A TECHNO-ECONOMIC STUDY OF THE RECYCLING OF MIXED PLASTICS TO USEFUL PRODUCTS

by

ESKANDAR SETOUDEH

Submitted for the
Degree of Doctor of Philosophy
of the
University of Aston in Birmingham

October 1981

To my family and to the
memory of my father

THE UNIVERSITY OF ASTON IN BIRMINGHAM

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SUMMARY

The techno-economic implications of recycling the components of mixed plastics waste have been studied in a two-part investigation: (a) An economic survey of the prospects for plastics recycling, the plastics waste arisings from retailing, building, automotive, light engineering and chemical industries have been surveyed by means of questionnaires and interviews. This was partially successful and indicated that very considerable quantities of relatively clean plastics packaging was available in major department chains and household stores. The possibility of devising collection systems for such sources, which do not lead to any extra cost, have been suggested. However, the household collection of plastics waste has been found to be uneconomic due to high cost of collection, transportation and lack of markets for the end products. (b) In a technical study of blends of PE/PP and PE/PS which are found in admixture in waste plastics, it has been shown that they exhibit poor mechanical properties due to incompatibility. Consequently reprocessing of such unsegregated blends results in products of little technological value. The inclusion of some commercial block and graft copolymers which behave as solid phase dispersants (SPDs) increase the toughness of the blends (eg EPDM in PE/PP blend and SBS in PE/PS blend). Also, EPDM is found to be very effective for improving the toughness of single component polypropylene. However, the improved mechanical properties of such blends have been accompanied by a fast rate of photo-oxidation and loss of toughness due to the presence of unsaturation in SPD's. The change in mechanical properties occurring during oven ageing and ultra-violet light accelerated weathering of these binary and ternary blends was followed by a viscoelastometric technique (Rheovibron) over a wide range of temperatures, impact resistance at room temperature ($20 \pm 1^{\circ}C$) and changes in functional groups (ie carbonyl and trans-1,4-polybutadiene). Also the heat and light stability of single and mixed plastics to which thiol antioxidants were bound to SPD segment have been studied and compared with conventional antioxidants. The long-term performance of the mixed plastics containing SPD have been improved significantly by the use of conventional and bound antioxidants. It is concluded that an estimated amount of 30000 tonnes/year of plastics waste is available from department chains and household stores which can be converted to useful end products. This justifies pilot-experiments in collaboration with supermarkets, recyclers and converters by use of low cost SPD's and additives designed to make the materials more compatible.

KEY WORDS: Techno-economic, Plastics waste, Solid phase dispersants (SPDs), Long term performance, Useful end product

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Last, but by no means least, my sincere appreciation to my mother for her patience and encouragement throughout this work.

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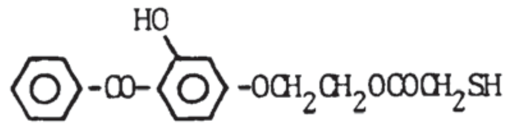
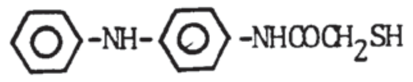
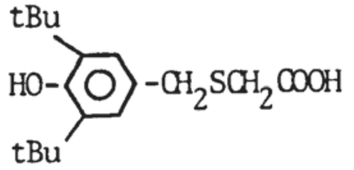
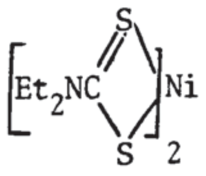
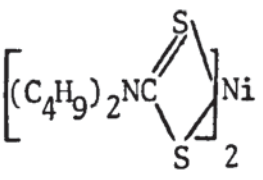
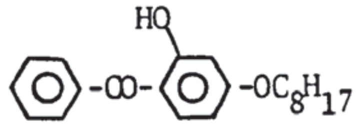
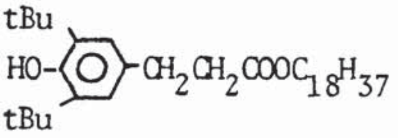
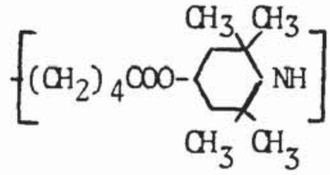
LIST OF ABBREVIATIONS

Chemical Structure	Name (abbreviation in brackets)
	4-Benzoyl-3-hydroxyphenyl-o-ethyl thioglycollate (EBHPT)
	4-(Mercaptoacetamido)diphenylamine (MADA)
	(3,5-Ditertiarybutyl-4-hydroxy) benzyl carboxymethyl sulphide (DBCMS)
	Nickel diethyl dithiocarbamate (NiDEC)
	Nickel dibutyl dithiocarbamate (NiDBC)
	2-Hydroxy-4-octyloxybenzophenone (UV531 - HOBP)



n-Octadecyl-3-(3',5'-di-tert-butyl-4-hydroxyphenyl) propionate (Irganox 1076)



Bis-(2,2,6,6-tetramethyl-4-piperidininy) sebacate (Tinuvin 770)

CHAPTER ONE

INTRODUCTION

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INTRODUCTION

1.1 General Introduction

A major advantage of thermoplastic polymers is their ability to be moulded into complex shapes of high quality much more cheaply than metals. This has led to a favourable technical and economic environment for the extensive replacement of traditional materials by polymers. However, the escallation of the raw material costs of plastics has provided economic incentives for the investigation of polymer recycling processes.

The main outlets for plastics are in the packaging and building industries, with other markets spread over a wide variety of manufactured products. The rapid growth of the plastics industry has occurred mainly as a result of penetration into markets previously held by more traditional materials, such as ferrous and non-ferrous metals, leather, glass and paper. Estimates of the annual savings of a range of materials brought about by substitution by plastics have been made as follows(1):

Metals	1.5 million tonnes
Paper and board	0.75 million tonnes
Wood	0.15 million tonnes
Others	0.60 million tonnes

The future increased demand of plastics is dependent on two parameters:

(a) the growth in world population, and

(b) the growth in demand per head.

H Teitge(2) has estimated the plastics demand for the years 2010, 2040 and 2080 (see Table 1.1). It has also been pointed out(2) that because of high wage levels in countries with high per head consumption and at the same time comparatively low price of plastics, the recycling of such plastics is still not economical. In future, the increase in the price of plastics as well as changes in the ratio of the wage to plastics price, will economically favour the recycling of plastics.

Table 1.1 Development of world plastics consumption(2)

Year	World population (1000 mill)	World plastics consumption* (in mill t)	Mean per head consumption (in kg)
1980	4.5	50	10
2010	7.6	144	20
2040	10.6	321	30
2080	12.2	724	60

* Without recycling

1.2 UK Consumption of Plastics

The consumption of plastics has been increasing steadily over the last ten years (apart from the recession of 1975 and 1980), although the rate of increase has varied (see Fig 1.1). For the period up to 1974, one can speak of a quasilinear increase. After the phase of recovery that followed the oil crisis, during 1976, a much reduced growth rate is apparent and there is a sharp drop in consumption in 1980 by 17.5% due to the recession. Table 1.2 breaks down the UK plastics consumption by polymer types between 1976 and 1980(3).

1.3 The More Common Types of Plastics and their Uses

Plastics can be classified into two classes(4):

(a) Thermoplastics which are not cross-linked (or not extensively so). These can be softened and moulded on heating and can thus be readily recycled when clean and segregated.

(b) Thermosetting resins (thermosets) which are cross-linked during processing (curing or hardening) to form three-dimensional structures. These cannot be recycled as such because the hardening is irreversible. The recycling potential of thermosetting resins is limited to their use as fillers or to the recovery of their intrinsic energy by incineration or pyrolysis.

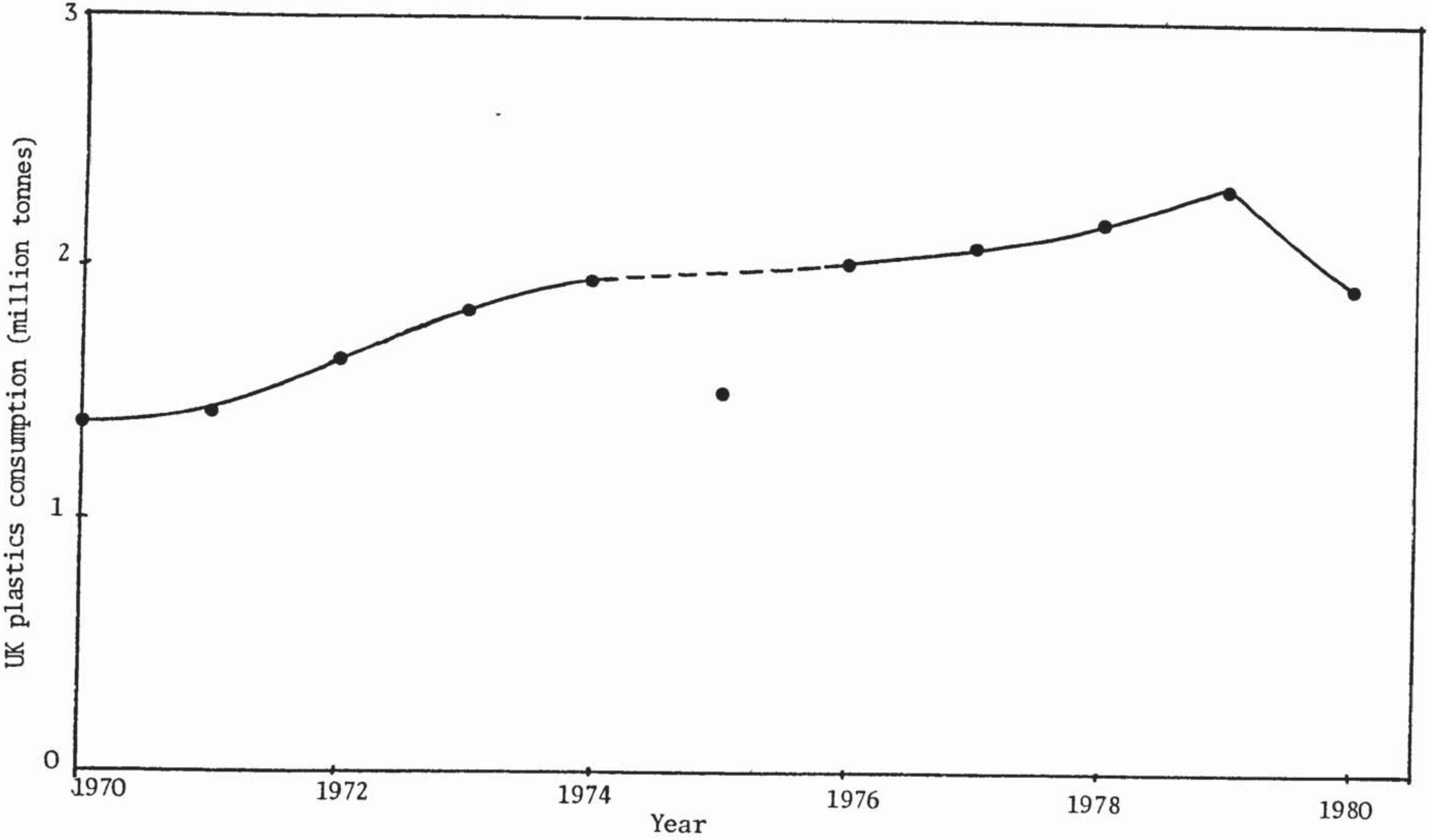


Fig 1.1 UK plastics consumption (1970-1980)

Table 1.2 UK consumption of plastics

Type of Plastics	Consumption 1000 Tonnes				
	1976	1977	1978	1979	1980
Thermoplastics:					
Low density polyethylene (LDPE)	417	425	455	502	415
High density polyethylene(HDPE)	120	135	150	176	160
Polypropylene (PP)	185	196	230	246	205
Polyvinyl chloride (PVC)	422	400	418	448	351
Polystyrene (PS)	160	150	166	166	131
Expanded polystyrene (EPS)	19	20	21	22	20
Acrylics	23	24	25	27	23
Polyamides	20	20	20	21	17
Acrylonitrile-butadiene-styrene copolymer (ABS)	36	37	45	59	43
Acetals	-	7	8	8	6
Polyester (saturated) films	14	16	17	21	17
Thermosetting:					
Amino plastics	136	163	138	137	120
Phenolic resin and moulding powder	60	63	73	80	60
Epoxides	13	14	14	15	13
Polyurethanes	71	84	89	95	84
Unsaturated polyester resins	58	69	65	61	45
Others:					
Total of small tonnage of both types with specialised applications*	287	271	258	288	245
TOTAL	2041	2094	2192	2372	1955

*Principally polycarbonates, polytetrafluoroethylene and saturated polyester moulding and blow moulding materials

1.3.1 The Major Thermoplastics(4)

(i) Polyethylene Two forms of polyethylene are produced, low density (LDPE), which is relatively flexible and high density (HDPE), which is relatively stiff. Polyethylene is used to make sheets, bags, milk bottles, detergent containers, stiff bottles for bleach etc, household utensils, toys and insulation and sheathing for cables.

(ii) Polypropylene Polypropylene is more rigid and lighter than polyethylene. It's main uses are for highly transparent packaging (eg crisps, snack food and biscuits), trays, furniture (chairs), car components, pipes, woven sacks and some carpets.

(iii) Polystyrene Polystyrene is a transparent polymer for drinking cups, small rigid containers (yoghurt, cream, eggs), foam forms for packaging and ceiling tiles, sheets for refrigerator liners and for transparent lighting fittings.

(iv) Polyvinyl chloride Polyvinyl chloride can be rigid or flexible depending on the amount of plasticiser incorporated, 0-10% plasticiser being used for rigid PVC. Rigid PVC is used for clear bottles (shampoos, detergents, orange squash) clear film for packaging, rigid sheet (corrugated sheets for buildings), pipes (rain water, mains, drains), gramophone records and car trims. Flexible PVC is used for cable insulation, flooring, car and furniture upholstery, shoe soles and raincoats.

(v) Acrylonitrile-butadiene-styrene (ABS) ABS is a tough plastic which is used for telephone and instrument cases, car trim and applications requiring high impact strength.

(vi) Acrylics (eg perspex) These polymers, which are usually methacrylate based, are durable and transparent and are used for windscreens, signs and light housings.

1.3.2 Lower Usage Thermoplastics

(i) Acetals Polyoxymethylene are used for metal replacement in engineering and building applications.

(ii) Nylons Polyamides are used for engineering and electrical applications in a wide range of industries.

(iii) Polycarbonates These are used where toughness and transparency are important (eg protective shields, baby feeding bottles).

(iv) Polytetrafluoroethylene (PTFE) This is used for non-stick and low friction applications (eg Teflon, Fluon).

(v) Polyester (PE) (especially polyethylene terephthalate) This is used for engineering applications and as a tough transparent film for photographic and reprographic purposes. A recent development is in so-called recyclable PET bottles into useful products (5).

1.3.3 Thermosetting Resins

(i) Formaldehyde based resins The main types are phenol formaldehyde (PF), eg Bakelite, urea formaldehyde (UF) and melamine formaldehyde (MF), eg Formica. These plastics or resins are used for tableware, electrical plugs, sockets and other electrical components. UF foam is used for cavity wall insulation.

(ii) Epoxy resins (polyethers) and unsaturated polyesters These plastics are used with glass fibre and other reinforcing agents for GRP boat hulls, car bodies, baths, portable buildings, etc.

(iii) Polyurethane (PU) This is used for furniture shells, furniture upholstery, insulation and in paints.

1.3.4 Additives (6)

Additives such as stabilisers, flame retardants, colourants, plasticisers, reinforcing agents and fillers may be added to plastics to modify and improve certain properties.

Flame retardants commonly used for plastics includes tricresyl phosphate and antimony trioxide.

Plasticisers are usually high boiling solvents or softening agents which are added to a plastic to facilitate processing or to increase flexibility or toughness. The principal plasticisers used today are dialkyl phosphates, such as dioctyl phosphate, aryl phosphate, such as tricresyl phosphate, and esters of aliphatic dicarboxylic acids such as dioctyl adipate. An addition of 30-50% plasticiser to PVC reduces the glass transition temperature of the polymer to give a flexible plastic with high elastic recovery.

A filler (or extender) is added to a plastic to modify its physical properties such as strength and hardness and to reduce the cost of the final product. The filler may be inorganic, for example clay, talc, mica, silica, asbestos and fibre glass or it may be organic such as various forms of cellulose derived directly from wood or vegetable fibre or obtained as a by-product from the textile industry, eg wood flour and chopped fabric. Fillers are usually compounded as 10-50% of the plastic. Antioxidants will be discussed in section 1.8.2·1f.

1.4 End-use of Plastics

The size of the plastics industry in the UK and its considerable growth rate is shown in Table 1.3(7). Packaging is seen as the most significant consumer of plastics, producing an even more

Table 1.3 UK plastics applications 1973 and predictions for 1980[7]

End Use	1973 Consumption		1980 Consumption		Waste Arisings	
	1000 tonnes	%	1000 tonnes	%	1000 tonnes	%
Packaging	550	30	730	25	730.0	43
Building	460	25	675	23	337.0	20
Electrical	200	11	280	10	-	-
Consumer non-durables	130	7	195	7	-	-
Automotive	110	6	420	14	210.0	12
Consumer durables	110	6	335	12	335.0	20
Miscellaneous*	270	15	255	9	76.5	5
Total	1830	100	2890	100	1688.5	100

* ie plastics used in any other application

significant proportion of the waste arisings.

1.5 Sources of Waste Plastics

According to their location of origin, plastics waste can be divided into the following groups.

1.5.1 'In Plant Waste'

This is the waste originating from the plastics processing industry in the form of sprues, runners, flash, rejected pieces, etc, which is homogeneous in nature. A major part of this material is already being reworked by re-incorporation into feed stock used in the plant. The remainder is contaminated and is generally unsuitable for further use due to, for example, partial decomposition as a result of excessive heat treatment, or due to accidental contamination by grease or other factory dirt.

1.5.2 'Industrial Waste'

This is the waste originating from further processing or treatment of intermediate plastics products (eg bulk containers in the dairy or sugar industries before packaging into smaller containers) which are frequently inhomogeneous in nature. Such waste is often constituted of mixtures of different polymeric materials or of different product formulations, or of mixtures of polymers with other material, such as paper or fabric. Such composite structures are used to develop the physical properties needed for particular applications, eg the use of coated fabrics as an alternative to leather. The complete separation of this mixed product into its primary constituents is not normally feasible on an economic basis and any utilisation will therefore have to be dependent on the development of techniques for processing mixed products and for separating them more efficiently.

1.5.3 'Domestic Waste'

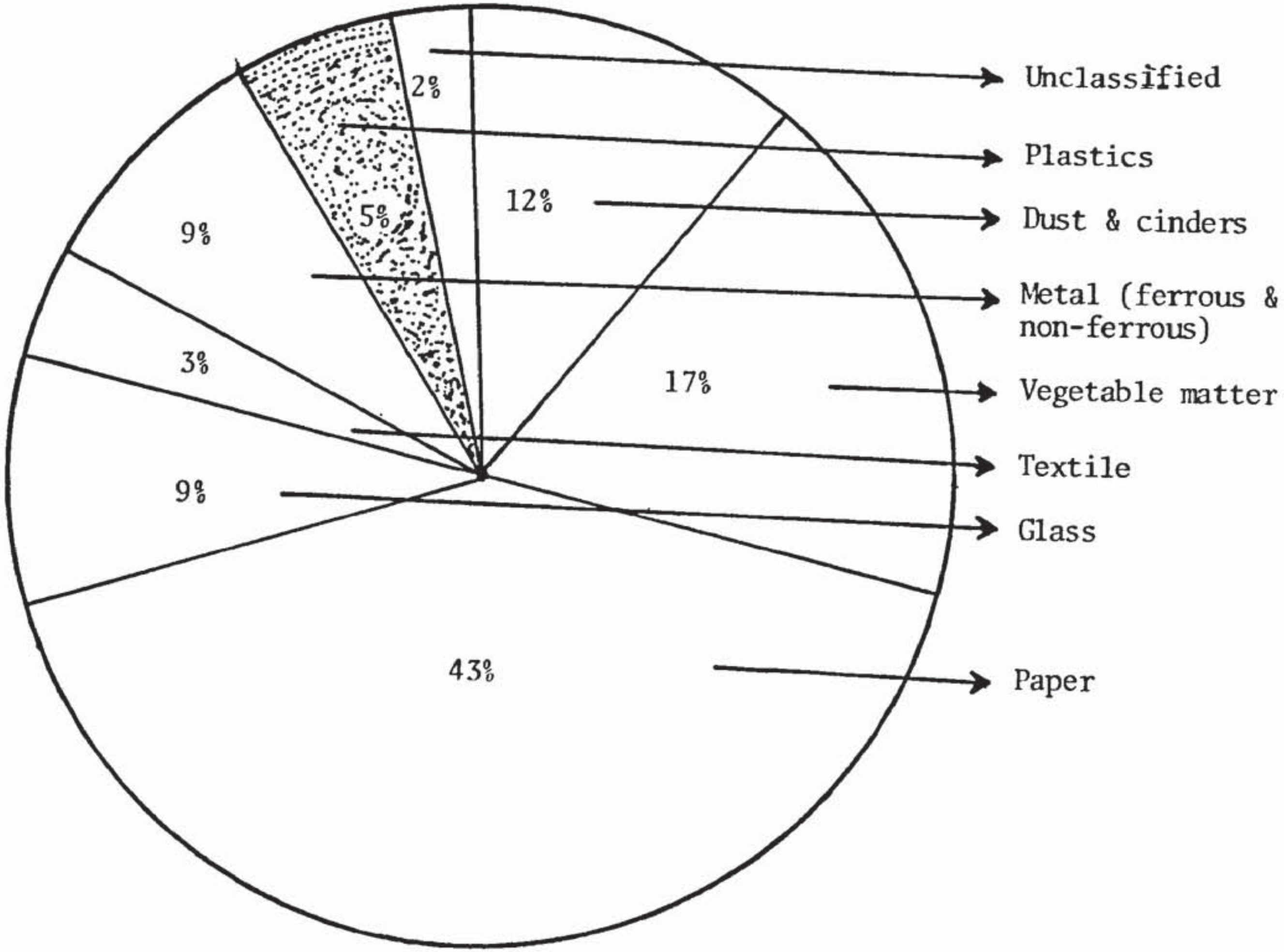
Domestic waste is the waste obtained from the collection of used or obsolete plastic objects or from refuse (eg household plastics waste). A number of studies(8-10) have indicated that the average plastic content of domestic and urban rubbish is about 4% by weight, and recent investigation has shown that this was increased to an average of 5% by 1980. Thus, for the UK, it has been estimated that the average composition of domestic refuse by weight in 1980 will be as shown in Fig 1.2(8). The most recent estimate of the quantity of domestic waste and commercial waste arising in Great Britain is 24 million tonnes(7,81).

1.5.3.1 Problems of Domestic Plastic Recovery

Problems encountered in domestic waste recovery can be classified as follows:

(a) Collection of waste Plastics waste, both industrial and

Fig 1.2 1980 estimated average composition of domestic refuse in UK



household, occur over a wide geographical area, often in relatively small quantities. Collection and segregation of such waste is expensive and uneconomic, unless the costs associated with collection, transport and sorting can be offset against the value of the recovered plastics.

(b) Low density to volume ratio One of the many advantages of plastics is their low weight and density but relatively high strength. Unfortunately, this is less of an advantage when plastics recovery is considered. The very high number of waste plastics items that would need to be collected to produce any significant recovery of actual plastics material is therefore unfavourable economically unless special baling equipment is introduced (this will be discussed fully in Chapter 2).

(c) Contamination Plastics waste is often contaminated by dirt, food or other substances that would have to be removed before the waste could be utilised. Even assuring a feasible sorting operation, the cost of such a cleaning operation would probably be prohibitive in many cases.

(d) Segregation of material types Plastics, unlike some of their competitor materials, are not a family of materials with similar properties, as plastics waste involves a combination of different materials, often as composites. These may be in various colours, shapes and be printed, decorated or labelled.

1.6 Re-use

In the consumer area, it is probably in re-use that plastics excell themselves. A glance in any kitchen or laundry, or a handyman's workshop, or a school art room, will reveal plastics being used in a wide range of secondary applications.

Bags, bottles, tubes and ice cream buckets are used as storage vessels, as flower pots, etc. If these containers went directly into the waste stream, it is obvious that new equivalents would need to be produced.

Re-use is also widely practiced with large plastic containers. Some drums and pails are retained for some time after use by farmers, building tradesmen, manufacturing firms and others for sorting, carrying and mixing applications.

Many plastics containers are also returnable; plastic crates for example, have widely been used for the transport and storage of fish, meat and other products, while bottle crates are used for for milk, beer and soft drinks.

While it is virtually impossible to quantify the extent to which containers are re-used or returned, this factor must be considered in estimating recycling potential.

1.7 Recycling

In the past few years, two problems relating to industrial working materials have been gradually forcing themselves into the awareness of the general public. Rawmaterials supply is becoming uncomfortably scarce, and the accumulation of materials in their used form is becoming uncomfortably plentiful. In such a situation, the concept of recycling is naturally attractive since at one stroke it offers a contribution at both ends of the problem.

The conservation of raw materials, particularly of the finite kind (eg oil) has been recognised as a social obligation and the recycling of certain waste materials could be one way of meeting not only the above obligation but also as a means of avoiding pollution of air, water and land. Since the majority of plastics have oil as a raw material source, the recycling and re-use potential of their waste must be taken into account.

1.7.1 Reasons for Recycling

(a) Energy savings Simply discarding our waste plastics is discarding our valuable energy. For example, recycling plastics into fabricated products saves some 85-95% of the energy of a typical plastic package(11) (see Table 1.4). This includes the energy of the petroleum feedstocks used to manufacture the resin.

Table 1.4 Energy savings in recycling various plastics(11)

End Product	Energy Content (%)	
	Resin	Fabrication
PVC $\frac{1}{2}$ gal container	85	15
HDPE 1 gal container	90	10
LDPE 1 gal produce bag	94	6
Polystyrene meat tray	83	17

Table 1.5 Recycling plastics as a product -vs- burning plastics as a fuel(11) (1000 lb of LDPE)

Fuel value (MM Btu)	20.050
Recycling value (MM Btu)	37.712
Saving in recycling	17.662
Saving increase	88%

It is true that simply burning plastic wastes as fuel saves energy but recycling these wastes into a fabricated product will frequently double the energy savings. For example, 1000 lb of high density polyethylene has a fuel value of 20 million Btu, but recycling 1000 lb of polyethylene wastes into a fabricated product will save as much as 39 million Btu - an 85% saving as shown in Table 1.5.

(b) Recycling for economic reasons The general economics of the plastics industry where raw material costs form a significant part of the price of the fabricated article has always provided a powerful incentive for some recycling. In practice, as with metal, glass and paper industries, efforts have always been concentrated on the reworking of clean and homogeneous wastes which arise in the factory itself or which are brought in from firms which have specialised in up-grading and reconditioning plastic materials. If prices of virgin material increases, as a result of higher oil prices, the incentive for this type of recycling will be higher so that the amount of material treated may increase slightly.

1.7.2 Various Recycling Operations

(i) Primary material recycling In this process the polymer itself is reprocessed into the same application as the original article. Examples are the recycling of unsold gramophone records into new ones and the remoulding of obsolete bottle crates.

(ii) Secondary material recycling In this, the polymer is reprocessed to give an object which differs from the original one. As such, it includes cases where because of the nature of the material being recycled in this way objects are produced whose physical properties and value are less than they were originally. Examples are the manufacture of shoe heels from used plastic cups and the production of fence posts from mixed plastic wastes.

(iii) Recycling into energy Incineration utilises the latest energy contained in a material to produce heat which can be used to supplement other sources of power.

(iv) Chemical recycling This describes the treatment of recovered plastics and other wastes to give a useful product which may be, nevertheless of a very different nature to the starting material (hydrolysis of nylon and pyrolysis of PMMA does substantially give back starting materials). However, most polymers do not give chemically useful pyrolysis products and they generally have only fuel value.

1.8 Technical Factors Governing the Recycling of Plastics

1.8.1 Technical Limitations to Recycling

From the point of view of the plastics processing industry, an incentive to recycle material exists when the operation gives rise to no penalty in terms of costs, resources, productivity or technical hazard. Since the escallation of oil prices began in 1973 (for future oil prices see Fig 1.3)(12), there has been a corresponding increase in the cost of plastics materials, and this fact in itself has been a major influence in increasing the attractiveness of recycling. Against this has to be set the technical problems which can arise unless due account is taken of certain basic needs of plastics processing. Amongst these, some of the most important are:

(a) The material must normally be a single type of polymer, and for many applications, of known and constant formulation. This requirement arises because within the family of plastics materials different polymers have distinctive physical properties and any unforeseen change in composition can, therefore, affect the quality or safety of the article being produced. In addition, some polymers are incompatible with one another and the surface properties which result when these are mixed together involves their processing on many types of equipment impossible (compatibility will be discussed fully in section 1.8.2.2).

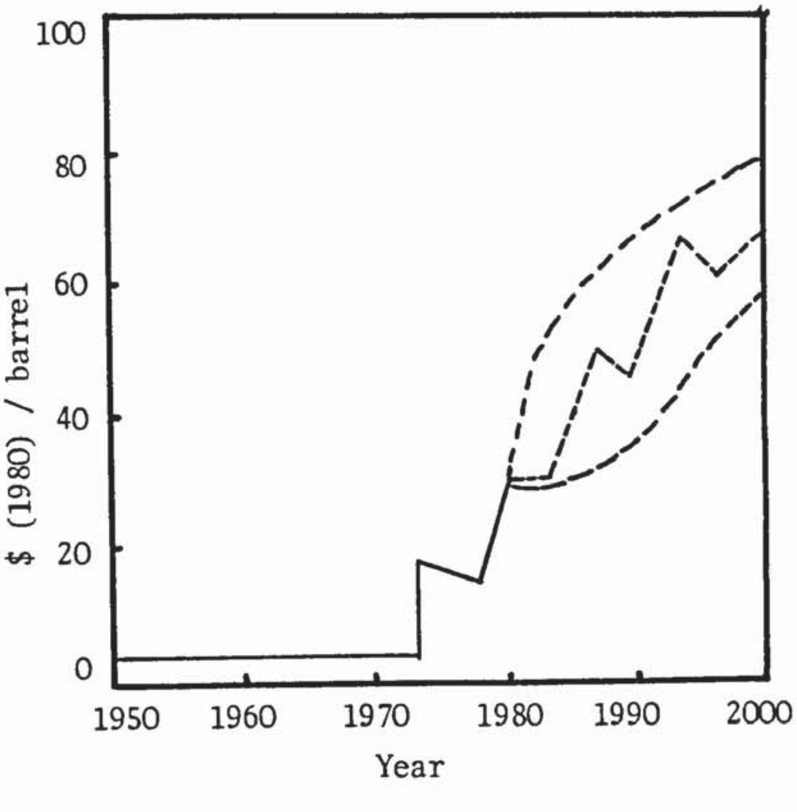


Fig 1.3 Future estimated oil prices (1980 - 2000)(12)

(b) The material must be free from contaminants and dry. Because the majority of plastics items are designed in such a way that a given property or effect is achieved with a minimum usage of materials, any system which permits discontinuities to be present in the structure of a product can give rise to failure in use. This is also important from a safety point of view since many plastics products are used for food packaging applications in which the presence of unknown and possibly tainting impurities is unacceptable.

(c) The material needs to be available on a regular basis. The majority of plastics processing operations are continuous in nature and their successful use depends on accurately matching the processing conditions to the raw material being handled. The use of recycled products can frequently call for some modification in these conditions and a 'stop go' availability can frequently mean that the process is not fully under control. As a result, not only can quality suffer, but also conversion efficiency can be reduced, thus affecting the cost of the final product.

1.8.2 Physical and Chemical Limitations to Recycling

1.8.2.1 Polymer Degradation during Processing and Service Life

Oxidation of polymers can primarily be viewed in two principle stages(13). The first is one which is manifested during the processing operation, characterised by the high temperature, thermal treatment and mechanical shear but only for a comparatively short time. The other occurs during service life of the fabricated articles subjected to relatively mild and/or intermittent oxidative attack. These oxidative processes manifest themselves as an adverse effect on the mechanical performance of the articles. Useful properties such as mechanical strength, electrical behaviour and aesthetic appeal are adversely affected.

The nature of the degradation reaction varies in rate and extent depending on the chemical(14,15) and physical(16,17) structures of the polymers. Initial molecular weight(18,19), the presence of chemical(20-22) and physical(23,24) impurities and the nature of the external environment(25) to which they are exposed, all affect the rate of the degradative processes.

Scott(25) points out that the most important accelerating environmental influences apart from oxygen which are deleterious to polymer stability are heat, light, mechanical deformation, contamination by metal ions and ozone.

1.8.2.1a Chemical Processes Involved in Thermal Oxidation

The chemical processes involved in thermal oxidation of polymers are now well understood as a result of extensive studies over the past thirty years(26). The most important feature of this process is the long kinetic chain free radical process (eq 1), which leads to the incorporation of many molecules of oxygen from a single free radical initiating species.

Chain propagating reaction $\qquad \mathrm{R\cdot + O_2 \longrightarrow ROO^\cdot}$ $\qquad \mathrm{ROO^\cdot + RH \longrightarrow ROOH + R^\cdot} \qquad (1)$

The formation of one molecule of hydroperoxide for each molecule of oxygen consumed is of fundamental importance to the kinetics of the process, since hydroperoxides are highly unstable materials which break down rapidly at processing temperatures giving rise to new free radicals which initiate new chains (eq 2). This gives rise to the well known auto-accelerating rate curve which is ultimately balanced by the bimolecular removal of alkyl peroxy radical from the system (eq 3).

$$\mathrm{2ROOH \longrightarrow ROO^\cdot + RO^\cdot + H_2O} \qquad (2)$$

$$\mathrm{2ROO^\cdot \longrightarrow Inert\ product} \qquad (3)$$

Under long term conditions, that is when the rate of initiation is low, the removal of a single free radical from the system will break a long kinetic chain involving many oxygen molecules.

1.8.2.1b Effect of Metal Ion Contamination

Very small amounts of transition metal ions have a marked effect on the induction period(27). Copper, manganese, cobalt and iron are particularly powerful thermal pro-oxidants in the form of soluble salts or metal complexes and their effect is to catalyse the breakdown of hydroperoxides to free radicals (eq 5).

$$ROOH + M^{+} \longrightarrow RO^{\cdot} + M^{2+} + {}^{-}OH \qquad (4)$$

$$ROOH + M^{2+} \longrightarrow ROO^{\cdot} + M^{+} + {}^{+}H \qquad (5)$$

The overall reaction is identical to normal thermal breakdown but it occurs thousands of times faster, effectively removing the induction period.

The more effective transition metal ions are not normally present in virgin polyolefins. Small amounts of titanium salts may be present from some polymerisation systems but their effects are small and are relatively easily controlled by antioxidants. The situation may be different in waste plastics. Iron, manganese and copper are widely distributed in biological materials and iron may also be introduced in the form of rust which is difficult to remove from agricultural packaging. Scott et al(28,28a) have found that the presence of ferric stearate accelerates thermal and photo-oxidation of the polyethylene and polypropylene.

1.8.2.1c Effect of Processing on Environmental Stability

The effect of processing on the environmental stability of plastics has been recently studied in some detail(27-31). It has been found that oxygen containing groups introduced during processing have a powerful photosensitising effect on the polyolefins during subsequent environmental exposure to normal weathering conditions. There is now a great deal of evidence to suggest that hydroperoxides formed during the processing operation are responsible for the photosensitisation by photolysis (eq 6). The formation of hydroperoxide is associated with the presence in the polymer of a minor amount of unsaturation, particularly vinylidene.

$$\mathrm{ROOH} \xrightarrow{h\nu} \mathrm{RO^{\bullet}} + {}^{\bullet}\mathrm{OH} \qquad (6)$$

Hydroperoxide is formed in an auto-accelerating mode and there is an induction period before vinylidene begins to disappear. The products formed by photolysis of carbonyl groups during photo-oxidation of polyolefins is of considerable importance to their behaviour during photo-oxidation.

1.8.2.1d Effect of Reprocessing on Polymers

It is clear then that peroxides formed during thermal processing are the cause both of melt instability of the polymer and of photo-instability. In the processed virgin polymer, these degradation problems can be controlled. In waste plastics from domestic or industrial sources (this does not refer to 'in house' factory waste which is normally recycled in small proportions with the virgin polymer feed without difficulty) the situation can be very difficult. In the first place, consumer waste, unless effectively cleansed, will contain small amounts of metal ions which are both thermal and uv pro-oxidants and in the second place the effect of light on thermally processed polymer is to introduce unsaturated groups which themselves act as pro-oxidants in a reprocessing operation. The effect of both transition metal ion contaminants and unsaturated photolysis products may be catastrophic unless new kinds of stabilising systems are developed to control their effect.

Sadrmohaghegh and Scott(32) have found a direct relationship between the initial concentration of hydroperoxide after processing and initial rate of carbonyl formation, with reprocessing of polyethylene in a closed mixer. The rate of photo-oxidation has been found to be auto-accelerating. In practice, most recycled polyethylene (with the exception of 'in house' recycled material) will have been subjected to some photo-oxidation during service. This point will apply particularly to packaging (eg containers, shrink wrap film, agricultural scaks, etc) which is potentially the major source of recyclable plastics waste.

It is found(32) that uv exposure, followed by recycling increases the sensitivity of recycled film to photodegradation considerably more than recycling alone; the effect is similar to that of three recycling operations without intervening uv exposure.

It is also found(28) that there is a sharp decrease in the embrittlement time of the polypropylene (unstabilised) with reprocessing. Fig 1.4 shows the chemical changes on the polypropylene with the number of recycling cycles.

1.8.2.1e Photo and Thermal Degradation of Polymer Blends

All types of polymers tend to degrade on weathering at least to some extent(33,34). The analysis of weathering behaviour becomes quite complicated in the case of polyblends because not only do the two phases age at different rates, but continuing interactions between the two phases remain of prime importance.

The most important target of oxidative attacks involves carbon-carbon double bonds. In fact, at the initial stage of oxidation, of rubber modified plastics, it is possible to consider that only the rubber phases oxidises, with no attack in the plastic portion. Hirai(34) has shown that polymers with a high double bond concentration are more oxygen sensitive than those having a low or zero concentration of double bonds.

Scott et al(35-40) have shown that rubber modified polymers undergo rapid loss of impact strength on photo-oxidation. This rapid loss of impact is found to be in parallel with decrease in the concentration of 1,2-dialkyl ethylene groups due to the rubber segments (polybutadiene).

