)

Polystyrene produced by free radical polymerization techniques is atactic and therefore non-cystalline. However,isotactic PS has been prepared by the use of Ziegler-Natta catalysts. Isotactic PS has a high crystalline melting point of 230 °C,which makes it a difficult to process,also it has less transparency and more brittelness than the atactic polymer.(158) For these reasons atactic polystyrene has achieved commercial importance.

The polystyrene used in the present study was atactic in"crystal" form named " Corinex General Purpose " and was supplied by Shell Chemical Company LTD.

5-11 Experimental

In order to study the effects UV-irradiation on LDPE/PS blends containing different ratios of the corresponding copolymers as a soild phase dispersant (SPD), different amounts the LDPE / PS copolymers (10,20 and 50 %) containing 40 % PS were added to LDPE. The samples were processed in the Torque Rheometer (see section 3-2) at 170 °C under N_2 gas for 30 minutes (closed and full chamber).After processing the samples were discharged from the mixer into cold water,then they compression moulded to prepare films with thickness about 0.01 cm.(see section 3 - 3). The samples were cut in small peices (2 X 2 cm), attached them to standard paper frame and mounted in the UV cabinet (section 4-). After different periods of time , the exposured samples were tested by IR-spectroscopy (section 4- 1) to study changes of some important functional groups influence in the mechanical properties of the samples. The results obtained by the IR-spectroscopy are shown in Figs 5-1 to 5-5 .

In order to obtain the effects of photo-oxidation on the mechanical and dynamic mechanical of the samples,the sample films were prepared by tensile strength and Rheovibron's cutter (see sections 4- 3 and 4- 5). The specimens attached to card-board papers and mounted in the UV cabinet.After different perids of time ,the samples were tested by the tensile measurement machin and by the Rheovibron. The samples tested by the Rheovibron were returned to the UV cabinet for the next tests. The results are shown in Figs 5-8-to5-11.

5-12 Results and Discussions

Infra-red spectrum of uv-irradiated ,LDPE,PS and LDPE/PS blends containing different ratios of the corresponding copolymers (10,30 and 50 %) are shown in Figs 5-1to5-5 . The IR specra of the processed LDPE shows a band at the 3555 cm^{-1} (Fig 5-1) which is due to O-H streching of hydroperoxide.(159)This band was calculated as hydroperoxide index (A 3555 / A 1895)cm^{-1},(see Fig 5-8). As was mentioned before, a good correlation was obtained between hydroperoxide measured by the IR spectroscopic method and hydroperoxide measured by the Iodometric technique (see sections 3- 4 and Fig 3-2).

Infra-red absorption spectrophotometry has been used to determine the nature of oxidation products and the rate of their formation during thermal and photo-oxidation of LDPE by Oaka,Richards(161) and Scott.(160) However , photo-oxidation of LDPE results in the build-up of different products,for example, hydroxyl,carbonyl and changes in the unsaturation groups described earlier. The rate of photo-oxidation was measured by the rate of formation of carbonyl (Fig 5-8,No1). It was found that the rate of carbonyl formation increases as the ratio of the SPD is increased in the samples ,since polystyrene has less photo-stability than low-density polyethylene. Scott and co-worker(160) have investigated the effect of concentration of PS during photo-oxidation of LDPE .

The change of vinylidene group at 890 cm^{-1} and formation of vinyl at 910 cm^{-1} are shown in Fig 5-8,Nos3 and 2 respectively.It was found that the vinylidene functional group concentration decreases slighty up to 100 hrs exposure and then decreases rapidly to the lowest value. Formation of the vinyl functional group up to about 100 hrs exposure is not considerable ,but then its concentration increases rapidly with exposure time.

Figures 5-2 and 5 - 11 show the development of the IR absorbance of polystyrene film on photo and thermal oxidation respectively. As was mentioned earlier, PS has less photo-stability and high thermo-stability than LDPE,so the development of the functional groups on thermal oxidation of PS is not discussed. However ,the Uv exposed PS film shows a broad peak at 3440 cm^{-1} and a slightly less intense but sharper band at 3540 cm^{-1}. These have been attributed to tertiary benzylic alcohol and secondary methylenic(3440 cm^{-1}) and tertiary hydroperoxide (3540 cm^{-1}) respectively (see Scheme 5-1, reactions 5-23 and 5-25). As it was mentioned formation of these functional groups are negligible(see Fig 5-9).

The IR spectra of Uv exposured PS shows a small but sharp peak at 1705 cm^{-1} which is attributed to the formation of carboxylic acid(162) (Fig 5-2) . Also ,peaks at 1720 cm^{-1} and 1705 - 1725 cm^{-1} have been attributed to formation of saturated carbonyl groups. A part from the groups mentioned above, a sharp and broad peak at 1735 cm^{-1} is seen. This peak has been attributed to formation of saturated ester group(164). The data obtained from photo- degradation of PS, LDPE and LDPE/PS blends containing the corresponding copolymers are shown in Figs 5-11, 5-8 and 5-10 respectively. As it is shown in Fig 5 -10 rate of formation of carbonyl group in LDPE/PS blend is more than that in the corresponding graft copolymer. It is believed that occupation of benzylic hydrogen by graft points decreases possibility of photo-oxidation of the SPD by benzylic hydrogen transfer mechanism and only photo-degradation of the sample takes place by methylenic hydrogen transfer mechanism (see Schemes 5-1 and 5-2).

The effects of photo-oxidation on the mechanical properties of the samples (LDPE, PS and LDPE/PS blends containing different ratios of the SPD) are shown in Figures 5-12 to 5-15 . It was found that the elongation at break, tensile strength and also impact strength of the samples decreased during photo -degradation and it was found that ,although the rates of mechanical deterioration of the blends are more than that of the corresponding copolymers during photo-oxidation ,this rate increases with increase in ratio of the SPD in the samples. As was mentioned earlier this effect is due to the low photo-stability of PS in the samples.

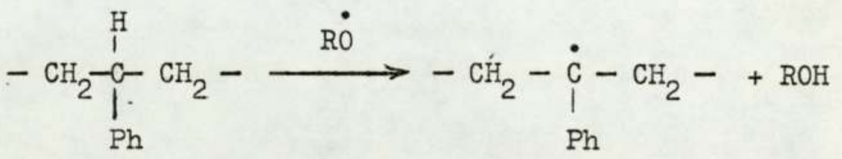
The complete dynamic mechanical spectra of PS,LDPE,LDPE/PS(50/-50) and the corresponding copolymer (containing 40 % of bonding after extraction) are shown in Figures 5-16 to5-18 respectively.

The tests were carried out from -100 to 110 °C for the uv exposured crystal PS film and from -140 to 110 °C for the other exposured samples. A small discrete damping peak was observed at -85 °C for PS sample before uv-irradiatin with maximum tan δ value 0.01. This discrete peak also has been reported by Scott and co-workers.(212) As the temperature was increased tan δ increased slightly to about 80 °C and then increased sharply to 100 °C which is the glass transition temperature (Tg) of the polymer (Fig 5-16). After 48 hrs irradiation the small damping peak became broader,smaller and shifted to higher temperature (80 °C).This might be due to some cross-linking reation taking place during photo-oxidation.It has been found that ,the corresponding complex modulus increased as the irradiation time increased.

The effect of uv-irradiation on the LDPE and LDPE-PS copolymer is to decrease the peak height at -120 °C .This peak is slightly is broadened and shifted to higher temperatures(-119 to 118 °C). This transition can be attributed to the cross-linking reactions of the exposed samples.The β transition also shifts to higher temperatures and this shift seams to be greater for the graft copolymer. This can be attributed to the decrease of molecular motion of LDPE by the grafted PS which may enhance cross-linking reactions in the samples.

Scheme No 5-1

In the following chemical equations Ph = C_6H_5.

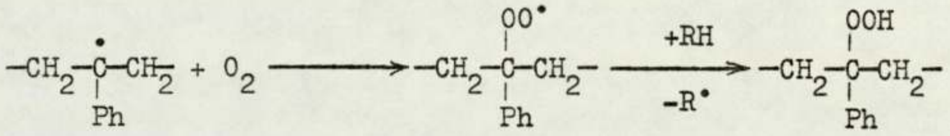


$$-CH_2-\underset{Ph}{\overset{H}{C}}-CH_2- \xrightarrow{R\dot{O}} -CH_2-\underset{Ph}{\dot{C}}-CH_2- + ROH$$

(5-22)

alkoxyl radical abstraction of

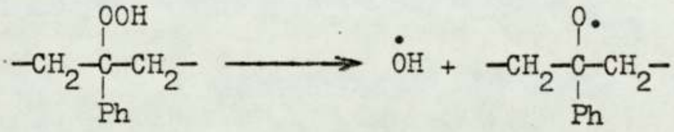
benzylic hydrogen



$$-CH_2-\underset{Ph}{\dot{C}}-CH_2- + O_2 \longrightarrow -CH_2-\underset{Ph}{\overset{OO^{\bullet}}{C}}-CH_2- \xrightarrow[-R^{\bullet}]{+RH} -CH_2-\underset{Ph}{\overset{OOH}{C}}-CH_2-$$

(5-23)

benzylic hydroperoxide
($3540\ cm^{-1}$)

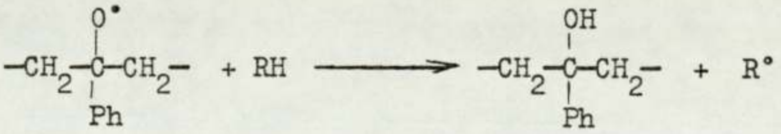


$$-CH_2-\underset{Ph}{\overset{OOH}{C}}-CH_2- \longrightarrow \dot{O}H + -CH_2-\underset{Ph}{\overset{O^{\bullet}}{C}}-CH_2-$$

(5-24)

alkoxyl radical

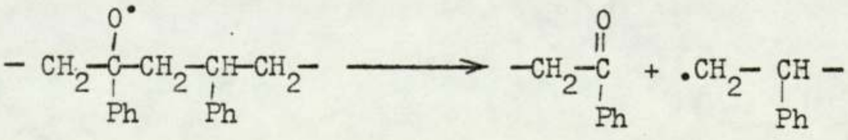
The alkoxyl radical abstracts hydrogen from the polymer chain (5-4) or undergoes scission (5-5).



$$-CH_2-\underset{Ph}{\overset{O^{\bullet}}{C}}-CH_2- + RH \longrightarrow -CH_2-\underset{Ph}{\overset{OH}{C}}-CH_2- + R^{\circ}$$

(5-25)

tertiary benzylic alcohol ($3440\ cm^{-1}$)

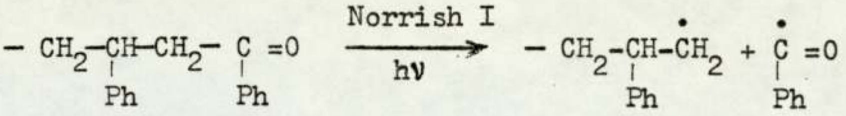


$$-CH_2-\underset{Ph}{\overset{O^{\bullet}}{C}}-CH_2-\underset{Ph}{CH}-CH_2- \longrightarrow -CH_2-\underset{Ph}{\overset{O}{\overset{\|}{C}}} + \cdot CH_2-\underset{Ph}{CH}-$$

(5-26)

acetophenone

Radical production is accompanied by a reduction in molecular weight. The acetophenone undergoes either Norrish type I or Norrish type II

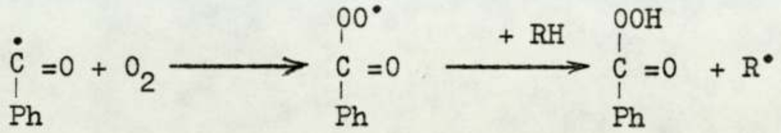


$$-\mathrm{CH_2{-}\underset{Ph}{CH}{-}CH_2{-}\underset{Ph}{C}{=}O} \xrightarrow[h\nu]{\text{Norrish I}} -\mathrm{CH_2{-}\underset{Ph}{CH}{-}\dot{C}H_2} + \mathrm{\underset{Ph}{\dot{C}}{=}O}$$

(5-27)

alkyl and acyl radical

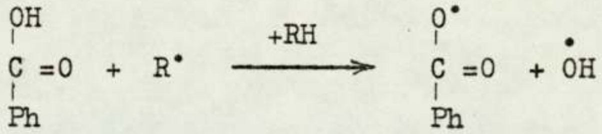
The acyl radical undergoes the following reactions.



$$\mathrm{\underset{Ph}{\dot{C}}{=}O} + \mathrm{O_2} \longrightarrow \mathrm{\overset{OO^{\bullet}}{\underset{Ph}{C}}{=}O} \xrightarrow{+\,\mathrm{RH}} \mathrm{\overset{OOH}{\underset{Ph}{C}}{=}O} + \mathrm{R^{\bullet}}$$

(5-28)

peracid

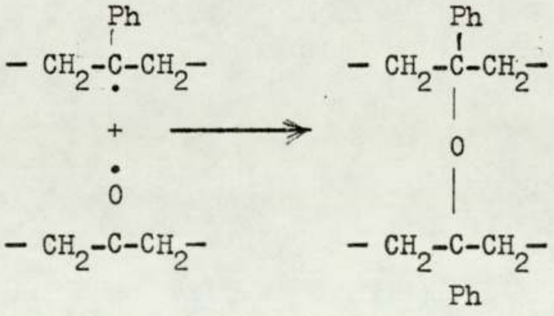


$$\mathrm{\overset{OH}{\underset{Ph}{C}}{=}O} + \mathrm{R^{\bullet}} \xrightarrow{+\mathrm{RH}} \mathrm{\overset{O^{\bullet}}{\underset{Ph}{C}}{=}O} + \mathrm{\dot{O}H}$$

(5-29)

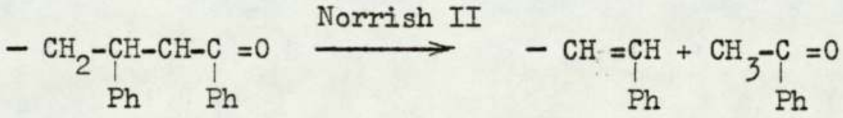
benzoic acid benzylic radical

The benzylic radical and alkyl radical form an ether linkage(1105-1000 $\mathrm{cm^{-1}}$).