The recent developments and the prominence of a new class of materials has stimulated an interest in the stability of polymer

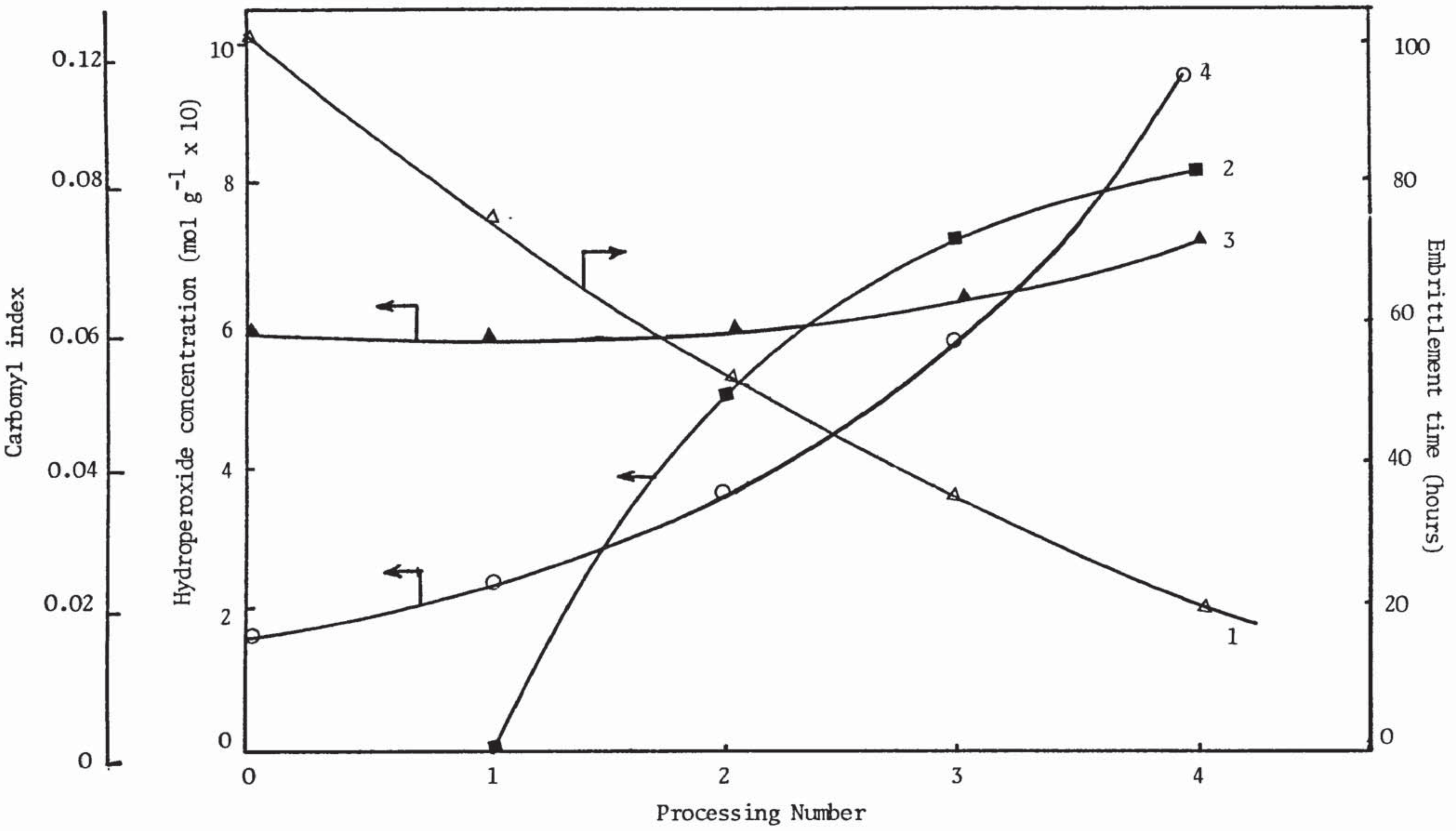


Fig 1.4 Relationship between functional group formation in PP during processing at 180°C and uv embrittlement time. 1 Embrittlement, 2 hydroperoxide concentration, 3 conjugated carbonyl index (1685 cm^{-1}), 4 saturated carbonyl index (1720 cm^{-1}) (Reproduced from C Sadrmohaghegh's Thesis)

blends. It is often surprising how the polymers in the blend influence the stability of each other in spite of the fact that this influence must usually act across the discrete phase boundary which exists between the constituents of the blend. This is quite different from the situation in copolymers in which the constituent monomers are chemically bonded to each other.

Scott et al(41,42) have studied the photostability of PE/PP, PE/PS and PE/PVC blends and have concluded that:

(i) PP, PS and PVC present in mixed plastics waste might be expected to increase photosensitivity.

(ii) This lower photostability of polymer blends (eg PE/PP, PE/PVC and PE/PS) is also reflected in their change in mechanical properties.

(iii) During uv irradiation, the tensile strength of the blends in all cases decreased initially but began to increase again at a later stage of oxidation. This increase was observed significantly at higher concentrations of PVC, PP and PS in LDPE. They believe that all these observations are due to the result from the net effect of two main reactions occurring during uv irradiation of blends; degradation at the interface and the interaction at the interface of the degradation products.

They have also shown(43) that during thermal oxidation, stabilised PVC acts as a heat stabiliser for LDPE/PVC blends, whereas unstabilised PVC acts as a thermal sensitiser.

Holmstorn et al(44) have made the following points on thermo-oxidative degradation of polyethylene.

(i) PVC and CPE adversely affect the thermo oxidative stability of LDPE. When unstabilised, PVC and CPE evolve large amounts of HCl during processing. Minor degradation of LDPE also occurs.

(ii) Stabilisation of the LDPE may be achieved by phenolic antioxidants. The tetra functional type of antioxidant used was much more effective than the bifunctional.

(iii) The stabilising effect of the antioxidants decrease more rapidly than usual when PVC was present.

(iv) Carbon black acted as a mild antioxidant and as a cross-linking agent during thermo oxidative degradation.

1.8.2.1f Some Possible Solutions to Polymer Degradation

Virgin polymers may be effectively stabilised in the melt stage before any appreciable quantity of hydroperoxide has been formed. This is normally achieved by the incorporation of small amounts of some compound which traps or removes free radicals. Notably, effective compounds are hindered phenols or aromatic amines which are converted by alkylperoxy radicals to stable free radicals incapable of continuing the kinetic chain (eq 7).

$$\begin{aligned} &ROO^{\bullet} + AH \longrightarrow ROOH + A^{\bullet} \\ &2A^{\bullet} \longrightarrow \text{Inert products} \end{aligned} \qquad (7)$$

(i) Chain-breaking antioxidants Conventional antioxidants are relatively ineffective in combating the deleterious effects of pro-oxidants produced during processing and subsequent environmental degradation. This is because they do not stop the formation of hydroperoxides by reaction 7 and these are, therefore, present to initiate photo-oxidation by 6 under environmental conditions.

Phenols and amines(27) do have some ability to inhibit the effects of metal ions in thermal oxidation. However, they show no protective effect when polymer films were exposed to uv light. The metal complexes produced are readily photolysed to give free radicals and the original metal ion in both the articles initiates photo-oxidation(25,30).

(ii) Preventive antioxidants Since both metal ions and uv light increase the rate of the chain-initiating process by catalysing the breakdown of hydroperoxide to free radicals by reactions 4,5 and 6 respectively, control of degradation in reprocessed polymer will depend on the development of more effective antioxidants which prevent the initiation process. These fall into three main classes(26,52):

(a) Metal deactivators The evidence suggests that metal ions exert their catalyst effect upon autoxidation by forming unstable co-ordination complexes with alkyl hydroperoxides, followed by electron transfer to give free radicals (see also section 1.8.2.1b). The deactivation of metal ions can be achieved in three ways:

(1) complexing the metal ions to its maximum co-ordination number by the various ligands,
(2) stabilising one valance state at the expense of the other, and
(3) forming an insoluble product, eg FeS.

(b) Uv absorbers(45,46) The most important function of uv screeners is that they prevent or reduce the rate of formation of initiating free radicals in the polymers. Important types of uv screening agents are orthohydroxy benzophenones, salicylates and benzotriazoles.

(c) Peroxide decomposers Some metal complexes, particularly those containing sulphur as one of the ligands, are powerful catalysts for the destruction of hydroperoxides.

Of these, the transition metal dithiocarbamates have been studied most extensively and nickel and cobalt dialkyl dithiocarbamates are amongst the most powerful thermal and uv antioxidants known. Peroxide decomposers are classified as follows:

(1) metal dialkyl dithiocarbamates(45,47),

(2) phosphite esters, cyclic phosphates, etc(48), and

(3) mono and disulphide compounds(49-52).

1.8.2.2 Polymer Compatibility

It is important to recognise that the incentive for the development of reprocessed products is not only economic but is also concerned with the conservation of non-renewable sources. If reprocessing is to make a contribution to the resource problem, solutions must be found which use less energy than starting with virgin raw materials. Therefore, it is economically desirable to eliminate complex separation processes and the use of energy-consuming cleansing operations if possible. Superficially, therefore, it would seem to be advantageous to reprocess mixed plastics in the ratio in which they are normally found in collected waste. Unfortunately, such mixtures give rise to fabricated products which are much inferior in mechanical performance (eg tear strength, impact strength, etc) to the original components used separately. This is due to the natural incompatibility of some of the common polymers (eg polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS)).

So, research and development on polymer blends is of value in order to obtain a better combination of properties for processing and for end use. This kind of research is important in the field of recycling of mixtures of domestic or industrial plastic scrap.

Scott et al(53,54) have investigated blends of low density polyethylene (PE) and polyvinyl chloride (PVC) and concluded that Young's modulus increased steadily from pure polyethylene to pure polyvinyl chloride whereas both tensile strength at break and elongation at break passed through a minimum at about 5% PVC. Optical and scanning electron microscopy related this mechanical behaviour to morpholocial changes in the two phase system under stress.

Blends of polyethylene (PE) and polypropylene (PP) have been widely investigated(54-60). It is found(54) that there is a limited compatibility (up to 5% PP) but all fall away to less than 10% of elongation at break of pure polyethylene at 20% of second component.

Paul and co-workers(61) investigated the mechanical properties of a simulated plastics waste mixture consisting of polyethylene (PE), polystyrene (PS) and polypropylene (PP) and polyvinyl chloride (PVC). No blend showed a higher property than the pure component having the largest value of the property. However, numerous blends were stronger than polyethylene, just as many were tougher than polystyrene. For certain properties, blends may be better than some virgin components, but with respect to the balance of properties, they are always inferior. Two different approaches for improving the mechanical properties of mixed plastics waste have been suggested:

(1) use of solid phase dispersants (SPDs) or compatibilisers, and
(2) chemical modification.

1.8.2.2a Solid Phase Dispersants (SPDs)

Schramm and Blanchard(62) have suggested chlorinated polyethylene (CPE) as a possible solid phase dispersant for polyvinyl chloride (PVC) and polyethylene (PE). Chlorinated polyethylene is prepared by the solid state chlorination of high density polyethylene (HDPE) slurry. During the chlorination process, the crystalline portions of the chain are not accessible for chlorination so that the parts associated with the crystalline region are all $-CH_2-$, while the amorphous parts consist of a mixture of $-CH_2-$ and $-CHCl-$. The $-CH_2-$ portion of the chain is compatible with polyethylene (PE) while $-CHCl-$ portion is compatible with polyvinyl chloride (PVC)(61).

Paul et al(61-64) used CPE solid phase dispersants with simulated palstics waste mixtures (binary and ternary) consisting of polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS). They drew the following conclusions from their work:

(i) CPE promotes toughness in blends that have a high proportion of PE and PVC. Blends consisting of PS are toughened to some extent by CPE, however, this may be due simply to the effect of CPE on other components.

(ii) The structure of the CPE plays some role in the extent of blend modification.

(iii) The use of CPE as a blend modifier has a potential application in the recycling of plastics recovered from municipal refuse. The CPE modification approaches appears to be more effective, however, when applied to mixtures containing principally PE and PVC.

Scott and co-workers have recently studied(54) the mechanical properties of three binary mixtures of incompatible polymers (LDPE/PP, LDPE/PS and LDPE/PVC) in the present of potential solid phase dispersants. They have concluded that it is possible to achieve an acceptable level of toughness in the composite products for the re-use of the materials in demanding applications. It is suggested that the main factor necessary to achieve good impact resistance and elongation at break of the polymer is the presence of a rubbery interphase between the heterophases. They have also suggested that in the case of blends (1 : 1 ratio) containing PE/PP and PE/PVC, ethylene-propylene-diene rubber (EPDM) appears to be the most effective SPD whereas for PE/PS, a butadiene-styrene block copolymer (SBS) is more effective.

It is found(65) that the mechanical properties of PP/LDPE blends depend greatly on the methods of processing used to fabricate the test specimens. Based on mechanical performance, the following order of effectiveness of different processing operations has been found.

Single gated injection moulding > compression moulding > double gated injection moulding

Weld lines appear to be especially serious for incompatible blends and should be avoided where possible. They have also found(65) that Epcar 847 improved the mechanical properties of LDPE/PP blends.

Scott and co-workers(43) have found that a cross-phase chemical interaction occurs in LDPE/PVC blends during high temperature processing under limited air, to give LDPE/PVC graft copolymers. A similar process also appears to occur during photo-oxidation of LDPE/PVC blends leading to improvement in blend properties. It is; also shown(66) that during melt blending of PS/LDPE a graft/block copolymer of PE/PS may be formed by using an initiator such as cumene hydroperoxide. The addition of this copolymer to PE/PS blend has improved its mechanical properties.

The addition of PS-g-LDPE blends in relatively low concentrations(67-70) diminished the particle dimensions significantly and led to improved mechanical properties.

Paul et al (71,72) have proved that addition of PS-g-PE, made by polymerising styrene onto polyethylene chains by co-radiation to a 50/50 PS/PE blend, diminished domain dimensions. Also, Wallrab (73) provided evidence of part homogenisation upon addition of PVC-g-PE to a 50/50 PVC/PE blend.

Professor Eli M Pearce (74) at the Polytechnic Institute of New York has initiated a programme designed to compatibilise plastic mixtures through the use of speciality polymers having a high potential for hydrogen bonding. In theory, domain barriers between components of an incompatible blend might be reduced through application of secondary bonding forces. Hydrogen bonds for example exert strong intramolecular forces between the polymer chains of nylon and cellulose. Dr Pearce is exploring the effectiveness of a class of specialised polymers designed to provide strong hydrogen bonding to one component of an incompatible blend.

1.8.2.2b Chemical Modification

Chemical modification of mixed plastics waste to produce material which would have properties similar to virgin resins and could be processed similarly to virgin materials would be the ideal way to recycle post-consumer plastics, assuming that the modification itself would not add too much to the cost of the material. This approach would require comparatively unsophisticated separation techniques to remove the plastics from wastes and would require no modification of existing plastics processing equipment. Chemical cross-linking has been investigated(75,76) as a possible superior means of up-grading the properties of mixed plastics waste. This approach would create, at a very small additional cost, materials with properties approaching those of some of the pure resins. Leidner(75) has found that, cross-linking of mixed plastics waste (by using about 3 pph of dicumyl peroxide 40C) results in tough, flexible highly impact resistant thermosetting material. He claimed that chemical cross-linking would add only about 3 C to the cost of 1 lb of recycled plastics.

1.9 Scope of the Present Project

Although the recycling of 'in house' plastics waste (in the form of off-cuts, flashing etc), has been practised for some time, the recycling of post-consumer waste presents much more formidable problems. This arises from the following causes:

(i) The waste is frequently contaminated by other materials which lead to difficulty in the recycling process (eg paper, metal foils, other plastics, organic materials).

(ii) The sources of plastics waste are variable with respect to the factors outlined in (i) and with respect to availability.

(iii) The recycling process modifies the performance of products made from recycled waste and this problem is exacerbated by the presence of contaminents.

(iv) Consumer waste cannot normally be recycled back into the primary application as can 'in house' waste. The viability of any recycling process therefore depends on the development of secondary applications which can tolerate a less technically defined product of more variable quality.

(v) In general, the technical performance of mixed wastes as a raw material for the converting industries is inferior to that of virgin polymers due to the material incompatibility of most of the common polymers.

(vi) Unless ways can be found of up-grading the mechanical and long term performance of products made from mixed plastics, the recycler will be limited to using carefully selected single component polymers from up-market products.

Previous work at Aston has been concerned with two main aspects of the recycling of mixed plastics(41):

(1) The mechanical behaviour of polymer blends and the effects of commercially available and synthesised solid phase dispersants (SPDs).

(2) The service behaviour of polymer blends and the development of melt and uv stabilisers for such blends.

The purpose of the present project is to examine the commercial feasibility of obtaining reproducible quantities of clean waste for reprocessing under the conditions defined as a result of Sadrmohaghegh's work and to compare this techno-economically with other recycling processes currently in use in the recycling industry.

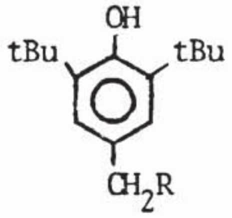
The technical aspect of the work is concentrated on long term performance of the blends which can now be produced and their application in selected applications. The main purpose of the work is to prepare adducts of antioxidant thiol containing polymers which could be used as compatibilisers, stabilisers to up-grade mechanical and long term performance of polymer blends (see below for antioxidant structure). This can be classified as follows.

(I) Attempts could be made to bind MADA and EBHPT on to polyethylene and polypropylene by use of mechanochemical processes.

(II) Attempts would be made to bind DBCMS, MADA and EBHPT onto ethylene-propylene diene monomer (EPDM) which is the most sensitive part of the blend to photo-oxidation, by use of mechanochemical processes.

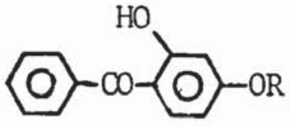
(III) Adducts obtained from I and II will be used as compatibilisers stabiliser of polymer blends and waste plastics.

(IV) The long term performance and mechanical properties of polymer blends containing these adducts is compared with blends containing conventional stabilisers and antioxidants.



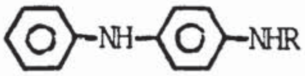
R = SCH_2COOH

(DBCMS)



R = $CH_2CH_2OCOCH_2SH$

(EBHPT)



R = $COCH_2SH$ (MADA)

CHAPTER TWO

ECONOMIC EVALUATIONS

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ECONOMIC EVALUATIONS

2.1 General Background

Large quantities of a plastics material of mixed composition could be recovered from refuse. Taking into consideration refuse arising from both domestic and commercial sources, as well as production scrap from the manufacturers of cable, carpets, laminates, etc, success with currently available processes and others being developed, could make available a raw material in quantities of serveral million tonnes annually in Western Europe alone(77).

Profitable business based on these possibilities and an expansion of plastics recycling will depend on the successful combination of developments in machinery and in compounding technology. These are essential requirements for the evolu tion of end products of high added value having the inherent characteristics of plastics. Developments in compounding technology include the extension and modification of the properties of recycled plastics by the incorporation of low cost fillers and additives designed to make the materials more compatible.

In the short to medium term, energy costs will continue to rise at a higher rate than prevailing inflation (see Fig 1.3)(12) and thus any scheme to recover energy will become increasingly attractive.

Similarly, the greater the energy content of any process, the comparatively less attractive it will become with time.

In order to establish a successful commercial plastics recycling operation, the following criteria have to be met:

(i) there is a continuous supply of scrap,
(ii) there is a technologically viable process for recycling,
(iii) there is an end use application and market for the recycled product, and
(iv) the economics of scrap supply, collection, processing and sale are such that a reasonable return on investment may be earned.

In the present study, the above criteria are fully discussed and assessed.

2.2 Economic Data: Sources, Categories and Volume of Waste Arisings

Contacts with the Packaging Industries Research Association (PIRA) and with the main organisations involved in recycling such as British Federation of Plastics (BPF) has provided data on the material availability of plastics wastes based primarily on published information and provided by polymer manufacturers and converters(78). This data gives no indication however of the availability of these materials for recycling or of their suitability for this purpose which depends on the specific situation at the point at which the plastics become waste. It is clear, the economics of collection dominate the overall viability of the recycling process.

2.2.1 Plastics Waste Arisings from In Plant Operations

Clean homogeneous plastics scrap is recycled 'in house' by the plastics processing industry or by independent recycler to produce granulates which are sold to the processers, either for admixture with virgin material or for use by itself in the production of products whose specifications permit the use of second grade material. 'In house' scrap consists of off-cuts, trims, sprues, runners, poor quality products, etc.

The available information on this area is rather sketchy and there is inadequate detail on levels of contamination and location of wastes. Estimates of the proportion of raw materials which become in plant scrap have been made as shown in Table 2.1(79).

Much of this in-factory reject material is directly reprocessed in the same factory and is, therefore, not waste. The quantity discharged as ex-factory waste has been estimated by Buttery(80) to be of the order of 100,000 tonnes/annum.

2.2.2 Plastics Waste Arisings from Domestic Refuse

A significant percentage of plastics is used as packaging materials

Table 2.1 Type and generation quota of waste in various processing methods. After [(79)]

Origin	Type and quantity of waste
Dry blending Banbury mixer	Powder, agglomerates, removed by screening drippings, aborted runs
Extrusion compounding	Chunks and strands from extruder purging. Wastes generated during faulty operation (overheating, impure feed). Custom compounding: 1-2% of throughput. In line compounding: 0.2% of throughput.
Injection moulding	Sprues and runners. Normally reground and reprocessed in amounts ranging from 1-15% of total feed. About 1% dirty grindings, floor sweepings, chunks from purging and contaminated mouldings.
Extrusion of pipe, rod, tubing and profiles	2-3% scrap for common extrusion processes. Up to 40-50% scrap for items machined from rod stock.
Film blowing	Start up, tail and reject film. Extruder purgings.
Sheet extrusion	Scrap generation: 15% in PE, 25% in PVC, 40% in oriented PP film.
Extrusion coating	6% loss in extrusion coating on paperboard, 5-6% in wire and cable coatings.
Coextrusion	9-10% scrap (sometimes 20%) generally sold to convertors.
Injection blow moulding	Practially no scrap.
Extrusion blow moulding	Amount of pinch-off, depending upon excess length of parison. Minimised by good design.
Rotational moulding	Removal of open sections and small amounts of trim flash.
Dip and sluch moulding	No cut off arises, since the material forms a solid solution on the mould. There is however a great potential for contamination of the plastisol or the fluidised solids bath resulting in rejected parts.
Casting	3-5% loss.
Calendering	Drippings from mixer and calender rolls (less than 1%).

Continued ...

Table 2.1 continued

Thermoforming	Trimmings arise in significant quantities.
Laminating	8% in high pressure lamination. Side trimmings or scrap cuttings when forming labels, bags etc from laminates.
Spreader coatings	6-10% scrap, little of which can be recycled.
Cellular plastics	5-10% in expanded PS.
Compression and transfer mouldings	2-5% flash (excess) material.

which soon become domestic waste (see Table 1.3). Toys, clothes and toilet articles have a service life of intermediate length, while cable-sheathing, machine parts and domestic appliances last for considerable time. Unless these synthetic materials are recycled, they eventually enter the refuse stream.

UK consumption of plastics in 1980 was about 2 million tonnes/annum in which over 50% of it is used for packaging and building purposes (see Table 1.3). A number of studies(7-10) have indicated that the average plastic content of domestic and urban rubbish in 1980 was about 4-5% by weight (see Table 2.2). The most recent estimate(81) of the quantity of domestic waste and commercial waste arising in the UK for 1980 was nearly 24 million tonnes and for 2000 around 33 million tonnes. The problem of disposal is thus likely to increase particularly as land fill will become more expensive and difficult as suitable sites, including those made accessible by transfer loading, are used up.

2.2.3 Household Collection

Two national proto-type schemes have provided(82,83) a source of information on household collection costs based on several years practical experience. These are the Huddersfield Waste Saver Campaign (Oxfam), and the Teesside Waste Saver Scheme. Both of these schemes have now been discontinued for economic reasons (ie in private cost terms) and, although neither of these organisations have kept detailed periodic records which permit

Table 2.2 Plastic content of UK household refuse(7)

		1968	1974	1980	2000	
Total plastic (%)		1	2	5	9	
Weight per household per week (kg)		0.1	0.2	0.7	1.5	
Weight per year (million tonnes)		0.2	0.4	1.2	3.0	
Composition of plastics waste in household refuse, 1970		Composition of plastics used in packaging, 1970				
Polyolefins	63%	Polyethylene Polypropylene			61% 8%	69%
Polystyrene Polystyrene	19%	Polystyrene				18%
Polyvinyl chloride	11%	Polyvinyl chloride				8%
Cellulos	4%					
Others	3%	Others				5%

an analysis to be made of the reasons for their failure (see however ref 82), Blackmore and Turner(83) have analysed the reasons for this in the case of Oxfam (Huddersfield Waste Saver Campaign) project. They point out that the extent of an initial ambitious scheme to collect and segregate glass, paper, textile, metals and plastics has been progressively reduced with time. Plastics were discontinued first due to the lack of any permanent outlet. Immediately before the Waste Saver (Oxfam) schemes were discontinued in 1978, only the most profitable waste materials were being collected, namely textile and paper. On the basis of private cost and benefit, the scheme made a loss of £4000 in 1978. However, by costing on the basis of social costs and benefits, a surplus of between £13000 and £17000 per annum was calculated for this scheme. This takes into account low cost of labour provided under the job creation scheme in an area of high unemployment, savings in waste disposal costs and savings in raw material import costs. However, such a form of evaluation is inappropriate to private industry and has, therefore, little likelihood of being applied in practice.

The primary reason for the discontinuation of both schemes was the escalating cost of transport, collection costs, maintenance problems and costs also caused severe difficulties(82,83).

2.2.4 Plastics Waste Arising from Industry and Commerce

The Brunel University group under the direction of Professor M Bevis have surveyed two specific areas; the arising of packaging waste in the horticultural and agricultural industries and the carpet, coating and related industries and have published their conclusions(84,85). These are as follows:

(a) Plastics waste arisings in the agricultural, horticultural and produce distribution industries(84)

A number of potentially important sources of plastics waste are identified which could be recycled in commercially available machines. The consequent products could find application in the source industries. Fertiliser sacks and silage covers are major candidates for collection and recycling. Although small containers, plant pots and trays are used in millions, there is no evidence for their accumulation and reclamation is unpromising. Similar conclusions apply to polyethylene cladding, screens and nets. Areas which should be investigated further include polypropylene twine, grow-bags and protective covers.

(b) Plastics waste arisings in the carpet, coating and related industries

A survey carried out by regions indicates large waste arisings in Yorkshire, the North East, North West, West Midlands, South East, South West, Wales, Scotland and Northern Ireland. The concentrations of activities provides for low waste collection and transport costs and the prospects for recycling appear to be attractive. The man-made materials are polypropylene and polyamides and existing commercial recycling should be able to handle them.

2.2.5 Plastics Waste Arisings in Retailing Industries

No information has so far been available from any source on the amounts of plastics waste arising in the form of packaging from manufacturing industry or from commercial retail outlets. The contact established with Plastics Recycling Limited (PRL) has proved very valuable in approaching the larger retail companies directly for information. The following sources were considered as a basis for a viable collection system.

(1) Supermarket and hypermarket retail chains and high street stores (mainly LDPE packages and wrappings)
(2) Breweries (HDPE, PP crates, wrapping film)
(3) Dairies (HDPE, PP crates, polydrums and containers)
(4) Bakeries and confectionary manufacturers (hygenic film, wrapping film)
(5) Tyre and tube manufacturers (protective film)

It was decided to approach the major companies involved with as concise a questionnaire as could be devised to produce the necessary information (see questionnaire (A), Appendix I). The results of this survey were disappointing in that only 21 responses (ie 19%) were received from 109 questionnaires sent out (see Table 2.3 for analysis of the results). Most productive were the supermarkets (6 responses out of 22), breweries (7 responses

Table 2.3 Analysis of replies to questionnaire from retailing companies

Nature of operation	Total no of companies in UK	Questionnaires sent out	Replies Rec'd	Replies Rec'd %	No of companies producing plastics waste (amount in 10^{-2}kg/week)					Average no of locations
					>20	10-20	5-10	1-5	<1	
Supermarkets and Town Centre Stores	200	22	6	27	3 50%	-	2 33%	1 17%	-	>50
Dairies (heat treatment milk)	11	11	3	27	-	-	1 33.3%	1 33.3%	1 33.3%	<5
Breweries	90	11	7	63	1 14.2%	-	-	1 14.2%	5 71.6%	<5
Bread & flour confect's	60	47	4	8.5	-	-	-	1 25%	3 75%	<5
Rubber tyre & tube co's	27	18	1	5.5	-	-	1 100%	-	-	<5
TOTAL	388	109	21	19	4 19%	-	4 19%	4 19%	9 42.8%	

out of 11) and dairies (3 responses out of 11). Because of insufficient response, a second letter was sent out to all the retailers who did not answer the first, asking them to return the questionnaire, if necessary marked 'No interest' (see Appendix I for second questionnaire (B) with some modification). There was a much better response to this letter and the number of companies replied altogether was 63 (ie 58%) out of 109 (see Table 2.4 for analysis of the results). Therefore there was an increase of 200% in response to the second letter.

The results obtained by the completion of the questionnaire should only be regarded as indicative of circumstances within a particular industry, as there were considerable variations in the information provided by respondants in any one industry. Direct contact with collaborating firms was found to be more satisfactory and the results of such interviews have been mentioned separately.

2.2.5.1 Analysis of the Survey on Supermarkets

The total of 29 questionnaires were sent out (see Table 2.4 for analysis of the results), 14 responses (ie 63.6%) were received. With analysing the replies according to the amount of waste arisings per week, it was found that 4 out of 14 (ie 28.5%) produced over 2000 kg/week, 2 (ie 14.2%) produces 500-1000 kg/week, 2 (ie 14.2%) produces 100-500 kg/week, 1 (ie 7.2%) produces below 100 kg of plastics waste per week and 5 (ie 35.7%) were not interested in the survey. The only problem is their number of locations

Table 2.4 Analysis of replies to questionnaires from retailing companies

Nature of operation	Total no of companies in UK	Sent Out	Replies Rec'd	Replies Rec'd %	No of companies producing plastics waste (amount in 10^{-2} kg/week)					Average no of locations	No of companies not interested
					>20	10-20	5-10	1-5	<1		
Supermarkets and Town Centre store	200	22	14	63.6	4 28.5%	-	2 14.5%	2 14.5%	1 7.2%	>50	5 35.7%
Dairies (heat treatment milk)	11	11	8	72.7	1 12.5%	-	1 12.5%	1 12.5%	2 25%	<5	3 37.5%
Breweries	90	11	11	100%	1 9%	-	-	1 9%	5 45%	<5	4 37%
Bread & flour confect's	60	47	20	42.5	-	1 5%	-	2 10%	7 35%	<5	10 50%
Rubber tyre & tube co's	27	18	10	55.5	1 10%	1 10%	2 20%	1 10%	3 30%	<5	2 20%
TOTAL	388	109	63	58	7 11%	2 3.2%	5 8%	7 11%	18 28.6%	<5	24 38.2%

which is over 50. A worthwhile collection system may be possible for some of the businesses with a minimum number of collection points (see however section 2.3 for a possible collection system).

2.2.5.2 Breweries and Dairies

In view of the fact that recyclers were aware of considerable quantities of broken crates being discarded in the vicinity of even small centres of population, it was decided to hold discussions with a major crate manufacturer (GPG International Limited). This company had initially expressed interest in collaborating in the research project but subsequently withdrew. Subsequently, the sales organiser (Mr F Wade) reported that very few crates were rejected as waste due to the high quality of the materials used. Later again, however, the company has changed its view and again expressed an interest in collaborating and negotiations progressed with the result that GPG have offered to provide information on plastics crate waste arisings in return for a technical study of the properties of their recycled products. A technical study of the up-grading plastics waste arising from polypropylene crates was carried out and will be discussed fully in Chapter 5.

The total of 11 questionnaires were sent out to dairies of which 8 (ie 72.7%) were received (see Table 2.4). Out of the 8 responses one company produces over 2000 kg/week (ie 12.5%), 1 produces

500-1000 kg/week (12.5%), 1 produces 100-500 kg/week (12.5%), 2 produce below 100 kg/week (25%) and 3 were not interested (37%) in the survey.

2.2.5.3 Bread and Flour Confectionaries

The total of 47 questionnaires were sent out of which 20 responses were received (ie 42.5%). Analysis of the results are as follows (see also Table 2.4):

1 company produces over 2000 kg/week plastics waste
2 companies produce 100-500 kg/week plastics waste
7 companies produce below 100 kg/week plastics waste
10 companies were not interested in the survey.

2.2.5.4 Rubber Tyre and Tube Companies

The total of 18 questionnaires were sent out of which 10 responses were received (ie 55.5%). Analysis of the results are as follows (see also Table 2.4):

1 company produces over 2000 kg/week waste plastics
1 company produces 1000-2000 kg/week plastics waste
2 companies produce 500-1000 kg/week plastics waste
1 company produces 100-500 kg/week plastics waste
3 companies produce below 100 kg/week plastics waste
2 companies were not interested in the questionnaire

2.2.6 Plastics Waste Arisings in Building and Automotive Industries

The following sources were considered as potential sources for a viable collection system:

- (i) domestic house builders (mainly LDPE packages, wrapping films)
- (ii) residential construction hotels, flats etc (wrapping film, LDPE packages)
- (iii) motor vehicle industry, wheeled tractors, motor cycle, tricycles and railway workshops (protective film, wrapping film, LDPE packages)

The results of this survey were disappointing in that only 36 responses were received (ie 36%) from 100 questionnairs sent out (see Table 2.5 for the analysis of the results), of which 14 companies were not interested in the survey. Most productive were the motor vehicle industry (21 responses out of 41, ie 51.2%). This cannot lead to any proper conclusions due to insufficient response.

2.2.7 Plastics Waste Arisings in Light Engineering and Chemical Industries

The following sources were considered as a basis for a viable collection system:

Table 2.5 Analysis of replies to questionnaire from building and automotive companies

Nature of operation	Total no of companies in UK	No sent Out	Replies Rec'd	Replies Rec'd %	No of companies producing plastics waste (amount in 10^{-2} kg/week)					Average no of locations	No of companies not interested
					>20	10-20	5-10	1-5	<1		
Domestic house builders	470	15	1	6.6	-	-	-	-	-	5-10	1 100%
Residential construction hotels, flats etc	320	26	10	38.5	-	-	-	-	7 70%	5-10	3 30%
Motor vehicle	310	41	21	51.2	-	-	3 14.3%	3 14.3%	8 38%	<5	7 33.4%
Wheeled tractors	14	11	2	18.1	-	-	-	-	-	-	2 100%
Motor cycle, tricycle, pedal cycle, railway workshop	15	7	2	28.5	-	-	-	-	1 50%	<5	1 50%
Total	1130	100	36	36	-	-	3 8.3%	3 8.3%	16 44.4%	<5	14 39%

(i) Light engineering industries (mainly LDPE packages, wrapping films); only the light engineering companies around Midland area were investigated.

18 questionnaires were sent out, only 4 responses (ie 22.2%) were received. Results are summarised in Table 2.6.

Findings were:

1 company produces between 100-500 kg/week plastics waste

2 companies produce below 100 kg/week plastics waste

1 company was not interested in the survey

(ii) Fertiliser companies (mainly LDPE packages, PP and HDPE containers):

47 questionnaires were sent out of which 17 replies were received (ie 36%). Results are summarised in Table 2.6. Significant findings were:

1 company produces over 2000 kg/week plastics waste

2 companies produce between 1000-2000 kg/week plastics waste

2 companies produce between 500-1000 kg/week plastics waste

4 companies produce between 100-500 kg/week plastics waste

5 companies produce below 100 kg/week plastics waste

3 companies were not interested in the questionnaire

(iii) Pharmaceutical chemicals and preparations:

Table 2.6 Analysis of replies to questionnaires from light engineering (Midlands area) and chemical companies

Nature of operation	Total no of companies in UK	No sent out	Replies Rec'd	Replies Rec'd %	No of companies producing plastics waste (amount in 10^{-2} kg/week)					Average no of locations	No of companies not interested
					>20	10-20	5-10	1-5	<1		
Light eng (Midlands)	18	18	4	22.2	-	-	-	1 25%	2 50%	<5	1 25%
Fertilizer company	47	47	17	36.1	1 5.8%	2 11.6%	2 11.6%	4 23.2%	5 29%	<5	3 18.8%
Pharmacutical Chemical & Preparations	136	31	12	38.7	-	-	-	1 8.4%	9 75%	<5	2 16.6%
Total	201	96	33	34.4	1 3%	2 6%	6 18%	2 6%	16 48.5%	<5	6 18.5%

The total of 31 questionnaires were sent out, 12 responses were received (ie 38.7%) of which 9 of them (ie 75%) produce below 100 kg of waste per week. Results are analysed in Table 2.6.

2.2.8 Public Image of the Packaging Industry

During the course of the present survey, great difficulty has been experienced in obtaining factual information from the packaging and associated industries. This appears to be associated with the extreme reluctance of the industry to admit that packaging is a source of plastics waste. Crate manufacturers are probably particularly sensitive because large quantities of broken crates are now appearing as litter on the shoreline after being discarded by shipping. The trade associations are very much involved in this and are in general opposed to the provision of information which might be subsequently used against them publically. This does not appear to apply so much to the retail stores (although two major high street stores did state 'we regret we cannot be of assistance in this connection as we are not manufacturers and as such do not have plastics waste'). The more favourable reaction from these companies doubtless reflects their interest in obtaining some economic benefit from recycling of the waste packaging. Several companies have asked to be kept informed of the outcome of these investigations, particularly if there is the possibility of them receiving payment for their waste.

2.2.9 Summary of the Survey

The analysis of the replies to questionnaires are summarised in Table 2.7. A total of 305 questionnaires were sent out of which 132 (ie 43.2%) responded. Of these, 44 were not interested in the survey (ie 33%). Supermarkets and hypermarkets appear to be a viable source of plastics waste. Assuming a supermarket produces 3 tonnes/week of waste on average, (eg Hintons), the waste arising from about 200 supermarkets (see Table 2.9) will probably be 600 tonnes/week or 30000 tonnes/year. This waste is potentially capable of being collected by the same kind of collection procedure practiced by Hintons (see Section 2.3) involving no extra charges over and above current practice.

It is also found from the survey that most of the waste produced is LDPE wrapping films or protective plastic bags (ie 34% and 35% respectively) and only 5% consists of crates/trays (for further details see Table 2.8).

2.3 Possible Collection System

The following points can be made, arising from a discussion with Hintons Limited, who operate 35 stores in the North East of England(87):

(i) They do all their own baling at the site of waste arising for reasons of space limitation, and as they already have the bales there is no capital cost involved in collection for

Table 2.7 Analysis of replies to questionnaire from the present investigation (sum of 305 companies)

Nature of operation	Total no of companies in UK	No sent out	Replies Rec'd	Replies Rec'd %	No of companies producing plastics waste (amount in 10^{-2} kg/week)					Average no of locations	No of companies not interested
					>20	10-20	5-10	1-5	<1		
Total	1720	305	132	43.2	8 6%	4 3%	10 8%	16 12%	50 38%	<50	44 33%

Table 2.8 Analysis of replies to questionnaire according to type of waste from the present investigation

(sum of 305 companies)

Nature of operation	Total no of companies in UK	No sent out	Replies Rec'd	Replies Rec'd %	Number of companies producing different cateogry of waste									
					Wrapping film	%	Protective plastic bags	%	Polydrums containers	%	Crates/ trays	%	Others	%
Total	1720	305	132	43.2	45	34	46	35	28	21	7	5	15	11

Table 2.9 Superstores/hypermarkets - analysis by TV regions(86) (Source, IGD)

TV Region	Number	Percentage
Granada (including Border)	50	23.0
Scottish TV and Grampian	21	9.7
Tyne Tees TV;	12	5.5
Yorkshire TV	34	15.7
Anglia TV	13	6.0
London Weekend TV	22	10.1
Southern TV	13	6.0
Harlech TV / Westward TV	15	7.0
ATV (Midlands)	37	17.0
Total	217	100.0

recycling.