$$\begin{array}{c} -\mathrm{CH_2{-}\overset{Ph}{\underset{\bullet}{C}}{-}CH_2{-}} \\ + \\ \mathrm{\dot{O}} \\ -\mathrm{CH_2{-}C{-}CH_2{-}} \end{array} \longrightarrow \begin{array}{c} -\mathrm{CH_2{-}\overset{Ph}{C}{-}CH_2{-}} \\ | \\ \mathrm{O} \\ | \\ -\mathrm{CH_2{-}\underset{Ph}{C}{-}CH_2{-}} \end{array}$$

(5-30)

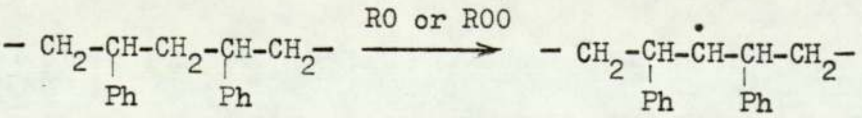


$$-\mathrm{CH_2{-}\underset{Ph}{CH}{-}CH{-}\underset{Ph}{C}{=}O} \xrightarrow{\text{Norrish II}} -\mathrm{CH{=}\underset{Ph}{CH}} + \mathrm{CH_3{-}\underset{Ph}{C}{=}O}$$

(5-31)

Scheme No 5-2

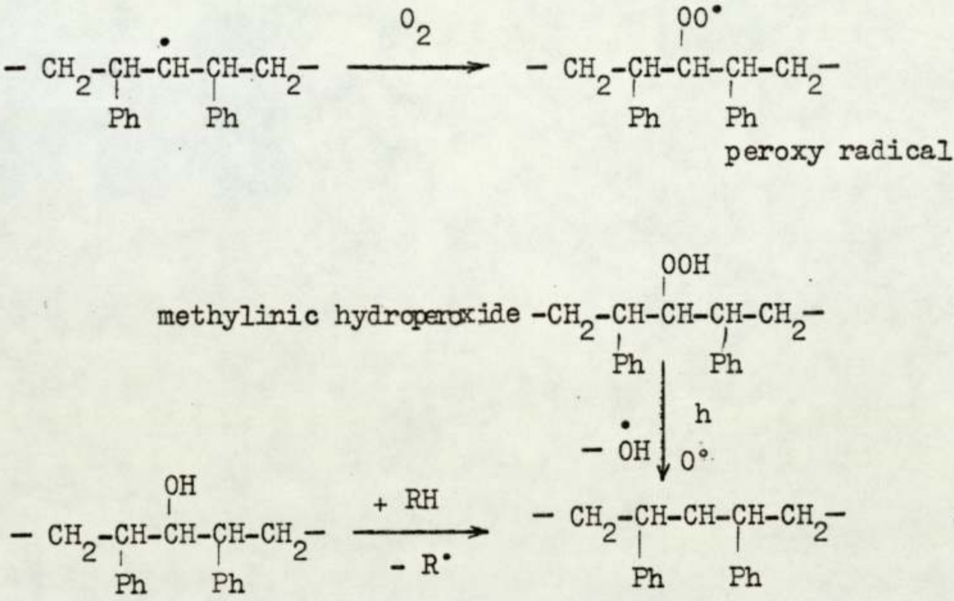
In this case abstraction of methylenic hydrogen takes place.



$$-\mathrm{CH_2{-}\underset{Ph}{CH}{-}CH_2{-}\underset{Ph}{CH}{-}CH_2{-}} \xrightarrow{\mathrm{R\dot{O}}\ \text{or}\ \mathrm{RO\mathring{O}}} -\mathrm{CH_2{-}\underset{Ph}{CH}{-}\dot{C}H{-}\underset{Ph}{CH}{-}CH_2{-}}$$

(5-32)

The alkyl radical undergoes the following reactions.

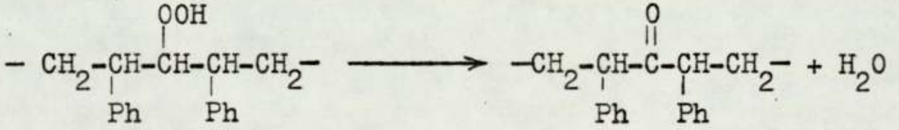


$$-CH_2-\underset{Ph}{CH}-\overset{\bullet}{C}H-\underset{Ph}{CH}-CH_2- \xrightarrow{O_2} -CH_2-\underset{Ph}{CH}-\overset{OO^\bullet}{CH}-\underset{Ph}{CH}-CH_2-$$

$$-CH_2-\underset{Ph}{CH}-\overset{OOH}{CH}-\underset{Ph}{CH}-CH_2- \qquad (5\text{-}33)$$

$$\big\downarrow \; h, \; -\overset{\bullet}{O}H$$

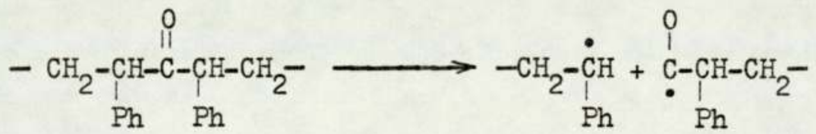
$$-CH_2-\underset{Ph}{CH}-\overset{OH}{CH}-\underset{Ph}{CH}-CH_2- \xrightarrow[-\,R^\bullet]{+\,RH} -CH_2-\underset{Ph}{CH}-CH-\underset{Ph}{CH}-CH_2- \qquad (5\text{-}34)$$



$$-CH_2-\underset{Ph}{CH}-\overset{OOH}{CH}-\underset{Ph}{CH}-CH_2- \longrightarrow -CH_2-\underset{Ph}{CH}-\overset{O}{\overset{\|}{C}}-\underset{Ph}{CH}-CH_2- + H_2O \qquad (5\text{-}35)$$

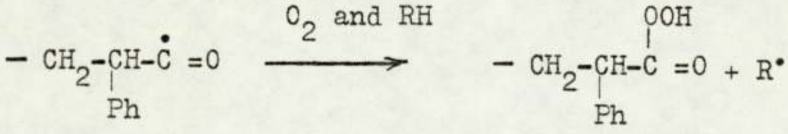
aryl ketone (1720 cm^{-1})

aryl ketone undergoes reaction Norrish type I.



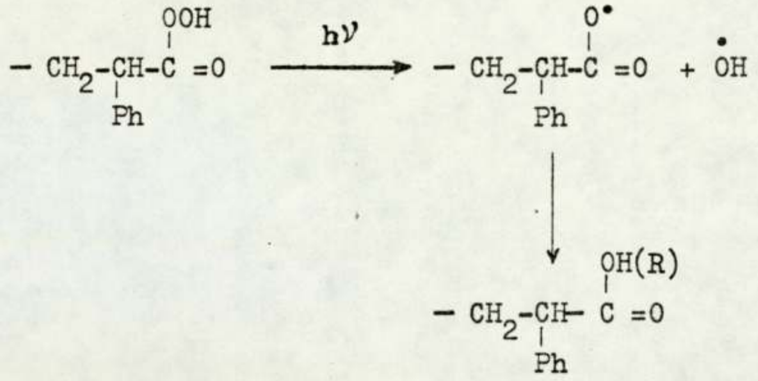
$$-CH_2-\underset{Ph}{CH}-\overset{O}{\overset{\|}{C}}-\underset{Ph}{CH}-CH_2- \longrightarrow -CH_2-\underset{Ph}{\overset{\bullet}{C}H} + \underset{\bullet}{\overset{O}{C}}-\underset{Ph}{CH}-CH_2- \qquad (5\text{-}36)$$

Formation of alkyl and acyl radical accompanied by chain scission.



$$-CH_2-\underset{Ph}{CH}-\overset{\bullet}{C}=O \xrightarrow{O_2 \text{ and } RH} -CH_2-\underset{Ph}{CH}-\overset{OOH}{C}=O + R^\bullet \qquad (5\text{-}37)$$

peracid (3280 cm^{-1})



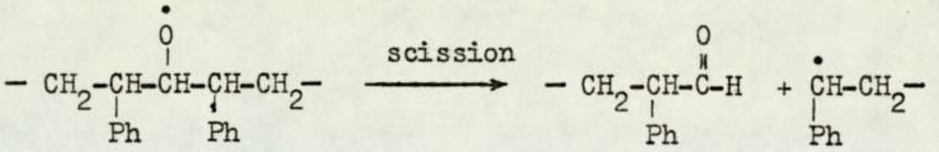
$$-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\overset{\mathrm{OOH}}{\mathrm{C}}=\mathrm{O} \xrightarrow{h\nu} -\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\overset{\mathrm{O^\bullet}}{\mathrm{C}}=\mathrm{O} + \dot{\mathrm{O}}\mathrm{H}$$

$$\downarrow$$

$$-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\overset{\mathrm{OH(R)}}{\mathrm{C}}=\mathrm{O} \qquad (5\text{-}38)$$

carboxylic acid (1705 cm^{-1})

or ester (1735 cm^{-1})



$$-\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\overset{\overset{\bullet}{\mathrm{O}}}{\mathrm{CH}}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\mathrm{CH_2}- \xrightarrow{\text{scission}} -\mathrm{CH_2}-\underset{\mathrm{Ph}}{\mathrm{CH}}-\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}-\mathrm{H} + \underset{\mathrm{Ph}}{\dot{\mathrm{C}}\mathrm{H}}-\mathrm{CH_2}- \qquad (5\text{-}39)$$

alkoxy radical

aldehyde (1720 cm^{-1})

Formation of aldehyde and alkyl radicals is accompanied by a reduction in molecular weight of the polymer.

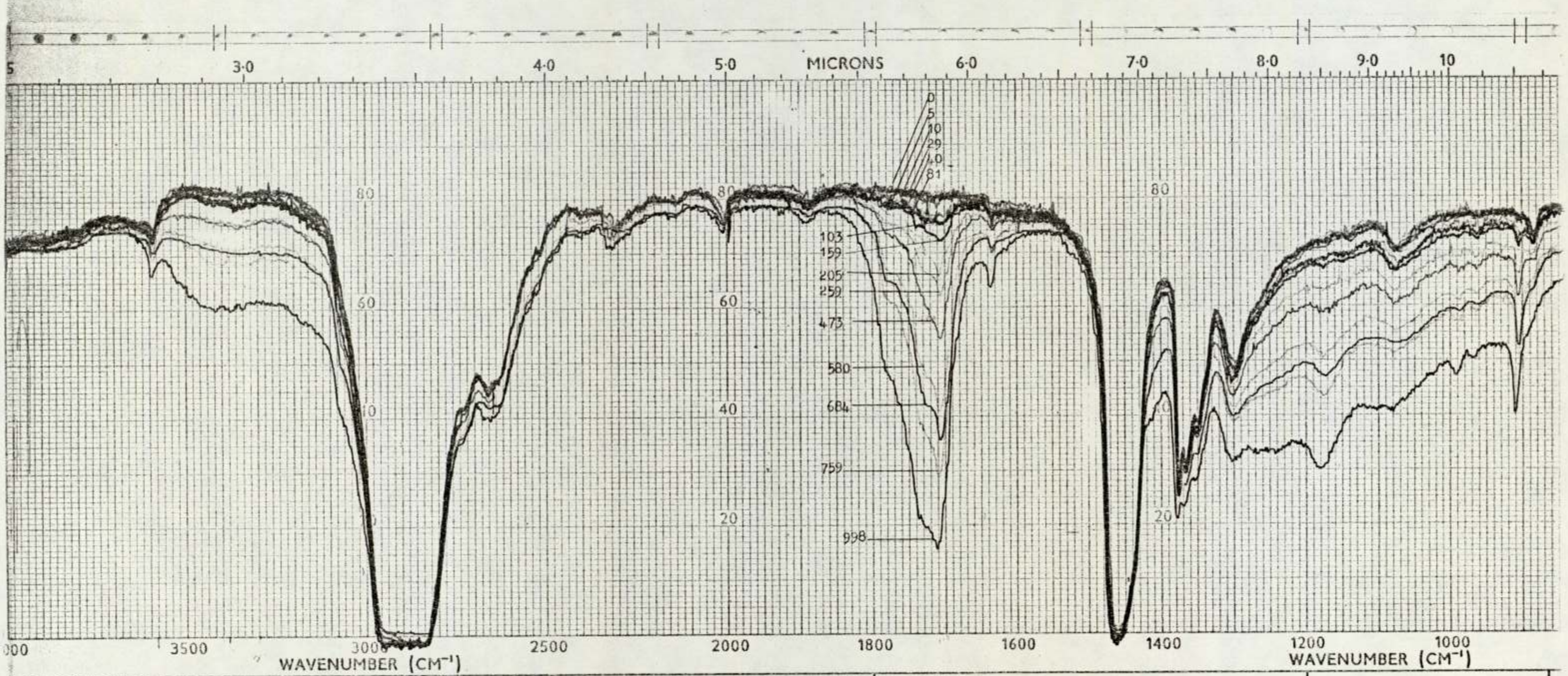


Fig 5-1 Change in hydroxyl (3500-3000 cm^{-1}, carbonyl (1800-1600 cm^{-1}, vinyl 910 cm^{-1} and vinylidene 889 cm^{-1} absorptin of LDPE during irradiation. (Nos on curves afe exposure time .

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

REMARKS

Composition = 100 % LDPE
Spead = M
Thickness = 0.01 cm
IR = Model 475

SCAN TIME

SLIT

OPERATOR

DATE

Fig 5-2 Changes in hydroperoxide (3500-3000 cm^{-1}) and carbonyl (1800-1600 cm^{-1}) absorptin during photo-oxidation of PS film. Numbers on curves indicate exposure time (hr).