(ii) The bales are returned to a central regional depot in otherwise empty delivery trucks which have just delivered goods to the store. There is, therefore, no additional cost in the transporting processes.

(iii) The baled waste is picked up by a local waste collection organisation at regular intervals (approximately three collections per week) for resale to recyclers. There is therefore no need for additional centralised storage capacity for waste plastics.

(iv) If the waste is collected directly from the stores under the normal lcoal authority waste collection scheme, an average charge of £100 per week for each location is levied by the authorities. There are clearly advantages in selling the waste at the current price of £30 per tonne paid by waste collection.

Hintons' experience could possibly be practiced by more than 200 supermarkets and hypermarkets (Table 2.9 analyses the number of supermarkets and hypermarkets according to TV regions). The only capital cost which should be taken into consideration, is the price of a baling operation, which can be used for baling paper as well as plastics.

If a supermarket is paying £100 per week for collection of about 5 tonnes of waste (ie £20 per tonne), it could profit by £40-£50 per tonne by selling it to a recycler in the way described above. In practice the cost of waste collection is likely to increase steadily as other costs (ie transport, wages, etc) rise.

2.4 Overall Economic Conclusions

The following additional points can be made from the survey:

(i) In the retail trade, plastics waste fall in to two main classes:

  (a) Pallet shrink wraps which are heavy gauge polyethylene and normally not contaminated. For example, Hintons produces approximately 1 tonne per week from all their outlets and this is sold directly for recycling (£30 per tonne).

  (b) Package shrink wraps which are generally a lighter gauge but contaminated with paper labels and are frequently surface printed with brand names etc. Approximately 5 tonnes per week of this is available from just one grocery retail chain in the North East of England (Hintons).

(ii) We can assume that similar amounts of waste plastics will be available from other chain stores (eg Tesco, Spar, Marks and Spencer, British Home Stores, Woolworths etc) but it has proved difficult to get this information. It would be useful to do some random assessment of the activities of local stores in order to confirm this.

(iii) There is a dearth of factual statistical information on the quantities of plastics waste arising from commercial sources, partly as a result of the activities of the Trades Associations.

(iv) Attempts to obtain such information by questionnaire has been only partially successful (ie only 43% of the questionnaires were answered).

(v) It seems likely that one reason for the difficulty in obtaining data about waste plastics is that the polymer fabricating industries are concerned about their public image and consequently they do not wish the topic of plastics waste and litter to become a subject for public debate.

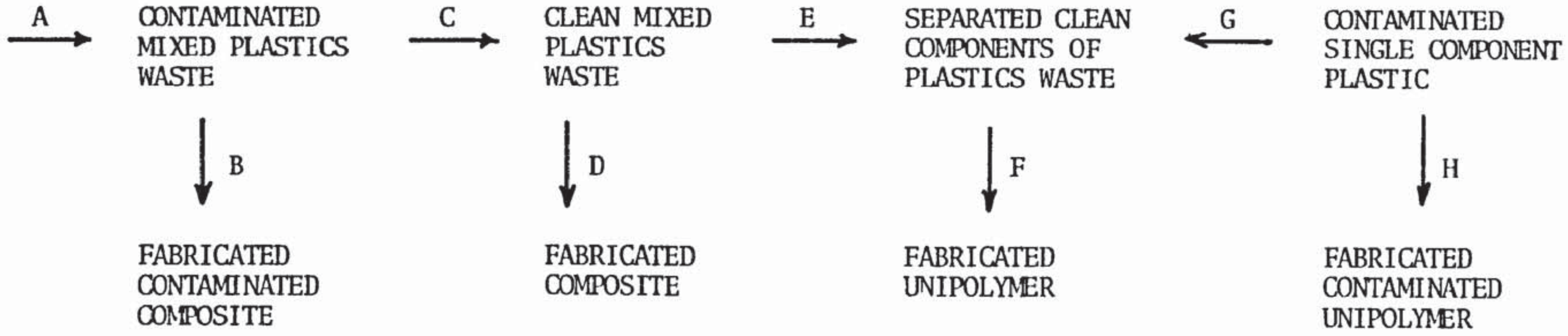
(vi) Household collection of plastics waste is uneconomical because of the high cost of collection, transportation and the present lack of markets for the heterogeneous products.

(vii) Very considerable quantities of relatively clean plastics packaging are available at the major department chains and household stores and managements are in general keen to see them recycled, if they can gain economically from such a procedure.

(viii) It is economically desirable to eliminate complex separation processes and the use of energy consuming cleaning operations if at all possible. Therefore, it would seem to be advantageous to reprocess mixed plastics in the ratio in which they are normally found in collected waste. Unfortunately, such mixtures give rise to fabricated products which are much inferior in mechanical performance (ie tear strength, impact strength etc), to the original component used separately. This is due to the mutual incompatibility of some of the common polymers. Therefore, the technical work of this project has been concerned with improving the mechanical and environmental properties of such mixtures in order to improve the quality of the fabricated products so that it is acceptable in the market (see Recycling Scheme Paper 74). Technical work is discussed fully in Chapters 5 and 6.

(ix) The use of solid phase dispersants (SPDs) to improve physical properties of plastics waste would affect the price of the end product. Therefore, it is very important to evaluate low cost fillers and additives for the

Recycling Scheme



A Collection from industrial or household sources

B Fabrication process capable of handling heterogeneous organic contaminated materials (involves the introduction of the new compounding additives to improve compatibility and long term performance)

C,G Cleansing process capable of removing organic contaminents, metal salts and complexes

D Fabrication process capable of handling heterogeneous materials (involves the introduction of solid phase dispersants, antioxidants and the stabilisers for long term performance)

E Physical separation process, flotation, solution etc

F,H Conventional conversion process; injection moulding, extrusion etc (may involve new compounding ingredients, antioxidants etc for high quality applications) evolution of end products of high added value having the inherent characteristics of plastics.

2.5 Processing of Mixed Polymers

2.5.1 General Background

The equipment used for the recycling of homogeneous scrap is basically similar to normal plastics processing equipment and is unsuitable for the homogenisation of mixtures of polymers or of mixtures of polymers with other materials. It is also unsuitable for handling large amounts of contamination unless the material is first cleaned by one of the various laundering processes now available from such companies as Krauss-Maffei and Reifenhauser(88).

The recycling of mixed plastics waste involves the homogenisation of the various different polymers, the dispersion in the plastics mass of the contaminants (ie non-thermoplastic materials) and the conversion of the mass directly into products which do not resemble the products from which the waste arose. Normally, these recycled articles enter the market for wood and concrete products and exhibit considerable advantages over both wood and concrete. Verity Smith points out(89) six criteria for processes available, three of which concern the design of the equipment, two concern its mode of operation and one is concerned with marketing. These criteria are summarised as follows:

(i) Efficient homogenisation The ess ential characteristics of a mixed plastics recycling machine is that it shall subject the mixture for a very short period to a high rate of shear at high temperatures. The high temperature and high rate of shear are necessary to obtain intensive mixing at a viscosity lower than that of normal plastics processing, permitting homogenisation in a semi liquid phase. The very short residence time is necessary to avoid decomposition of less stable polymers in the mixture, especially PVC.

(ii) Conservation of energy The most efficient way of conserving the energy content of waste plastics is by recycling but this must be performed efficiently. This means that the homogenisation process should be as adiabatic as possible because the most efficient way to bring the plastics mix to melting temperature is by frictional heat within the material. In other words, the energy is derived from the drive motor rather than from external heating.

(iii) One-step operation To cool and pelletise the homogenised plastic mass in the manner used by independent recyclers who have a market for the pellets is not practical. In the first place, there is no market for mixed plastics pellets. In the second place, this would involve the loss of the considerable heat content of the melt coming from the recycling machine plus the expenditure of considerable heat energy to convert the material bulk to the processing temperature. It is necessary that the recycling process includes one step production of the finished or at least semi-finished article without the intervention of a granulate stage.

(iv) Consistency of feedstock Raw material for a given product must have a roughly constant composition and provision must be made for ensuring this. This criterion is important and is completely independent of the process used.

(v) Maximisation of plant output It may appear obvious that the output from the machine must be maximised. It has not always been realised that amortisation of the plant is the largest element in the cost of transforming plastics waste into plastics products. Therefore the proportion of productive hours to inactive hours is much more important in the overall cost accounting than is the case with conventional plastics processing, while the cost of raw materials is an almost negligible factor. The Japanese attempts to operate large, capital intensive recycling plant on an eight hour per day basis have proved not to be commercially viable.

(vi) Choice of product The choice of the finished product has the largest influence on the profitability of the enterprise of all the decisions open to the operator of a recycling plant.

2.5.2 Development of Machinery for Processing of Mixed Polymers

The choice of recycling machines at present on the market is limited to five types: the Reverzer, designed by Mitsubishi Petrochemical Company in Japan and marketed by Rehsif SA; the Remaker, built by Kleindiant in Germany and marketed by Berstorff; the Flita, designed by Flita GmbH in Germany and marketed by Davo (Reifenhauser Group); the Klobbie, built by Rehsif SA in Belgium and a machine built by Fabrique Nationale Herstal in Belgium.

All five machines are basically different from each other in the means employed to homogenise the mixture of polymers. The Reclamat process (UK) which is used by Plastics Recycling Limited (PRL) is also discussed in section 2.5.2.5.

2.5.2.1 Reverzer

The Reverzer(13) employs a short, deep-cut extruder screw on the discharge end of which is mounted a large fluted double cone case in which is mounted an annulus giving a zone of intensive mixing between the periphery of the cone and the annulus. Homogenised material is degassed and passed to an accumulator provided with a screw piston which discharges the material from a nozzle.

Three alternative methods of processing the material are available. The original Japanese process, flow moulding, involves the filling of simple sheet metal moulds directly from the nozzle of the

Reverzer. A set of about 20 moulds is used, the moulds being transported by a conveyor system through a spray tunnel where they are cooled before the product is ejected and the mould returned for refilling (see Fig 2.1) (90).

The advantages of the flow moulding process are obvious. The use of externally cooled sheet metal moulds, coupled with the fact that 20 different moulds can be circulated at the same time, permits remarkably economic market development work. The maximum shot weight attained so far is 50 kg; the minimum practical shot weight is about 5 kg. Multiple cavity moulds can be used.

A maximum output of 500 kg/h is possible depending on the design of the moulds, the type of scrap used and the design of the mould transfer system, production rates of between 350 and 500 kg/h are obtained.

The Revertzer can also be adopted to the production of continuous sections by extrusion. This involves the use of a special die head and calibrator together with a modification of the usual type of haul-off and saw system. The investment is much lower than for flow moulding. Sections are at present limited to about 10 cm x 10 cm maximum.

Finally, a new process of compression moulding using the Reverzer is the subject of a recent patent application by Rehsif. This permits an extension of the basic Reverzer idea into more technical

Fig 2.2 Cost estimates for Reverzer process.

* At the time of editing, US $ = 300 yen

items, such as pallets, stadium seats and cable drums, where large surface areas require more pressure than is available in the flow moulding process.

The cost estimates for the Reverzer process is shown in Fig 2.2.

2.5.2.2 Remaker(89)

The Remaker represents a totally different approach to recycling techniques. Similar in appearance to a conventional injection moulding machine, the Remaker is actually an intrusion moulder. A continuously rotating screw plasticises the material and injects it at relatively low pressure through a large diameter gate into moulds, mounted in a conventional press. The low pressure permits the use of aluminium moulds.

The machines are made in three sizes having shot volumes of 1000, 2700 and 4000 cc and locking forces of 305 KN, 1500 KN and 3000 KN respectively.

The dwell period of the material in the heated cylinder imposes certain limitations. The machine will not handle mixtures containing PVC and the machine has limitations in handling rigid compositions. For small flexible items, the Remaker is undoubtedly the most successful recycling system on the market.

2.5.2.3 Flita(89)

The Flita system is totally different from either the Reverzer or the Remaker. It employs a roller mixer comprising a mill roll eccentrically mounted in a cylindrical mixing chamber, plasticising the material by shearing it against the wall of the mixing chamber. Like the Remaker, it relies on external electric heating. Material is discharged from the Flita, is moulded by compression moulding in separate presses. The degree of homogenisation achieved is less with either the Reverzer or the Remaker, but it is sufficient for many purposes, notably perforated paving blocks for parking etc. Output rates are of the order of 200 kg/h.

2.5.2.4 Klobbie(91)

The Klobbie machine is being developed by Rehsif on the basis of an original invention by E J C Klobbie of Lankhorst Toawfabrieken in the Netherlands. It can handle mixed plastics waste with a minimum content of 50% polyolefins (and up to 20% PVC and 20% paper) and has a maximum output of about 70 kg/h, producing finished products up to 100 x 100 x 2200 mm dimensions and 18 kg maximum weight. Typical end products include fence posts, flooring elements and similar simple shapes, especially for use in agriculture and horticulture.

The essential technical aspect of the 'Klobbie' system is the use of an adiabatic extruder, operating at very high screw speed and shear rate, and achieving a very high integration of plastics and paper fibres. The fact that the machine can not only handle mixed plastics, but also a percentage of paper or similar non-plastics, greatly extends its field of use. It can reprocess plastics coated paper.

The system begins with a conventional granulator (see Fig 2.3) feeding directly into a storage hopper which is in turn linked with the production hopper. There is the possibility of adding other ingredients (or other plastics) at these stages, after which the mixture is sucked to the extruder hopper. Hence a small amount of blowing agent is added (to counteract shrinkage which would be considerable with such a massive plastics moulding) and pigments, masterbatch and other ingredients can be added at this final stage. The mixture is then force-fed into the extruder using a high torque electric feeder, working through a gear box.

The extruder and screw is conventional with belt drive, but operating at about 350 rpm (compared with the 100 rpm usual on a conventional extruder). This produces very high shear and frictional heat so that external heat is required only at the start up. The plasticised melt is then extruded at low pressure directly into the mould.

The Klobbie machine costs about £100000 which compares very favourably with the cost of £400000 for the Mitsubishi developed Reverzer system.

Fig 2.3 'Klobbie' plastics recycling machine(91)

2.5.2.5 The Reclamat Process (UK)(4)

The Reclamat process (UK) also makes a board product. Waste film is crumbed, compounded with a black masterbatch plastic, extruded and granulated. Heavier gauge wastes are fragmented. The board product is formed on a belt in sandwich form with the specially prepared film waste forming the outer layers and the fragmented material the cone. Successive passes through ovens cause the layers to sinter. A press is used for final forming of boards. The product is aimed primarily at the agricultural market where its non-absorbent, weather-proof qualities are advantageous. The Plastics Recycling Limited of Worcester, England operates with this technique.

Table 2.10(85) represents output and capital costs of selected plastics recycling processes. However, there is no detailed information available about operating costs.

Table 2.10 Output and capital costs of selected plastics recycling processes

Process	Replag		Regenoform	Klobbie	Remaker		
					05	07	09
Output per hour (kg) Maximum attainable, actual determined by material, product thickness etc	500	1000	200	140	50	150	300
Maximum shot weight of mouldings (kg)			25+	10+	1	2.7	5
Output per year (tonnes). Maximum attainable at 100% unit capacity factor. 4000 hours per year. 6000 hours per year, and at 80% unit capacity factor	 2000 3000 2400	 4000 6000 4800	 800 1200 950	 560 840 700	 200 300 250	 600 900 700	 1200 1800 1450
Capital investment (£)		<1.75m	<0.35m	<0.05m	<0.04m	<0.065m	<0.125m

Basic machinery, including size reduction equipment and mould costs. Regenoform (XI mould), Klobbie (X10), Remaker (X1), Replag two roll coating line is quoted; and in all cases the cost excludes transport, transport equipment, building and installation costs.

CHAPTER THREE

GENERAL EXPERIMENTAL PROCEDURES USED IN TECHNICAL WORK

CHAPTER THREE

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3.1 Materials

(i) Unstabilised low density polyethylene (LDPE) in granular (bead) form, identified as 'Alkathene', supplied by Imperial Chemical Industries Limited.

(ii) Unstabilised polypropylene (PP) in powder form, identified as 'Propathene' HF 18, supplied by Imperial Chemical Industries Limited.

(iii) Ethylene propylene diene rubber (EPDM) supplied by Esso Petroleum Company under the trade name of Vistalon 6505.

(iv) Styrene-butadiene-styrene (SBS) copolymer was supplied by Shell Chemicals (UK) Limited, under the trade name of TR 1101.

3.2 Sample Preparation

3.2.1 Melt Processing

The samples were processed on a RAPRA torque rheometer(92) which is essentially a small mixing chamber, containing mixing screw contra-rotating at different speeds. Throughout the processing operation for various blends high shear rate (72 rpm) was used. It has a good temperature control and a continuous read-out is provided of both melt temperature and the torque required for mixing. The chamber may be operated either open to the atmosphere or sealed by a pneumatic ram. A full charge was 35 g of polymer and when this charge was used, the chamber was sealed and processed for varying periods. When it was desired to process in the presence of oxygen, a charge of 20 g was employed and the chamber was left open to the atmosphere.

On completion of processing, the polymer sample was rapidly removed and quenched in cold water to prevent further thermal oxidation.

3.2.2 Preparation of Polymer Films

The films were obtained by compression moulding of processed samples using stainless steel glazing plates. The plates were thoroughly cleansed before use to ensure smooth surfaces and a special grade of cellophane paper was used to prevent the film sticking to the plates. Control of film thickness was achieved by using a standard quantity of polymer, about 6 g was found to produce a film of approximately 1.5×10^{-2} cm (0.006"). The weighed amount of the polymer was placed between the glazing plates and inserted into an electric press whose platens were maintained at 160 $\pm$ 2°C and 180 $\pm$ 2°C for polyethylene and polypropylene polyblends respectively. The pressing of films involved three stages:

(a) pre-heating for 1.5 minutes without applying any pressure,

(b) final pressing, for 1.5 minutes, with a pressure of 85 kg cm^{-2} (60 tonnes on a 12 inch diameter ram), and

(c) water cooling the plates to 50-60°C and removing the plates from the press and the films stored in the dark at 0°C. Portions of uniform thickness and dimensions were cut for testing.

3.3 Determination of Torque -vs- Time Curve

An idealised torque -vs- processing time curve(93) is depicted in Fig 3.1. Initially, there is a sharp rise in the torque when the polymer is introduced into the processing chamber of the RAPRA torque rheometer (point a). As the polymer gradually melts, the torque decreases and reaches a minimum (point b). This is then followed by a slight increase in torque due to the transition from the rubbery to the melt phases (point c). The time to reach point c is called fusion of flex time. The fusion time of a particular polymer shows a strong dependence on mechanical stress, temperature and the presence of additives. Irreversible changes due to thermal oxidative degradation (eg cross-linking or chain scission) during further processing of the polymer may be reflected by the subsequent increase or decrease of torque.

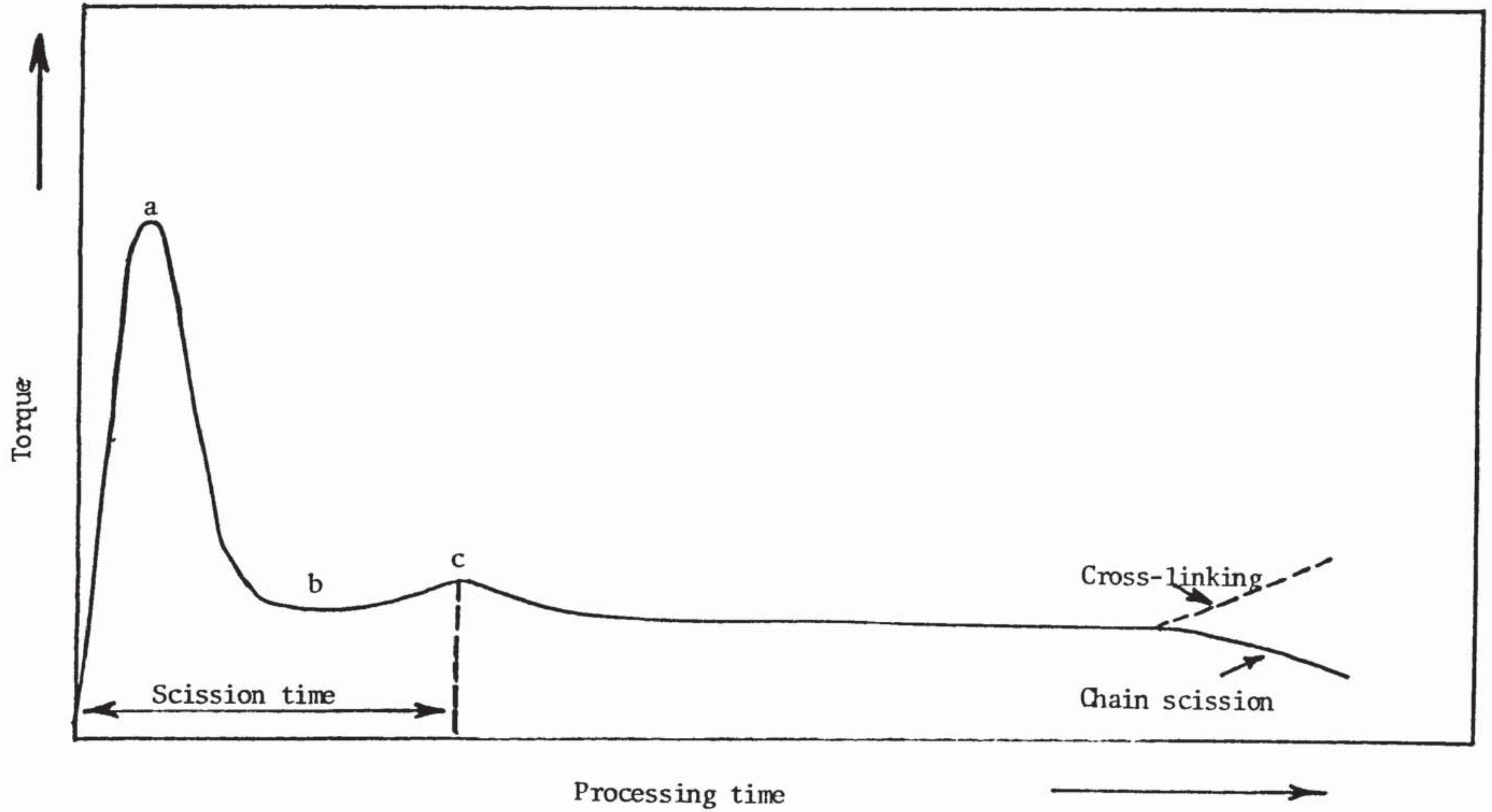


Fig 3.1 An idealised torque -v- processing time curve

3.4 Measurement of Melt Flow Index (MFI)

Melt flow index was determined on low density polyethylene (LDPE), polypropylene (PP) and polyblend samples which have been processed with or without additives. The apparatus used was as described in the British Standard method for determination of MFI (94). The melt flow index is a measure of the melt viscosity of the polymer which in turn is related to the molecular weight. The melt flow index (MFI) is defined as the amount of polymer in grammes extruded through a standard die in a given time (usually 10 minutes). A low melt flow index corresponds to a high melt viscosity and since melt viscosity is directly related to the molecular weight of a polymer, a low MFI corresponds to a high molecular weight and vice-versa (95). A strict relationship obviously only applies to polymers of the same chemical constitution, but it also is restricted to polymers of the same density since density also affects melt viscosity. In the case of polyethylene and EVA, the standard temperature is 190°C but for polypropylene the temperature is 230°C in order to allow for its higher melting point.

The appropriate relationship of MFI with molecular weight ($\bar{M}n$) and melt viscosity (η^*) are given by the following two equations respectively (in the case of LDPE) (96):

$$\sqrt{\bar{M}n} = 188 - 30 \log \text{MFI}$$

$$\eta^* \text{ (poise)} = 7.5 \times 10^4 \frac{1}{\text{MFI}}$$

Since thermal oxidation brings about changes in the molecular weight of the polymer by virtue of such reactions as chain scission, cross-linking etc, these are expected to be reflected in the melt flow index values. Hence melt flow index measurement provides a means of detecting any oxidation which may occur during heat treatment of the polymer.

The temperature was brought to a steady extrusion temperature of 190 ± 0.5°C and 230 ± 0.5°C for polyethylene and polypropylene respectively, before beginning an experiment. The barrel was then charged with 4.0 g of polymer, damping down with the charging tool to exclude air. The time taken to charge the barrel should not exceed one minute. Four minutes of melting and homogenation was allowed then the polymer was allowed to extrude under constant load of 2.16 kg, through a die 0.0930 and 0.0465 diameter respectively for polyethylene and polypropylene.

The extrudate was cut with a suitable sharp-edged instrument. The time interval for the first extrudate was 60 seconds and was discarded, then six successive cut offs were taken each at the end of 30 seconds; any cut off that contained air bubbles was rejected and each cut off was weighed separately and their average weight was determined. If the difference between the maximum and minimum values of the individual weighings exceeded 10% of the average, the test result was discarded and the test repeated on a fresh portion of the sample. The melt flow index was calculated from the following relation:

$$\text{MFI} = \frac{600 \times \text{average weight of cut off in gram}}{(\text{interval time in seconds})}$$

3.5 Ultra-violet Exposure Cabinet

Uv irradiation of the samples was carried out in the ultra-violet cabinet. Ultra-violet cabinet comprised a metal cylinder of about 110 cm in outer diameter and having a concentric circular rotating drum whose circumference was 15 cm from the periphery of the metal cylinder (photograph number I). Thirty-two fluoroescent 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 each sample. The cylinder cabinet was opened to the atmosphere on both the lower and upper sides and the circulation of air in the cabinet was ensured by the driven ventilator situated under the rotating frame.

The samples were attached to a separately made hard brown paperboard with aluminium foil backing which was mounted vertically on the circumference of the rotating wheel fixed inside the cabinet. In this position, the light beam fell perpendicularly on the surface of the film. The temperature recorded inside the cabinet with the lamp on was $30 \pm 1^{\circ}\text{C}$.

The radiation source consisted of the cylindrical array of 20 W

Photograph I

fluorescent tube lamps, positioned on the inner side of the cabinet. 24 lamps, type C (Phillips Actinic Blue 05) 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 Fig 3.2A and Fig 3.2B for the lamp A1 and lamp C respectively. The maximum in the relative intensity of the lamp A1 is at 317 nm and of the lamp C, 374 nm. The available wavelength with the above combination of lamps was between 280 nm and 500 nm and the radiation intensity I_0 at the sample surface was $I_0 = 44.3 \text{ W/m}^2$.

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

3.6 The Accelerated Thermal Oxidation of Processed Polymers

Experiments on low density polyethylene and blends were carried out in a Wallace oven at 110 ± 2°C. Polypropylene was examined at 140 ± 2°C in the presence of air. Each sample was suspended in a separate cell to prevent the cross-contamination of the additives by volatilisation and was subjected to an air flow of 3.0 cu ft/h (85 litres/h).

3.7 Measurement of Brittle Fracture Time of Polymer Samples

This is essentially a destructive test method. Films of identical

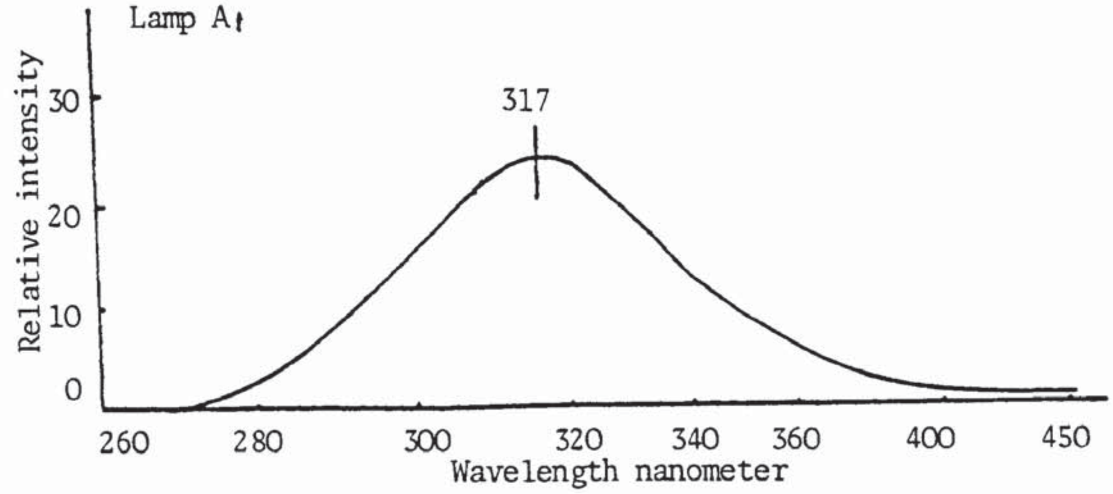


Fig 3.2A Spectral distribution of fluorescent lamp type A1 (Westinghouse sunlamp FS20)

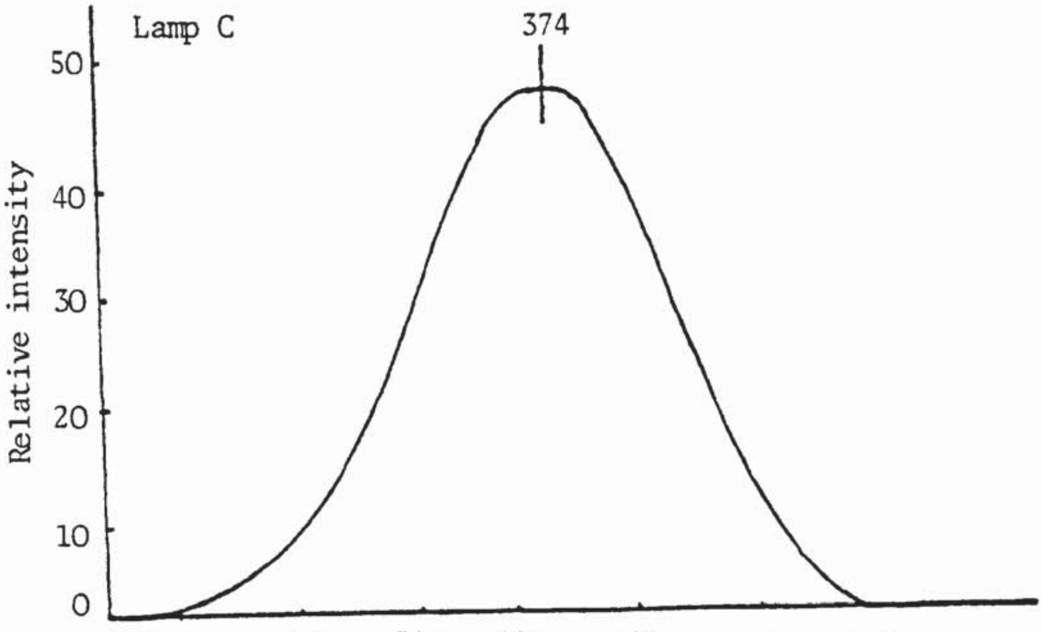


Fig 3.2B Spectral distribution of fluorescent lamp C (Phillips Actinic Blue 05)

size (2 cm x 3 cm) and of uniform thickness (0.015 cm, 0.006") containing different additives and percentages of second polymer along with a control sample were irradiated and were periodically checked and their time to embrittlement was determined by folding the film back on itself 180° manually. Each polymer sample was carried out in duplicate. The reproducibility of the results was found to be acceptable. Variation from the mean value was of the order of ± 5%.

3.8 Infra-red Spectroscopy

All infra-red spectra were recorded using a Perkin-Elmer infra-red spectrophotometer model 599. The spectra from 4000 to 200 cm^{-1} were recorded at medium scan speed.

Infra-red spectroscopy has been widely used to determine the nature of oxidation products and rate of formation of these products during thermal and photo-oxidation of polymers. It is a non-destructive test and particularly useful for quantitative purposes since the same test sample can be used repeatedly. Since thermal and photo-oxidation of polymers results in the build-up of different oxidation products, for example hydroxyl, carbonyl, carboxyl, vinyl, etc, the kinetics of the growth of these functional groups, as the irradiation proceeds, have been followed by observing the change in the characteristic absorption peaks at different wavelengths and these were assigned by a comparison with the values for the long chain ketones, aldehydes, acids, esters, etc.

PROCEDURE

In all quantitative analyses, the following combined form of Beer Lambert's equation was used(98):

$$A = \log_{10} {}^{I_o}/_{I} = ECl$$

where: A = absorbance or optical density

I_o = intensity of radiation effectively entering the sample

I = intensity of radiation emerging from the sample

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

C = concentration of absorbing group present in the sample in mole/litre

l = path length of radiation in the sample in cm

The samples were exposed for regular intervals of time and the spectra were run on the same chart paper for comparison purposes.

To minimise errors due to variation in film thickness, as well as errors due to the instrument, and internal standard, a characteristic absorption peak was used. The growth and decay of observed absorption peaks (for functional groups) were expressed as indices which were defined as the ratio of the absorbance of functional group peaks to that of the reference peak.

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

3.8.1 Calculation of Absorbance

The base line technique$^{(99)}$ was used to calculate the optical density or absorbance due to various functional groups. This was done as shown in Fig 3.3A by drawing a straight line (base line) tangential to adjacent absorption maxima or shoulders, then erecting a perpendicular through the analytical wavelength until it intersects the base line. At 'A' the concentration of the functional group to be determined is zero and at 'B' there appears an absorption peak whose height serves to calculate the concentration. Before the commencement of any spectral measurement, the spectrophotometer was adjusted to read 100% transmittance at 2800 cm^{-1} and this was known as the background line.

However, with an absorption such as shown in Fig 3.3B, the proper location of base line is less obvious but in the present work to determine the absorbance of peak 'A' the base line is to be either a, b, or c, depending on the width of the shoulders B, C and D. If all three shoulders, B, C and D, are narrow, 'a' is used as the base line and so on.

3.9 Ultra-violet Spectroscopy Studies

The uv spectroscopy of the additive containing polymer and polyblend films and model solutions were carried out using the Unicam uv/visible spectrophotometer model SP800. For the former, an unprocessed additive-free polymer film of identical thickness

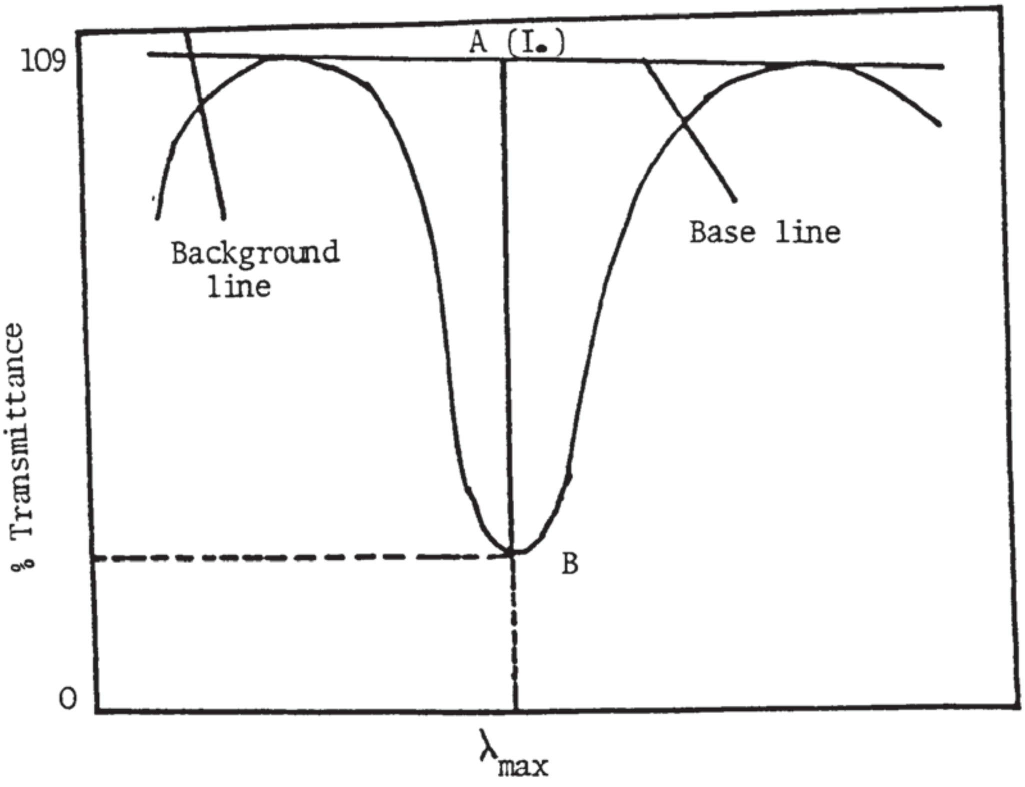


Fig 3.3A

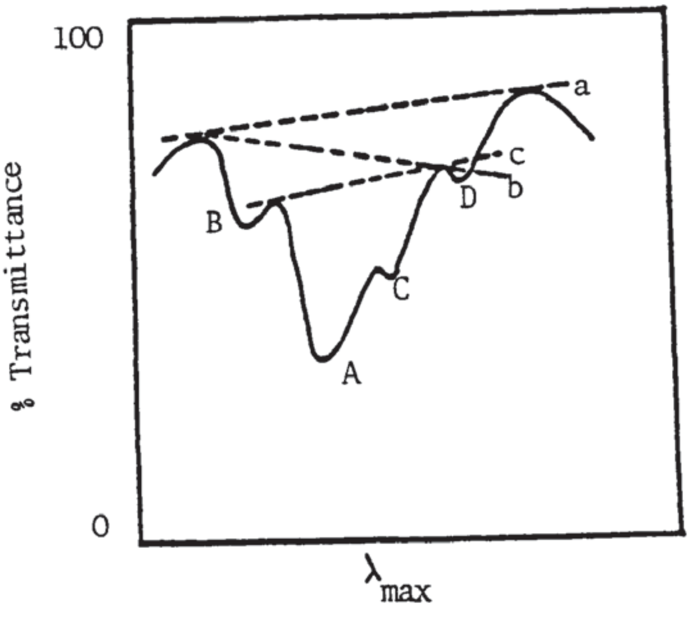


Fig 3.3B

was used (as a compensator) in the reference beam. In the case of the model solutions, the spectra were recorded using quartz cells of 10.0 mm path length with the pure solvent being used in the reference beam.

3.10 Solution Casting

Films were cast from solution of ethylene-propylene diene rubber containing different additives in chloroform. In order to find the optimum volume of solvent, 5 g of EPDM was weighed and was dissolved in different volumes of chloroform. It was found that 160 cc of chloroform gives rise to a homogeneous solution. The homogeneous solution was obtained after solution was kept for 50 hours. The solution was then cast onto a glass plate. In order to achieve an even thickness, a known volume of solution was cast each time.

3.11 Measurement of Impact Strength

The polymer films were cut into thin strips (about 1.5 cm wide) and mounted on cardboard for exposure in the uv cabinet and also for oven ageing. Samples of exactly equal thickness were chosen for replicate impact studies but the thickness of the samples at other exposure times varied between 0.006" to 0.007" (0.015 cm to 0.018 cm). The impact strength of the films was measured before and during photo and thermal degradation by means of a small falling weight impact tester. This apparatus enables the measurement of impact tests to be carried out on very small specimens.

This apparatus consisted of (see Fig 3.4) a metallic tube (A) fixed to a square steel block (B); this block can be fitted onto another square steel block (C) by means of two pins (D and E). In the middle of (C), there is a round hole on which the film is mounted. The sample is clamped between (B) and (C) before testing. A slit was drilled along the length of the metallic tube and a ruler attached alongside the tube to enable measurement of heights. A pin was moved along the slit to the height required and the weight was introduced into the tube so that it settled on the pin. The pin was withdrawn in quick movement giving free way to the dart-like weight to fall onto the sample. If an adequate weight and height are used, the dart perforated the sample, penetrating into the block (C). Five tests were performed for each sample and the average impact strength computed. The impact strength of a film was taken as the energy required to break the film per unit thickness. Hence the impact strength was calculated in erg cm^{-1}.

$$E = \frac{m \times g \times h}{\text{thickness } (t)}$$

where: m = mass of falling weight (g)

g = 981 cm sec^{-2}

h = height of the falling weight (cm)

t = thickness of the film (cm)

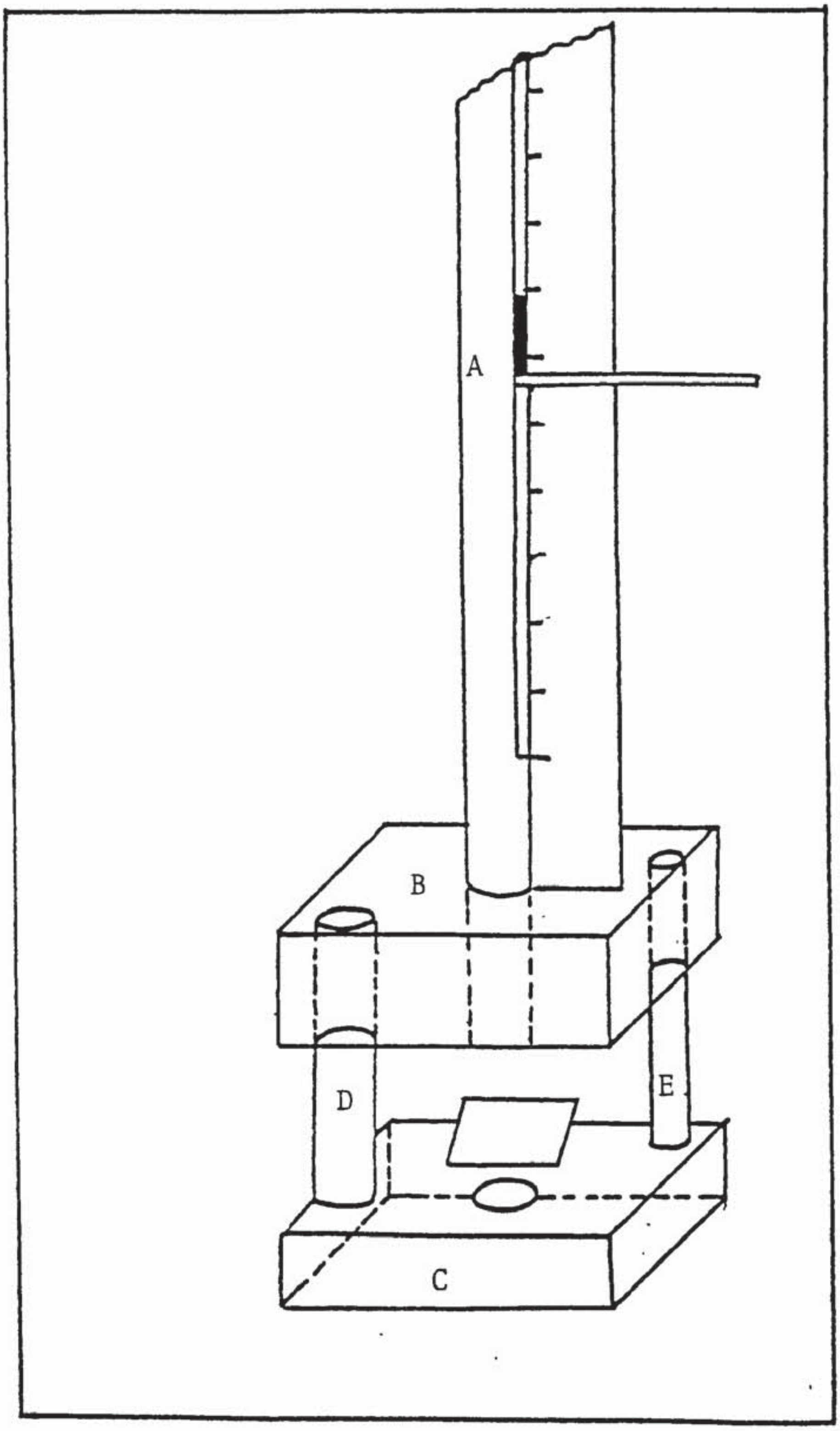


Fig 3.4 Experimental film impact tester

3.12 Measurement of Tensile Strength

The tensile tests were carried out on an Instron Tensile Tester (model TMSM) using cross-head speed of 2 cm per minute. Tests were carried out on 5-8 samples from each run and the average result was taken. The error involved in the measurement was in the region of 15%. The dimensions of the dumb-bell test piece was as follows:

Length	5.0 cm
Breadth	0.35 cm
Thickness	0.015-0.020 cm
Gauge length	3 cm
Temperature	$21 \pm 1^{\circ}C$

Specimen number, average thickness and blend composition was recorded for every test. From the stress-strain curves obtained, modulus, tensile strength, yield strength and elongation at break were recorded. The results being calculated from the equations given below:

$$\text{Tensile strength (TS)} = \frac{\text{force at break}}{\text{thickness x width}}$$

$$\text{Yield strength (YS)} = \frac{\text{force at yield}}{\text{thickness x width}}$$

$$\text{Percentage elongation (E\%)} = \frac{\text{chart length x crosshead speed}}{\text{chart speed x gauge length}} \times 100$$

$$\text{Modulus} = \frac{\text{chart length x crosshead speed x initial slope}}{\text{gauge length x thickness x width}}$$

3.13 Measurement of Dynamic Mechanical Properties

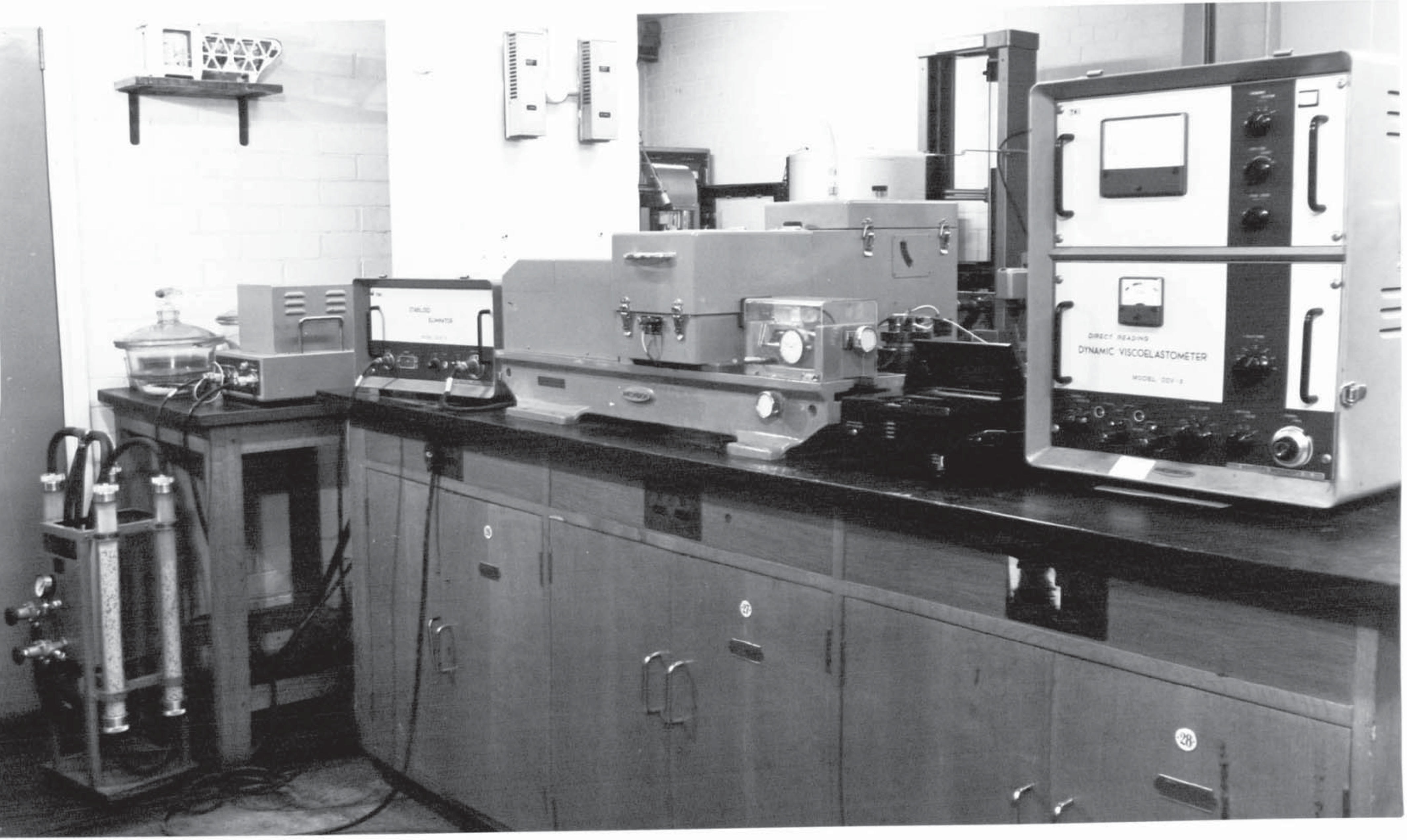
3.13a Procedure

The Rheovibron model DDVII (photograph II), Toyo Measuring Instrument Company Limited (TMI), Tokyo(100) was used at ambient temperature and over a temperature range from -100°C up to 0°C. All measurements were made at a frequency of 110 hertz (Hz). Specimens (3 mm x 60 mm) were stamped out using a steel cutter from compression film. The sample chamber was cooled to -100°C fairly quickly, maintaining constant tension in the sample to prevent 'kinking' or fracture. After reaching equilibrium, the liquid nitrogen was allowed to boil off and readings were taken as the chamber slowly returned to ambient temperature; the air must be dry and for this purpose it must be passed through the columns containing silica gel and molecular sieves and they must be dried before each measurement. Readings can also be taken during the cooling operation, but the former method (while the chamber slowly returns to ambient temperature) was found(101) to give more accurate results owing to better temperature control. The Rheovibron instrument was calibrated before each measurement.

3.13b Theory and Derivation of Basic Dynamic Equations

The purpose of using the Rheovibron is to measure the temperature

Photograph II



dependence of the complex modulus and mechanical damping of high polymers at a definite frequency.

Modulus of elasticity is a measure of stress accompanying a unit deformation and for material obeying Hook's law it is the ratio of stress to strain. It also provides a measure of recoverable potential energy. However, not all materials follow Hook's law ideally and the energy utilised in deforming a body is not fully recoverable, a part is always lost as heat. The extent of this energy dissipation, however, varies from material to material.

Mechanical damping is a measure of loss of energy as heat and is defined by the ratio of the energy dissipated as heat to the energy stored as potential energy. The mechanical damping can be calculated as logarithmic decrment (Δ) which is the logarithmic ratio of amplitudes of two successive damped oscillations (Figs 3.5a and 3.5b). High polymers are the best known examples of the class of material known as viscoelastic having characteristics of both viscous liquids and elastic springs. If a stress is suddenly applied to a polymeric material. The resulting strain reaches some value immediately and then decays or relaxes over a period of time.

The sinusoidal experiments involving viscoelastic appears to show two stress components, one in phase with the applied strain (δ') or parallel to the direction of the strain, (Fig 3.5a) and the other out of phase with the applied strain (δ'') or perpendicular to the direction of the strain.

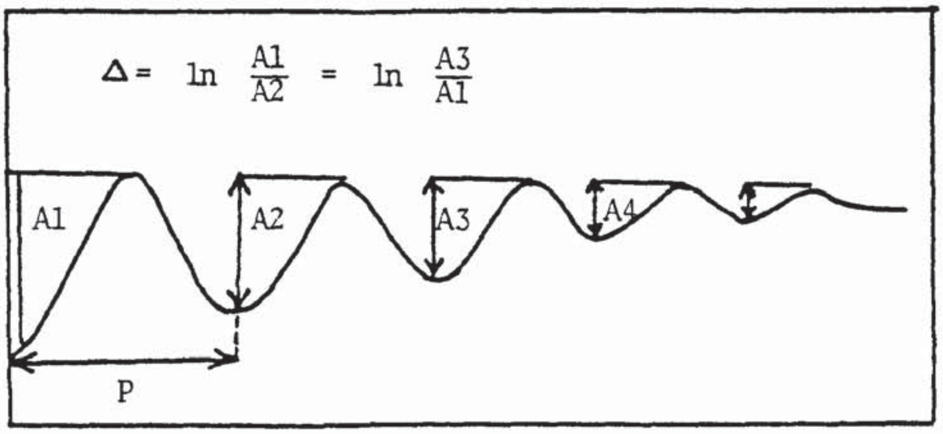


Fig 3.5a Schematic representation of typical damped oscillation curve.

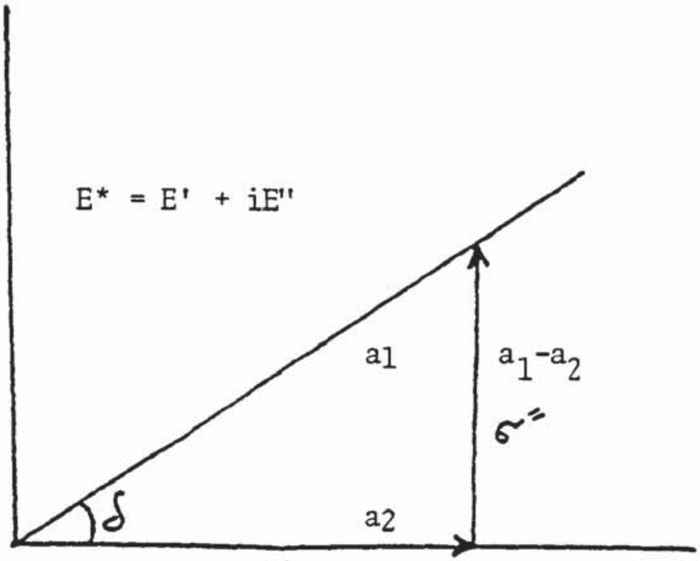


Fig 3.5b Vector diagram

The magnitude of two stresses is given by:

$$'\delta = E' \text{ x strain} \tag{3.1}$$

$$''\delta = E'' \text{ x strain} \tag{3.2}$$

Where: E' and E'' are real and imaginary parts of the complex modulus defined as $E^* = E' + iE''$.

The quantities of E' and E'' are also called storage and loss modulus respectively. The former is related to the stored and recoverable energy and the latter is related to the damping terms which determines the dissipation of energy into heat when the material is deformed.

The equation $E^* = E' + iE''$ can also be expressed in terms of the absolute value of complex modulus of elasticity /E*/ and phase angle δ between the stress and strain.

$$E^* = E' + iE'' = \frac{\delta_{max}}{\varepsilon_{max}} \tag{3.3}$$

where: $$E' = \frac{\delta'}{\varepsilon_0} = \frac{\delta_0}{\varepsilon_0} \operatorname{Cos} \delta = E^* \operatorname{Cos} \delta \tag{3.4}$$

$$E'' = \frac{\delta''}{\varepsilon_0} = \frac{\delta_0}{\varepsilon_0} \operatorname{Sin} \delta = E^* \operatorname{Sin} \delta \tag{3.5}$$

The ratio of out-phase modulus to in-phase modulus,

$$\frac{E''}{E'} = \frac{E^* \operatorname{Sin} \delta}{E^* \operatorname{Cos} \delta}$$

The ratio of E''/E' is called loss tangent, loss factor, dissipation factor or mechanical damping.

$$\frac{E''}{E'} = \tan\delta \qquad (3.6)$$

Therefore the mechanical dissipation factor is proportional to the ratio of the energy loss to the energy stored during a cycle of deformation.

3.13c Principles Involved in the Rheovibron

Both ends of the sample are fixed to transducers, one of which is a transducer of displacement, ΔL (Model T-7), and the other of which is a transducer of generated force, ΔF, (Model T-1) which are shown in Figs 3.6a and 3.6b.

The specimen is deformed sinusoidally with the help of the driving device and the sinusoidal stress which is generated at the other end of the specimen is out of phase with the applied strain and differing by a phase angle, $\tan\delta$.

To obtain the angle, δ, both the magnitude of the oscillating displacement, ΔL, and oscillating force, ΔF, are transformed in the electrical output by strain (T-7) and stress (T-1) gauges respectively, specified for strain and stress detection(102,103).

The output voltages of T-1 (stress transducer) and T-7 (strain transducer) are indicated by vectors $/a_1/$ and $/a_2/$ respectively,

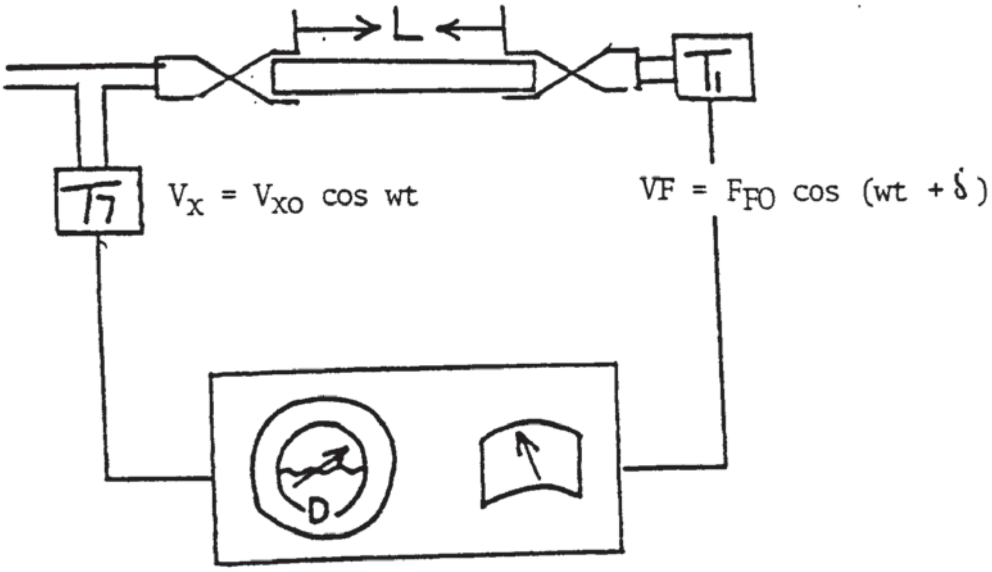


Fig 3.6a Schematic representation of the Rheovibron DDV-II dynamic tensile tester

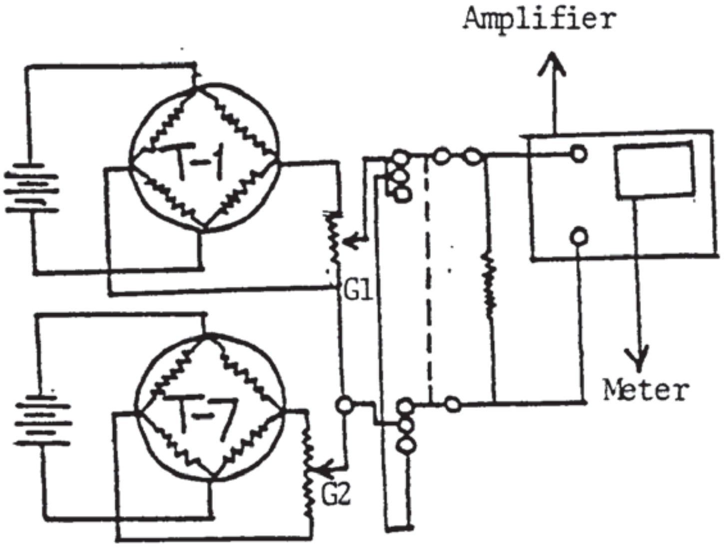


Fig 3.6b General concept of Rheovibron

are adjusted to unity, $/a_1/=/a_2/=1$ by attaining full scale deflection, vector substraction is made by changing the output circuits of the two gauges. This enables the value of tan δ to be read directly from the meter. After the condition of $/a_1/=/a_2/=1$ is satisfied, tan δ is given by the equation (3.7) which it (tan δ) can be read directly from the meter.

$$
\begin{aligned}
/a_1-a_2/ = \quad a_1^2 + a_2^2 &= 2a_1a_2 \text{ Cos } \delta \\
&= \sqrt{2-2 \text{ Cos } \delta} \\
&= \sqrt{2(1-\text{Cos } \delta)} \\
&= 4 \text{ Sin}^2 \delta/2 \\
&= 2 \text{ Sin } \delta/2 \\
&= \tan \delta \ (\ \delta \text{ being very small}) \qquad (3.7)
\end{aligned}
$$

The complex modulus embracing both viscous and elastic components can be calculated from the following equations:

$$
/E^*/ = \frac{\delta_{max}}{\varepsilon_{max}} = \frac{\Delta F/S}{\Delta L/L} = \frac{\text{force}}{\text{area}} \Big/ \frac{\text{length}}{\text{elongation}} = \frac{\Delta F}{S} \cdot \frac{L}{\Delta L} \qquad (3.8)
$$

where: ΔF = oscillating load or amplitude of tensile force

S = cross-section of samples (cm^2)

L = length of the sample

ΔL = oscillating displacement of the sample of amplitude of elongation

If the supply and output voltages of the transducers T-1 and T-7 are E_1, E_2 and C_1, C_2 respectively, then the relation of ΔF and ΔL can be calculated as follows:

$$\Delta F = \frac{C_1}{E_1 f_1} \quad , \quad \Delta L = \frac{C_2}{E_2 f_2}$$

where f_1 and f_2 are the calibration factors of the transducers T-1 and T-7 respectively.

Putting these values into equation 3.8,

$$/E^*/ = \frac{C_1}{C_2} \cdot \frac{L}{S} \cdot \frac{f_2}{f_1} \cdot \frac{E_2}{E_1} \qquad (3.9)$$

By adjusting the dividers G_1 and G_2, condition $^{C_1}/C_2 = {}^{C_2}/C_1$ is set, since the products of $C_1G_1 = C_2G_2$ are made equal at the time of measuring tan δ ($/a_1/ = /a_2/ = 1$).

Replacing these values in equation 3.9,

$$/E^*/ = \frac{f_2}{f_1} \cdot \frac{L}{S} \cdot \frac{E_2}{E_1} \cdot \frac{G_2}{G_1} \qquad (3.10)$$

Now, $\frac{Lf_2}{Sf_1}$ is constant for the sample and transducer used and $\frac{E_2}{E_1}$ is previously calibrated. Therefore /E*/ is only dependent on the reading of G_1 and G_2.

Calculation of oscillating load, ΔF

This is obtained from the following equation:

$$F = 10^4 \text{ dynes } . \frac{10^3}{D} . N$$

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

D = value of the dynamic force dial at the time of measuring tan δ

N = the value of the tan δ range at the time of measuring tan δ and obtained from Table 3.1

Calibration of oscillating displacement, ΔL

$$\Delta L = 5 \times 10^{-3} \text{ AN cm}$$

where: 5×10^{-3} cm = calibration value of T-7 gauge

A = the value of the amplitude factor when measuring tan δ and obtained from Table 3.1

Putting the above values of ΔF and ΔL in the equation of complex modulus (equation 3.8),

$$/E^*/ = 2 \times \frac{1}{AD} \times \frac{L}{S} \times 10^9 \text{ dynes cm}^{-2} \qquad (3.11)$$

Since during the displacement of sample, there is also a slight displacement in the check rod and T-1 rod which gives an error in the final L values. To eliminate this, an error constant 'k' is included in the above equation and the final equation of complex modulus of elasticity takes the form:

Table 3.1

Tan δ range or amplitude factor	N or A
0 db	31.6
10	10.0
20	3.16
30	1.0
40	0.316
50	0.1
60	0.0316

$$/E^*/ = 2 \ \frac{1}{A(D-K)} \ \times \ \frac{L}{S} \ \times \ 10^9 \text{ dynes cm}^{-2} \qquad (3.12)$$

where: L = sample length (cm)

S = cross section area (cm^2)

A = value corresponding to amplitude factor selected (usually A was equal to 1.0)

D = dynamic force reading on dial

K = error factor

3.14 Microscopy Examination

The versatility of the Vicker's photoplan optical microscope enables both polarised light and phase contrast microscopy to be used to investigate the polymer and the degree of dispersion of second polymer in the first polymer matrix (continuous phase). The instrument had provision to take photographs, of the slide in view. Photographs were taken under polarised light and phase contrast conditions.

Polarised microscope specimens were examined using glass slides which were cleaned by putting them into a saturated solution of sodium hydroxide and methanol for 24 hours. The slides were taken out and washed with distilled water.

A glass slide was placed on a hot plate and above it another slide was placed. The first slide acts as a heat transfer medium and prevents any dirt from the hot plate getting on to the second slide. A small piece of the polyblend is placed on the second slide and when it was melting a cover slide placed above it. Using a glass rod the cover slide is pressed and when the glass cools the polyblend is firmly sandwiched between the glass slides. This was placed in the microscope and its photograph was taken.

3.15 Continuous Cold Extraction Technique

During the hot extraction of polypropylene films, it was found that oxidation of polypropylene takes place. Also the ethylene-propylene diene rubber was found to shrink during hot extraction. Therefore a cold extraction technique was designed in which extracting solvent was in continuous movement. The apparatus (Fig 3.7) consisted of a three-necked round bottomed blask (A) fitted to column (B). When the extraction solvent boils, it passes through the column (B) in to a condenser (C), which leads in to a soxhlet (D). Samples are placed in the soxhlet (D) and when this is filled, solvent is returned to flask (A) through the connecting tube (E). It is found that continuous cold extraction is as efficient as hot extraction (by choice of the appropriate solvent) and has certain advantages over the hot extraction. Two main advantages are:

(i) the extraction is carried out at room temperature so the possibility of polymer samples oxidising is minimised, and

(ii) due to the lower temperature, the stream of nitrogen gas is not necessary.

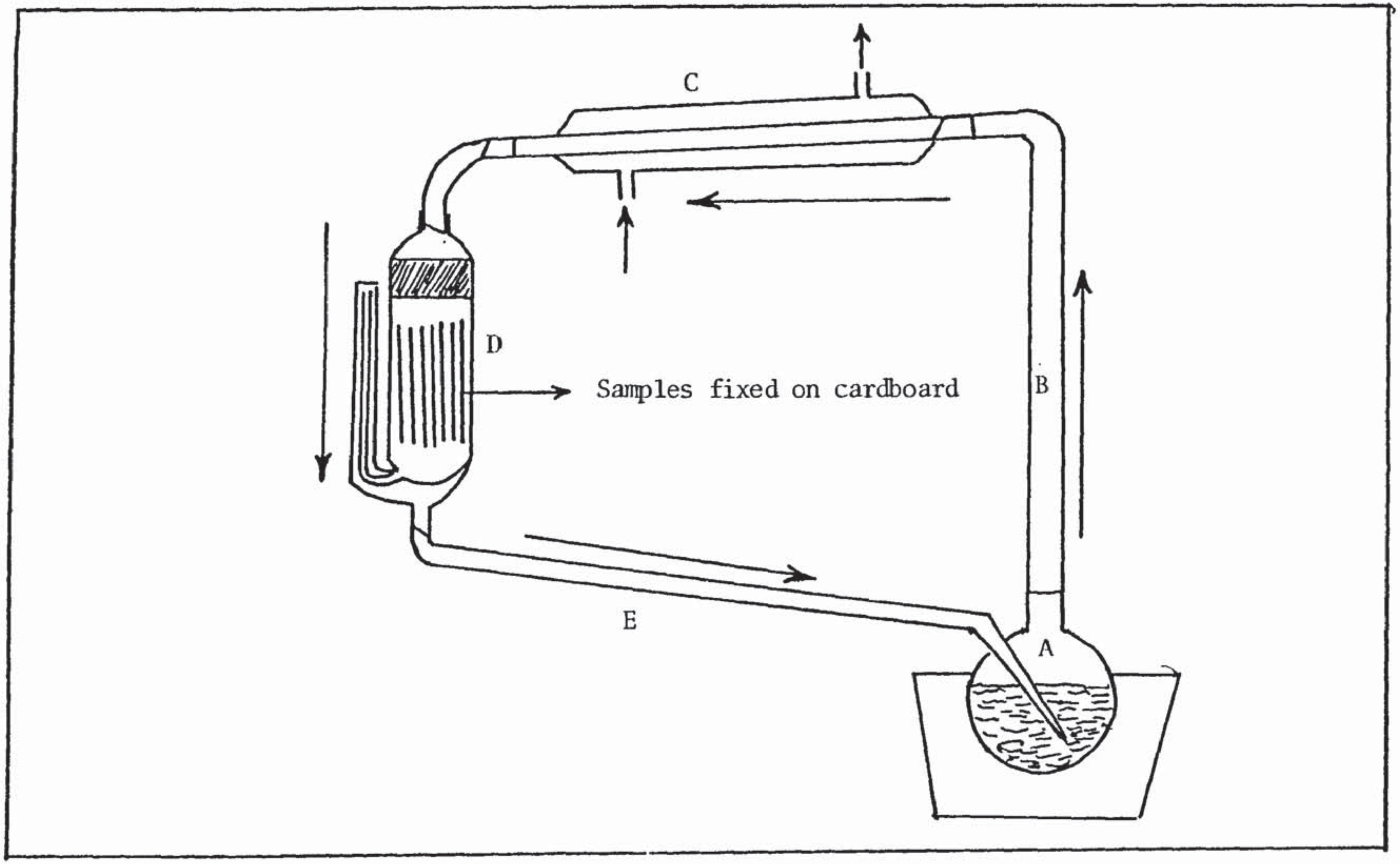
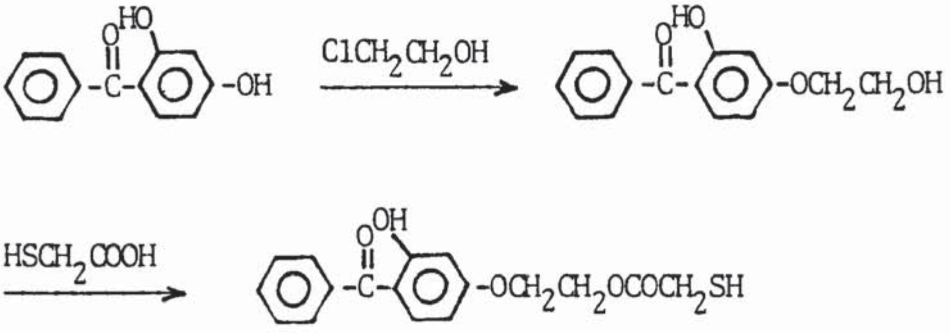


Fig 3.7 Continuous cold extraction apparatus

3.16 Chemical Synthesis and Characterisation of Additives

3.16.1 Chemical Synthesis of 4-Benzoyl-3-hydroxyphenyl-O-ethyl thioglycollate

The following two stage process was used in the synthesis of this compound(104).



3.16.1a Preparation of 2-Hydroxy-4-(β-hydroxy-ethoxy)-benzophenone(105)

21.4 g (0.1 M) of 2,4-dihydroxybenzophenone and 0.4 g (0.1 M) of sodium hydroxide were dissolved in 125 ml of distilled water, 8.1 g (0.1 M) of ethylene chlorohydrin were added all at once to the above solution, and the mixture was stirred at 90-95°C for 4 hours and then 125 ml of distilled water at 95°C was added to it. The solution was allowed to stand overnight with stirring at room temperature. The next day, the precipitate obtained was washed several times with distilled water and mechanical stirring continued during 24 hours. A white powder was obtained, melting point 90°C, and was used for the next stage without further purification.

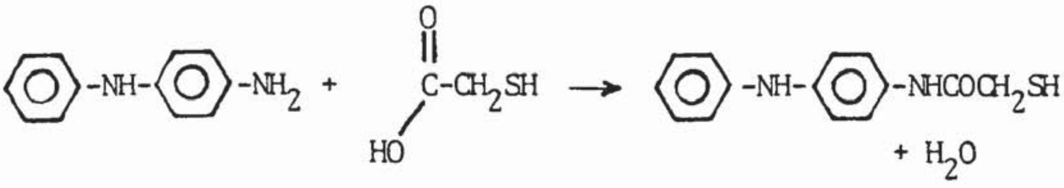
Ir data	Phenolic OH and alcoholic OH	3310-3500 cm^{-1}
	Benzophenone carbonyl	1630 cm^{-1}
	Aliphatic $-CH_2$	2920 cm^{-1}
Nmr data	Aromatic protons	2.3-2.5 τ (multiplet)
	Phenolic protons	2.2 τ (singlet)
	Alcoholic hydroxyl proton	4.0 τ (singlet)
	Methylenic protons	6.5-6.7 τ (multiplet)
Uv data	Benzophenone group absorption at 330 nm.	

3.16.1b Preparation of 4-Benzoyl-3-hydroxyphenyl-O-ethyl thioglycollate (EBHPT)

25.8 g (0.1 M) of 2-hydroxy-4-(β-hydroxy-ethoxy)benzophenone and 10 g (0.109 M) of thioglycollic acid were dissolved in 200 ml of toluene. 0.5 ml of concentrated sylphuric acid were added to this solution. The flask was fitted with a Dean and Stark and the solution was refluxed (in an oil bath at 115°C) until the theoretical amount of water was removed (6 hours). The solution was washed to neutral pH with sodium bicarbonate solution and distilled water. It was then dried with anhydrous magnesium sulphate. Toluene was removed by rotary evaporation to give a red liquid which gave yellow crystals in a refrigerator. The melting point of this compound was found to be 54°C (literature, 54°C)(104). The ir spectroscopy of the compound (EBHPT) is shown in Fig 3.8.

Ir data	H-bonded phenolic -OH	3200-3400 cm^{-1}
	Ester carbonyl	1720 cm^{-1}
	Thiol group -SH	2550 cm^{-1}
Uv data	Benzophenone group absorption	330 nm
Nmr data	Aromatic proton	2.3-2.6 τ
	Methylenic proton	6.2-6.5 τ
	Phenolic proton	2.2 τ
	Thiol proton	7.2 τ
	3 Aromatic protons	3.2-3.7 τ

3.16.2 Synthesis of 4(Mercaptoacetamido)diphenylamine (MADA) (106)



The method employed in the synthesis was the one described by the Goodyear Tyre and Rubber Company, Research Division. The 4-(mercaptoacetamido)diphenylamine (MADA) was prepared according to the above scheme.

The compound was obtained by the amidation of para-amino-diphenylamine

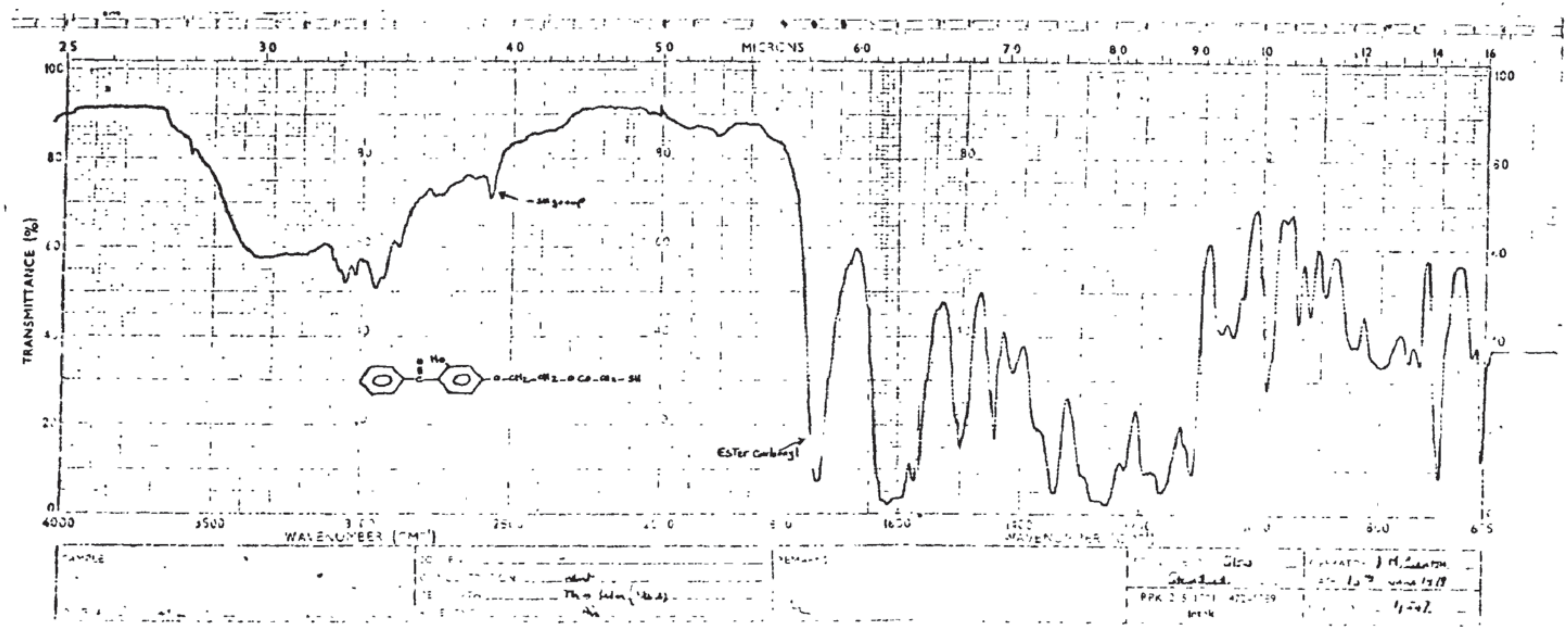


Fig 3.8 Infra-red spectroscopy of 4-benzoyl-3-hydroxyphenyl-o-ethyl thioglycollate (EBHPT)

with thioglycollic acid in refluxing xylene.

A mixture of 18.4 g (0.1 M) of para-amino-diphenylamine, 9.2 g (0.1 M) of thioglycollic acid and 150 cc of technical grade xylene was heated to reflux (about 140°C) in a 500 ml flask under nitrogen gas for about 10 hours.

The residue was diluted with n-hexane and allowed to cool down to room temperature and left overnight. A crystalline product was obtained and by recrystallising this product from toluene and methanol (4:1 v/v), a powder product was obtained. It is crystalline white, melting point of 135-136°C, yield 70%. The product is very sensitive to oxidation, therefore the recrystallisation should be carried out under a nitrogen atmosphere. Ir spectroscopy of the compound (MADA) is shown in Fig 3.9.