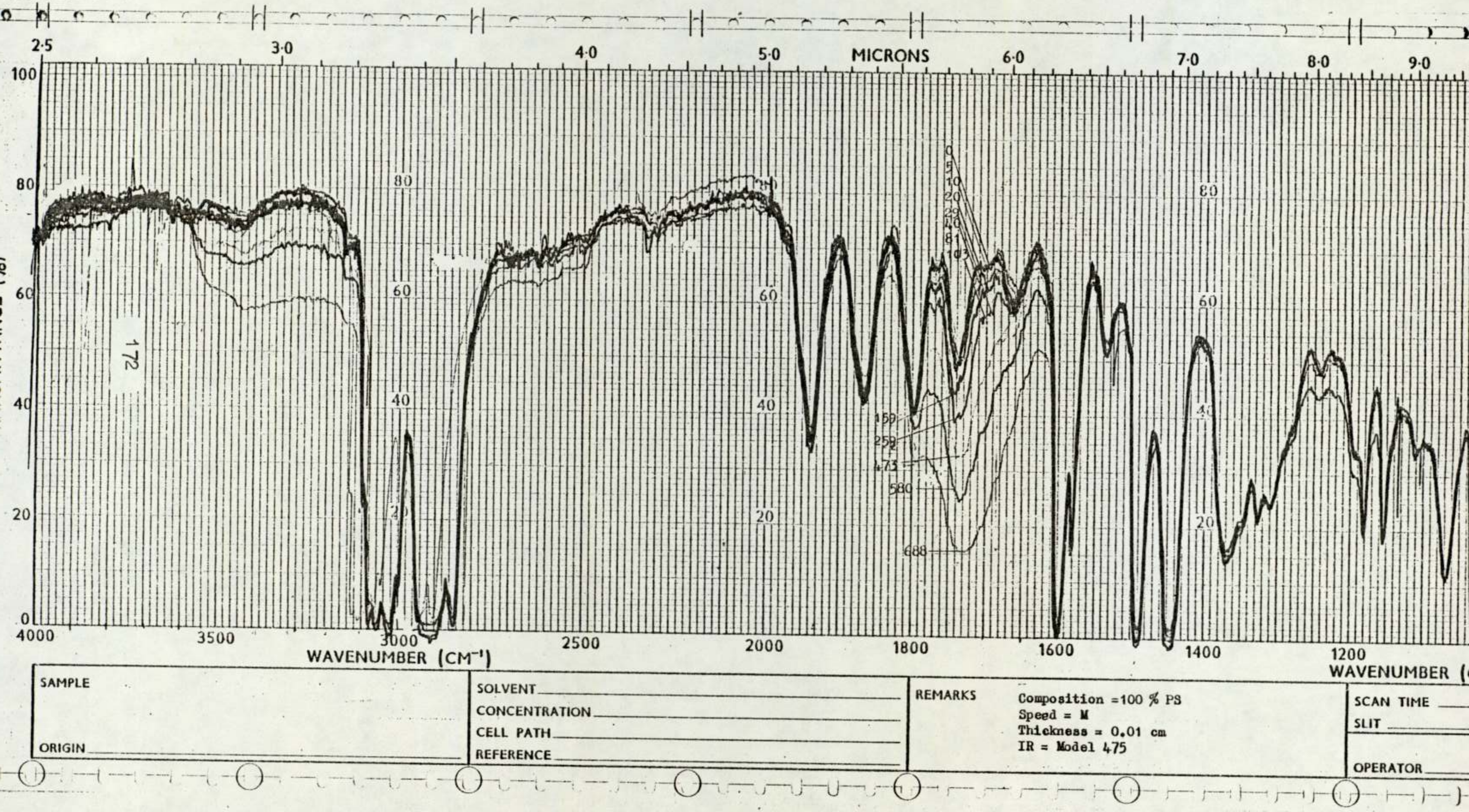
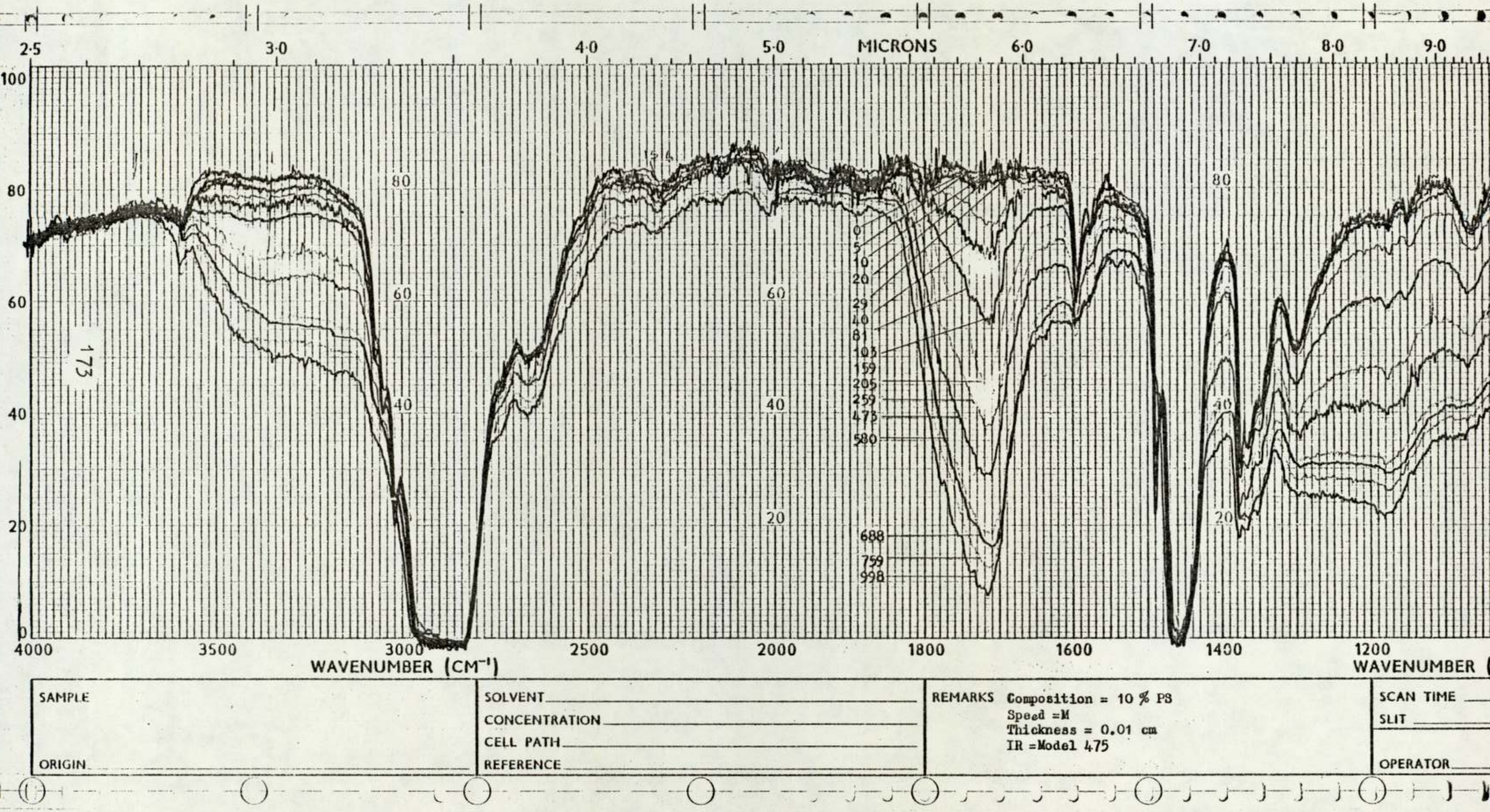
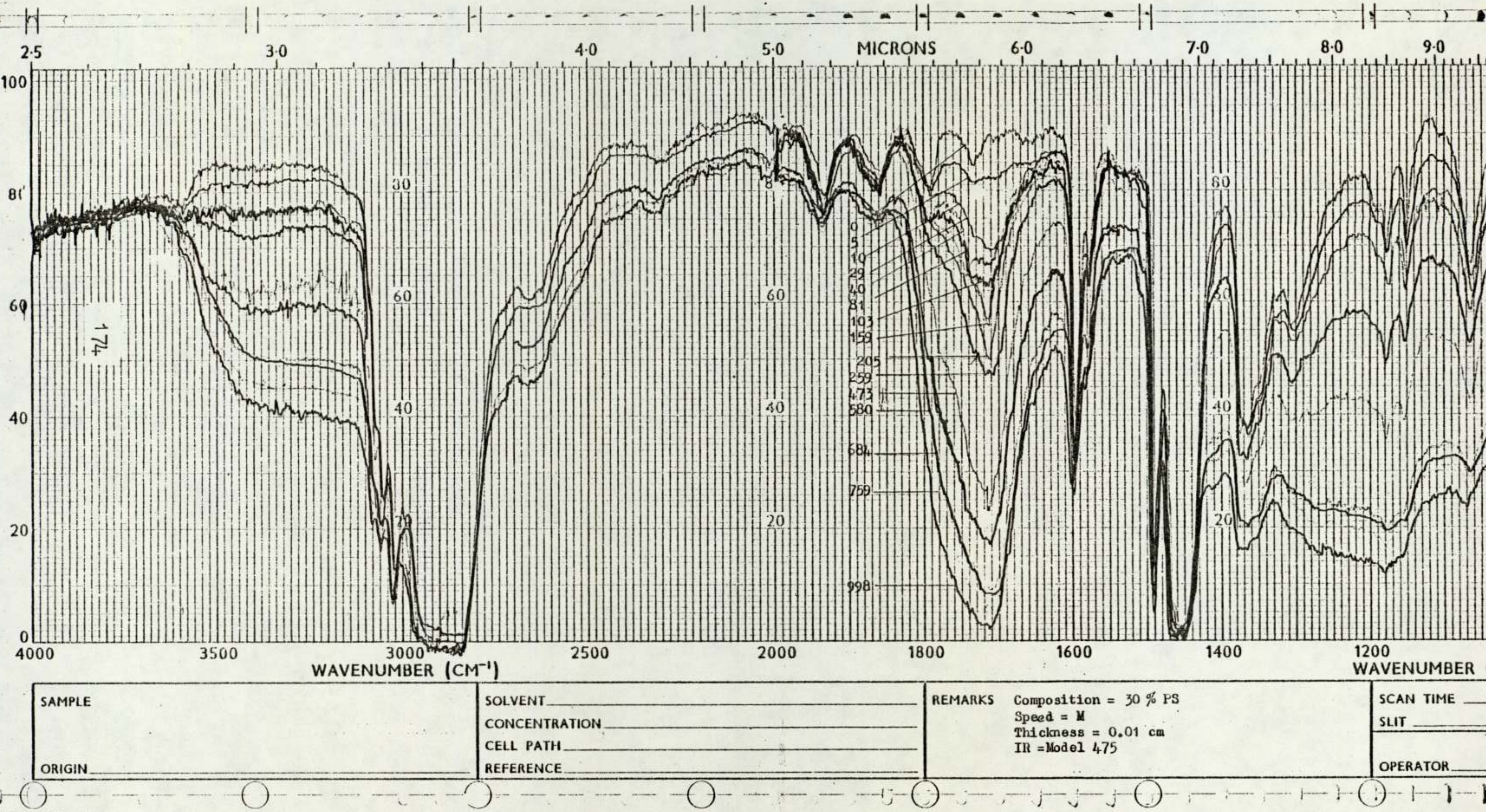


Fig 5-3 Changes in hydroperoxide(3500-3000 cm^{-1}) and carbonyl (1800-1600 cm^{-1}) absorption during photo-oxidation of LDPE/PS containing 10 % SPD.Numbers on curves indicate exposure time (hr).



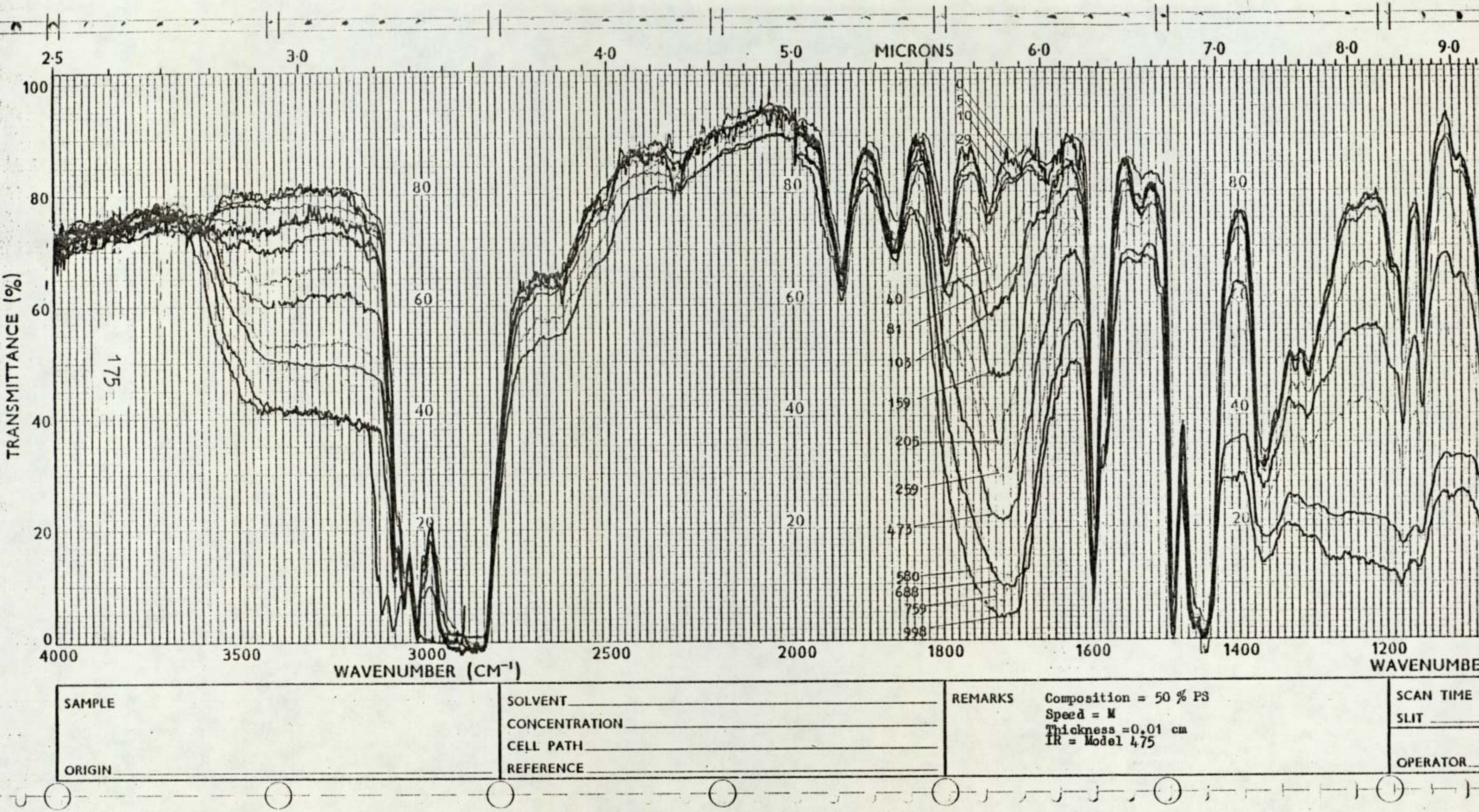
REMARKS Composition = 10 % PS
Speed =M
Thickness = 0.01 cm
IR =Model 475

Fig 5-4 Change in hydroperoxide(3500-3000 cm^{-1}) and carbonyl (1800-1600 cm^{-1}) absorption during photo-oxidation of LDPE/PS containing 30 % SPD .Numbers on curves indicate exposure time (hr).