Ir data	Aromatic ring	880 cm^{-1}
	Secondary amine (-NH)	3450 cm^{-1}
	Secondary amine (carbonyl)	1650 cm^{-1}
	Thiol group -SH	2561 cm^{-1}
	$-CH_2-$ alkyl	1440-1460 cm^{-1}
	Amide -NH-	3260 cm^{-1}

3.16.3 Preparation of (3,5-ditertiarybutyl-4-hydroxy)benzyl carboxymethyl sulphide (DBCMS)

This was prepared according to the following scheme:

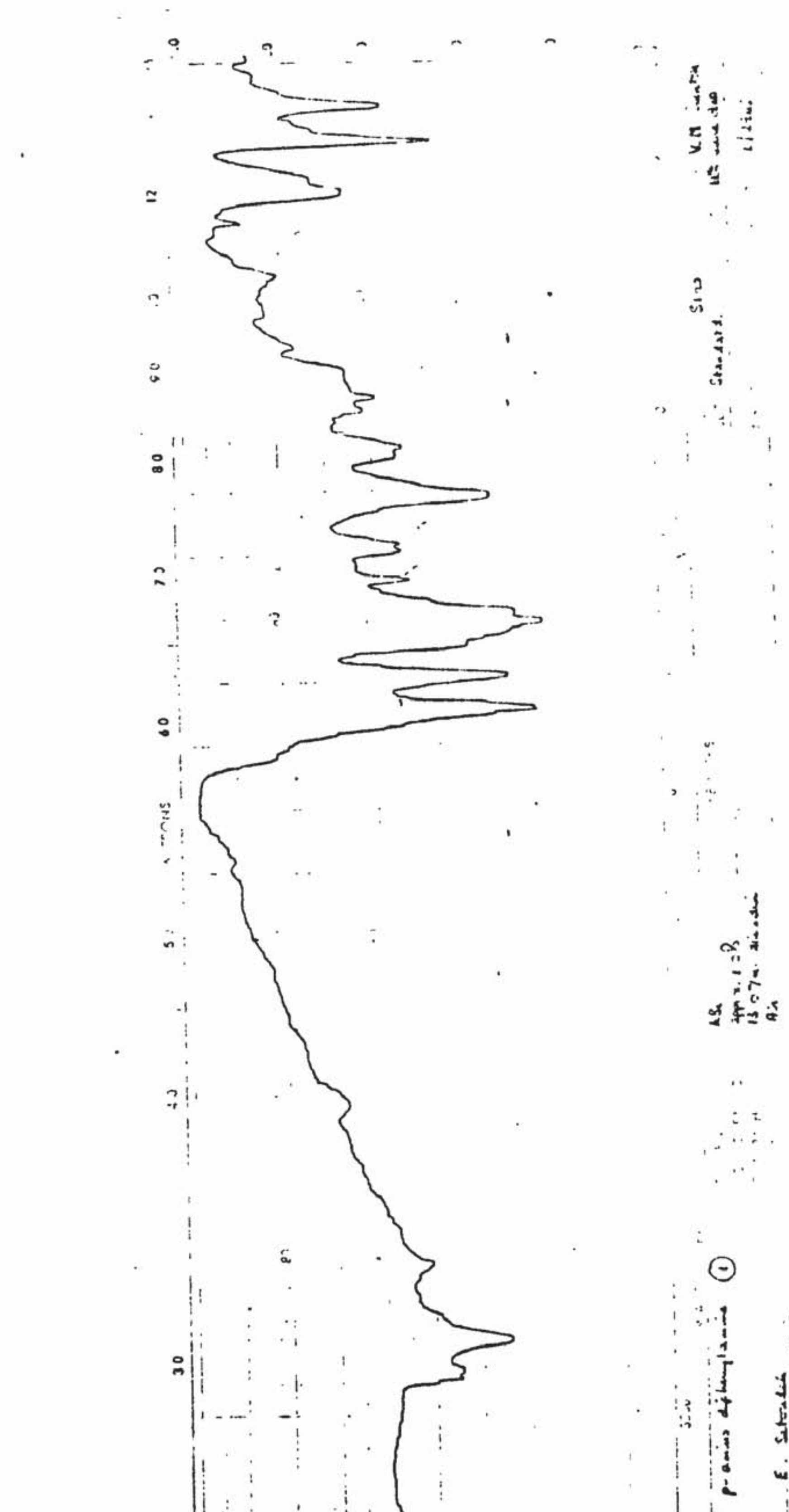
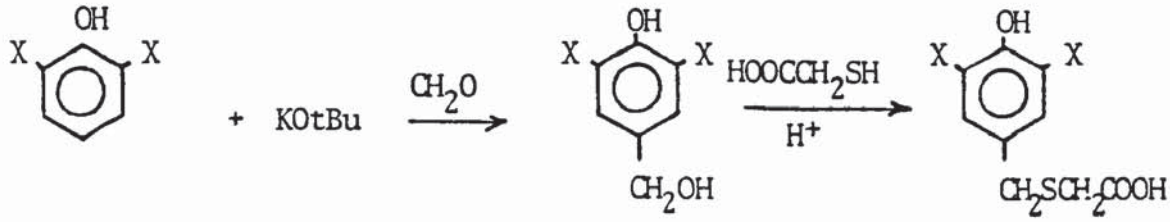


Fig 3.9 Infra-red spectroscopy of 4-(mercapto acetamido) diphenylamine (MADA)



where: $X = -C(CH_3)_3$

3.16.3a Preparation of 3,5-ditertiarybutyl-4-hydroxybenzyl alcohol(107)

53.5 parts by volume of a 7.5% solution of formaldehyde in tertiary butyl alcohol, 50 parts of a 500 g/l solution of 2,6-ditertiarybutyl phenol and 14 parts of a 50 g/l solution of potassium tertiary butoxide in the same solvent were mixed at 20-22°C and stirred under a nitrogen atmosphere for 30 minutes. The mixture was then poured into ice water and two layers formed, the upper organic layer solidifying. The solids were washed with water, stirred with hexane, filtered and air dried. A crystalline white solid of 3,5-ditertiarybutyl-4-hydroxybenzyl alcohol (BHBA) was obtained, melting at 137°C. Ir spectroscopy of the compound (BHBA) is shown in Fig 3.10.

Ir data		
	Free phenolic -OH	3600 cm^{-1}
	Hydrogen bonded -OH	3300-3500 cm^{-1}

3.16.3b Reaction of 3,5-ditertiarybutyl-4-hydroxybenzyl alcohol with Thioglycollic Acid(108)

29.5 g (0.125 M) of 3,5-ditertiary butyl-4-hydroxybenzyl alcohol

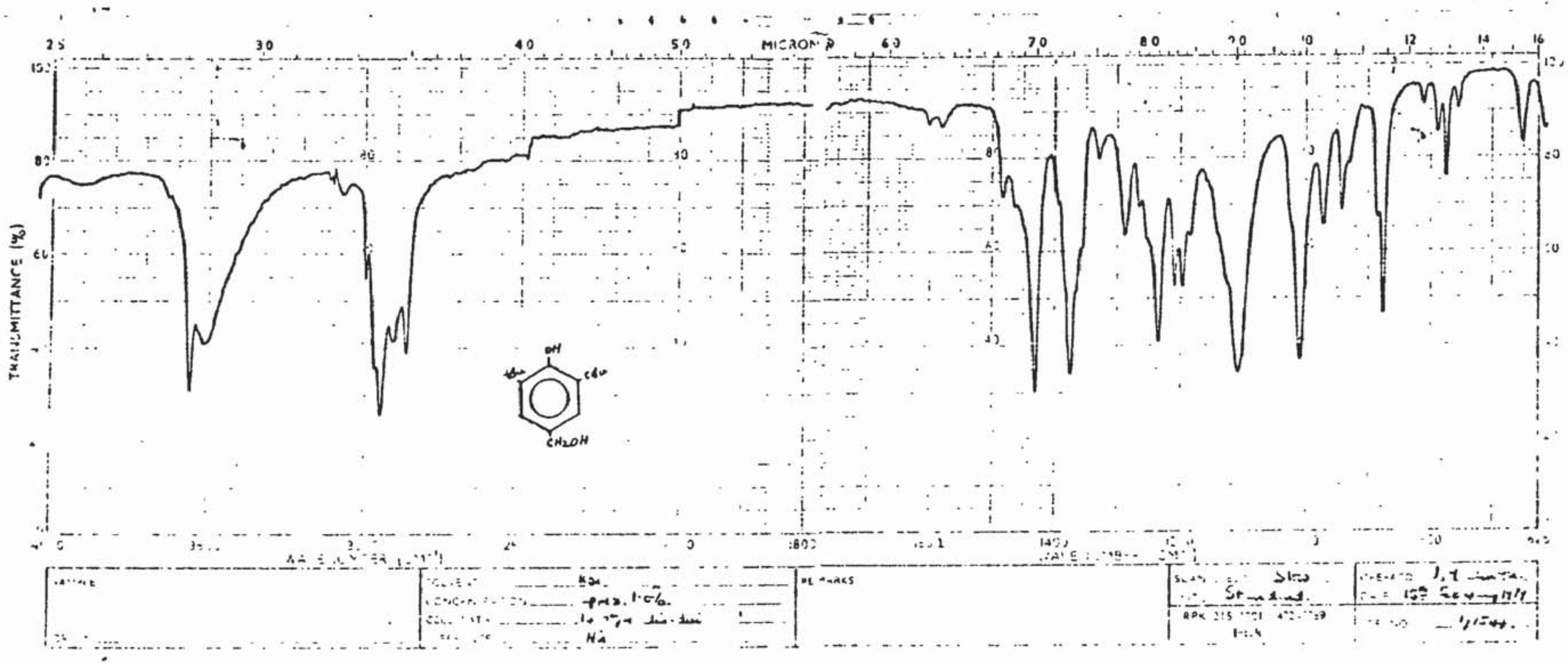
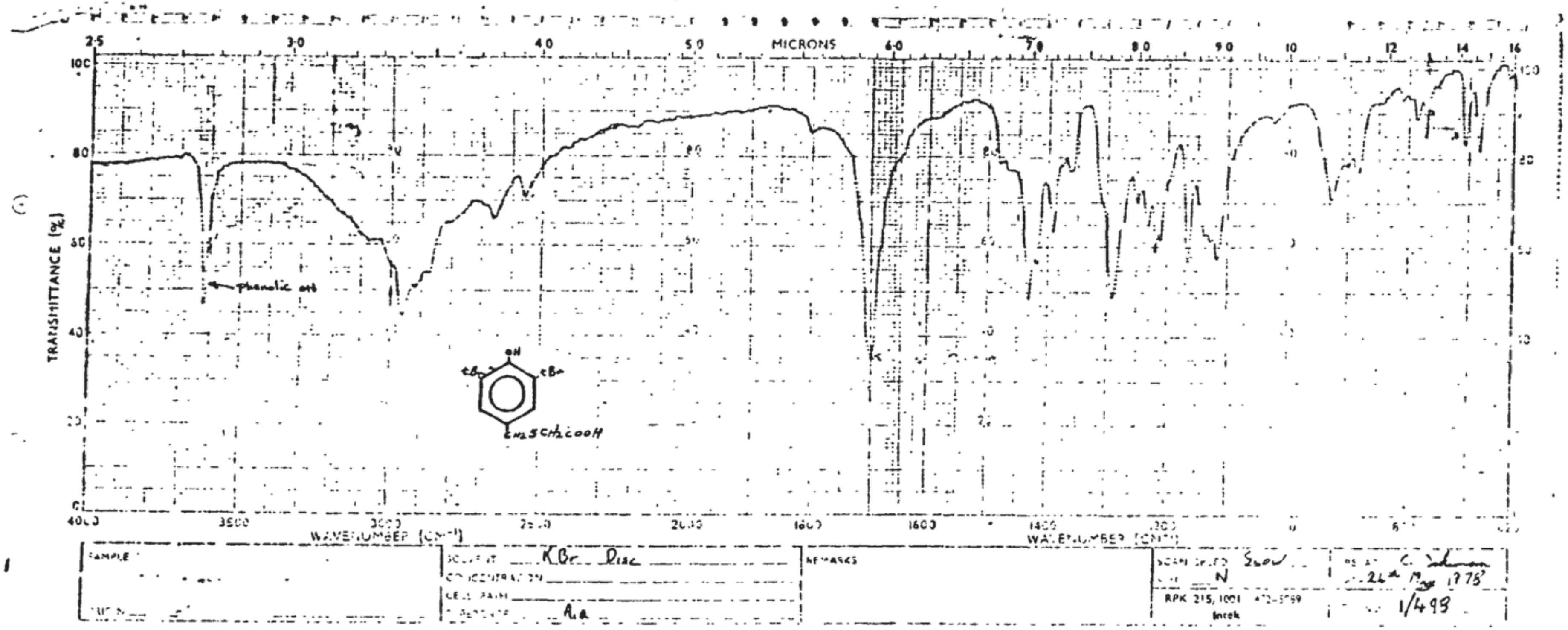


Fig 3.10 Infra-red spectroscopy of 3,5-ditertiary-butyl-4-hydroxybenzyl alcohol (BHBA)

was poured in to a 500 ml flat bottomed flask. 200 ml of toluene was added and the mixture stirred by means of a magnetic follower. 11.5 g (0.125 M) of the thioglycollic acid was poured into the solution followed by a few drops of concentrated sulphuric acid. The flask was fitted with a Dean and Stark apparatus with condenser. The reaction was heated at 120°C in an oil bath. The completion of the reaction was judged by stoichiometric amount of water produced. The product was washed with distilled water and then with sodium bicarbonate (2% solution) to neutralise the medium. It was then dried with anhydrous magnesium sulphate, filtered and dried. A white solid was collected, melting at 98-99°C. Ir spectroscopy of the compound (DBCMS) is shown in Fig 3.11.

Ir data	Phenolic -OH	3640 cm^{-1}
	Acidic carbonyl	1700-1710 cm^{-1}



SOLVENT KBr Disc

CONCENTRATION

CELL PATH

REFERENCE A.R.

SCAN SPEED Slow

N

C. Johnson

26th May 1978

1/493

Fig 3.11 Infra-red spectroscopy of (3,5-di-tertiary-butyl-4-hydroxy)benzyl carboxy methyl sulphide (DBCMS)

CHAPTER FOUR

MECHANOCHEMICAL BINDING OF THIOL ANTIOXIDANTS TO POLYMERS

CHAPTER FOUR

MECHANOCHEMICAL BINDING OF THIOL ANTIOXIDANTS TO POLYMERS

4.1 Mechanochemical Binding of Thiol Antioxidants to Ethylene-propylene Diene Monomer (EPDM)

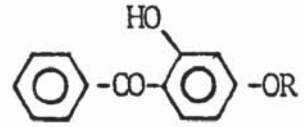
4.1.1 General Background

It has been demonstrated that antioxidants and stabilisers containing a thiol group can be readily added to olefinic double bonds in polymers in the presence of an added radical generator(109-116). It is also known, however, that many polymers readily generate free radicals under conditions of high shear above their glass transition temperatures(117-122) (eg in a shearing mixer during processing(123,124)). More recently, direct evidence has been found for macroradical formation by esr spectroscopy. The free radicals have been trapped by freezing the masticated polymer in liquid nitrogen below the glass transition temperature(125) and their reaction with stable-free radicals previously introduced into the system(126,127) has been followed.

Therefore, the free radicals formed in the scission of the molecular chains of a polymer can react in several ways; (i) with oxygen to form alkylperoxy radicals, (ii) with other radicals present in the mixture and (iii) with the double bonds of the rubber.

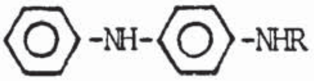
4.1.2 Attempted Ethylene-propylene Diene Monomers (EPDM) Adduct Formation with Stabilisers Containing Thiol Groups during Mechanochemical Process

The uv stabilisers such as 4-benzoyl-3-hydroxyphenol-o-ethyl thioglycollate (I, EBHPT) and 4-(mercaptoacetamido)diphenylamine (II, MADA) and a thermal stabiliser, such as 3,5-di-tertiary-butyl-4-hydroxybenzyl carboxy methyl sulphide (III, DBCMS) were used for adduct formation with EPDM during processing in the torque rheometer.



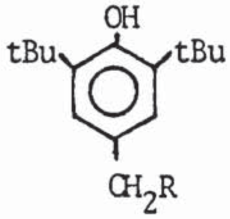
(I) R=$CH_2CH_2OCOCH_2SH$

EBHPT



(II) R=$COCH_2SH$

MADA



(III) DBCMS

R=SCH_2COOH

4.1.2a General Procedure

The mechanochemical reaction carried out using the prototype RAPRA torque rheometer which is essentially a small mixing chamber, containing mixing screws contra-rotating at different speeds (see 2.2.1 for further details). A full charge of 35 g of compounded polymer (polymer + additive) was processed for various times and temperatures with the chamber closed to the atmosphere. Attempt was made to find the optimum temperature and time in which maximum binding was obtained. For this purpose, a range of temperatures from 50 to 200°C was chosen. After the optimum temperature had been defined, the processing time was varied (ie from 3 minutes to 20 minutes). On completion of mixing, the polymer was rapidly removed and quenched in cold water to prevent further thermal oxidation. The material was compression moulded at 140°C for 2 minutes (1 minute preheat with no pressure and 1 minute under pressure) into sheets of thickness 0.015 - 0.02 cm using a special grade cellophane as a mould release agent. These polymer sheets were soxhlet extracted using acetone or methanol as a solvent (see 2.15). It was found that 4-5 days of cold extraction was enough to remove all non-bound antioxidants. (Hot extraction caused the EPDM films to shrink and hence the cold extraction technique, which is as efficient as hot extraction, was developed (see 2.15)). The extracted films were placed in a vacuum oven at 30°C overnight in order to eliminate the solvent. They were analysed by ir spectroscopy in order to determine the amount of bound antioxidant.

4.1.2b Estimation of Bound Stabilisers

Ir spectroscopy was used to determine the amount of antioxidants (I, II and III) bound to the EPDM. This technique has been previously used by several workers(110,128,129) for estimation of the amount of bound antioxidants containing hydroxyl, carbonyl aromatic groups. The absorbance of the benzophenone group at 1630 cm^{-1}, aromatic group at 1600 cm^{-1} and phenolic hydroxyl at

3640 cm^{-1} were taken respectively for I, II and III in films with thickness of 6 to 8 x 10^{-3} ins (0.006 - 0.008"). The amount of bound antioxidant was measured using the calibration curve discussed in 4.1.3.

4.1.3 Calibration Curve

The calibration curve was made by casting rather than incorporation by melt mixing in the torque rheometer(130) for the following reasons:

(i) the loss of additives was minimised, and

(ii) oxidation of the antioxidants due to heat and mechanical shear was prevented.

Procedure

5 g of EPDM was weighed out accurately, dissolved in 160 cc of chloroform which was found to give homogeneous solution. 0.04 g (0.8%) of antioxidant (I) was added to this solution, left for 48 hours. It was cast on a glass plate in films with the thickness of 6 to 8 x 10^{-3} inches and were analysed by ir spectroscopy technique. This was repeated for three other concentrations (ie 1, 1.5 and 2%) of antioxidant (I).

The intensity of absorbance at 1630 cm^{-1} due to the presence of the benzophenone group in compound (I) was proportional to the amount of added antioxidant. In order to eliminate errors due to sample thickness and instrument variables, a reference peak at 800 cm^{-1} was used. The ratio of the absorbance at 1630 cm^{-1} to that of 800 cm^{-1} was taken as benzophenone index and plotted as a function of antioxidant added per hundred gram of EPDM (phr). The calibration curve was used for the estimation of bound antioxidant (I). The calibration curve is shown in Fig 4.1.

$$\text{Benzophenone Index} = \frac{\text{Absorbance at } 1630 \text{ cm}^{-1}}{\text{Absorbance at } 800 \text{ cm}^{-1}}$$

In the case of compounds (II) and (III), the same procedure was followed. The absorbance at 1600 cm^{-1} due to the presence of aromatic group in compound (II) was taken and its ratio to the reference peak at 800 cm^{-1} measured (aromatic index). The calibration curve used for the estimation of bound antioxidant (II) is shown in Fig 4.2.

$$\text{Aromatic Index} = \frac{\text{Absorbance at } 1600 \text{ cm}^{-1}}{\text{Absorbance at } 800 \text{ cm}^{-1}}$$

Finally, in compound III the absorbance at 3640 cm^{-1} due to the phenolic OH was measured and the phenolic index was plotted against the concentration of compound III in 100 g of EPDM. The calibration curve is shown in Fig 4.3.

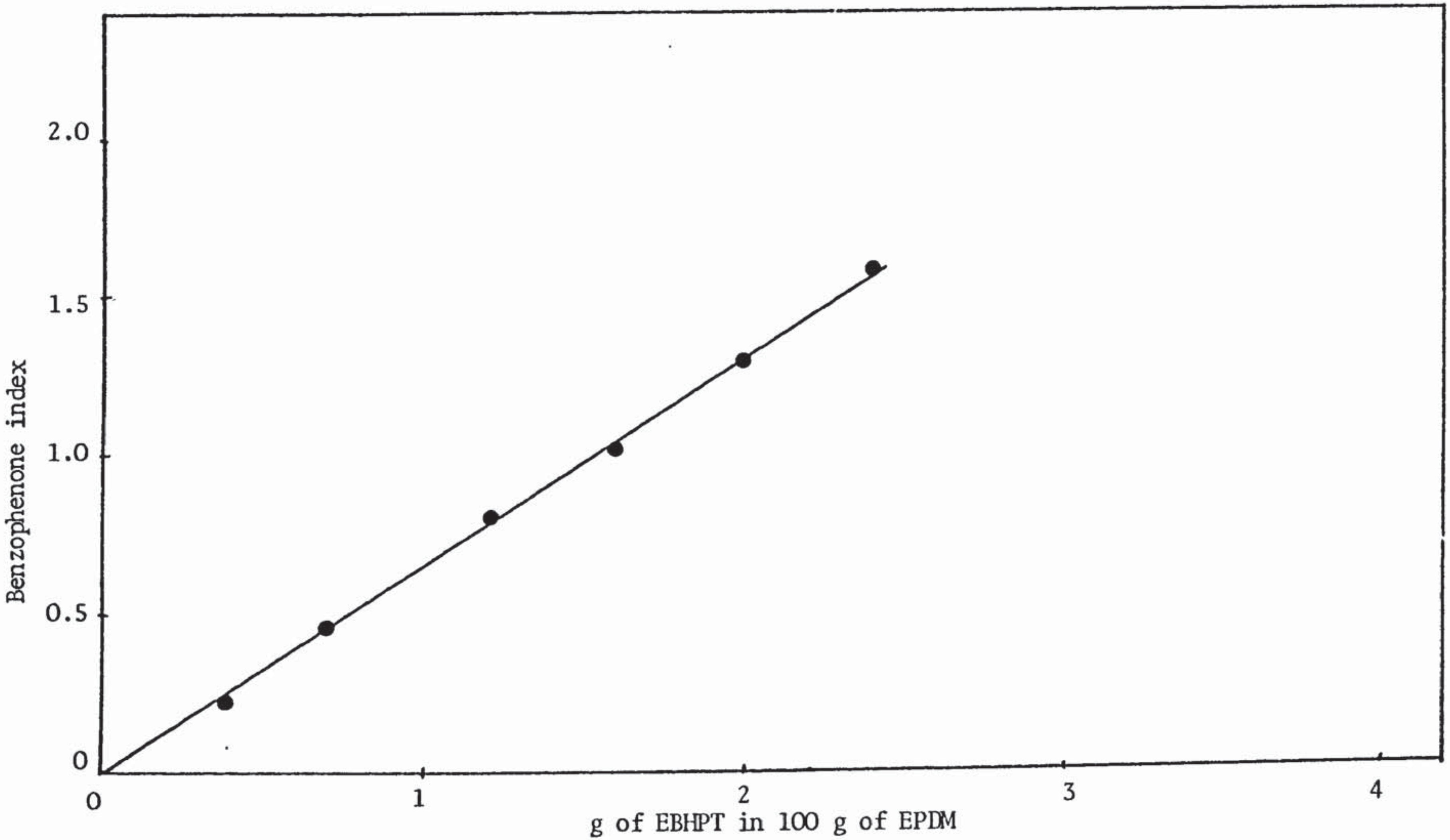


Fig 4.1 Calibration curve for EBHPT made by measuring absorbance of benzophenone group of EBHPT in EPDM cast film

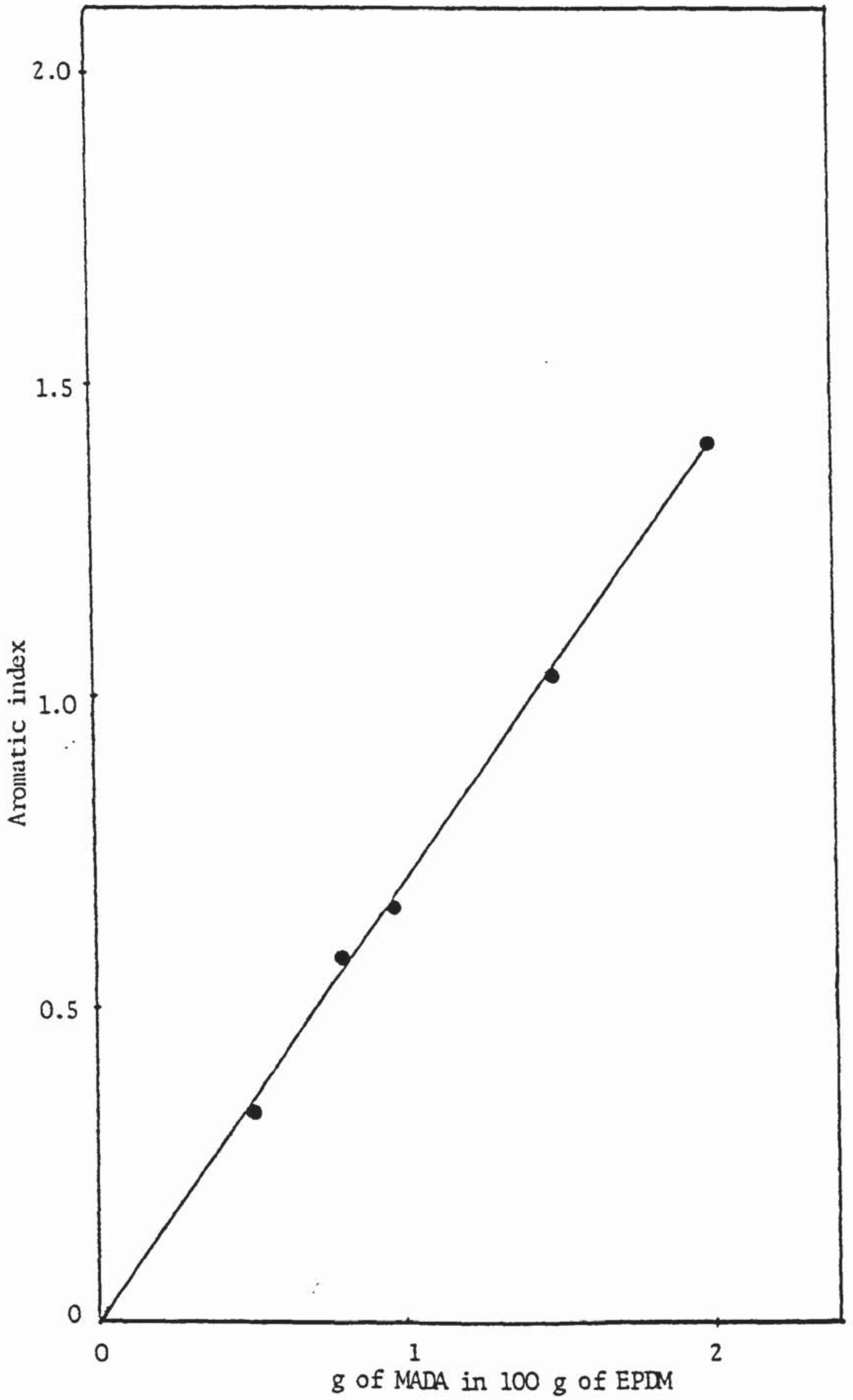


Fig 4.2 Calibration curve for MADA made by measuring of aromatic group of MADA in EPDM cast film

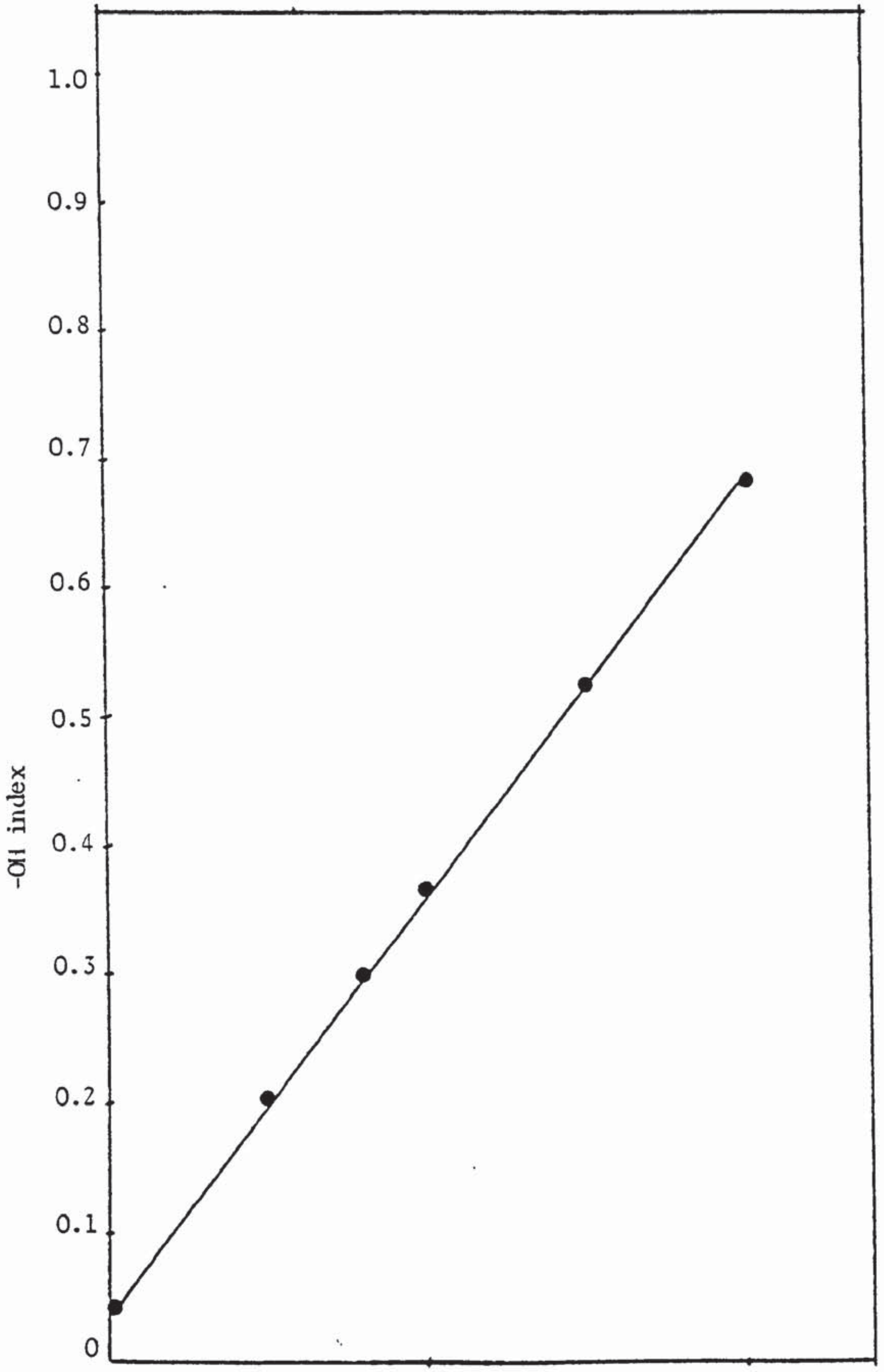


Fig 4.3 Calibration curve for DBCMS made by measuring of OH group of DBCMS in EPDM cast film

$$\text{Phenolic OH Index} = \frac{\text{Absorbance at } 3640 \text{ cm}^{-1}}{\text{Absorbance at } 800 \text{ cm}^{-1}}$$

4.1.4 Mechanochemical Binding of EBHPT (I) to Ethylene-propylene Diene Monomer (EPDM)

The binding was carried out according to the procedure in section 4.1.2a with the modification that EBHPT was compounded into EPDM using a cold mill for 1 to 1.5 minutes. The polymer was then cut to small pieces and processed in the torque rheometer. This was done because EBHPT was in a liquid form, therefore, direct compounding in the torque rheometer was difficult. After processing, the polymer was compression moulded to films with thickness of 6 to 8 x 10^{-3} inches (0.015 - 0.017 cm) and extracted, the amount of bound EBHPT was analysed using ir spectroscopy technique described in section 4.1.2b. The benzophenone index was measured and the amount of EBHPT bound was calculated using calibration curve (Fig 4.1, section 4.1.3).

In order to find out the optimum processing temperature, a set of experiments was carried out with 2% (0.7 g) of EBHPT. The processing time was kept constant at 5 minutes and the processing temperature was varied ranging from 70 to 150°C. The extent of binding of EBHPT in EPDM as a function of processing temperature is shown in Fig 4.4. The correlation between torque -vs- processing time at different temperatures (ie 60 - 140°C) is shown in Fig 4.5. It is clear that by increasing the processing

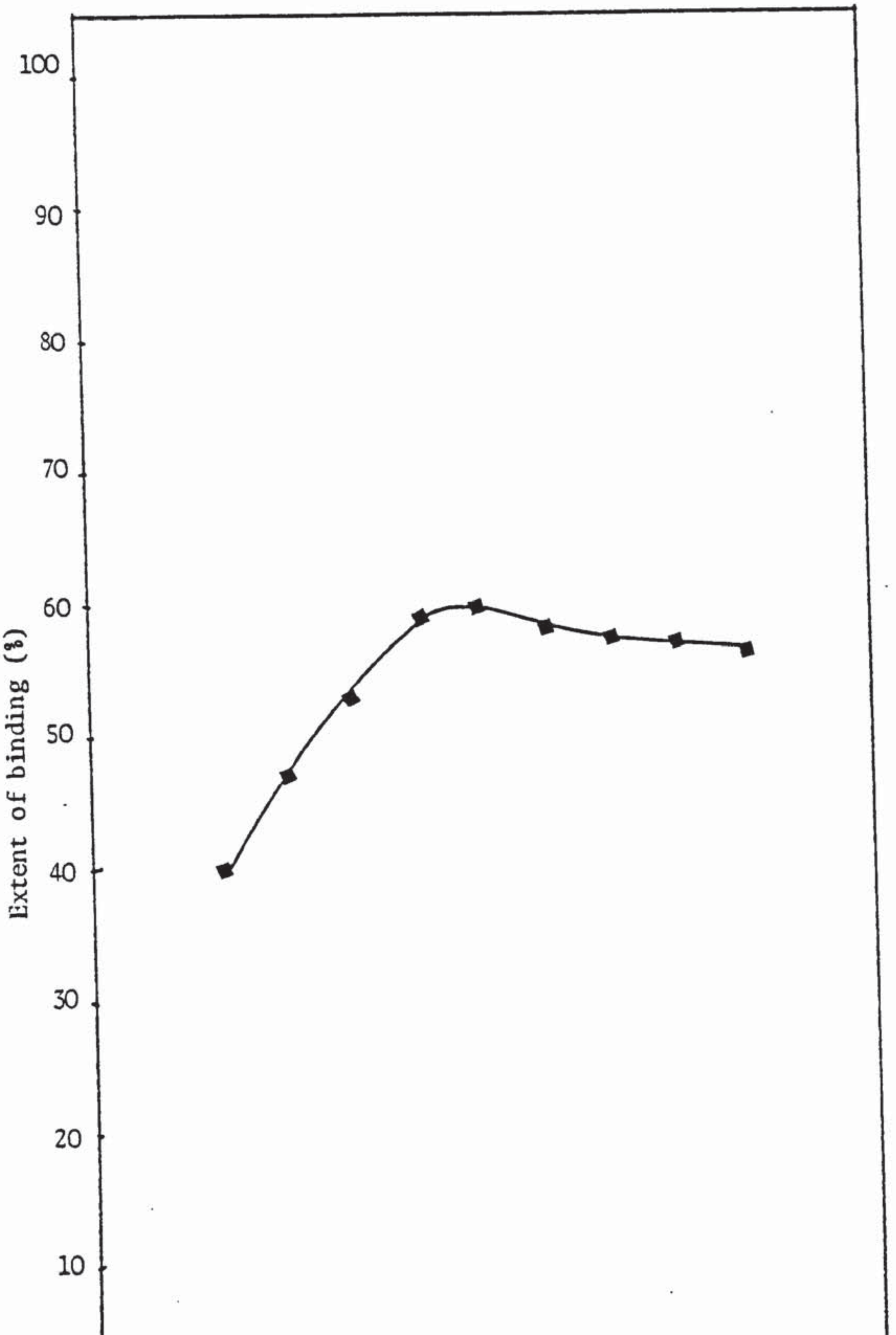


Fig 4.4 The extent of binding of EBHPT as a function of processing temperature (torque rheometer) in EPDM

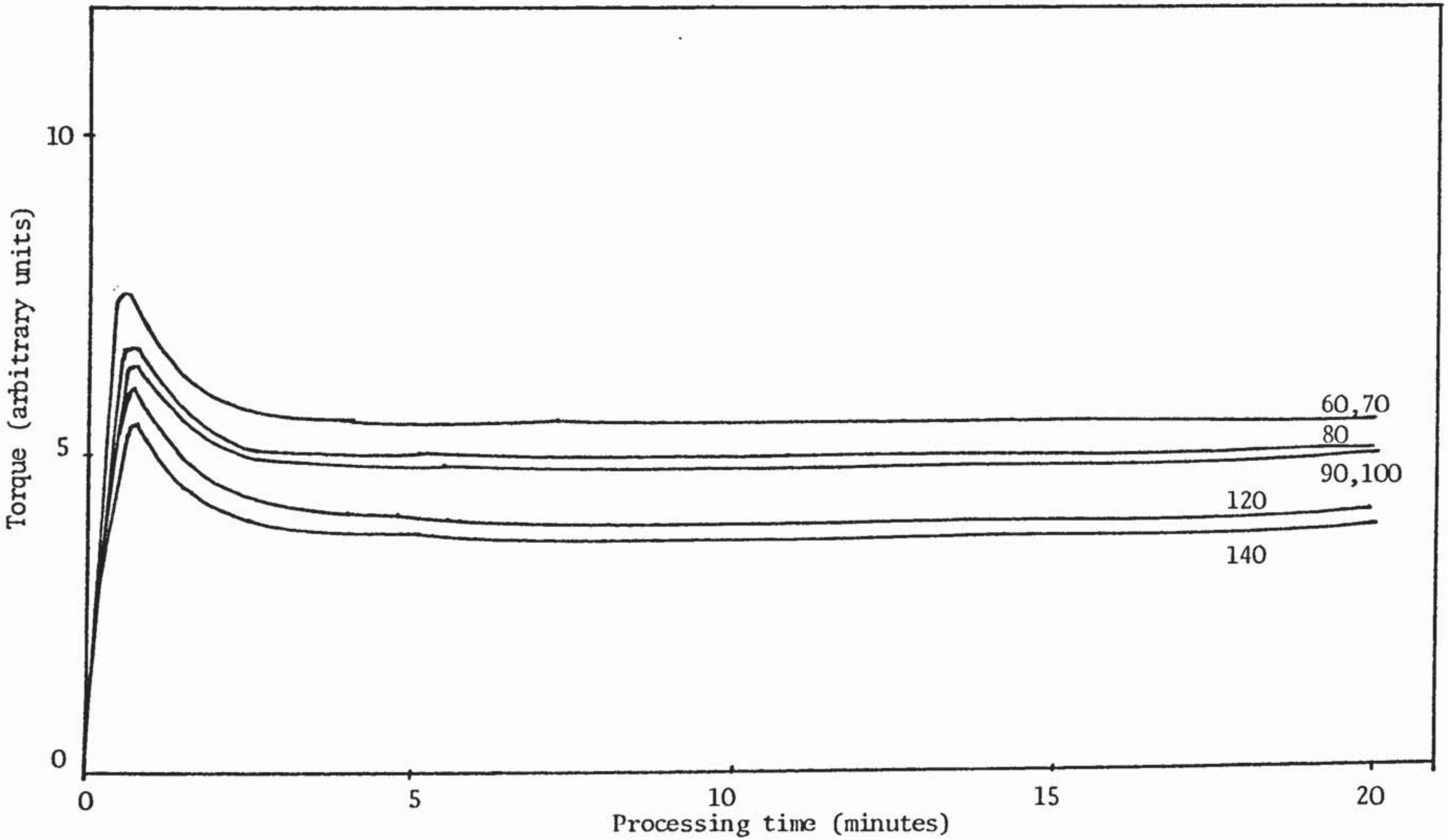


Fig 4.5 Dependence of torque of EPDM on the processing time at different temperatures, full and closed chamber (figures on the curves indicate the processing temperature, ^{o}C)

temperature the amount of torque decreases due to the higher viscosity.