Composition = 30 % PS
Speed = M
Thickness = 0.01 cm
IR =Model 475

Fig 5 -5 Change in hydroperoxide(3500-3000 cm^{-1}) and carbonyl(1800-1600 cm^{-1}) absorption during photo-oxidation of LDPE/PS containig 50 % SPD . Nos indicate exposure time(hr)



Composition = 50 % PS
Speed = M
Thickness =0.01 cm
IR = Model 475

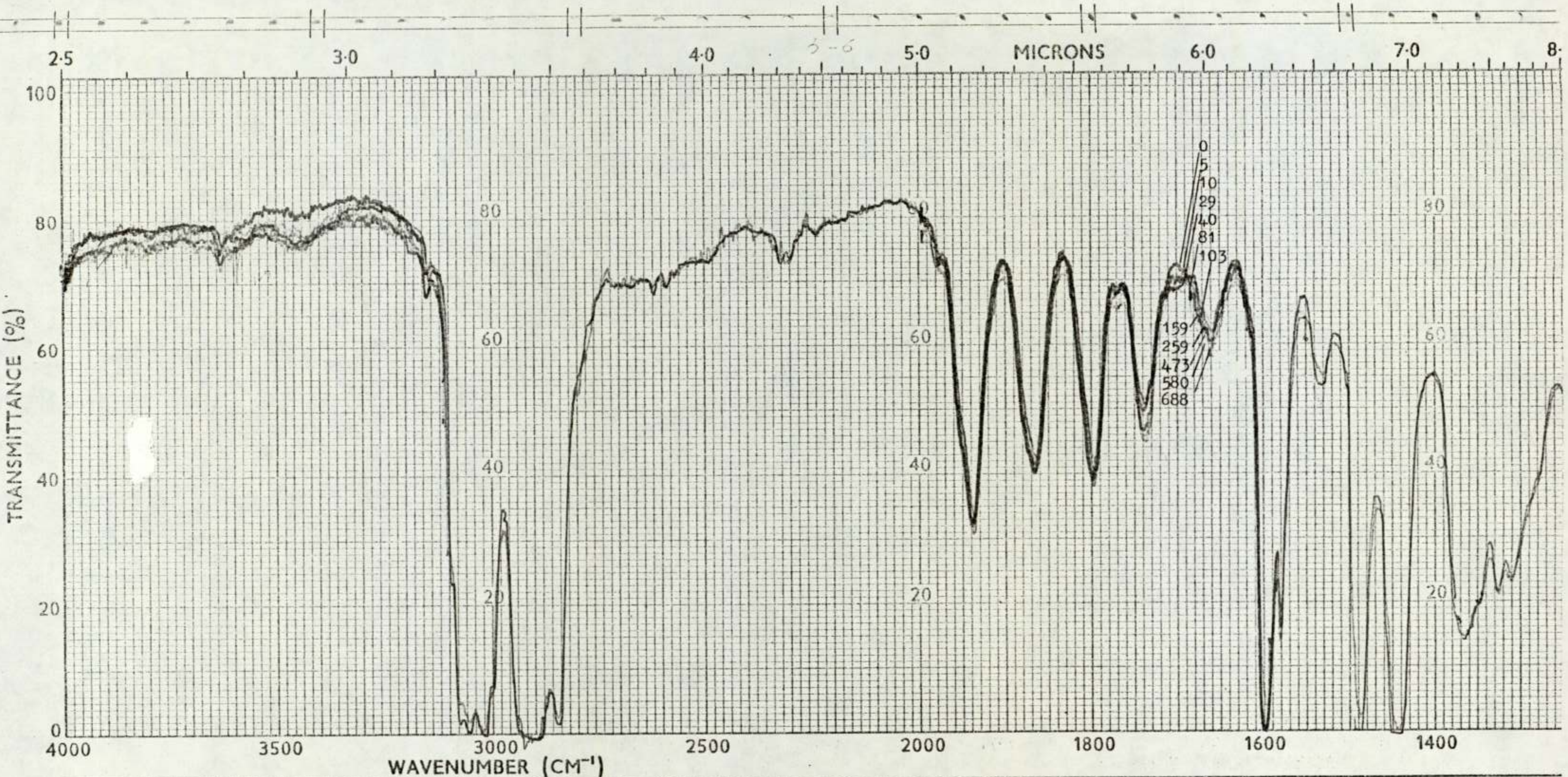


Fig 5-6 Change in hydroperoxide(3500-3000 cm^{-1}) and carbonyl(1800-1600 cm^{-1}) absorption of PS during thermal oxidation.Nos indicate time of oven ageing.

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

REMARKS Composition = 100 % PS
Speed =M
Thickness = 0.01 cm
IR = Model 475

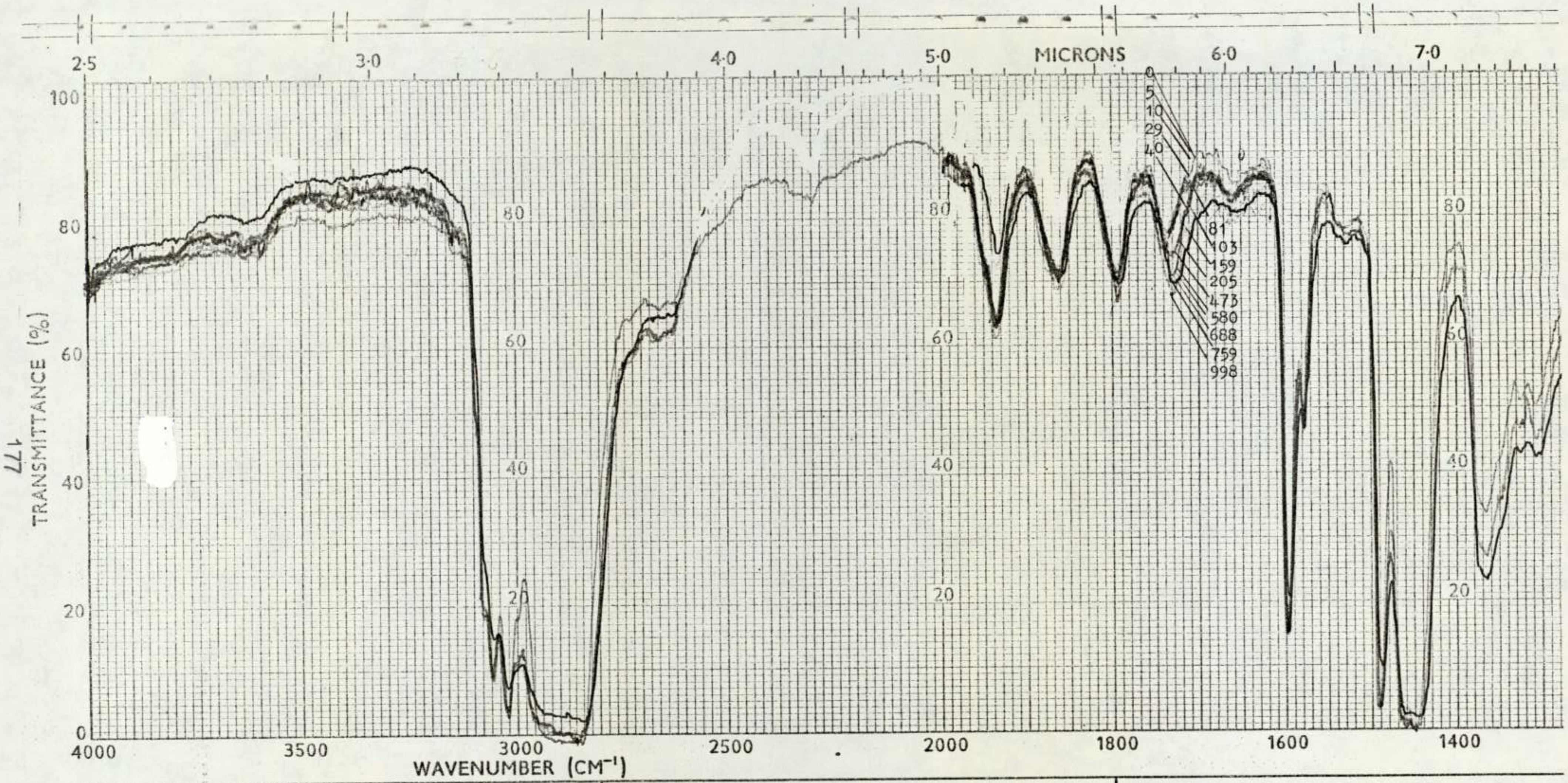


Fig 5-7 Change in hydroperoxide(3500-3000 cm^{-1}) and carbonyl(1800-1600 m^{-1})absorption of LDPE/PS con-50 % SPD during thermal oxidation.Nos indicate thermal ageing time.

SOLVENT

CONCENTRATION

CELL PATH

REFERENCE

REMARKS

Compositin = 50 % Ps
Speed = M
Thickness = 0.01 cm
IR =Model 475

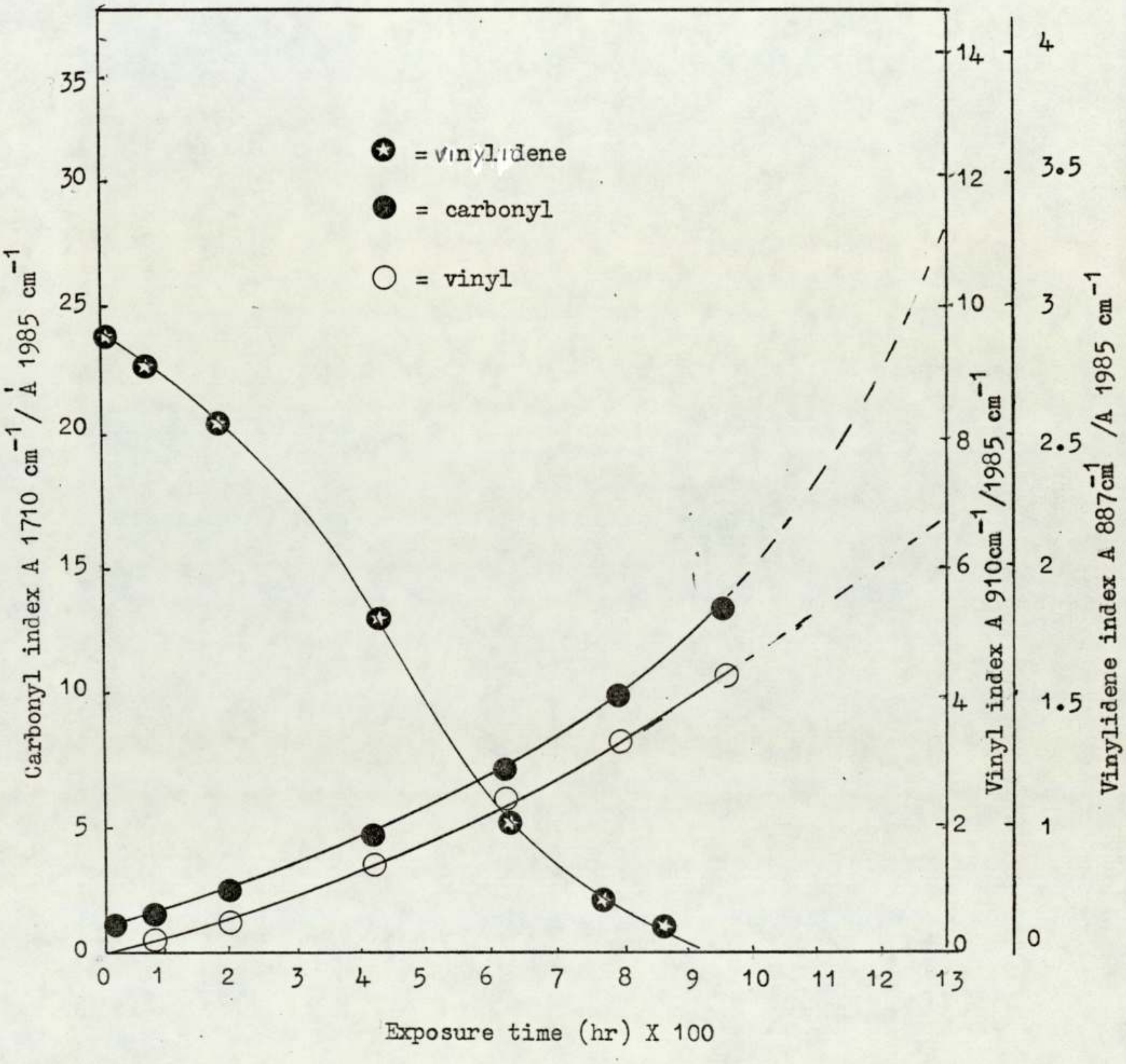
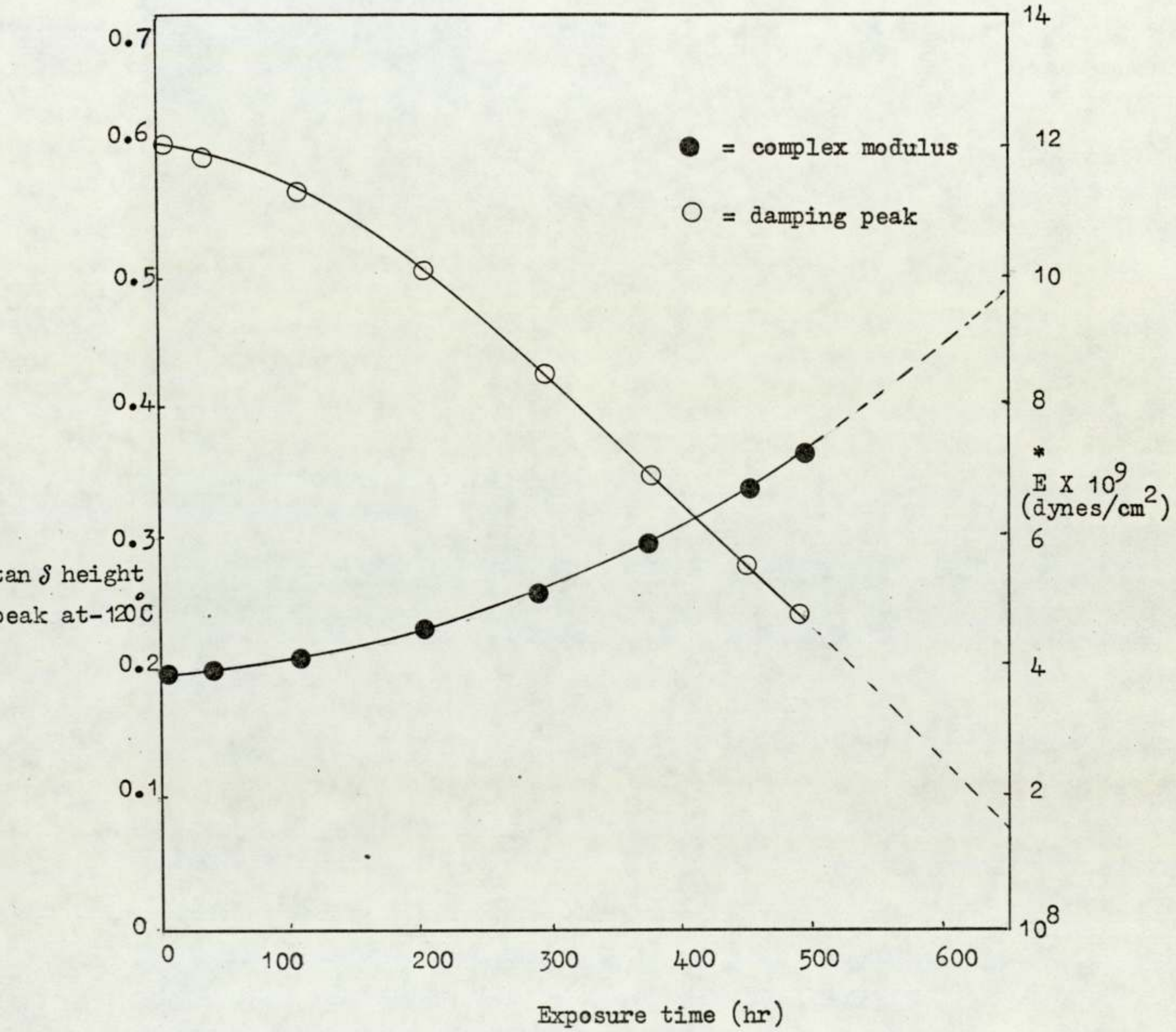


Fig 5- 8 Changes of carbonyl, vinyl, and vinylidene groups during photo- degradation of LDPE.



5-9 Changes of complex modulus and loss modulus tan δ height peak during photo-degradation of LDPE.

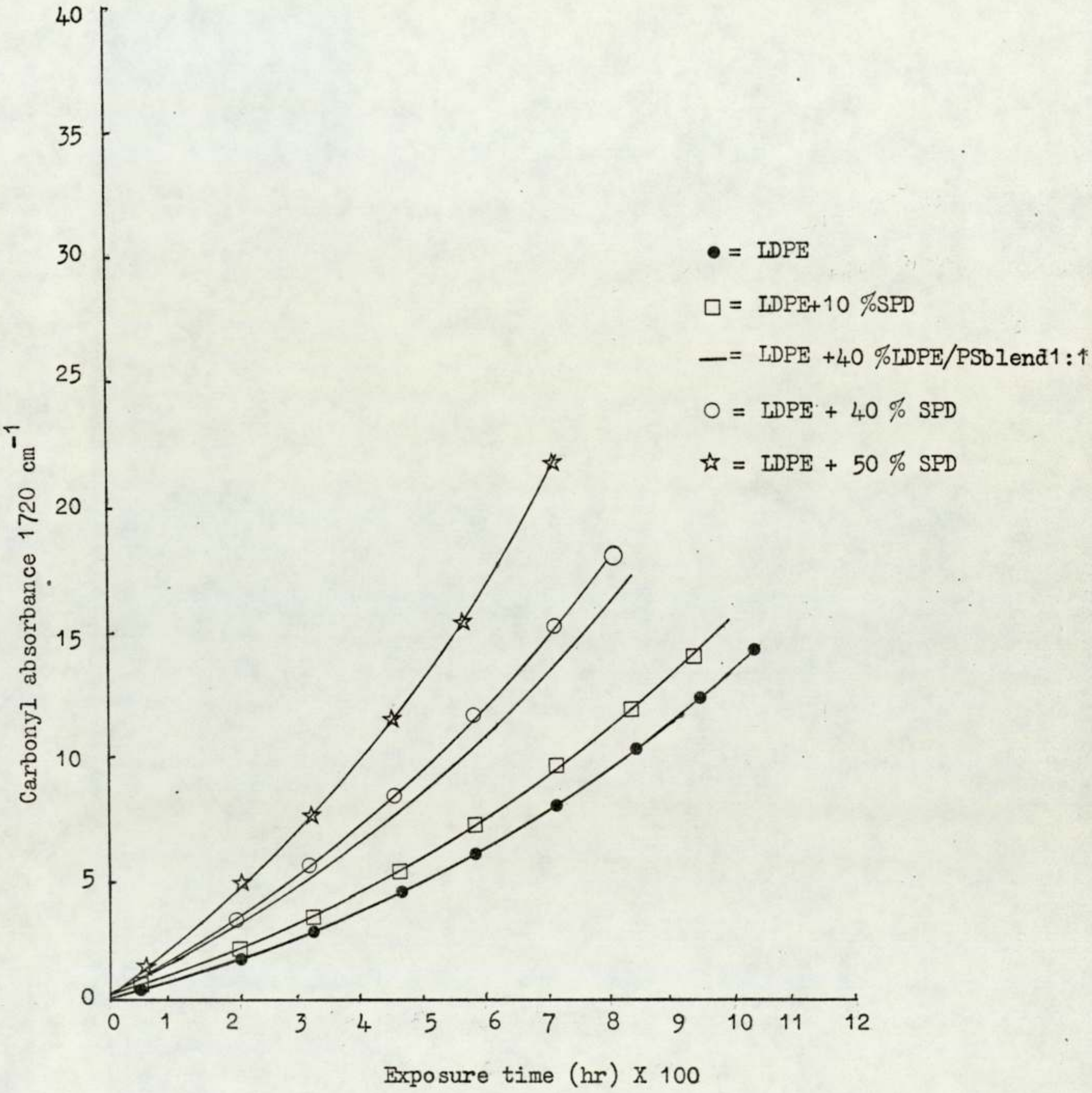


Fig 5-10 Effect of different ratios of PS on formation of carbonyl in LDPE / PS blends during irradiation

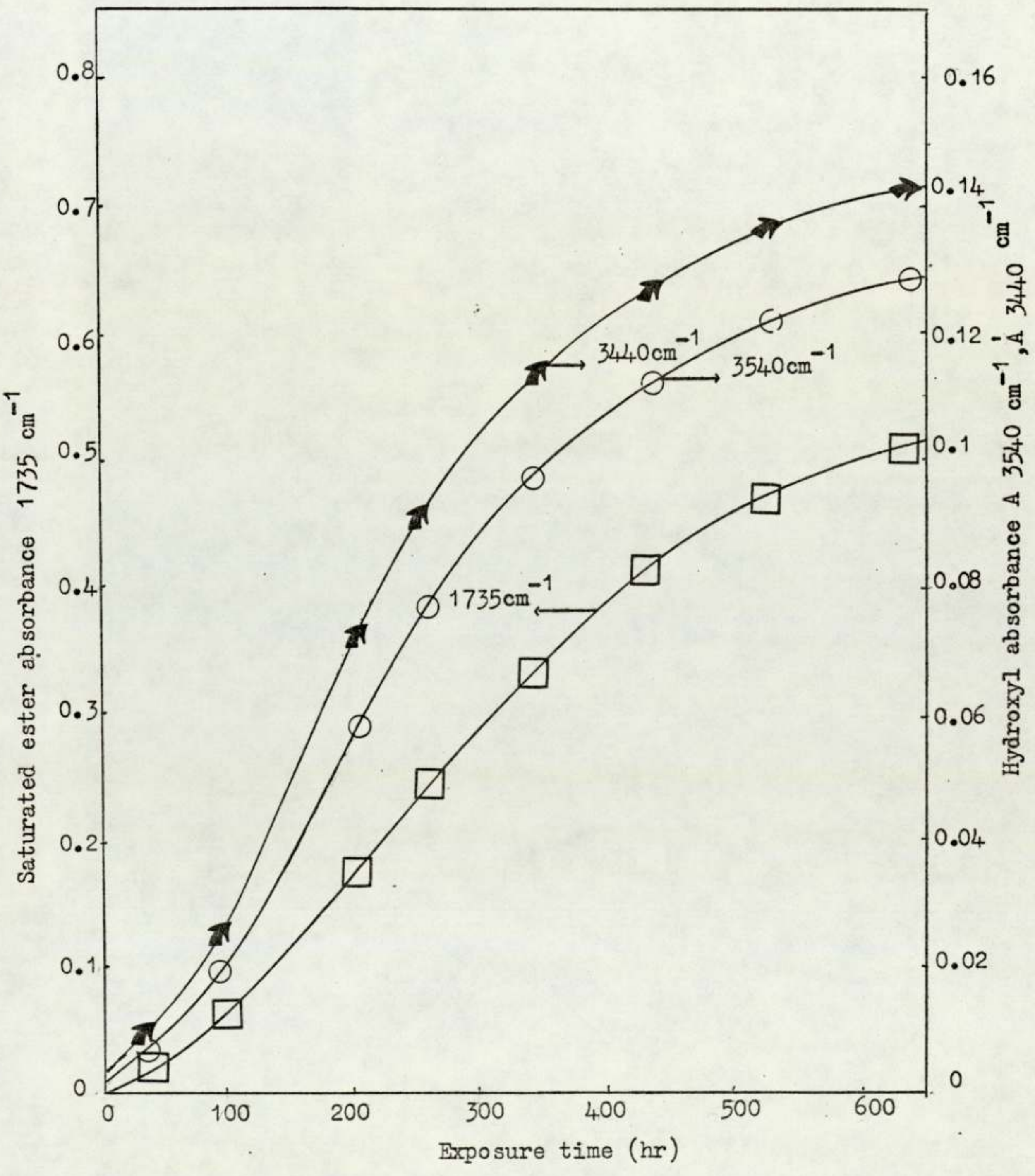


Fig 5-11 Development of some functional groups in PS film during photo-oxidation.

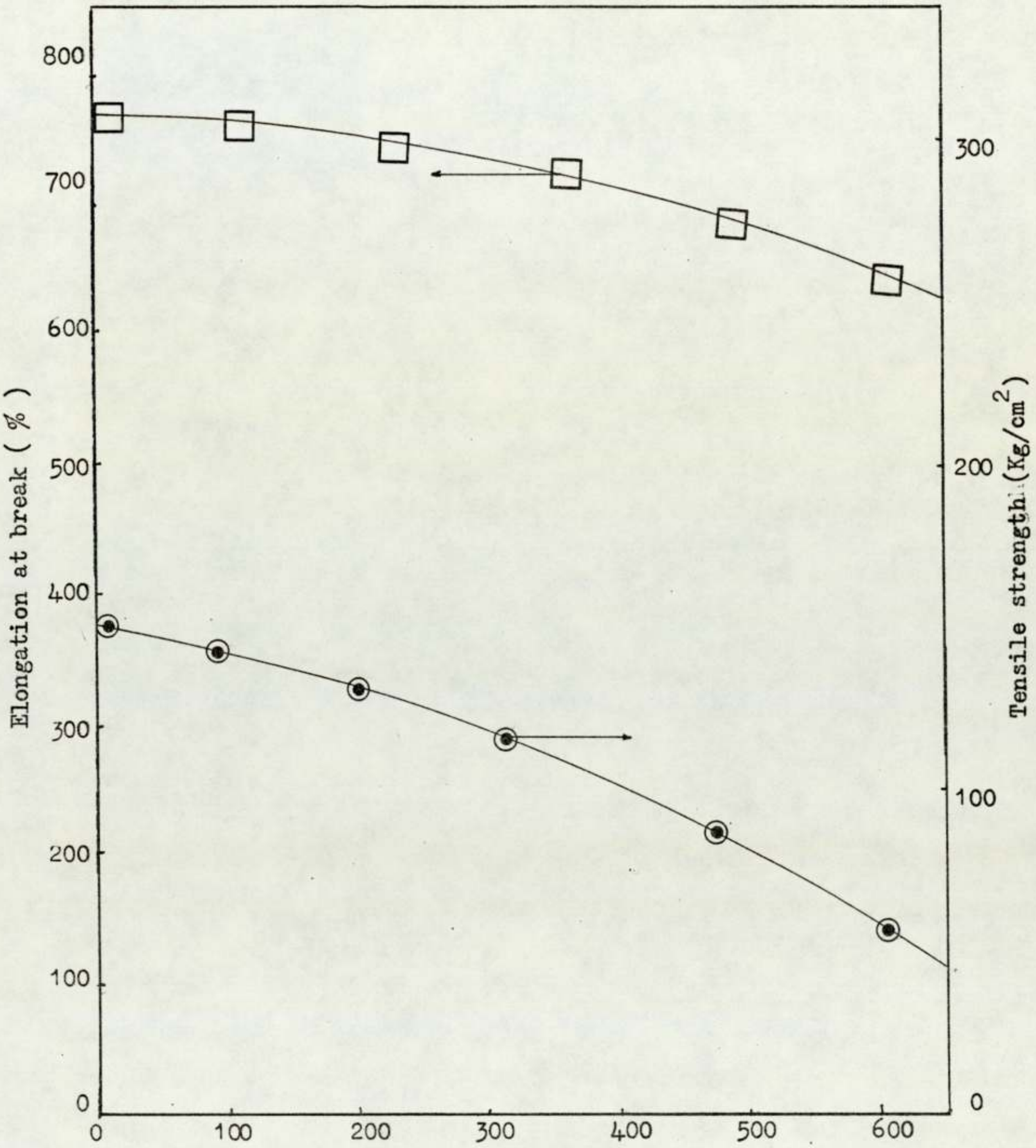


Fig 5-12 Changes of elongation at break and tensile strength of unprocessed LDPE during photo-degradation.