The other processing factor which affects the extent of binding during the mechanochemical process is time. In order to explore the optimum processing time, a set of experiments was carried out with 2% (0.7 g) of EBHPT. All processings were carried out at optimum processing temperature (ie 100°C) and all conditions were kept constant. Processing time was varied, ranging from 3 to 20 minutes. The extent of binding of EBHPT in EPDM as a fucntion of processing time is shown in Fig 4.6.

4.1.5 Masterbatch Formation

The above results (section 4.1.4) showed that the optimum temperature and time for obtaining maximum binding with EBHPT was 100°C and 15 minutes respectively. Similar conditions were used for masterbatch formation (2, 5 and 10%) with EBHPT. The extent of binding of EBHPT in EPDM as a function of EBHPT concentration is shown in Fig 4.7. Masterbatches obtained were used as compatibiliser, stabiliser for blends of polyethylene/propylene and polypropylene/ethylene-propylene diene rubber (see Chapters 5 and 6).

4.1.5.1 Results

The extent of binding of EBHPT as a function of EBHPT concentration

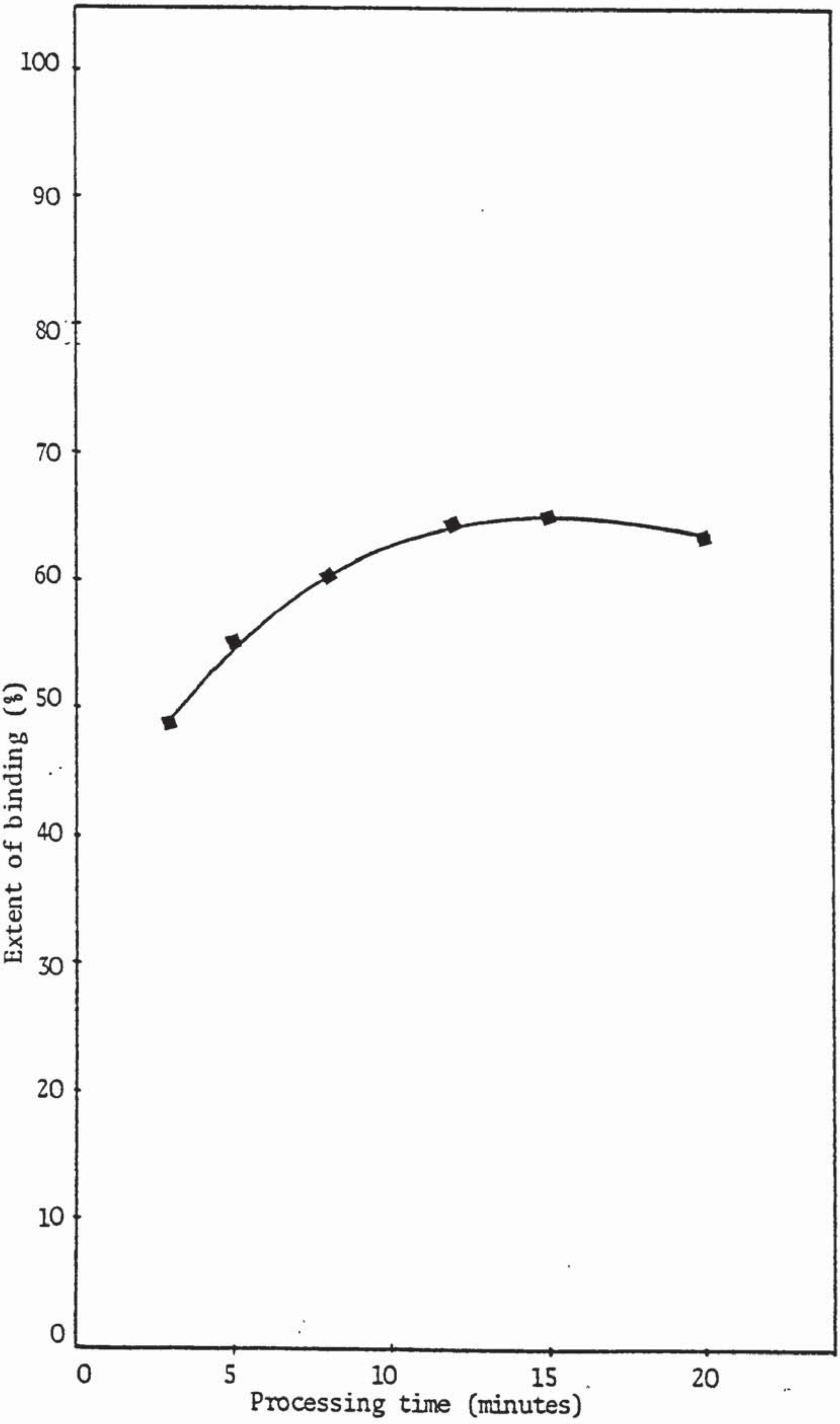


Fig 4.6 The extent of binding of EBHPT as a function of processing time (torque rheometer) in EPDM

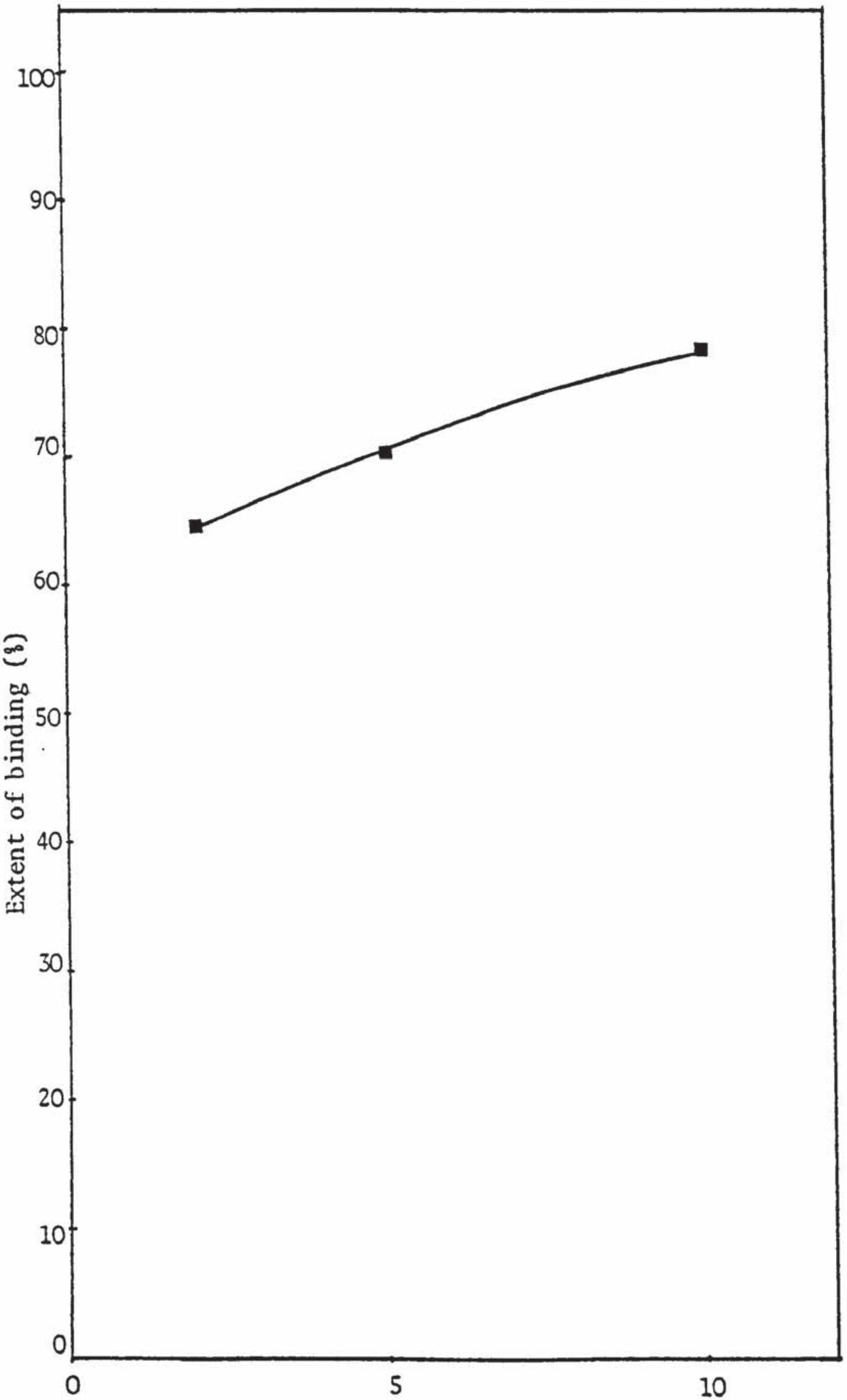


Fig 4.7 The extent of binding of EBHPT as a function of EBHPT concentration (g/100 g) in EPDM

is shown in Fig 4.7. It was not possible to measure the amount of EBHPT binding directly on the films containing 5% and 10% of EBHPT. Therefore, they were diluted into 2% extracted and the amount of bound measured as in section 4.1.2b, by the use of calibration curve, Fig 4.1. As can be seen from Fig 4.7, the amount of binding increases as the concentration of EBHPT is increased from 2 to 10%. With 2% of EBHPT about 65% binding was obtained whereas by increasing it to 5 and 10% the extent of binding was increased to about 70 and 77% respectively.

4.1.6 Mechanochemical Binding of MADA (II) onto Ethylene-propylene Diene Monomer (EPDM)

The procedure mentioned in section 4.1.2a was followed for the binding and the amount of MADA bound was analysed by ir using the calibration curve in Fig 4.2. The aromatic index was measured and the amount of the bound estimated as section 4.1.2b using the calibration curve (Fig 4.2).

4.1.6.1 Masterbatch Formation

The optimum temperature and optimum time of processing obtained for EBHPT was 100^{o}C and 15 minutes respectively. Similar conditions were used for masterbatch formation (2, 5 and 10%) with MADA.

4.1.6.2 Results

The extent of binding of MADA as a function of MADA concentration is shown in Fig 4.8. The amount of binding increased from 75% for 2% MADA up to 82 and 87% for 5 and 10% respectively. Also the changes in torque -vs- processing time of EPDM containing 2% EBHPT and MADA is shown in Fig 4.9. It clearly indicates that EPDM containing EBHPT has lower torque at initial and later stages which could possibly be due to the cold mill effect (ie 1.5 minutes) or better plasticising effect of EBHPT.

4.1.7 Mechanochemical Binding of DBCMS (III) onto Ethylene-propylene Diene Monomer (EPDM)

The binding was carried out according to the procedure in section 4.1.2a. The amount of DBCMS bound was estimated using calibration curve in Fig 4.3. The ratio of the absorbance at 3640 cm^{-1} due to phenolic -OH group of DBCMS to that of the reference peak at 800 cm^{-1} was taken as phenolic -OH index, and the amount of bound DBCMS was directly calculated using calibration curve (Fig 4.3).

The chemical structure of DBCMS differs from EBHPT and MADA. Because DBCMS was a monosulphide and did not contain any thiol group, therefore, the processing temperature and processing time of the binding was studied independently. In order to obtain an optimum processing temperature, a set of experiments was carried out with 2% (0.7 g) of DBCMS. The processing time was kept

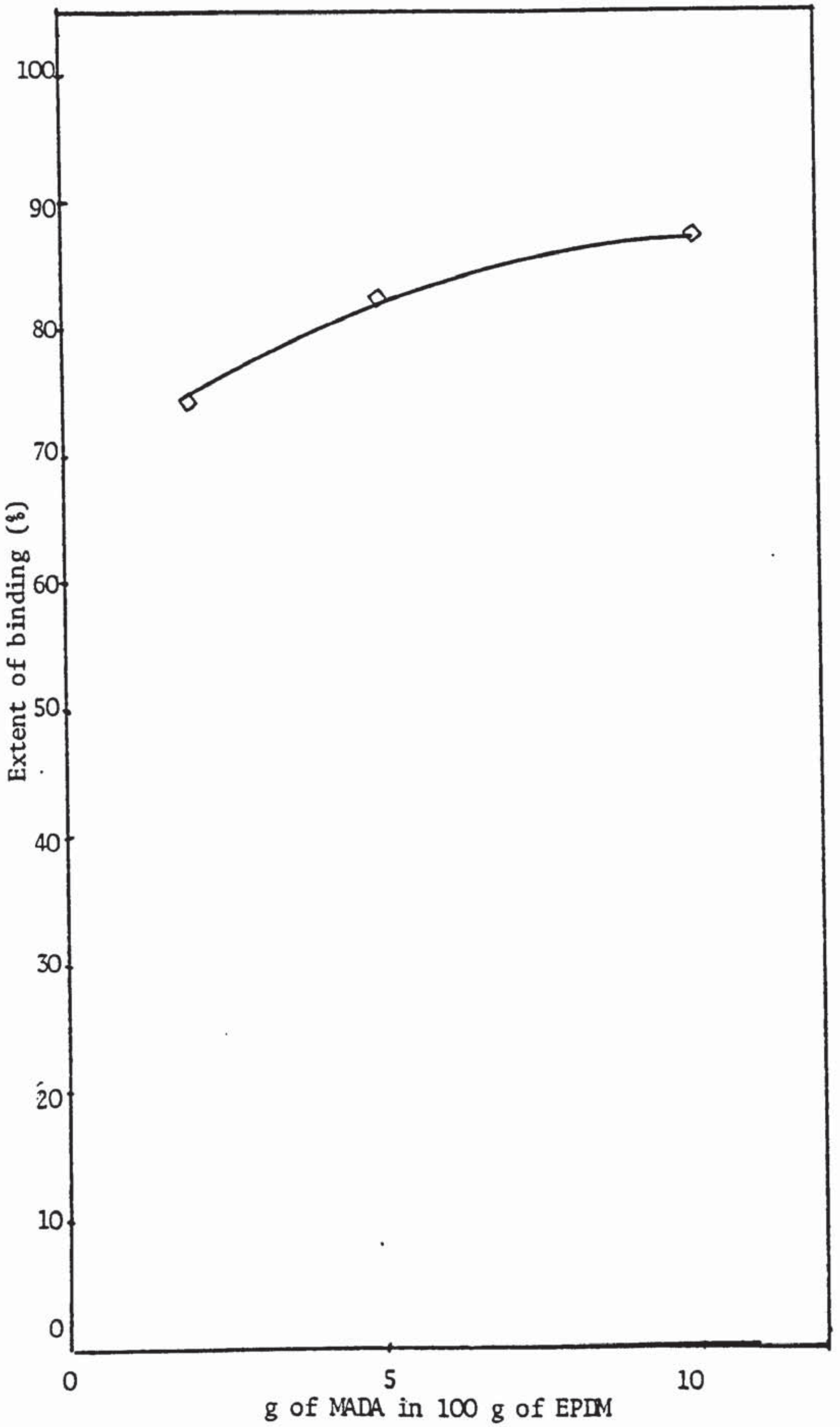


Fig 4.8 The extent of binding of MADA as a function of MADA concentration (g/100 g) in EPDM

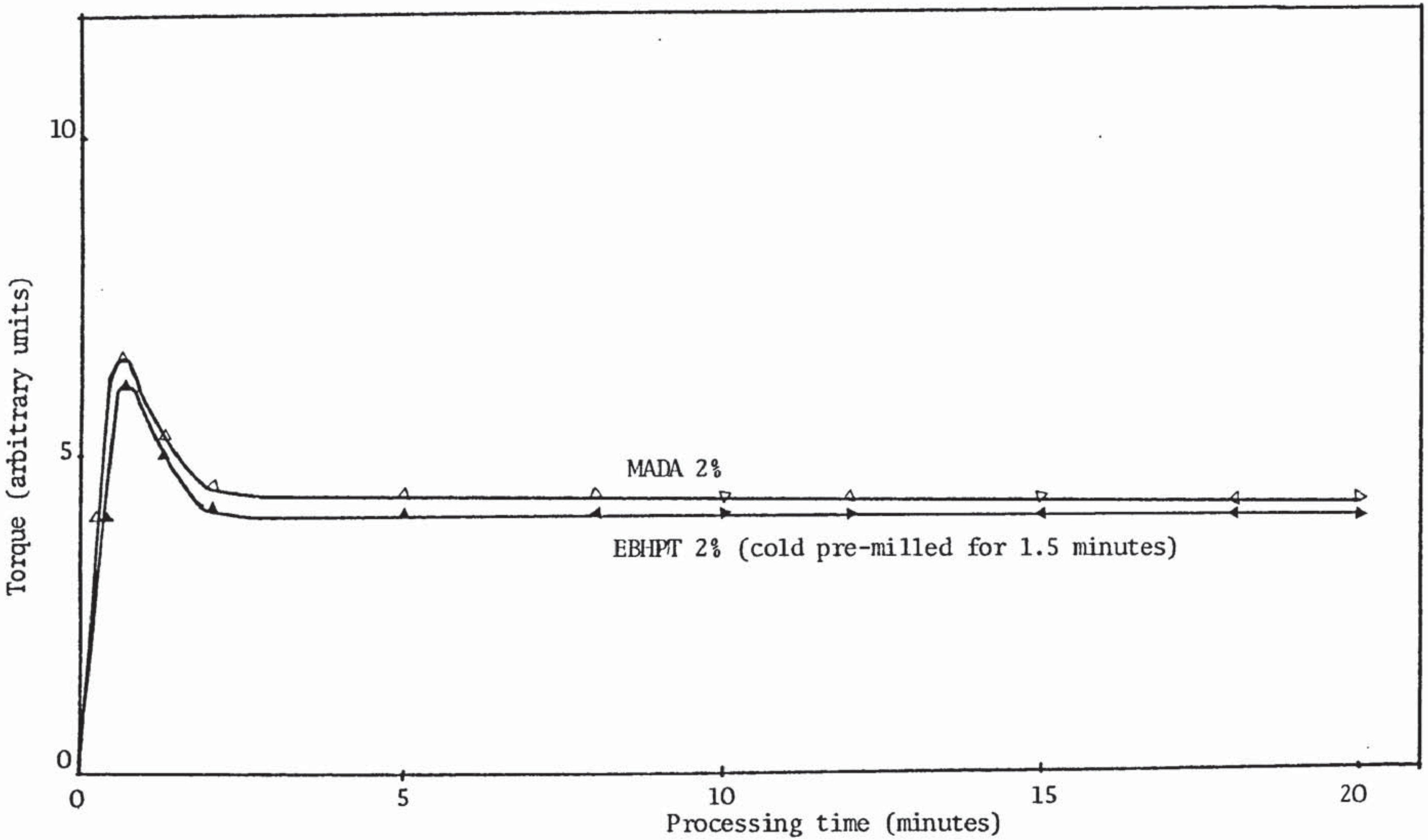


Fig 4.9 Dependence of torque of EPDM containing MADA and EBHPT on the processing time at 100°C, closed chamber

constant at 5 minutes and the processing temperature was varied ranging from 60 to 200°C. The extent of binding of DBCMS as a function of processing temperature is shown in Fig 4.10.

To find out the optimum processing time, a set of experiments in which the processing temperature was kept constant (ie 200°C) was carried out with 2% (0.7 g) of DBCMS. The extent of binding of DBCMS as a function of processing time is shown in Fig 4.11. Results of the maximum binding obtained during mechanochemical binding of EBHPT, MADA and DBCMS onto EPDM at optimum temperature and time are summarised in Table 4.1.

Table 4.1 Estimation percentage of binding of stabilisers at optimum temperature and time

Concentration of stabiliser (pph)	Estimated percentage of binding		
	EBHPT, I	MADA, II	DBCMS, III
2	65	75	35
5	70	82	-
10	77	87	-

The ir spectroscopy of pure EPDM, EPDM containing bound EBHPT, MADA and DBCMS extracted and unextracted are shown in Figs 4.12, 4.13, 4.14 and 4.15 respectively.

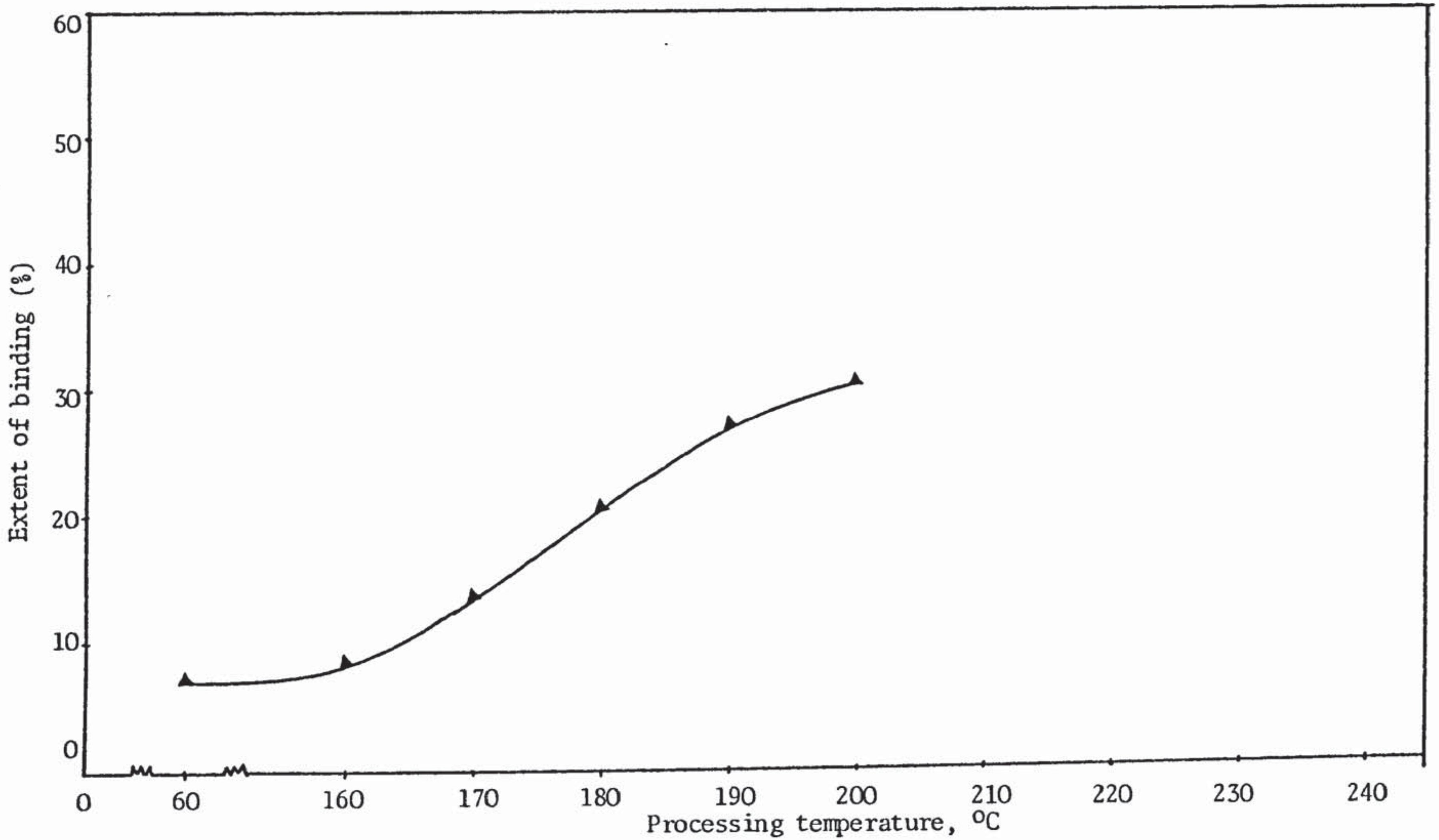


Fig 4.10 The extent of binding of DBCMS as a function of processing temperature (torque rheometer) in EPDM

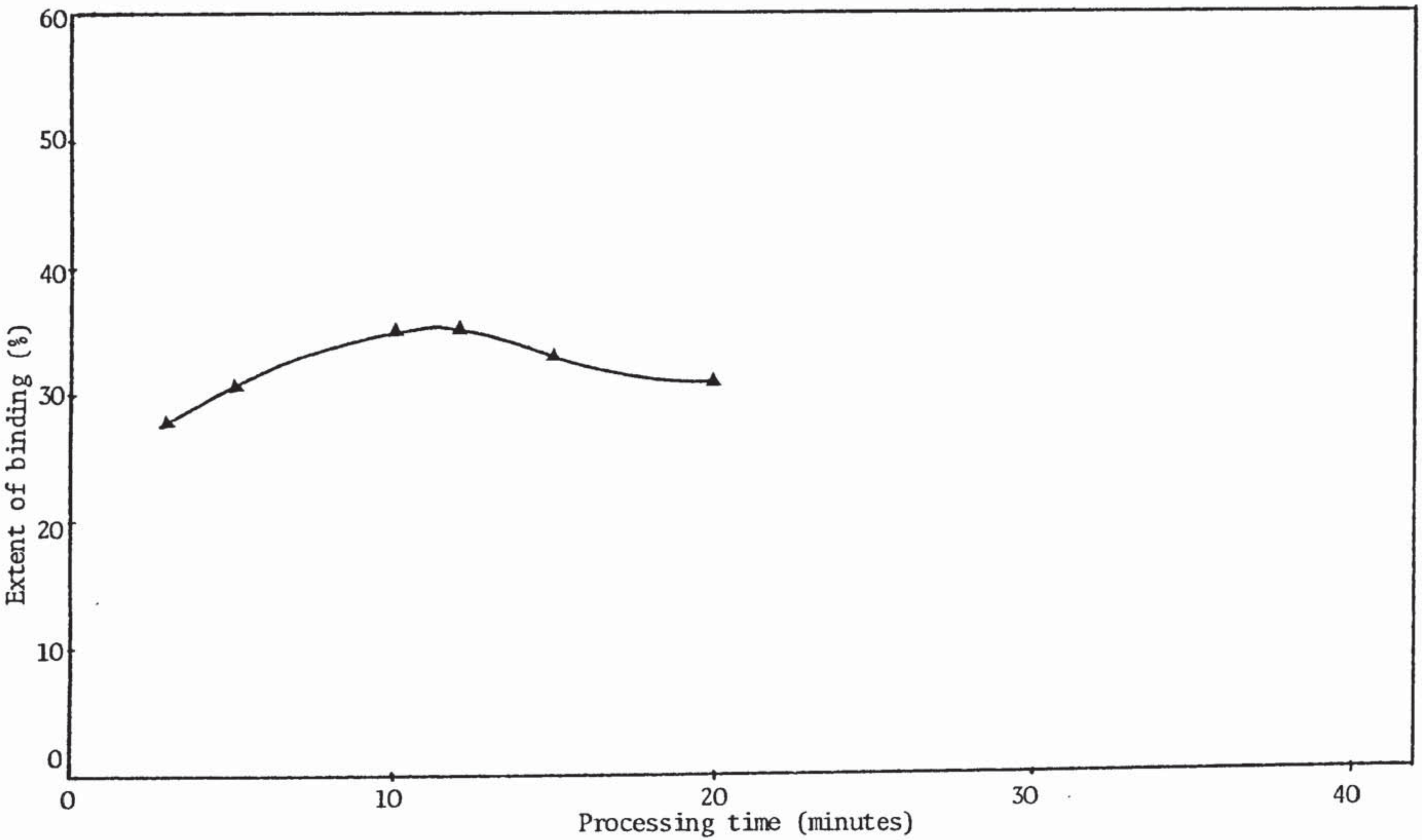


Fig 4.11 The extent of binding of DBCMS as a function of processing time in EPDM. Processing temperature was 200°C in all the times

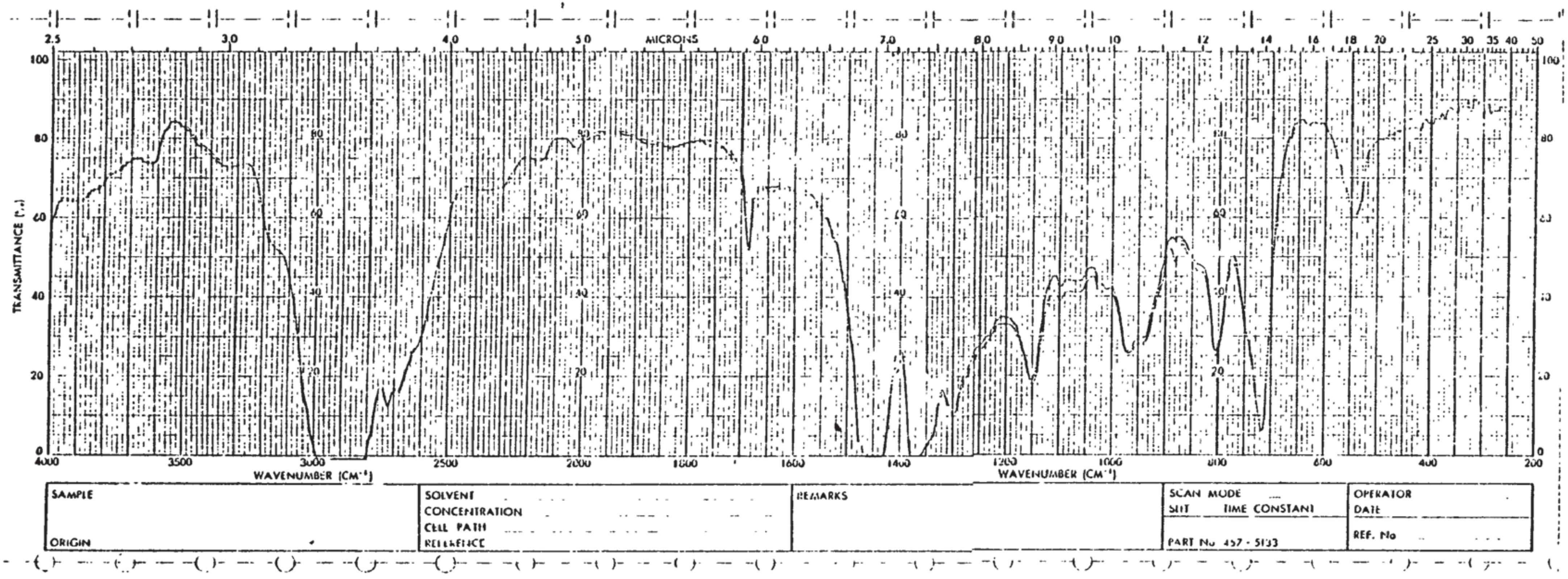


Fig 4.12 Infra-red spectroscopy of EPDM (100%) film

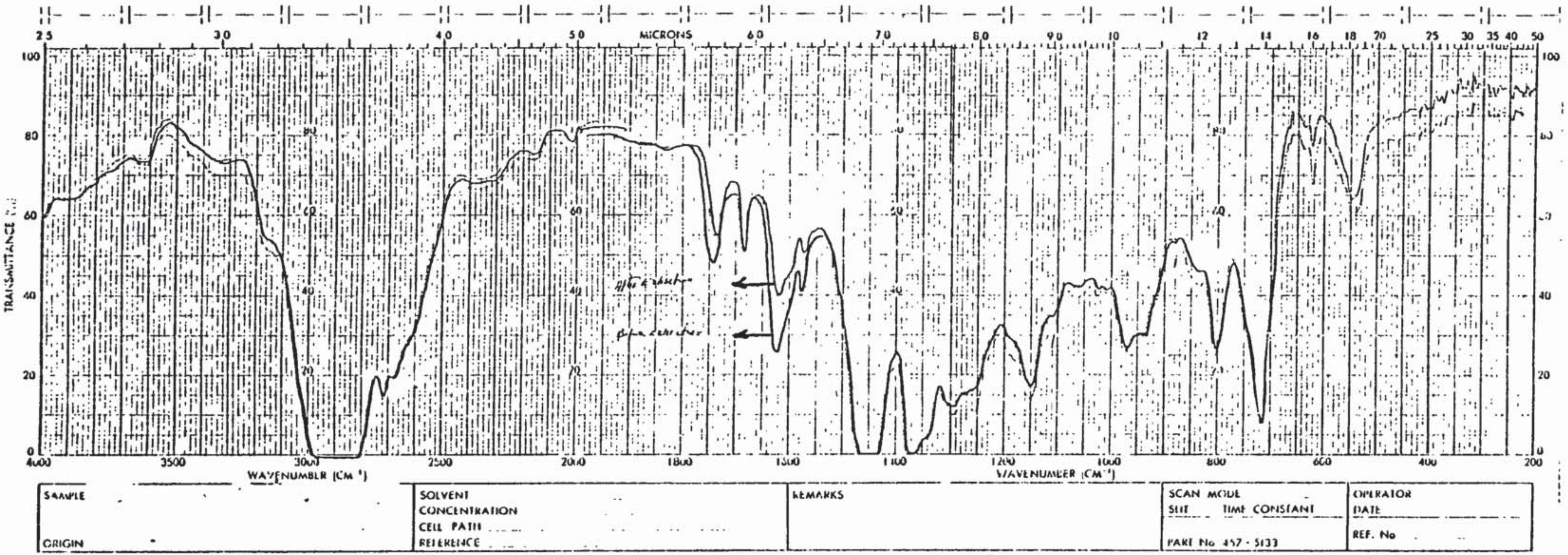


Fig 4.13 Infra-red spectroscopy of EPDM film containing EBHPT (2%) bound before and after extraction

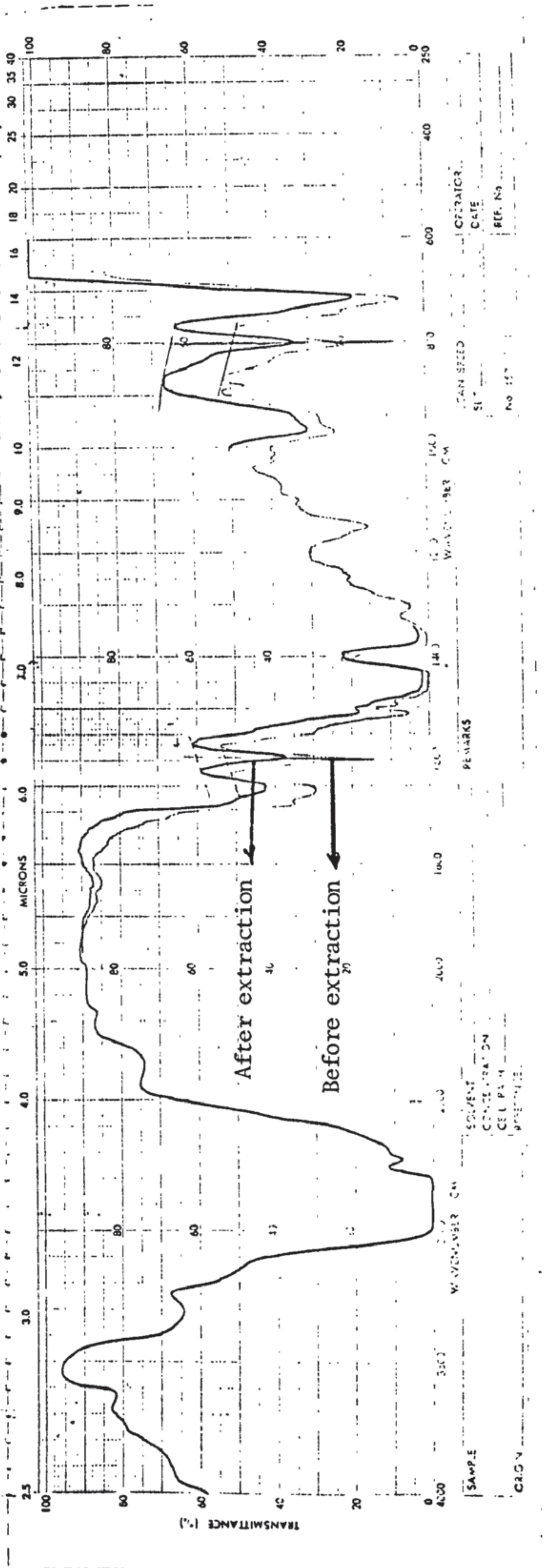


Fig 4.14 Infra-red spectroscopy of EPDM film containing MADA (2%) bound before and after extraction

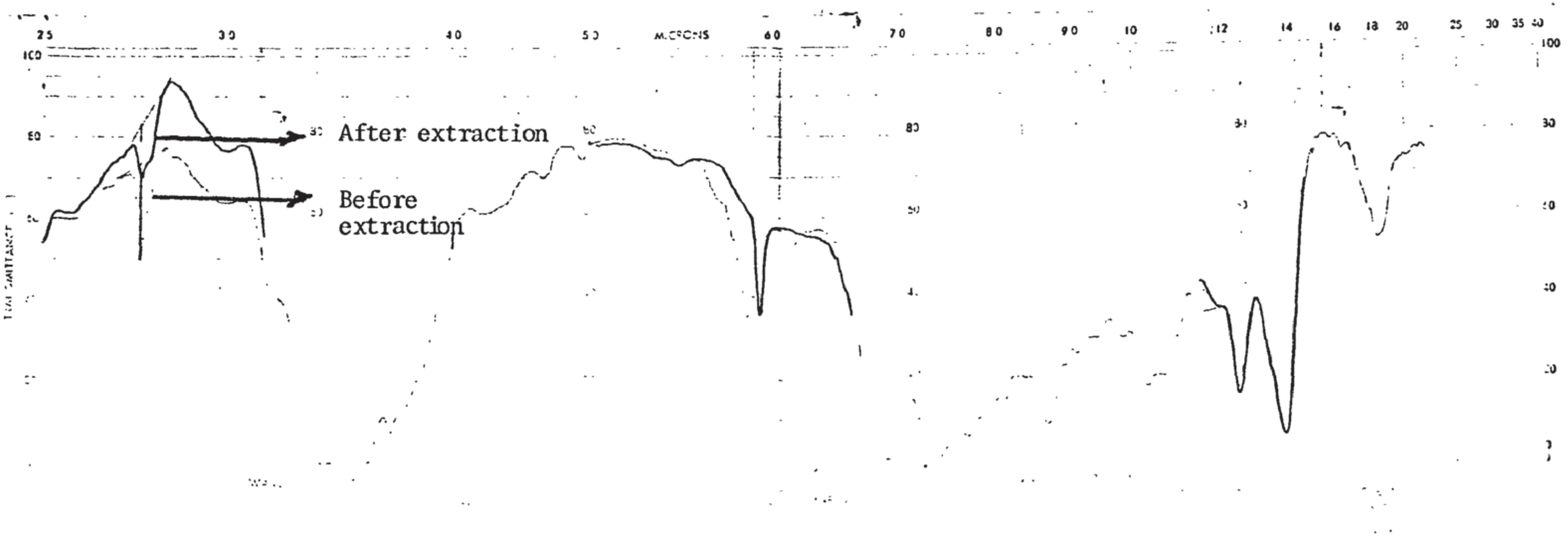


Fig 4.15 Infra-red spectroscopy of EPDM film containing DBCMS (2%) bound before and after extraction