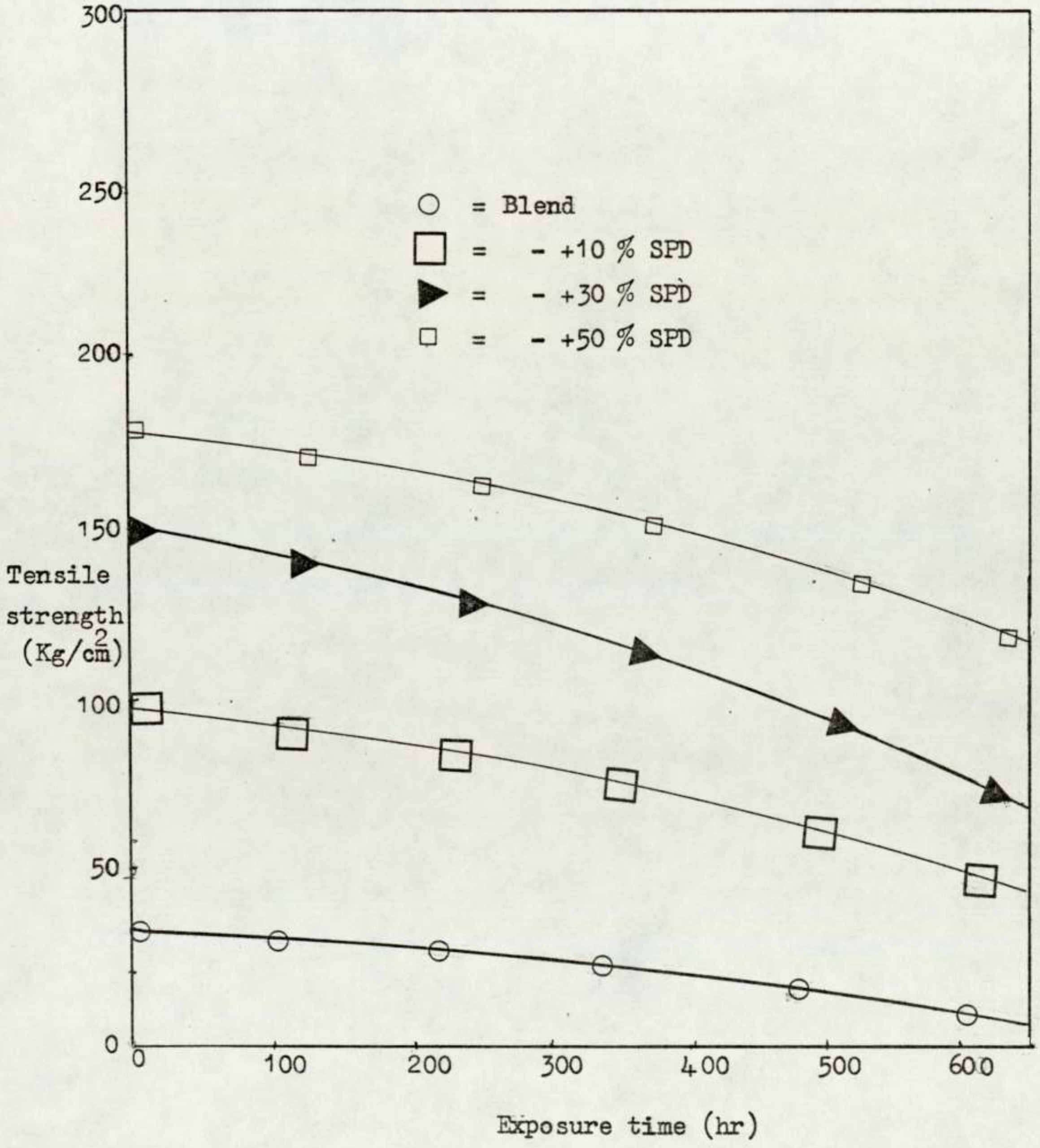


Fig 5-13 Changes of tensile strength as a function of exposure time (photo-oxidation) for LDPE/PS blends(50/50) containing different ratios of SPD.

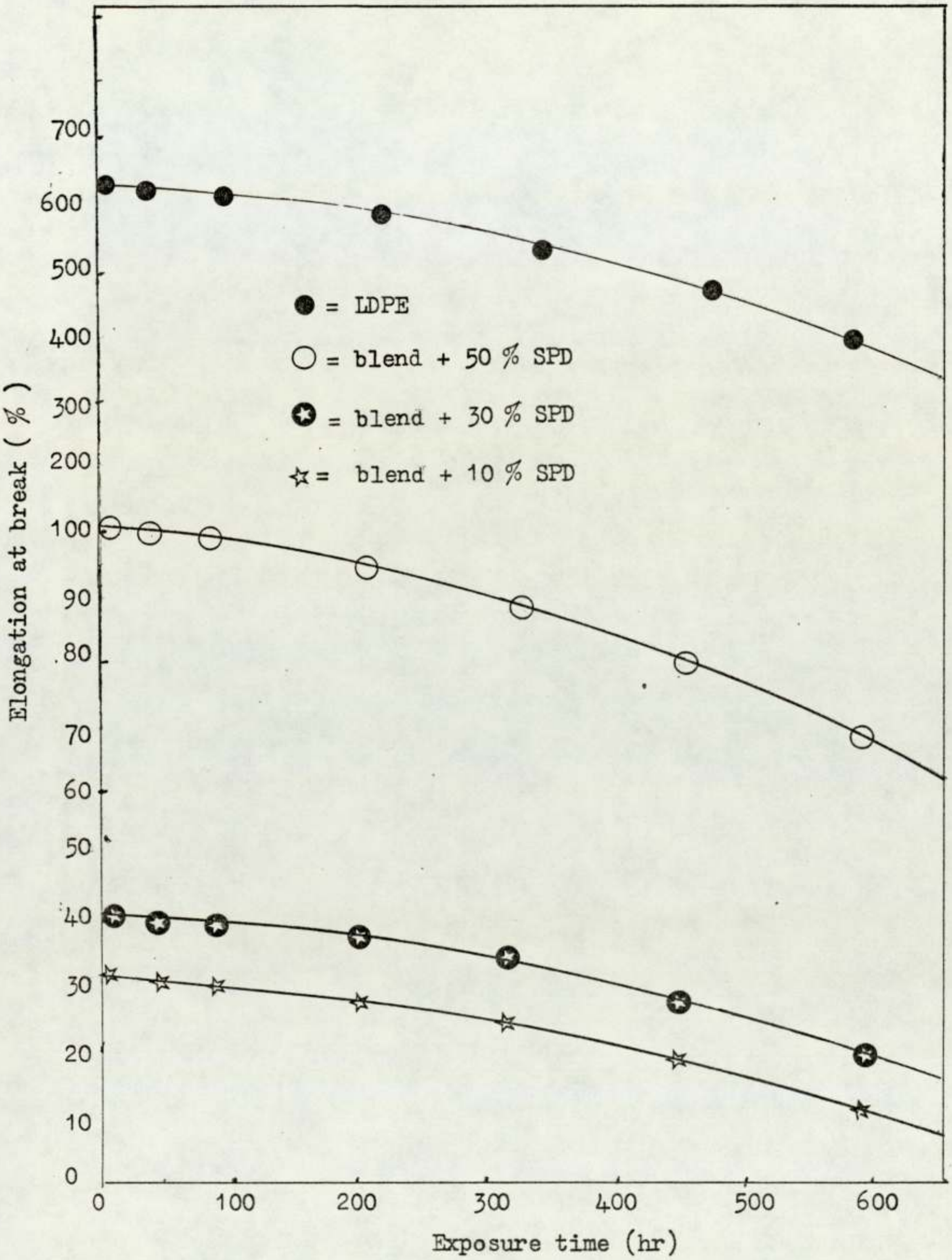


Fig 5-14 Changes of elongation at break as a function of exposure time for LDPE and LDPE/PS blends(50/50) containing different ratios of SPD.

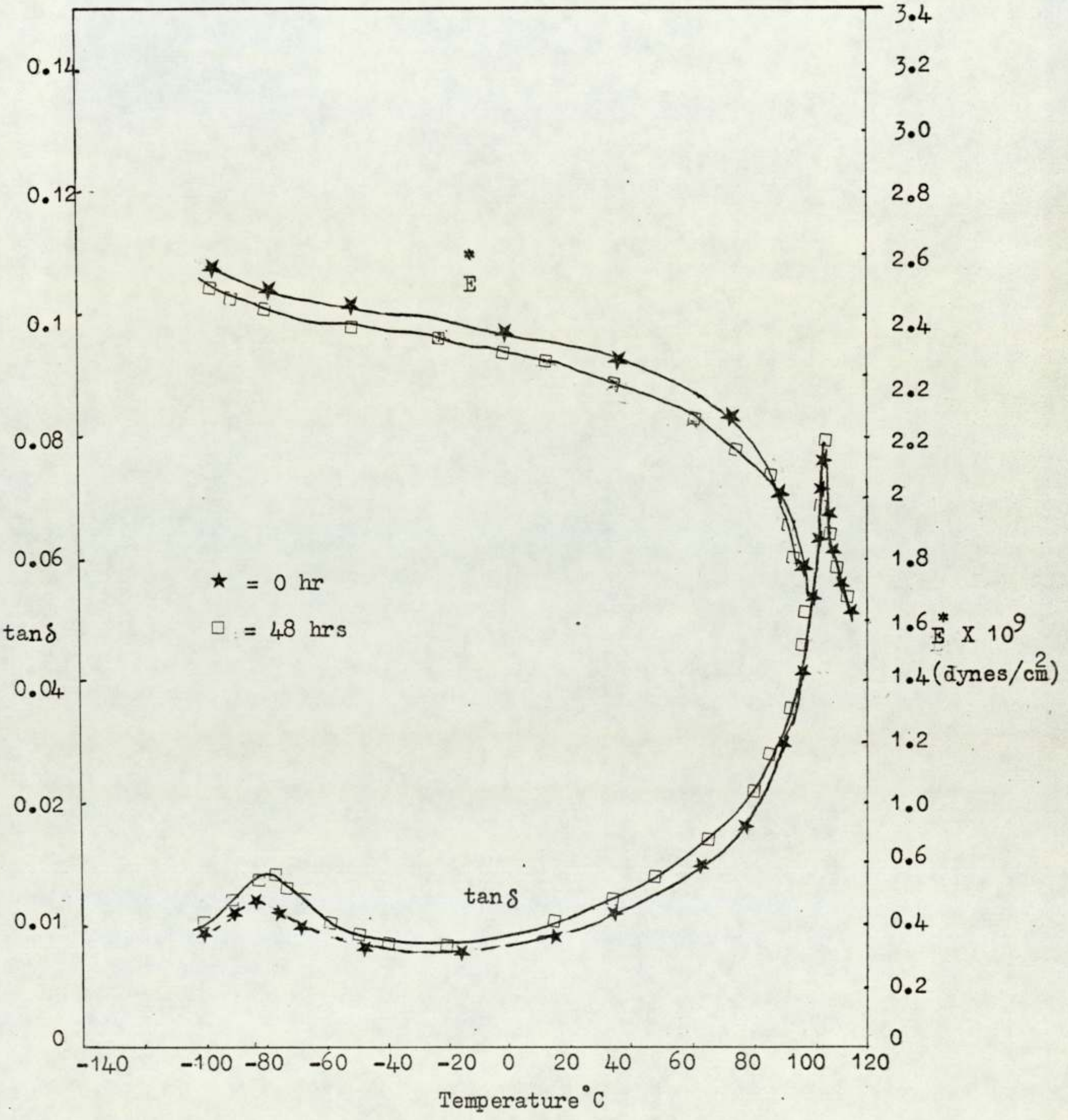


Fig 5-16 Changes of tan δ and complex modulex ($\overset{*}{E}$) of PS film as a function of temperature before and after photo-degradation.

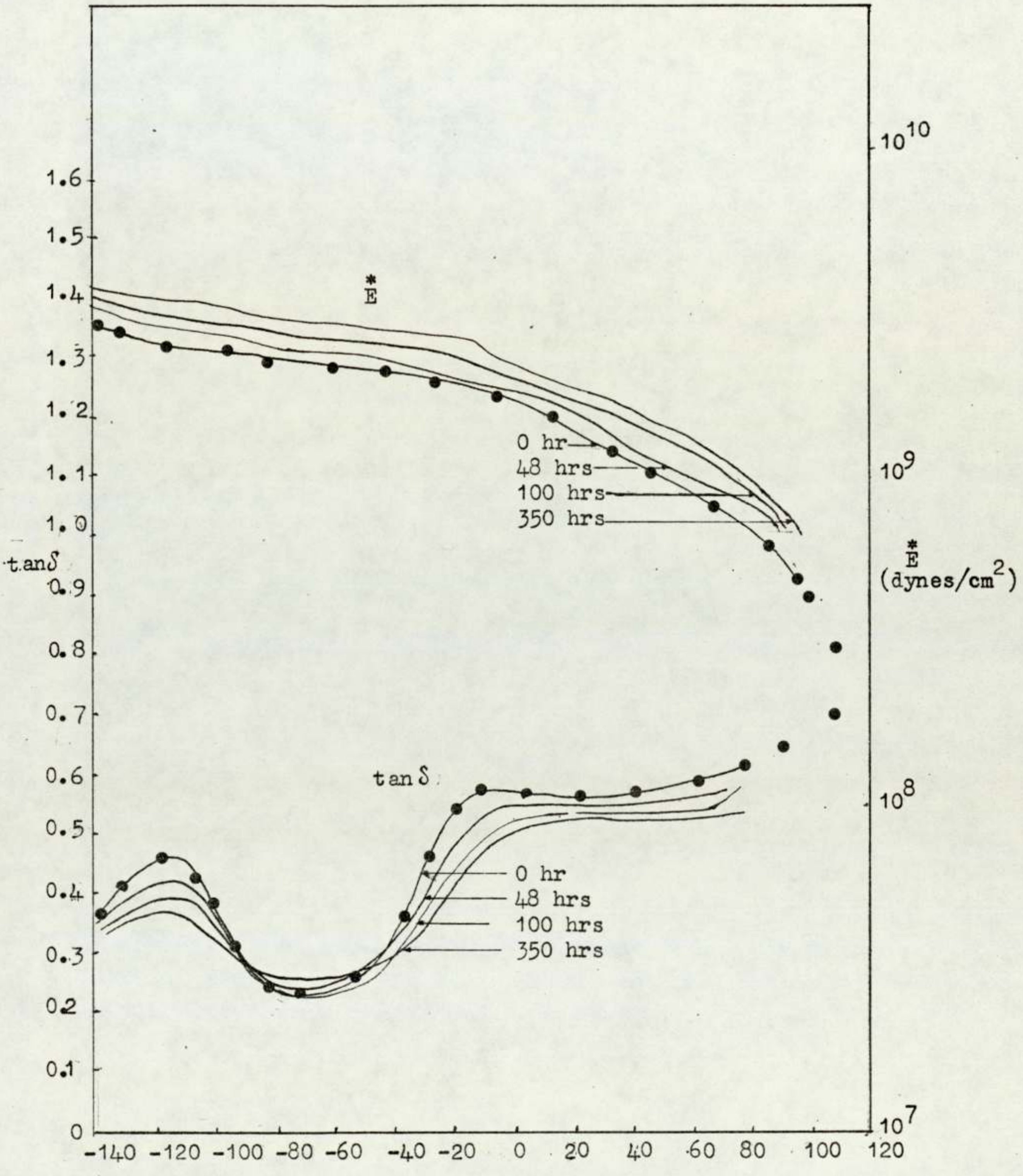


Fig 5-17 Changes of tan δ and complex modulus ($\overset{*}{E}$) of LDPE as a funtion of temperature during UV radiation.

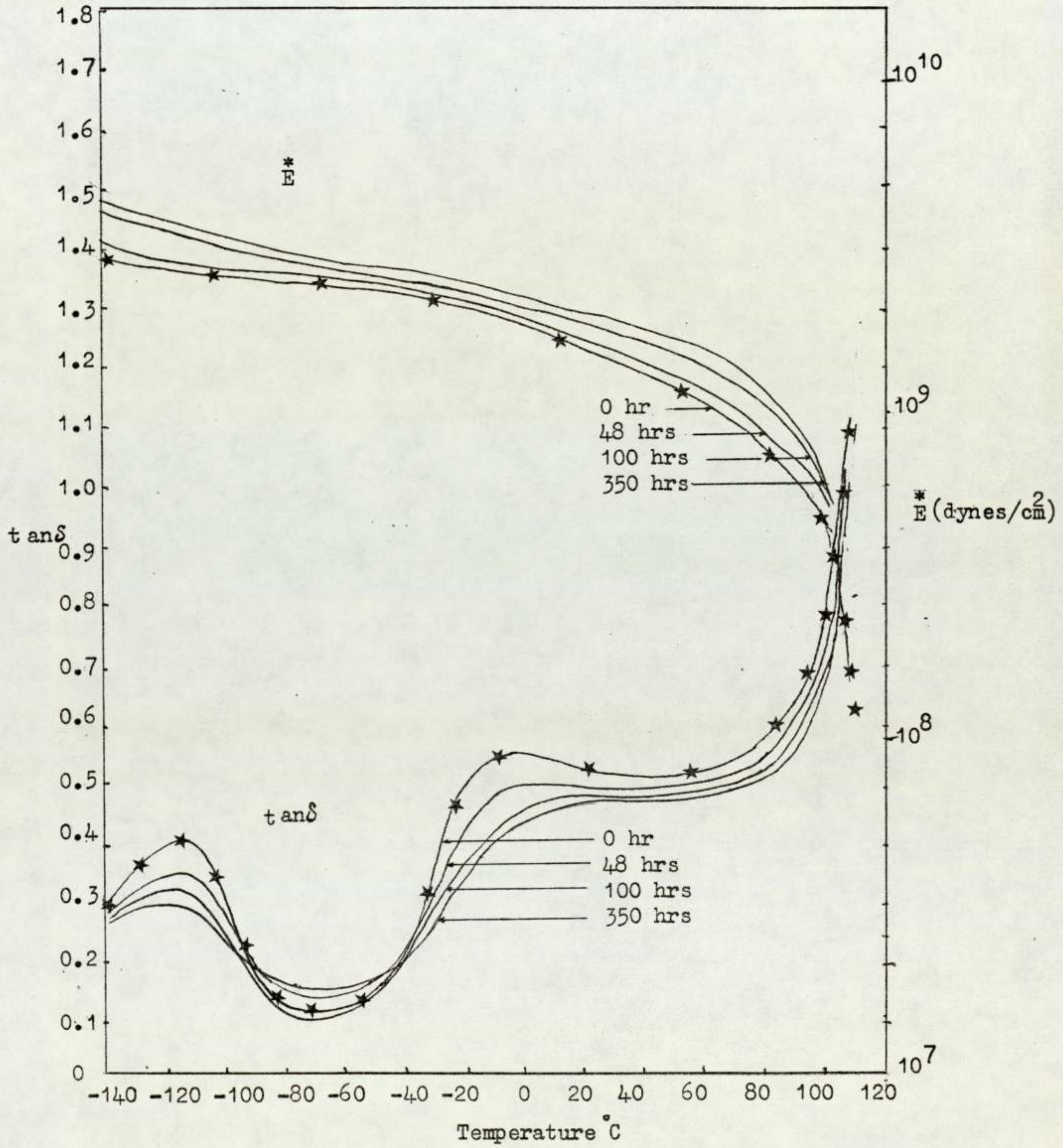


Fig 5-18 Changes of t anδ and complex modulus ($\overset{*}{E}$) of LDPE-PS copolymer as a function of temperature during UV radiation.

Conclusions

The results of this study show that, it is possible to graft styrene onto the processed LDPE in the absence of free radical initiator and also it was grafted onto the unprocessed LDPE in the presence of free radical initiators such as benzoyl peroxide (BPO) and cumene hydroperoxide (CHP).The copolymer was also prepared by mechano-chemical method (polymer-polymer interchange) in the presence of CHP as an effective intiator.This method was found to be more effective than the chemical method for preparation of LDPE-PS copolymers as interfacial agent to improve mechanical properties (specially impact strength) of the corresponding blends.

Apparently,the competition between the extent of the bonding and thermo-mechanical degradation of the individual polymers during processing which cause cross-linking reactions which increase with the processing time(30 minutes), and temperature (170°C) is responsible for this optimum. The ideal process would cause uniform bonding of PS to all LDPE chain without occurance of cross-linking or interaction between the same free radical fragments.

The mechanism of improvement of mechanical properties of the blends is believed to involve increased interfacial adhesion provided by the SPD in the incompatible polyblends.

From the results of a study of photo-degradation, it was concluded that as the ratio of the SPD increases in the modified polyblends,photo instability of the polymeric system is increased. This effect was examined by the IR-spectroscopy by measuring absorption peak at 1720 cm^{-1} which results from formation of carbonyl group which is related to the photo-oxidation of the samples.

Dynamic mechanical measurements from -140°C to 120°C showed that the blends and grafts of LDPE and PS show one Tg at -120°C which is called γ transition. This transition is believed to be due to the motion of a limited number of $(-CH_2-)$ groups in the LDPE main chain. The second transition was shown at -20 to 20°C. It is believed this transition which is named β transition is related to the movement of the polymer chain (LDPE) in the vicinity of branch or graft points. So, this transition shift for the graft copolymers are more than that of the corresponding blends. The third transition was shown at 100°C for crystal PS before processing. This transition shifts to lower temperatures (to about 90°C) depending on the processing time or irradiation time of the polymer, since according to the equation, $Tg = Tg_{o} \frac{K}{\overline{Mn}}$, glass transition of the polymer depends on the number average molecular weight of the polymer (in the above equation, K is the constant characteristic and for PS = 1.75×10^5. For this polymer with number average molecular weight of 10^4, glass transition about 83°C and for infinite number average molecular weight glass transition about 100°C has been observed.(172)

From the optical microscopy studies it was concluded that, in the copolymers of LDPE and PS, the PS particles are distributed in a more homogeneous manner than that in the corresponding polyblend, and it was observed that addition of the SPD decreases the domain size of of the blends and this effect is reflected in improvement of mechanical properties of the blends.

SUGGESTIONS FOR FURTHER WORK

The use of LDPE-PS copolymers, made by a mechano-chemical method, as solid phase dispersants in the presence of cumene hydroproxide (CHP) has been shown to be an effective way of improving mechanical properties. However, the improvement of the mechanical properties was not as great as that shown by other SPD's (chlorinated polyethylene, ethylene-propylene-diene and styrene butadiene rubbers) [160] A possible reason could be the side reactions occurring during the mechano-chemical processing of the polymers. In order to achieve a higher extent of binding, attempts should be made to reduce side reactions by the following methods:

1. Varying the grades of polyethylene (i.e. molecular weight and degree of crystalinity) should allow more interchange reactions and increase the extent of binding.
2. Increasing the shearing forces acting on the polymers during processing should increase the extent of mechano-chemical reaction.
3. Using initiators with life-time higher than CHP such as dicumyl hydroproxide and ditertiary butyl peroxide.
4. Addition of LDPE-PS copolymers as an interfacial agent during the processing in order to improve the mechanical properties of the blends. The increased surface area of the dispersed phase should increase the probability of reaction across the interface.

Another problem encountered during the course of this work was the effect of photo-degradation of the SPD's leading to inferior mechanical properties of the samples. To overcome this problem attention should be directed towards photo-stabilisation of the blends by means of UV stabilisers .

Appendix No 1 General properties of crystal polystyrene

(Carinex General Purpose)

Resistance to :	Alkalis	Excellent
	Acids	Generally good, but attacked by stronly oxidising acids.
	Oxygen	Good
	Solvent	Soluble in ester, aromatic hydrocarbons ketones, higher alcohols and chlorinated hydrocarbons.
	Water	Excellent.

Physical properties	Unit	Value
Specific gravity		1.05-1.07
Specific heat	Kg/Kg/ C	0.134
Viscosity	Centipoise	1.9
Melt index	g/ 10 mins	10
Monomer content	%	0.3
Mechanical properties		
Tensile strength	MN/m^2	40
Elongation	(%)	2
Modulus	MN/m^2	3500
Impact strength	MN/m^2	0.1
Flexural strength	Joules/6.4	60

REFERENCES

1 G.Scott,A.Gaffar and P.Crowther,Eur Poly J 14, 631 (1978)

2 D.R.Paul,C.E.Locke and C.E.Vinson.Poly Eng Sci,17,157,(1972)

3 W.H.Barenster and D.H.Heikens.Polymer,4,574,(1973).

4 C.E.Locke and D.R.Paul,J App Poly Sci,17,2597,(1973)

5 M.U.Amin,PhD Thesis,Univ of Aston in Birmingham,(1973)

6 C.Sadrmohaghegh,PhD Thesis,Univ of Aston in Birmingham,(1979)

7 W.M.Barenster,D.H.Heikens and P.Piet, Polymer,15,120,(1974)

8 C.E.Locke and D.R.Paul, J App Poly Sci, 17,2791,(1973).

9 A.J.Warner,C.H.Parker and B.Baun,"Solid Waste Management of Plastics" a report to Manufacturing Chemical Association(1971)

10 C.Sadrmohaghegh,PhD Thesis,Univ of Aston in Birmingham (1979)

11 M.E.Banks,N.D.Lusk and R.S.Ottinger"New Chemical Concepts for Utilization of Waste Plastics"EPA Pub No SW16C (1971)

12 Anon,Mod Plast, 47,50.(1970)

13 N.L.Dorbing,H.E.Hull and R.F.Testin, Public Health Pub No1908, (1971)

14 Anon,Chem Eng,77,88 June15 ,(1970)

15 J.D.Milgren,"Recycling of Plastic" presented at the ACS Symp Chemical Technology for Research Recovery Washington DC,June, (1971)

16 J.L.Holman(Bureau of Miners),Chem Eng News,47,7,May 31(1971).

17 W.A.Mack"Recycling Waste Plastics at a profit presented at National Conference on Waste Recycling,Denver,(1971). Also See Ref No16

18 D.R.Paul,Reuse of Plastics Recovered from Solid Wastes Progress" report to EPA,(May1971)

19 R.J.Sperker and S.L.Rosen,Poly Eng Adv.Sci 16(4) April (1976)

20 D.R.Paul,C.E.Vinson and C.E.Locke,Poly Eng Sci 12,157,(1972)

21 D.R.Paul and S.Newman, Polymer Blends 2, 35 (1978)

22 D.R.Paul, C.E.Vinson and C.E.Locke,Poly Eng Sci 12, 157(1972)

23 N.G.Gaylord in"Copolymers,Polyblends, and Composites" Adv in Chem Ser, 142, 76. Amer Chem Soc,WashingtonD.C,(1975)

24 S.L.Rosen,Poly Eng Sci,7,115 (1967)

25 D.R.Paul and S.Newman Polymer Blends Vol 2,36,(1978)

26 D.W.Landstedt and E.M.Bevilacqua,J Polymer Sci 63,423,(1960)

27 V.N.Kuleznev,L.S.Krokhina and B.A.Dogadin,Kolloid Zhurn,29, 170-171 (1967)

28 F.Ide and A.Hasegawa,J App Poly Sci ,13,308,(1973)

29 J.N.Schramm and R.R.Blanchard,paper presented at SPE,Cherry Hill New Jersey October 1970)

30 M.E.L.McBain and E.Hutchinson"Solubilization and Related Phenomena" Acadamic Press New York (1955)

31 G.E.Molau in"Block Polymers" (S.L.Aggarwal Ed),P 79,Plenum, New York (1970)

32 D.J.Meier,J Poly Sci C28, 81,(1969)

33 G.Riess and Y.Jolivet in "Copolymers,Blends and Composite Adv,in Chem Ser 142, 243,Amer,Chem Soc ,Washington,D.C (1975)

34 A.Tager, Physical Chenistry of Polymers, Moscow, (1978)

35 A.Darnay and W.E.Frankin"The Role of Packaging in Solid Waste Management,1966-1976,Public Health Service Pub No 1855(1969)