4.1.8 Discussion

Staudinger and Bondy(131) suggested that cold mastication is not a conventional thermal reaction but that the required energy is supplied directly as mechanical energy, the molecules being ruptured by the shearing forces imposed during the deformation of the bulk rubber. This hypothesis was expressed more specifically by Kauzman and Eyring(117) as the direct breakage of C-C bonds of the polymer backbone into free radicals:

$$\text{R-R} \xrightarrow[\text{energy}]{\text{mechanical}} 2\text{R}\cdot \qquad (1)$$

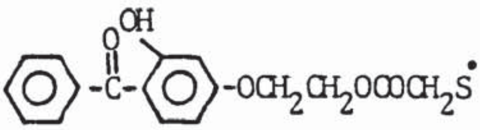
It was reported that polymerisation initiated by mechanical degradation occurs with a wide range of polymer-monomer systems and constitutes a general method of preparing block copolymers(120,132). Degradation of natural rubber during mastication has been shown to proceed(132) via two alternative mechanisms, oxidative scission at high temperatures and mechanical scission at low temperatures. The low temperature, cold mastication has received the greatest attention on a basis of chemical reaction. The mechanism of mastication involves the primary step of mechanical scission of a polymer chain into polymeric free radicals at carbon-to-carbon or other covalent bonds. The reaction of the polymer radicals can be summarised as follows:

Recombination: $2R\cdot \longrightarrow R{-}R$ (2)

Peroxy radical: $R\cdot + O_2 \longrightarrow RO_2\cdot$ (3)

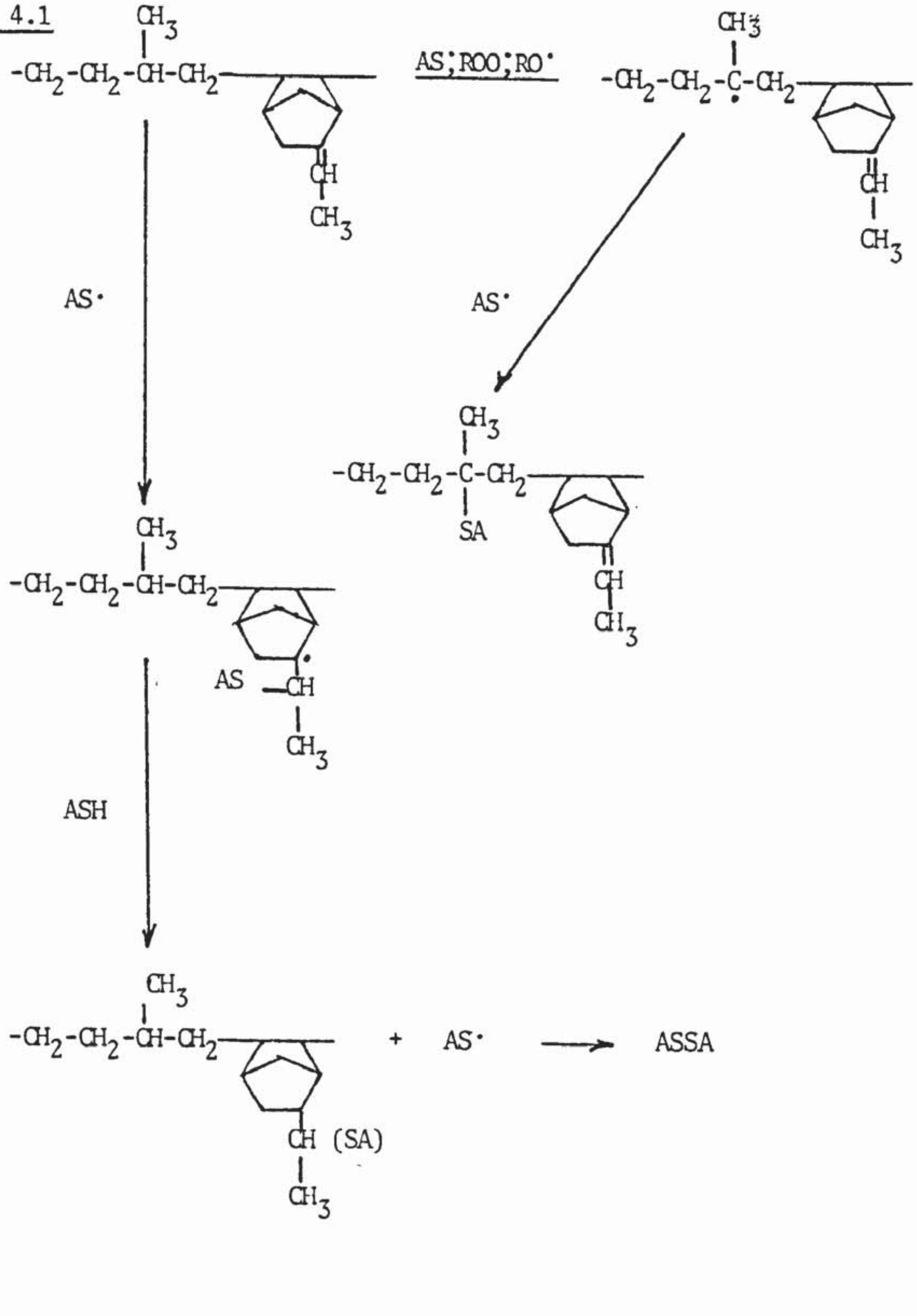
Reaction with formation
of a radical acceptor: $R\cdot + HS{-}Ph \longrightarrow RH + Ph\dot{S}$ (4)

In the absence of oxygen or other radical acceptors, the free radicals recombine (2). In the presence of oxygen the free radicals react to give alkenylperoxy radicals (3)$^{(122)}$. The $RO_2\cdot$ radicals so formed are deactivated by hydrogen abstraction from other rubber molecules to produce peroxides. The introduction of thermal oxidation products, however, such as alkoxy radicals ($RO\cdot$) and alkylperoxy radicals ($RO_2\cdot$) into the polymer might be expected to initiate the binding process as the hydroperoxide is known to behave as an effective initiator at high temperatures or in the presence of light. The alkylperoxy radical might be expected to abstract hydrogen from the rubber backbone or from the thiol group (ASH) to generate the $AS\cdot$ radical. The thiyl radicals ($AS\cdot$) may then add to the double bonds of rubber or alternatively they might react with the polymeric radical in the rubber backbone. $AS\cdot$ can have one of the following structures:



or

Scheme 4.1



There is also the possibility of the polymer backbone radicals to recombine and lead to the formation of cross-linking.

$$R^{\cdot} + R^{\cdot} \longrightarrow R\text{-}R$$

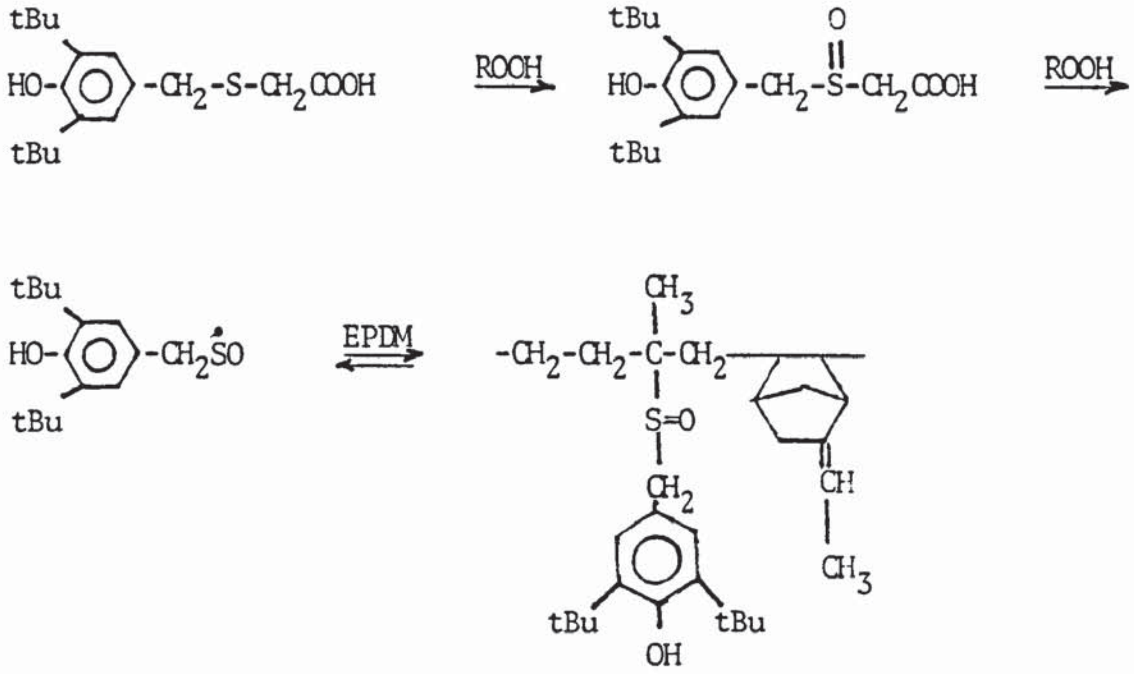
There are several important factors which could affect the binding reaction during mechanochemical masterbatch formation. These are: temperature, plasticity, rate of shear, initial molecular weight and the compatibility of the stabiliser. Polymers must be brought in to a deformable state during processing either by raising the temperature or by addition of plasticiser (Fig 4.5 clearly indicates the decrease in torque by increasing the processing temperature due to decrease in bulk viscosity).

The results clearly show that the temperature of the reaction plays a major role in determining the extent of binding. It can be seen from Fig 4.4 that the extent of binding increases by raising the temperature from 70 to 100°C and with a further rise in temperature it decreases about 10%. It appears that maximum yield of bound antioxidant can be obtained when processing operations are carried out at 100°C. This may suggest that apart from the effect of shear and air, some solubility is required to ensure better dispersion and compatibility of the antioxidant with the rubber.

Attempts to optimise the yield of bound antioxidant obtained by varying the processing time. The result given in Fig 4.6 shows that the maximum yield can be obtained after a period of 15 minutes processing. This behaviour is probably due to the fact that high torque (shear) at the start of the reaction (see Fig 4.9) produced a substantial concentration of alkyl radicals which quickly reacted with the thiol antioxidant and so initiated binding (see scheme 4.1).

In the initial stages, alkyl radicals seem to be the sole source of initiation but after about 3 - 5 minutes, the fall in viscosity as a result of molecular rupture is probably responsible for the slowing down in the rate of binding, because with the fall in viscosity, less alkyl radicals are being produced. The reversions observed in the processing may be explained in terms of oxidation of both bound and unbound antioxidant and the subsequent cleavage of (-S-C-) links. However, the decrease in the extent of binding at temperatures above 110°C could possibly be due to the lower torque and decreased shear (see Fig 4.5). Also the increase in the extent of binding with increasing the antioxidant concentration has been indicated to be due to the molar ratio of $[ROOH]/[S]$ which is fully discussed in section 4.2.8.

It can be seen from Fig 4.10 that DBCMS (compound III) was less reactive towards binding than EBHPT and MADA. This might be due to the structural differences of DBCMS (which was a monosulphide not a thiol). The mechanism of binding reaction in this case is not yet clearly known but it has been suggested(130) that the sulphenyl radical due to the further reaction of sulphenic during processing might attack double bond in the polymer or polymer radicals to give adduct with the following structure:



The increase in the extent of binding at higher temperatures (ie 170-200°C) as shown in Fig 4.10 might therefore be due to better oxidation (or thermolysis) of DBCMS which leads to higher binding (ie 30% at 200°C). However, it was not possible to continue the processing above 200°C due to technical problems. The decrease in the extent of binding (Fig 4.11) above 10 minutes (ie optimum processing time) might be due to the oxidation of the adduct through sulphur atom followed by thermolysis. These results confirm this suggestion since it was reported(133) that the oxidation products of sulphides function as more active inhibitors of autoxidation than sulphides themselves, and it was found that sulphoxides derived from monosulphides are the precursors of the active inhibitors. The activity of sulphoxides as inhibitor appears to be due to their instability leading to products which convert hydroperoxides to inactive products without formation of free radicals.

4.2 Mechanochemical Binding of Thiol Antioxidants to Polyolefins

4.2.1 General Background

Significant amounts of stabilisers can be lost from plastics due to oxidation, volatilisation and solvent extraction during fabrication and end-use. The problem is most severe for articles with a high surface area to volume ratio such as fibres and film. Plant and Scott(134) investigated the stabilisation of polypropylene fibres with antioxidants of molecular weight ranging from 200 to 700. The weight loss of stabiliser increased with an increase in temperature from 100 to 200°C and decreased with an increase in stabiliser molecular weight. These limitations have prompted extensive work on the production of high molecular weight uv stabilisers and their blending with polymers which was recently reviewed by Bailey and Vogl(135). These stabilisers are usually made by either copolymerisation with the monomer of the polymer to be stabilised or by synthesising a polymeric uv stabiliser. For semi-crystalline polymers like polyethylene, copolymerisation will reduce the crystallinity and hence the mechanical strength(136). In addition, recent work by Hodgeman(137) has shown that rigorous control over monomer purity is required otherwise chromophores which promote degradation will be introduced by this method. If the polymeric uv stabiliser approach is applied, problems will probably arise in blending the two polymers successfully.

An alternative approach to using a polymeric additive is to graft copolymerise a polymerisable uv absorber to the polyolefin substrate. This method should overcome the compatibility and volatility problems without substantially affecting the crystallinity of the substrate.

Burchill et al(138) have grafted 2-hydroxy-4-(3-methacryloxy-2-hydroxypropoxy)benzophenone (HMB) to low density polyethylene using a mutual gamma radiation technique in the presence of cupric chloride to inhibit homopolymerisation. Adams and Braun(139) have successfully grafted 2,6-di-tert-butyl-4-vinyl phenol to polystyrene.

Evans and Scott(140) have shown that the antioxidant 3,5-di-tert-butyl-4-hydroxybenzyl acrylate (DBBA) may be grafted to the surface of polymer artifacts. The antioxidant activity of the resulting 'efficiently dispersed' antioxidant is very much higher than that of low molecular weight antioxidants containing the same functional group. Even after extraction with an effective solvent for the antioxidant-monomer and derived polymer, the oxidative stability of the polymer films is very much greater than that of polymer containing the antioxidant-monomer or antioxidant-polymer incorporated by a conventional melt technique without extraction. It is also found(141) that 3,5-di-tert-butyl-4-hydroxybenzyl mercaptan (BHBM) became chemically combined to polypropylene to the extent of 68% of the antioxidant present when films containing BHBM were exposed to uv irradiation.

The chemical binding of thiol antioxidants into saturated polymers is of considerable practical importance due to their substantivity in aggressive environments. Therefore, an attempt was made to formation of adduct of polyethylene and polypropylene with stabilisers containing thiol groups during mechanochemical processing.

4.2.2 Attempted Polyethylene and Polypropylene Adduct Formation with Stabilisers Containing Thiol Groups during Mechanochemical Process

The uv stabilisers such as 4-benzoyl-3-hydroxyphenol-o-ethyl thioglycollate (I, EBHPT) and 4-(mercaptoacetamido)diphenylamine (II, MADA) were used for adduct formation with polyethylene and polypropylene during processing in the torque rheometer. Compound II (MADA) was also used as a melt and thermal stabiliser (see section 4.1.2 for chemical structures of compounds I and II).

4.2.2a General Procedure

The mechanochemical process was carried out using the prototype RAPRA torque rheometer (see section 2.2.1). A full charge of 35 g of compounded polymer (polymer + additive) was processed for various times, keeping temperatures constant (ie 150 and 180°C for polyethylene and polypropylene respectively) with the chamber closed to the atmosphere. On completion of mixing, the polymer was rapidly removed and quenched in cold water to prevent further oxidation. The material was compression moulded for 3 minutes (1.5 minutes without pressure and 1.5 minutes with pressure) at 150 and 180°C for polyethylene and polypropylene respectively. The films of thickness 0.015 - 0.018 cm obtained were hot extracted using acetone as solvent (extraction temperature at soxhlet was 50°C). It was found that 30 hours of hot soxhlet extraction was the minimum extraction time to remove the non-bound antioxidants. The extracted polymer films were placed in a vacuum oven at 30°C for at least 5 hours to recover the solvent and dry. Then the amount of bound antioxidant was analysed by ir spectroscopy.

4.2.2b Estimation of Bound Stabilisers

Ir spectroscopy was used to determine the amount of MADA (compound II) bound to polyethylene and polypropylene. Absorbance at 1600 cm^{-1} due to the presence of aromatic group in compound II (MADA) was measured in films with thickness of 6 to 8 x 10^{-3} inches (0.006 - 0.008 cm). The amount of bound MADA was measured using the calibration curve in section 4.2.3.

Uv spectroscopy was used to measure the amount of EBHPT bound to polyethylene and polypropylene. The direct method of uv spectroscopy technique by using polymer films containing EBHPT was not possible due to less compatibility, therefore, an indirect method of measuring the amount of EBHPT in the acetone extract was used (see below). The amount of EBHPT bound was determined using calibration curve in section 4.2.4.

4.2.3 Quantitative Determination of 4-(Mercaptoacetamido) Diphenylamine (MADA)

The calibration curve was made by using the prototype RAPRA torque rheometer (see section 2.2.1). A set of experiments were carried out according to the procedure 4.2.2a. Samples of PE and PP containing different percentage of MADA were processed for 10 minutes at 150 and 180°C for polyethylene and polypropylene respectively. The material was compression moulded for 3 minutes (1.5 minutes without pressure and 1.5 minutes with pressure) at temperatures mentioned above for each polymer. The films with the thickness of 6 - 8 x 10^{-3} inches (0.006 - 0.008") obtained were analysed by ir spectroscopy technique. The intensity of the absorbance at 1600 cm^{-1} due to the presence of aromatic group in MADA was proportional to the amount of added antioxidant. In order to overcome the errors dur to sample thickness and instrument a reference peak at 1895 cm^{-1} and 900 cm^{-1} were used for polyethylene and polypropylene respectively. The ratio of the absorbance at 1600 cm^{-1} to that of reference peak was taken as aromatic index and plotted as a function of MADA added per hundred grams of polymer (ie polyethylene or polypropylene).

The calibration curve obtained was used for the estimation of the bound MADA. Figs 4.16 and 4.17 represent the calibration curve for polyethylene and polypropylene respectively.

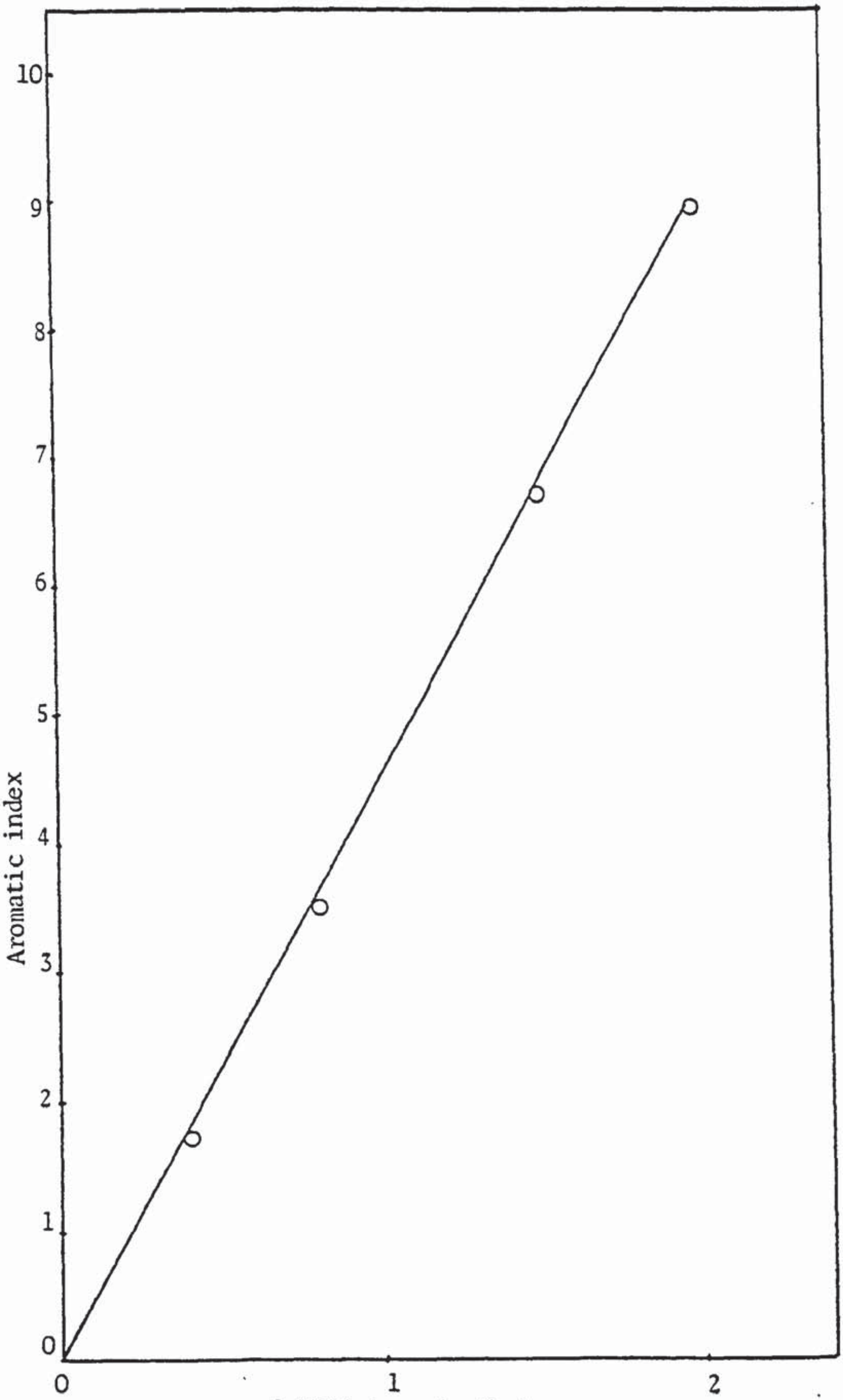


Fig 4.16 Calibration curve for MADA made by measuring of aromatic group of MADA in polyethylene, processed in torque rheometer for 10 minutes at 150°C, closed chamber

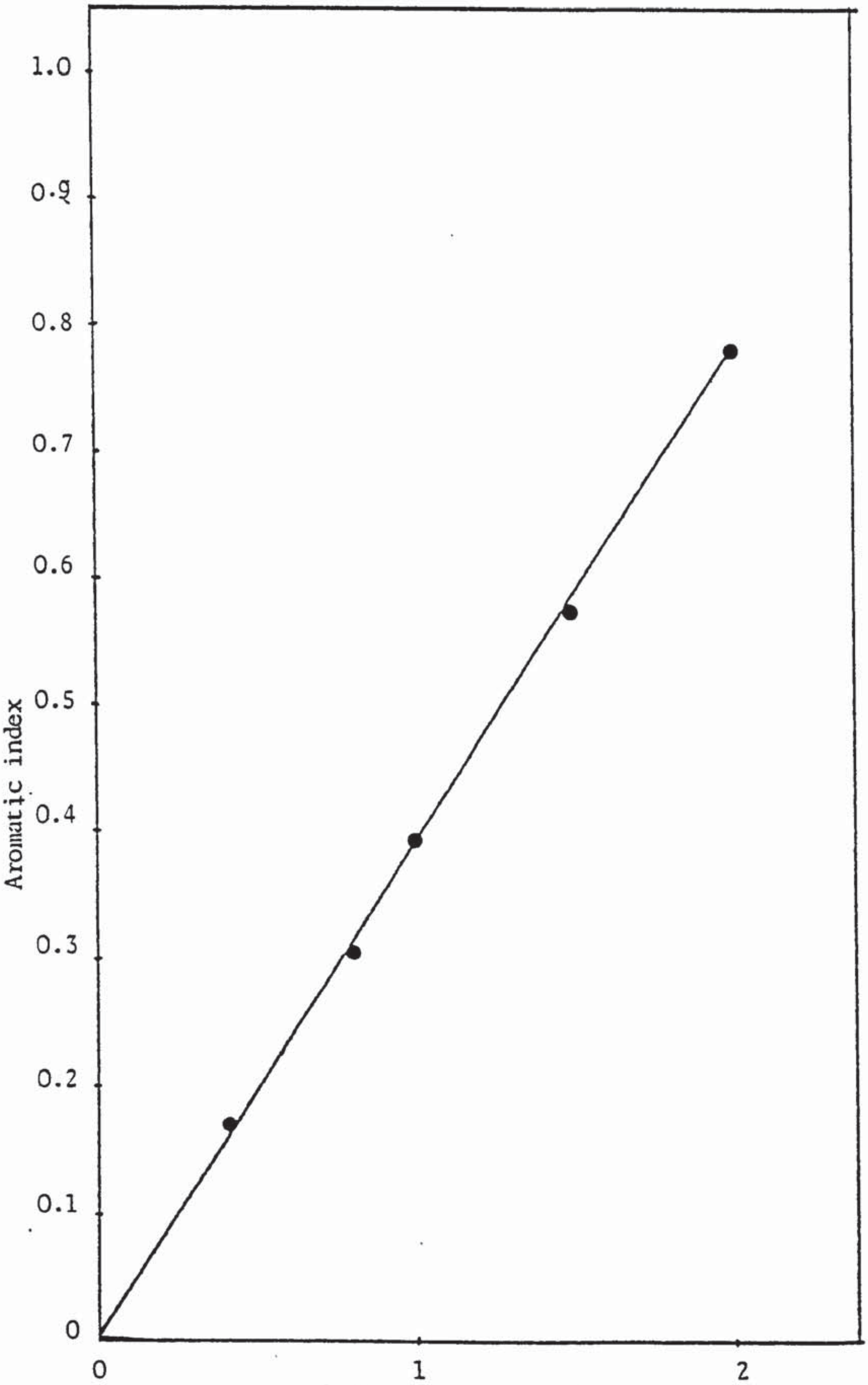


Fig 4.17 Calibration curve for MADA made by measuring of aromatic group of MADA in polypropylene, processed in torque rheometer for 10 minutes at 180°C, closed chamber

$$\text{Aromatic index in polyethylene} = \frac{\text{Absorbance at } 1600 \text{ cm}^{-1}}{\text{Absorbance at } 1895 \text{ cm}^{-1}}$$

$$\text{Aromatic index in polypropylene} = \frac{\text{Absorbance at } 1600 \text{ cm}^{-1}}{\text{Absorbance at } 900 \text{ cm}^{-1}}$$

4.2.4 Quantitative Determination of 4-Benzoyl-3-hydroxyphenyl-o-ethyl Thioglycollate (EBHPT)

It has been shown(110) that 2-hydroxybenzophenone derivatives in chloroform solution show an absorption maximum in the uv region of 300 - 350 millimicrons. This absorption was used in the estimation of these derivatives. Acetone extractions of polyethylene and polypropylene were evaporated and the residue was dissolved in chloroform. The solution was filtered and the filtrate was used to obtain a uv spectrum using chloroform as a blank. The concentration of the stabiliser was read off using a calibration curve made as follows. The calibration curve was made by preparation of different concentrations of EBHPT in chloroform. These solutions were used to obtain uv spectra. A calibration curve was plotted of the absorption maximum at 330 millimicrons against the corresponding weight of EBHPT. Calibration curve is shown in Fig 4.18.

4.2.5 Mechanochemical Binding of MADA onto Polyethylene

The mechanochemical process was carried out according to the

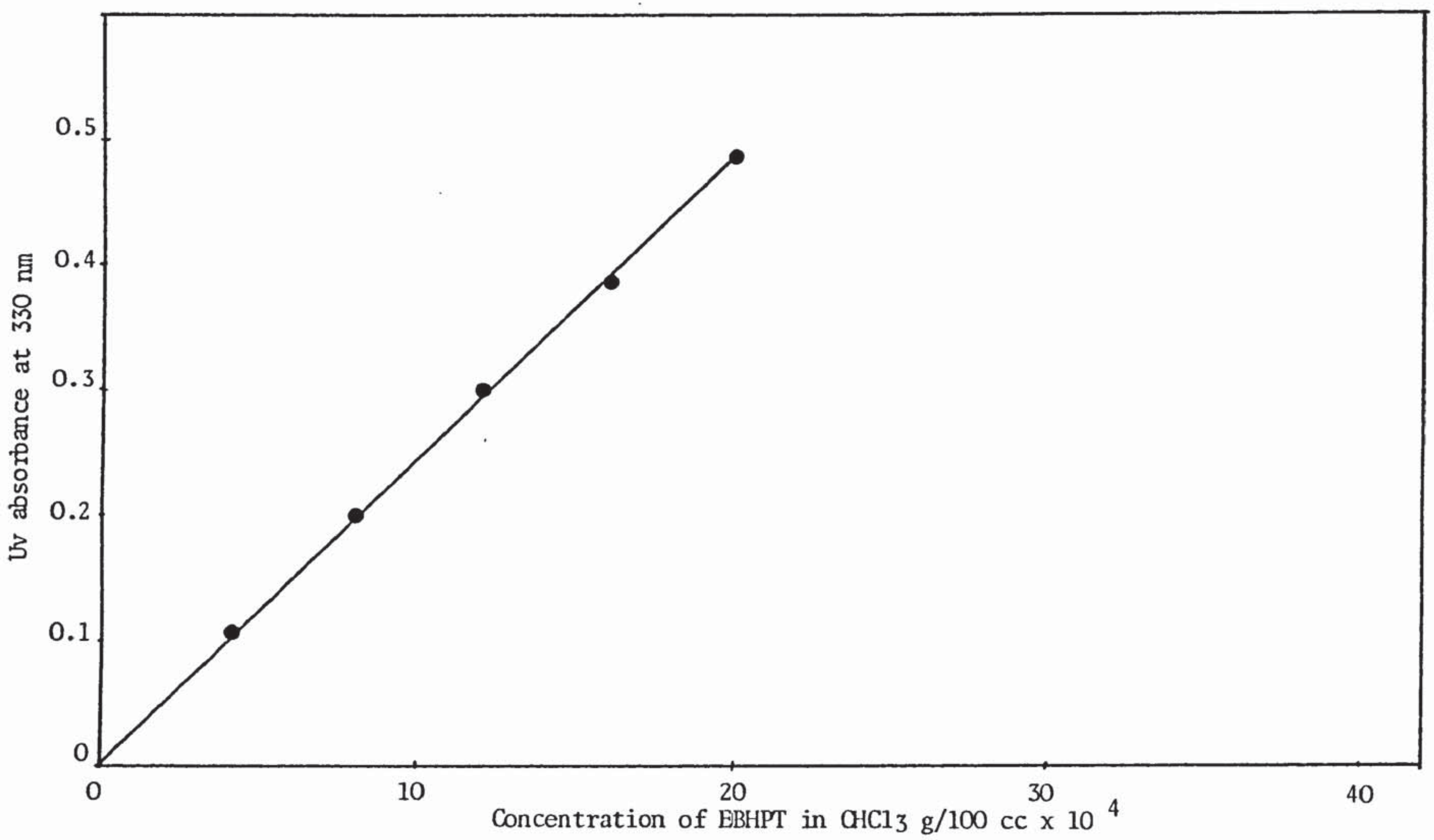


Fig 4.18 Calibration curve for EBHPT made by uv spectroscopy, measuring absorbance at 330 nm

procedure given in 4.2.2a. Polymer films after extraction were analysed by ir spectroscopy and the MADA bound was found using calibration curve in Fig 4.16, mentioned in section 4.2.3.

In order to obtain maximum MADA bound, optimum grafting time was obtained by keeping the processing temperature and MADA concentration constant (ie 150°C and 2% respectively for temperature and MADA concentration). The concentration of MADA was also varied in a set of experiments to find the effect of MADA concentration on the extent of binding. This was done by keeping the processing temperature and processing time (ie 150°C and 15 minutes respectively) constant. It was found that the extent of binding increased from 55% to 85% by increasing the MADA concentration from 0.4 to 2% respectively. Results are shown in Figs 4.19 and 4.20. The variation in torque of polyethylene samples containing 2% MADA with the processing time is shown in Fig 4.21, which indicates changes in the viscosity of polymer during processing.

4.2.6 Mechanochemical Binding of MADA to Polypropylene

The mechanochemical binding was carried out according to the procedure outlined in 4.2.2a, and the amount of MADA bound was calculated directly on the film using calibration curve in Fig 4.17, discussed in section 4.2.3.

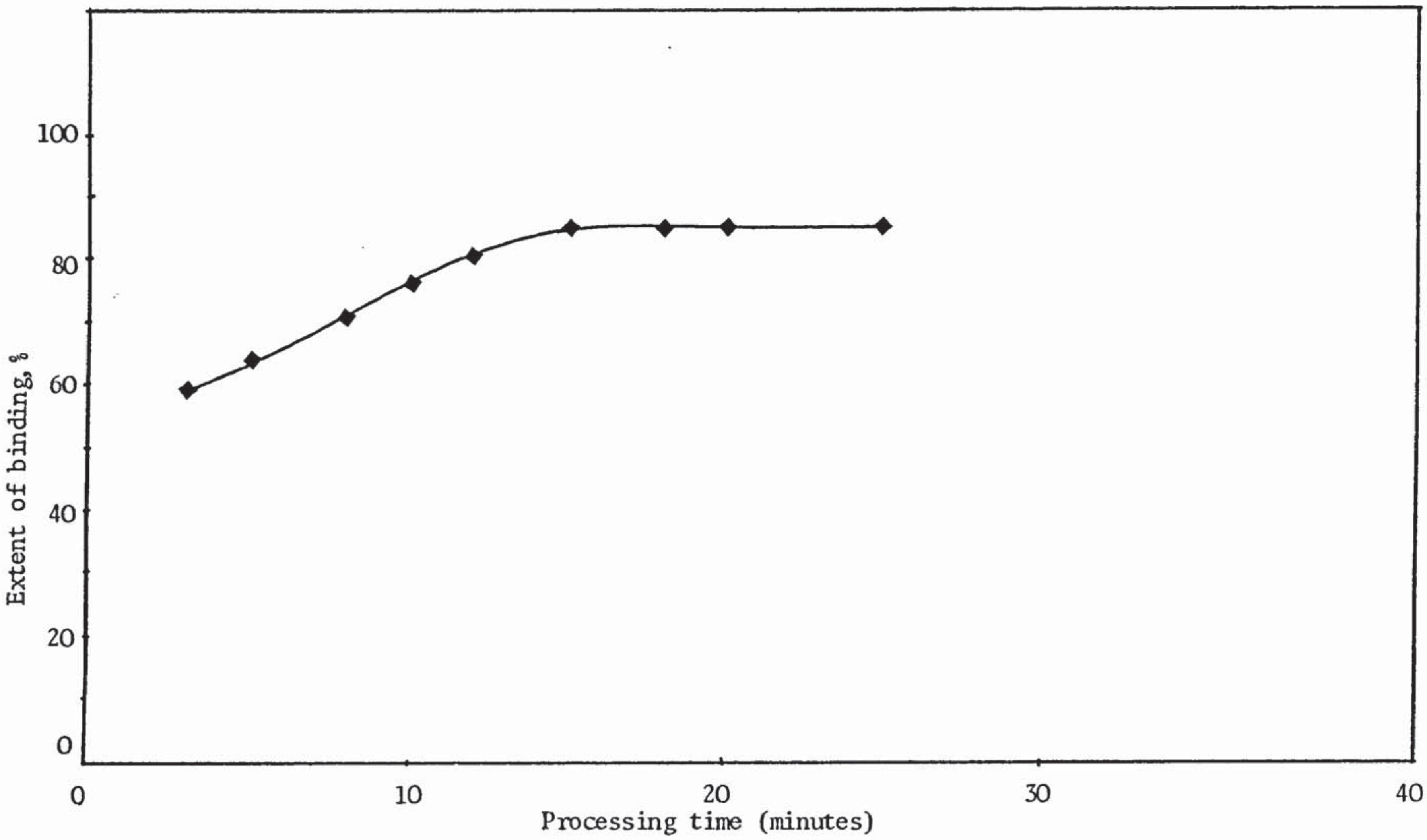


Fig 4.19 Effect of processing time on the extent of binding of MADA on polyethylene. All samples were processed at 150°C, closed chamber (ext 100 hours)

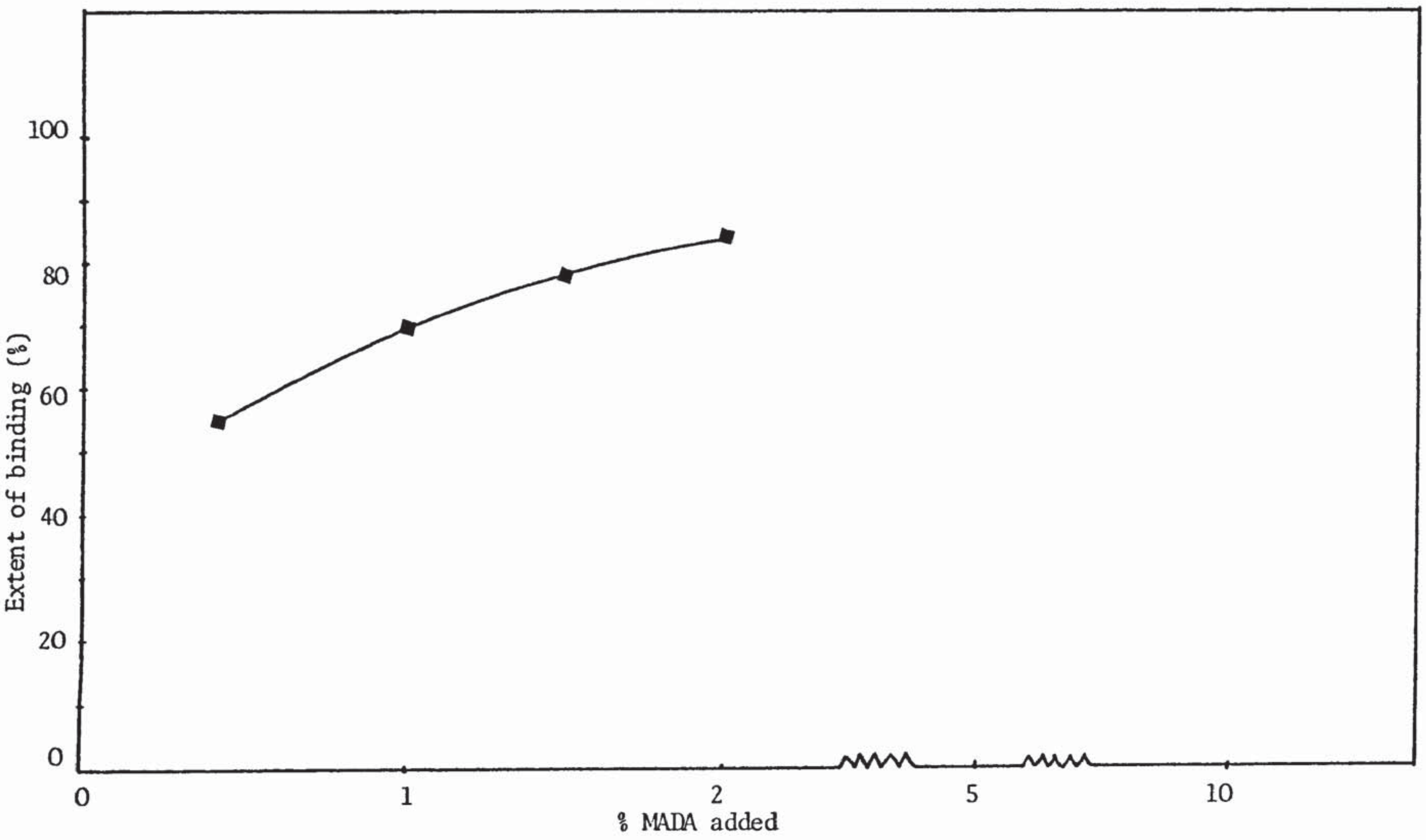


Fig 4.20 Effect of MADA concentration on the extent of binding on polyethylene. All samples processed at 150^{o}C, closed chamber for 15 minutes (ext 100 hours)

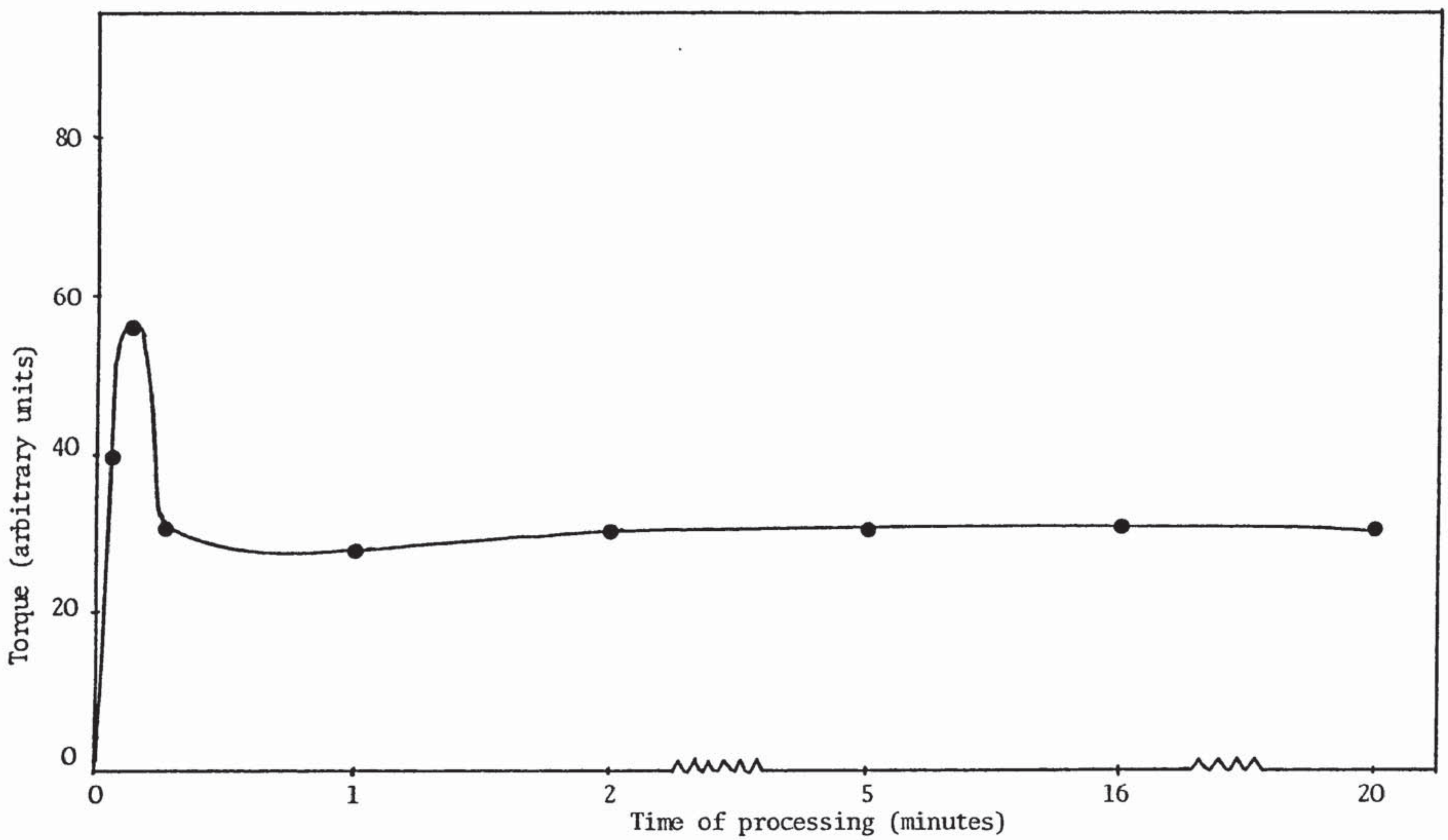


Fig 4.21 Dependence of torque of polyethylene melt on the processing time at 150°C, closed mixer chamber (concentration of MADA = 2%)

Results

Optimum processing time was obtained by a set of experiments with keeping the processing temperature constant at 180°C and the concentration of MADA at 2%. The results are shown in Fig 4.22. It was found that maximum MADA was bound to polypropylene at 15 minutes processing time.