36 D.R.Paul and S.Newman 2 , 49, (1978)

37 D.R.Paul and C.E.Vinson, Poly Eng Sci,12,157,(1972)

38 C.E.Locke and D.R.Paul,J Appl Poly Sci ,17,,2597, (1973)

39 W.M.Barentsen and D.Heikens, Polymer 14 ,579 (1973)

40 W.L.Carrik ,J ,Poly,Sci,(A-1) 8,215,(1970)

41 W.M.Brentsen and D.Heikens,Polymer,14,579,(1973)

42 J.N.Schramm and R.R.Blenchard,paper presented at SPE,Cherry Hill,New Jersey,October (1970)

43 D.R.Paul.C.E.Locke and C.E.Vinson,Poly Eng Sci.13,202,(1973)

44 D.R.Paul and S.Newman,Polymer Blends,Vol 2,53,(1978)

45 D.R.Paul and S.Newman,Polymer Blends,Vol 2,55,(1978)

46 F.Ide and A.Hasegawa,J,APPl Poly Sci,18,963,(1974)

47 D.R.Paul and S.Newman,Polymer Blends,Vol 2,56, (1978)

48 J.L.Amos,Poly Eng Sci,14,(1974)

49 S.L.Rosen ,Poly Eng Sci,7,115,(1967)

50 O.W.Lundstedt and E.M.Bevilacqua,J Poly Sci,24,297,(1957)

51 D.R.Paul,and S.Newman,Polymer, Vol2 ,39,(1978)

52 G.E.Molau in " Block polymer " Plenum Ed,New York, (1970)

53 D.R.Paul and S.Newman,Polymer Blends,Vol 2,57 (1978)

54 T.D.Pendle in "Block and Graft Copolymerization"(R.J.Ceresa, Ed) Vol 1,P 83,Wiley ,New York,(1973)

55 J.W.Schurer.A.deBoer and G.Challa.Polymer 16,201 (1975)

56 C.F.Paddock,U.S.A. Patent,3,758,435,(1973). Chem Abstr ,80, 48968 (1974)

57 THasegawa,K.Kishida and K.Tamia,Japanese patent,39656(1974) Chem,Abstr,82,18107,(1975).

58 E.H.Merz G.C.Claver and M.Baer,J Poly Sci,22,325, (1956)

59 Y.Minoura,H.Iino and M.Tsukasa,J,App,Poly,Sci,9,1299,(1965)

60 J.L.Otoole,A.A.Reventas and T,R.Von Toerne,Modern Plastics,41 (7) 149,(1964)

61 B.W.Bender,J App Poly Sci,9,2887,(1965)

62 A.Tager"Physical Chemistry of Polymers" chapter 19,(1978)

63 A.Dobry and F.Kavenoki,J Poly Sci 2, 90 (1947)

64 A.Tager "Physical Chemistry of Polymers" Moscow (1978)

65 N.U.Kuleznev,L.S.Korokhina and B.A.Dogadkin,Kollid Zhurn 29, 170,(1967)

66 G.Scott and C.Sadrmohaghegh to be published

67 S.S.Voyutsky,Autoadhesion and additive in polymers, Moscow , (1964)

68 S.R.Rosen,Polym Eng and Sci, 119 April (1967)

69 R.J.Kern,J.Polym Sci 21, 19 (1956)

70 A.D.Melstyre,J App Polym Sci 17, 29 (1963)

71 R.Buchdahl and L.E.Neilson,J Polym Sci,15, 1 (1955)

72 G.Gee,Rubb, Chem and Tech,18,71 (1943)

73 P.A.Small,J Appl Chem,3,71 (1953)

74 G.E.Molau,J Polym Sci,34,1276 (1956)

75 T.R.Paxton,J App Polym Sci,7,1499 (1963)

76 S.L.Rosen,Polym Eng Sci 116,April,(1967)

77 C.Sadromohaghegh,PhD Thesis Aston University in Birmingham (1979)

78 J.M.G.Cowie.Polymers:Chemistry and Physics of Modern Materials,54(1973).

79 M.Matsuo,G.nozaki and Y.Jyo,Polym Eng Sci,9(3) 197 (1969)

80 M.Takajanagi .Mem.Fac.Eng ,Kyushi.Univ,23,11,(1963).

81 L.E.Neilson,Mechanical Properties of Polymers,Reihol,177 , 171,175,(1962)

82 L.J.Haghes and G.L.Brown,J App Polym Sci, 5,580 (1961)

83 L.H.Sperling,D.W.Taylor and D.R.Bardman,J.App.Polym.Sci,14 73,(1970)

84 M.Bear,J.Polym.Sci, A-2,2,417 (1964)

85 E.P.Cizak (US)pat 3,383,435 (1968)

86 M.Bank,J.Leffingwell and C.Thies,J Polym Sci A-27,795(1969)

87 K.Schmeider 1,5,7,(1962)

88 E.Jinkel and H.V.Herving Kolloid-Z,148,57,(1963)

89 M.L.Dannis,J.App.Polym.Sci 7 231,(1973)

90 S.G.Turley,J Polym Sci,C-1,101 (1963)

91 R. Buchdahl and L.E.Neilson,J App Polym Phys,21,482,(1950)

92 A.A.Movsum.Zade,Vysokmol,Soedin,6,1340,(1964)

93 V.J. Schramm,J App Polym Sci,1,251 ,(1959)

94 P.V.Papero,E.Kuba and L.Roland,Text Res J,37,823,(1967)

95 L.H.Sperling and O.W.Friedman,J Polym Sci,A-27,425 (1969)

96 L.J.Hughes and G.L.Brown,J App Polym Sci,7,59,(1963)

97 G.Holden,E.T.Bishop and N.R.Legge,in the Proceedings of the Int Rubb.Conf,(1967) Maclaren

98 W.D.Neiderhauser and W.Bauer.J ,US pat 3,641,199,(1972)

99 S.L.Rosen.Polym.Eng and Sci,April 120,(1967)

100 3076781 Feb.5,1963 (Farbwerke Hoechst) chlorinated polyolefins US Pat

101 Report on nomenclature in the Field of Macromolecules,J Polym Sci ,8.257,(1973)

102 H.Battaered and G.W.Treger"Graft Copolymers" chapter 1, (1973)

103 D.C.Allport and W.H.Janes."Block Copolymers" (1973)

104 R.J.Ceresa. Block and Graft Copolymers,Pub,London (1962)

105 R.J.Ceresa, Block and Graft Copolymers, 11,(1962)

106 P.J.Flory,J Amer Chem Sci,59,241,(1937)

107 J.R.Roland and L.M.Richards,J Polym Sci 9,61(1952)

108 G.Smets and M. Glaesen,J Polym Sci,8 289 (1952)

109 L.C.Bateman Industr Eng Chem,49,704,(1957)

110 E.M.Bevilaque J Polym Sci,24,292,(1957)

111 G.Smets and A.Hertoghe.Makromol Chem .,17,189,(1956).

112 Encyclopedia of Polymer Science and Technology 2,489,(1965).

113 P.W.Allen and F.M.Merrett,J Polym Sci,22,193.(1956).

114 P.W.Allen,G.Ayrey,G.Moore and J.Scalan J Polym.Sci,36, 55, (1959).

115 W.L.Hawkins. Polymer Stabilization.p 168 London (1973)

116 H.A.Battaerd and G.W.Tiger.Graft Copolymers.,London (1967)

117 C.H.Bamford and R.G.W.Norrish.J Chem Sci 1504 and 1521,(1938)

118 G.Odian,T.Tacker,A.Rossi and E.Ratchik,J Polym Sci,57, 11, (1961)

119 W.R.Moore.Polymer Chemistry.(London),p,37,(1962).

120 H.C.Haas and P.M.Kamath.J.Polym.Sci,24, 143 and 85,(1957).

121 L.Carrick.J Polym Sci,8,215,(1970).

123 T.L.Cottrell,The Strength of Chemical Bonds, London (1958)

124 R.J.Ceresa,Block and Graft Copolymers,p 65,(1962)

125 A.A.Berlin,Adv Chem Moscow,27,94,(1958)

126 N.K.Baramboim, Mechano-chemistry of Polymers,translated from Russian by R.J.Mosely ,edited by Watson,Rubber and plastic Research Association of Great Britain (1964)

127 H.Grohn and C.Visiliu-oprea.Analel Univ ,Buchrest,Ser Stint Nat . 14 (1) ,27,(1965)

128 N.K.Baramboim and Y.U.Simako, Polym Sci U.S.S.R (English), 8,235,(1966)

129 M.Pike and W.F.Watson. J Polym Sci,9,229,(1956)

130 D.C.Allport and W.H.Janes,Block Copolymers 36,(1973)

131 H.Grohn and K.Bishop , Chem Tech ,11,384,(1959)

132 A.Casale and R.S.Porter,Adv in Polym Sci,17.30,(1975)

133 D.J.Angier,W.F.Watson,J Polym Sci ,18,129,(1955)

134 A.A.Berlin,Usp Khim,27,94,(1958),CA52/11456b

135 M.S.Akutin and B.N.Artememko,Plst.Massy,9,64 (1967)

136 A.Casale and R.S.Porter.Adv in Polym Sci 17,62,(1975)

137R.J.Ceresa. Block and Graft Copolymers ,93 (1969) London

138 D.J.Angier and W.F.Watson J Polym Sci,20,235,(1950)

139 D.Mangaraj and B.C.D oan,J.Polym Sci,13,630,(1975)

140 Aldrich Catalogue Handbook of Organic and Biochemicals(1977-1978)

141 A.Scott,Ph.D Thesis Aston University in Birmingham (1976)

142 M.Amin, Ph.D Thesis Aston University in Birmingham (1973)

143 K.T.Paul,RAPRA,2,29,(1972)

144 F.M.Rugg,J.J.Smith and R.C.Bacon,J Polym Sci 13,535,(1954)

145 J.C.W.Chien and C.R.Boss,J Polymer Sci A1 1579 (1977)

146 A.Scott PhD Thesis Aston University in Birmingham (1976)

147 K.Chakraborty PhD Thesis University of Aston in Birmingham (1977)

148 K.T.Paul,RAPRA Members,J,273-281 Nov (1963)

149 C.E.Locke and D.R.Paul,J App Polym Sci 17,2603,(1973)

150 C.Sadromohaghegh PhD Thesis Aston University in Birmingham (1979)

151J.H.Briston,Plastics films Page 21

152 Renfrew and Morgan,POlythene 169-170,(1948) London

153 C.E.Locke and D.R.Paul,J App Polym Sci,17,2600 (1973)

154 Ewing, Instrumental methods of Chemical Analysis, Mc Graw, Hill page 82 (1960)

155 C.Sadromohaghegh PhD Thesis Aston University in Birmingham (1979)

156 M.U.Amin PhD Thesis,page 78,Aston University in Birmingham(1973).

157 H.Staudinger, and A. Steinhofer,Ann ,517,35 (1935)

158 K.J.Saunders Organic Polymer Chemistry ,London(1973)

159 K.Charkroborty Ph.D Thesis Aston University in Birmingham (1977)

160 G.Scott and C.Sadrmohaghegh,Ph.D Thesis Aston University (1979)

161 Oak and Richards,J Chem Soc, 2429 (1949)

162 L.J.Bellumy, Infra-red Spectroscopy of Complex Molecules,Methuen

163 and Co.Ltd.London (1958)

164 J.R.Dyer, Aplication of Absorption Spectroscopy Compounds,London(1965)

165 F.H.Lohmann,j Chem Ed 32,155, (1955).

166 C.Sadrmomaghegh Phd Thesis Aston University in Birmingham,(1979)

167 L.E.Nielsen,Mechanical Properties of Polymers,177, (1962)

168 W.F.Billmeyer,Text-book of polymer science, London (1967)

169 M.U,Amin PhD Thesis, Aston University (1973)

171 R.J.Martinovich, SPE,Technical papers ,9,1,(1963)

172 L.E.Neilsen, Mechanical Properties of Polymers New York Vol 1 (1974)

173 Instruction Mannual for Rheovibron DDVII Toyo Measuring Instruments Co.Ltd,Tokyo,(1969)

174 A.Tager,Physical Chemistry of Polymers ,67,(1978)

175 C.Sadrmohaghegh PhD Thesis ,36, (1978),Aston University.

176 W.L.Hawkins,Polymer Stabilization 3, London (1972)

177 A.Tager Physical Chemistry of Polymers, Moscow (1978)

178 L.A.Wall,M.R.Harvey and M.Tryon J Phys Chem, 60,1306,(1965)

179 R.H.Sansen,W.H.Martin and T.De Benedictis,Trans.Inst.Rubber Ind, London 39,(6) T 301 (1963)

180 W.L.Hawkins Polymer Stabilization 8, (1972) London

181 C.E.Rogers.Physics and Chemistry of the Organic Solid State pt 11

Iinterscience, New York,p 510, (1956).

182 R.M.Barrer, Diffusion in and through solids ,Cambridge Press(1941)

183 H.D.Keith and A.Weissbery,Eds,Physics and Cemistry

184 A.J.Brydson ,Plastic Materials.London , 105, (1966)

185 Renfrew and Morgan , Polyethylene ,London , 88 and 94 ,(1957)

186 Cross,Richards and Willis, Diss Faraday Soc, 9, 235, (1950)

187 A.Elliot,E.J.Ambrose and R.B.Temple J Chem Phys 16, 877,(1948)

188 Harlen,W.Simpson ,F.B.Waddington and A.C.Baskett.J Ploym Sci 18,589, (1955)

189 M.Dole,C.D.Keeling and D.G.Rose,J Am Chem Sci,76,4304, (1954)

190 M.U.Amin PhD Thesis Page 189-190,Aston University ,(1973)

191 C.W.Bunn.Trans Faraday Soc 35 482,(1939)

192 G.Cotten and W.Sacks J Polym Sci Part A, 11345, (1963)

193 M.U.Amin PhD Thesis Aston University,(1973)

194 Oakes and Richards, J Chem Sci 2929,(1949)

195 F.M.Rugg,J.J.Smith and L.H.Wartman.Accad Sci 57, 398,(1954)

196 F.M.Rugg,J.J.Smith and R.C.Bacon.J Polym Sci 13,535,(1954)

197 J.P.Luongo,J Polym Sci 42,139,(1960)

198 B.J.Bacon.J App Sci 2,281,(1959)

199 Aggrawell and sweeting,Chem Rev 57,665,(1957)

200 Bellamy, The Infra-red Specroscopy of Complex Moleculs,(1957).

201 D.J.Carlsson and D.M.Wiles,Macromolecules 2 (6),587,597,(1969)

202D.L.Wood andJ.D.Loungo. Mod.Plastics,38,132,(1961)

203 L.H.Cross,R.B.Richards and H.A.Willis.Dis,Faraday,Soc 9 235,(1950)

204 Irvin . Chem Phys J.25, 549. (1956)

205 W.M.Barentsen, D.Heinkens and P.Diet.Polymer . 15,Feb ,(1974)

206 E.H.Kerner,Proc,Phys Soc London, 498,808,(1956).

207 D.R.Paul and C.E.Locke J Appl Polym Sci 17,2597-2617 (1973)

208 R.F.Boyer,Rubber Chem Technol, 36,1303 (1963)

209 D.E.Kline,J.A.Sauer and A.E.Woodward,J Polym Sci 22 ,455 (1965)

210 A.H.Wilbourn,Trans Faraday Soc,54,717 (1958)

211 T.F.Schatzki,J Polym Sci 14C,139 (1966

212 G.Scott,A.Scott and A.Ghaffar,Europ Polym J ,11, 271 (1975)

213 F.Harlen,W.Simpson,F.B.Wadington,J.D.Waldron and A.C.Baskett,J Polym Sci,18, 589 (1955)

214 M.Dole,C.D.Keeling and D.G.Rose, J Am Chem Soc,76,4304 (1954)