The effect of increasing the concentration of MADA on the extent of binding was also carried out with processing time of 15 minutes in all samples. It was found that by increasing the MADA concentration from 0.4 to 2%, the extent of binding increased from 66 to 75%. Results are shown in Fig 4.23. Infra-red spectroscopies of polyethylene and polypropylene containing MADA bound are shown in Figs 4.24 and 4.25 respectively.

4.2.7 Mechanochemical Binding of EBHPT onto Polyethylene and Polypropylene

The mechanochemical grafting was carried out using procedure 4.2.2a, and the amount of EBHPT bound into polyethylene and polypropylene was obtained using calibration curve in Fig 4.18 (section 4.2.4).

Results

The mechanochemical process of obtaining EBHPT bound polyethylene

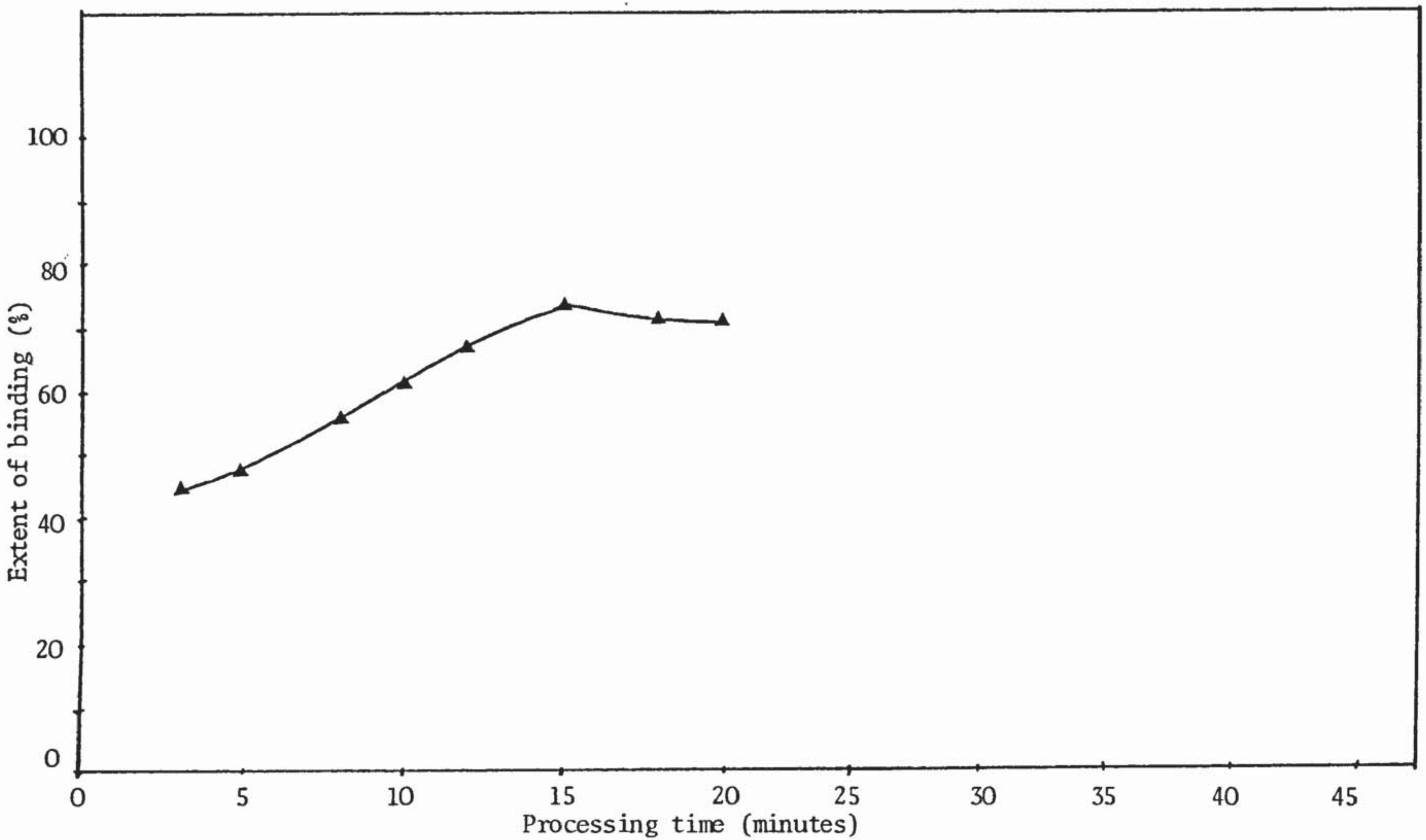


Fig 4.22 Effect of processing time on the extent of binding of MADA on polypropylene. All samples processed at 180°C, closed chamber and extracted for 100 hours

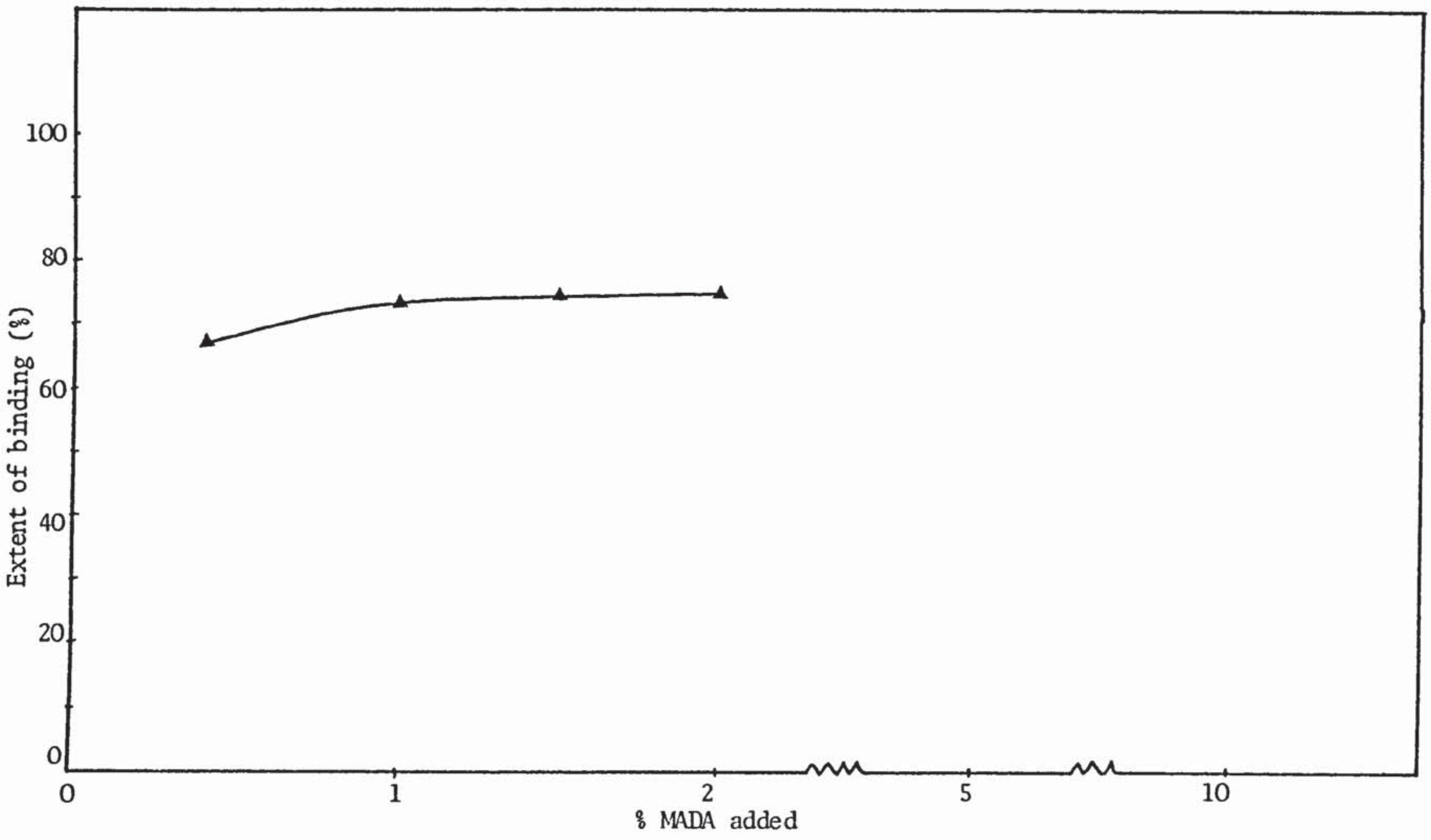


Fig 4.23 Effect of MADA concentration on the extent of binding on polypropylene. All samples were processed for 15 minutes at 180°C in a closed chamber

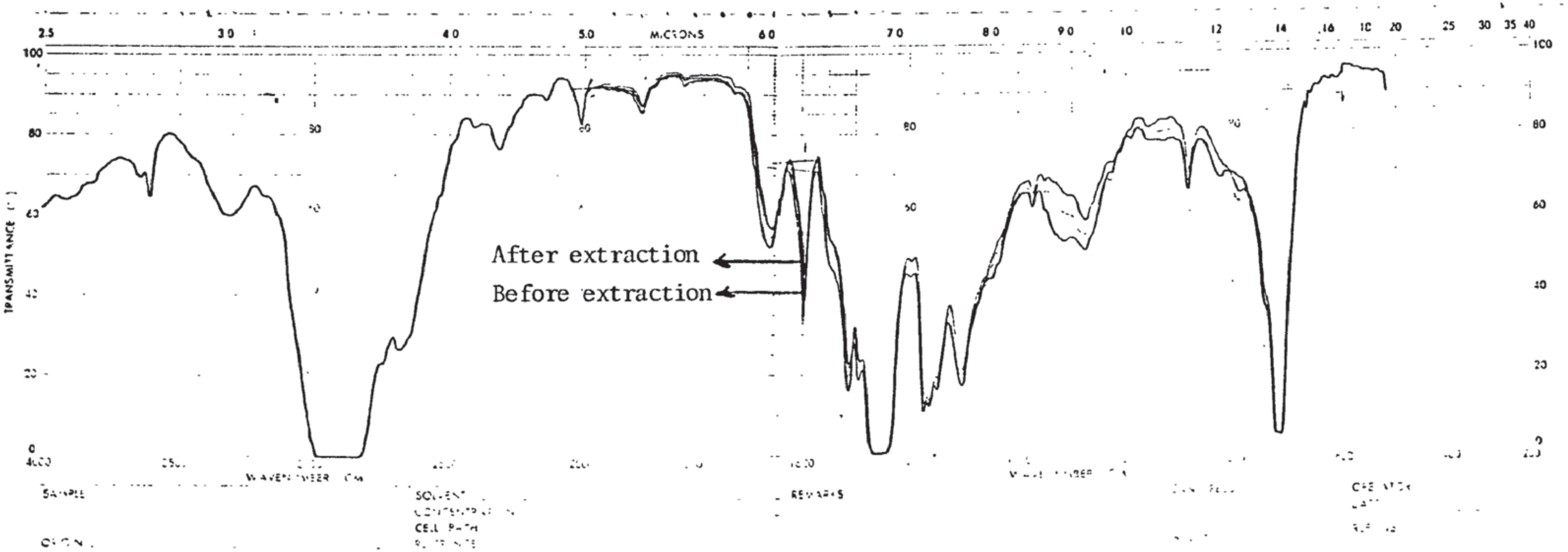


Fig 4.24 Infra-red spectroscopy of polyethylene film containing MADA (2%) bound before and after extraction

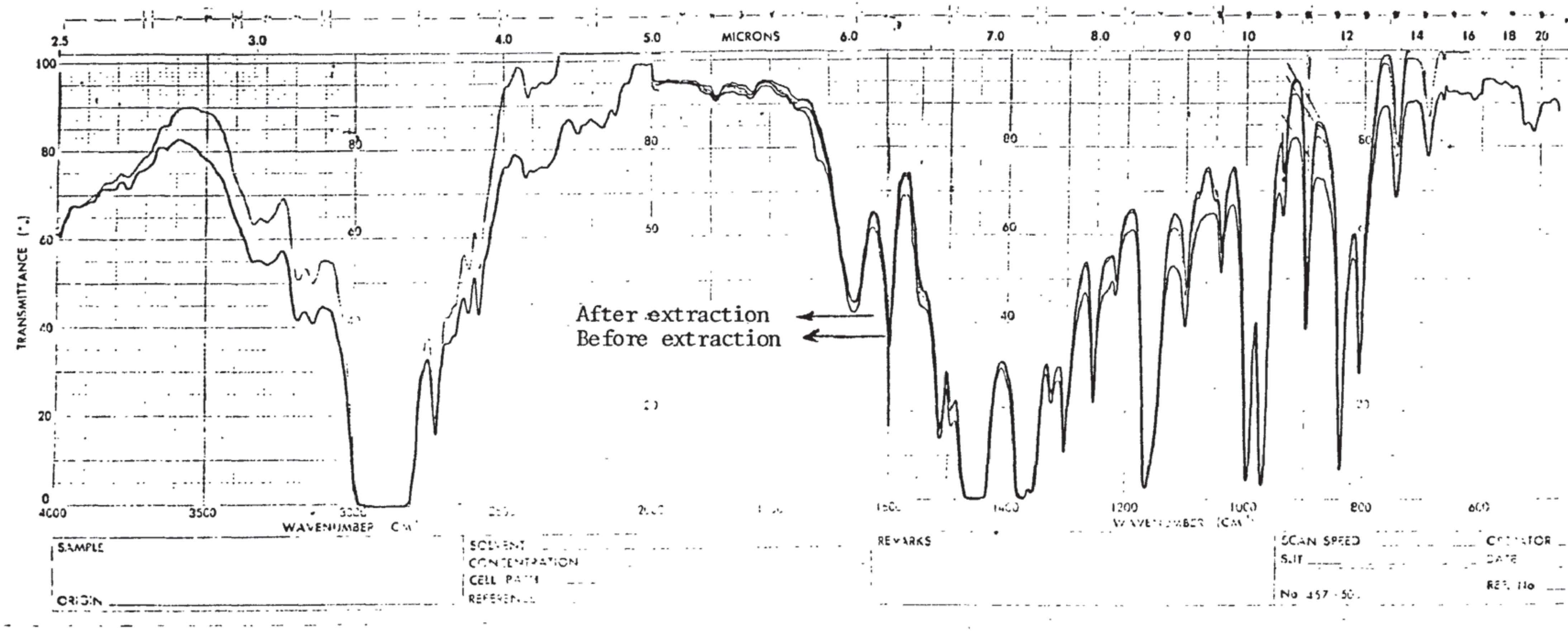


Fig 4.25 Infra-red spectroscopy of polypropylene film containing MADA (2%) bound before and after extraction

and polypropylene was not successful. It was found that only 20% of 2% EBHPT remained after extraction with acetone. The extent of binding may possibly be increased by addition of hydroperoxide to the system. Results of the maximum binding obtained during mechanochemical binding of MADA and EBHPT (ie at 2%) to polyethylene and polypropylene at optimum processing time of 15 minutes are summarised in Table 4.2.

Table 4.2 Estimation percentage of binding of stabilisers at optimum times

Stabiliser	Concentration of stabilisers (pph)	Estimated percentage of binding	
		Polyethylene	Polypropylene
MADA (II)	2	83	75
EBHPT (I)	2	15-20	20

4.2.8 Discussion

It is evident from the results presented that sulphur containing antioxidant (MADA) becomes readily bound to polyethylene and polypropylene when incorporated into polyethylene and polypropylene at processing temperatures (ie 150 and 180°C respectively for polyethylene and polypropylene).

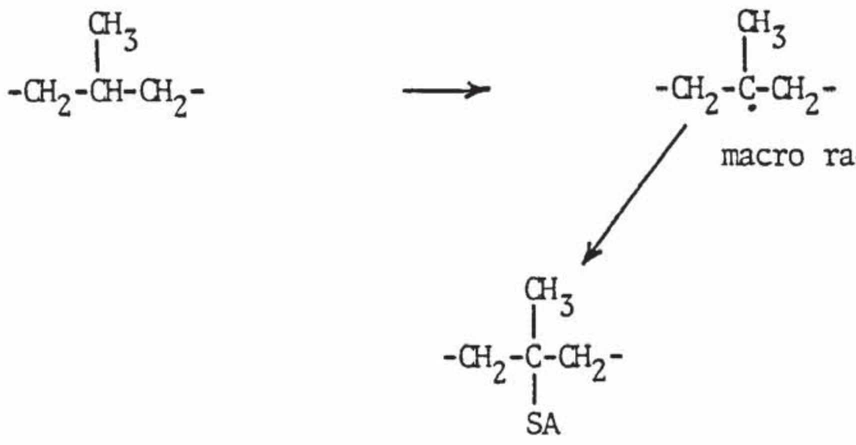
The processing of thermoplastic polymers shows evidence of thermal oxidative and mechanochemical processes, and which one predominates depends on the inherent oxidisability and detailed rheology of the polymers(142). In the case of polymers with higher glass transition temperatures (ie Tg), the mechanochemical formation of chemical 'defects' in the polymer is the primary process and this leads to accelerated oxidative degradation during the later stages of the polymers history(143).

It has been established by ESR that mechanical fracture of solid polymers produces free radicals through scission of the polymer chains(144). Free radicals formed by mechanical action are called 'mechano radicals'.

In the present instance, it seems likely that the presence of a small amount of dissolved or occluded oxygen in the mixer, coupled with the high shearing forces operating in the polymer are not only inducing the well known radical chain addition of the initial thiols to the polymer but are also converting some of the adduct and possibly the by product disulphides formed under these conditions to thiol sulphinates and related oxygenated species which are the precursors of the peroxidolytic antioxidants. (The effect of this oxygenated species on ageing of polymer films is described in section 4.4.)

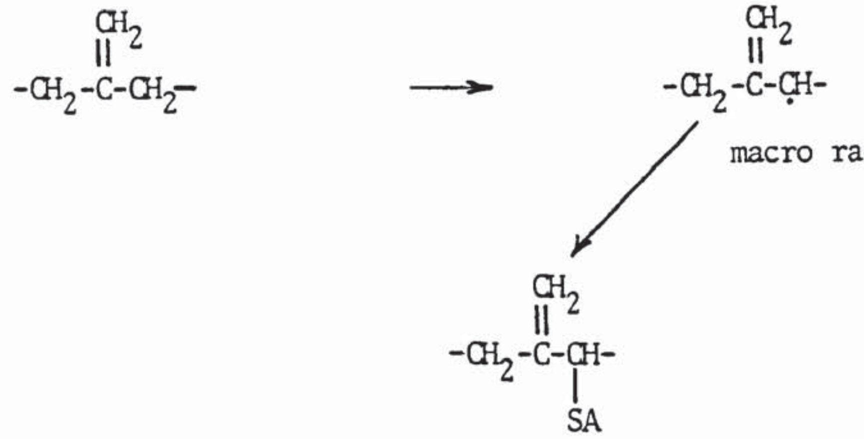
$$R\text{-}R \xrightarrow[\text{heat}]{\text{mechanical stress}} \underset{\text{mechano radical}}{R\cdot + R\cdot} \qquad (1)$$

$$AS\cdot + R\cdot \longrightarrow R\text{-}SA \qquad (2)$$


macro radical

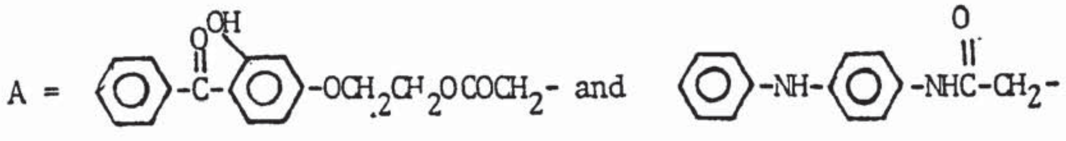
$$-CH_2-\overset{CH_3}{\overset{|}{CH}}-CH_2- \longrightarrow -CH_2-\overset{CH_3}{\overset{|}{\underset{\cdot}{C}}}-CH_2- \longrightarrow -CH_2-\underset{SA}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2- \qquad (3)$$

In the case of polyethylene, the same binding mechanism might operate; in this case, the allylic position is the most readily oxidisable.


macro radical

$$-CH_2-\overset{CH_2}{\overset{\|}{C}}-CH_2- \longrightarrow -CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{\cdot}{CH}- \longrightarrow -CH_2-\overset{CH_2}{\overset{\|}{C}}-\underset{SA}{\underset{|}{CH}}- \qquad (4)$$

where A can be:



An important question arising from these results is the high level of binding obtained at higher concentrations of MADA (this is particularly clear in the case of polypropylene). Preliminary experiments have indicated(145-147) that this is associated with the ratio of hydroperoxide to sulphur compound (S) present in the system. At high molar $[ROOH]/[S]$ ratio (>1) the sulphur compounds are all highly effective ionic catalysts for peroxide decomposition(146) and no free radicals are formed. At lower ratios (<1), the reaction is slower and only free radical derived products are formed initially. With increasing reaction time, however, ionic reactions predominate, and the hydroperoxide is no longer a potential source of $X^{\cdot}$ in scheme 4.2, section 4.4.

It follows from this that when the ratio of O_2 to S is high, ionic decomposition of the resultant hydroperoxides will compete effectively with redox reactions between ROOH and S leading to inhibition of the adduct reaction between S and the polymer (see also scheme 4.2, section 4.4.). The decrease in the binding efficiency at higher processing times could possibly be due to the oxidation of sulphur containing adducts which leads to breakage of the antioxidant moiety from the polymer backbone.

4.3 Dilution of Masterbatch to Lower Concentration

Dilution of 2% masterbatches of polyethylene and polypropylene containing MADA and EBHPT were carried out at the melt stage. Dilutions in the melt were made before and after extraction to the concentration of 3×10^{-4} mol of antioxidant in 100 g of polymer. To make 3×10^{-4} mol/100 g bound MADA and EBHPT, 3.9 (plus 96.1 g of virgin polymer) and 4.65 g (plus 95.35 g of virgin polymer) of MADA and EBHPT masterbatches (2%) were taken respectively and processed in the torque rheometer. Processing temperatures of 160 and 180°C were used for polyethylene and polypropylene respectively.

4.3.1 Functional Group Measurements

In general ir absorption regions of oxygen containing functional groups were routinely followed for light and heat aged films at intervals. Perkin-Elmer grating spectroscopy model 599 was used for following changes in the polymer films.

Evaluation of the degree of degradation (or stabilisation) is based on the extent of carbonyl group build up during the course of the reaction. To account for variations in film thickness and instrumental errors in intensity measurements, use is made of internal reference bands in LDPE (1895 cm^{-1}) and in PP (2730 cm^{-1}) which are unaffected by oxidation. A carbonyl index is, therefore, defined as the ratio of the carbonyl absorption at 1710 cm^{-1} to the appropriate reference band. The carbonyl absorption at 1710 cm^{-1} was determined using the base line method.

4.3.2 Results of Photo and Thermal Oxidation of Polypropylene containing MADA Bound

Fig 4.26 shows the changes in melt flow index (MFI) (samples containing 3 x 10^{-4} mol/100 g of unextracted MADA bound) during thermal processing in simulated commercial mixing operation at 180°C, with closed and open chamber. It is clear that there is no significant change in MFI of the sample after 25 minutes of open chamber processing. This confirms that the melt degradation of the polymer is completely inhibited by the antioxidant under these conditions and results in Fig 4.27 also confirm that oxidative degradation is inhibited as evidenced by the constancy of the initial carbonyl concentration for all the samples before thermal oxidation. The effect of increased concentration of antioxidant (ie 3, 4.5 and 6 x 10^{-4} mol/100 g) increases the induction period of the unextracted samples from 18 hours for 3 x 10^{-4} mol/100 g to 38 hours for 6 x 10^{-4} mol/100 g. Exhaustive solvent extraction (with acetone for a minimum extraction time of 48 hours) of the samples reduces the induction period slightly. Moreover, the increased induction period to oxidation of the extracted polypropylene films (containing different concentrations of MADA) compared to that of the control (no additive) indicates the presence of polymer-bound antioxidants.

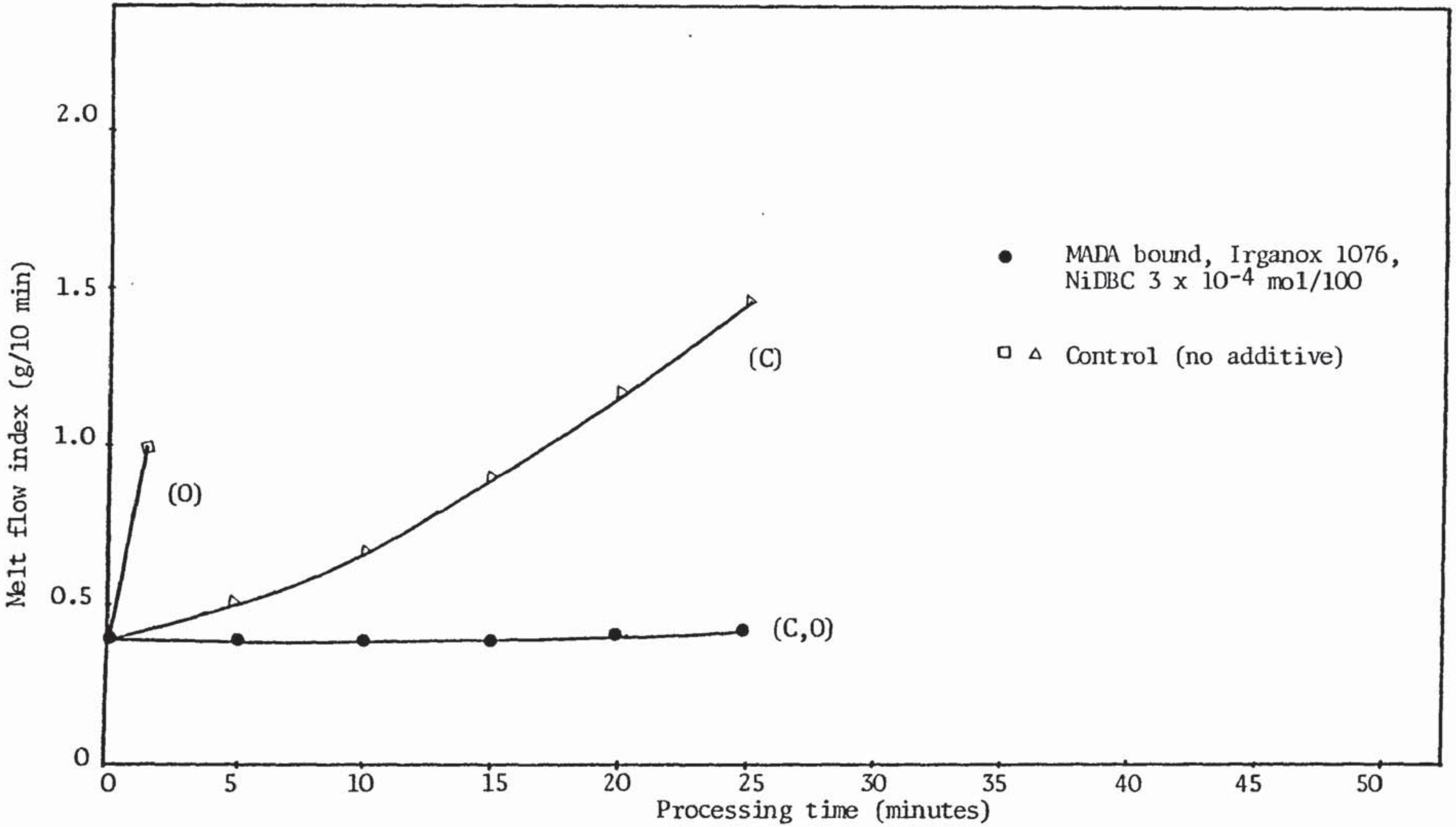


Fig 4.26 Effect of processing in open (O) and closed (C) mixer at 180°C on MFI of PP containing 3×10^{-4} mol/100 g of bound and commercial antioxidant

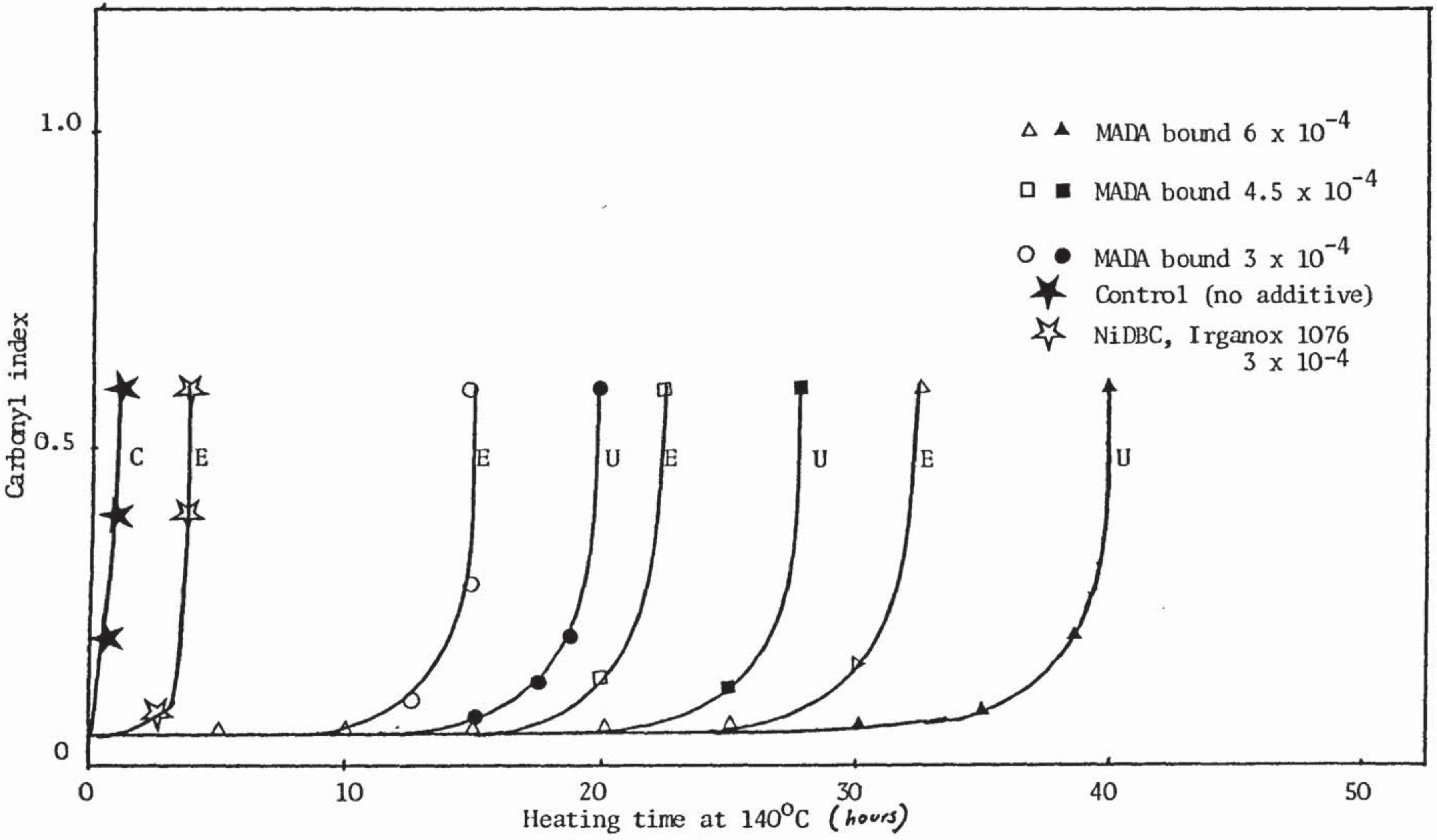


Fig 4.27 Thermal oxidative stabilities of PP films at 140^{o}C in air containing different concentrations of bound MADA. All samples processed at 180oC for 10 minutes, closed chamber (U = unextracted, E = extracted, C = control)

It is clear from Fig 4.27 that under conditions where loss of antioxidant by solvent extraction is important, the bound antioxidant is much superior to commercial antioxidants such as NiDBC and Irganox 1076 (3 x 10^{-4} mol/100 g, extracted) as an additive. Table 4.3 compares the induction period to onset of carbonyl formation and embrittlement time during thermal oxidation at 140°C of polypropylene films containing MADA bound extracted and unextracted.

It is known(20) that during processing of PP, hydroperoxides are produced and that they are responsible for a subsequent decrease in uv stability of the fabricated polymer. It was therefore of some interest to examine the effect of MADA bound on the uv stability of polypropylene. Figs 4.28 and 4.29 show the formation of carbonyl as a function of uv irradiation time for polypropylene films containing different concentrations of MADA bound, processed for 10 minutes in a closed chamber at 180°C. It is clear from Fig 4.28 that with increasing the concentration of the MADA bound, the stability to uv light increases (see Table 4.4 for embrittlement times). The uv stability of PP films containing MADA bound and commercial UV531 (uv absorber) is compared in Fig 4.29. It clearly shows the superior uv stability of the PP films containing MADA bound after acetone extraction in comparison with UV531 which was leached out during extraction (see Fig 4.29). The embrittlement time of the PP films containing different concentrations of MADA bound during uv irradiation is shown in Fig 4.30. It clearly demonstrates the linear relationship between the embrittlement time of the films with the antioxidant concentration. It also indicates

Table 4.3 Induction period to onset of carbonyl formation and embrittlement times in the oxidation of polypropylene films (140°C). All samples are processed at 180°C, 10 mins in closed chamber

	Control	PP containing bound MADA (3 x 10^{-4}mol or 0.077 g/100 g)		PP containing bound MADA (4.5 x 10^{-4}mol or 0.115 g/100 g)		PP containinb bound MADA (6 x 10^{-4}mol or 0.15 g/100 g)	
		Unext	Ext	Unext	Ext	Unext	Ext
Induction period (h)	-	15	11	23	18	36	28
Embrittlement time (h)	40 mins	20	15	28	23	40	33

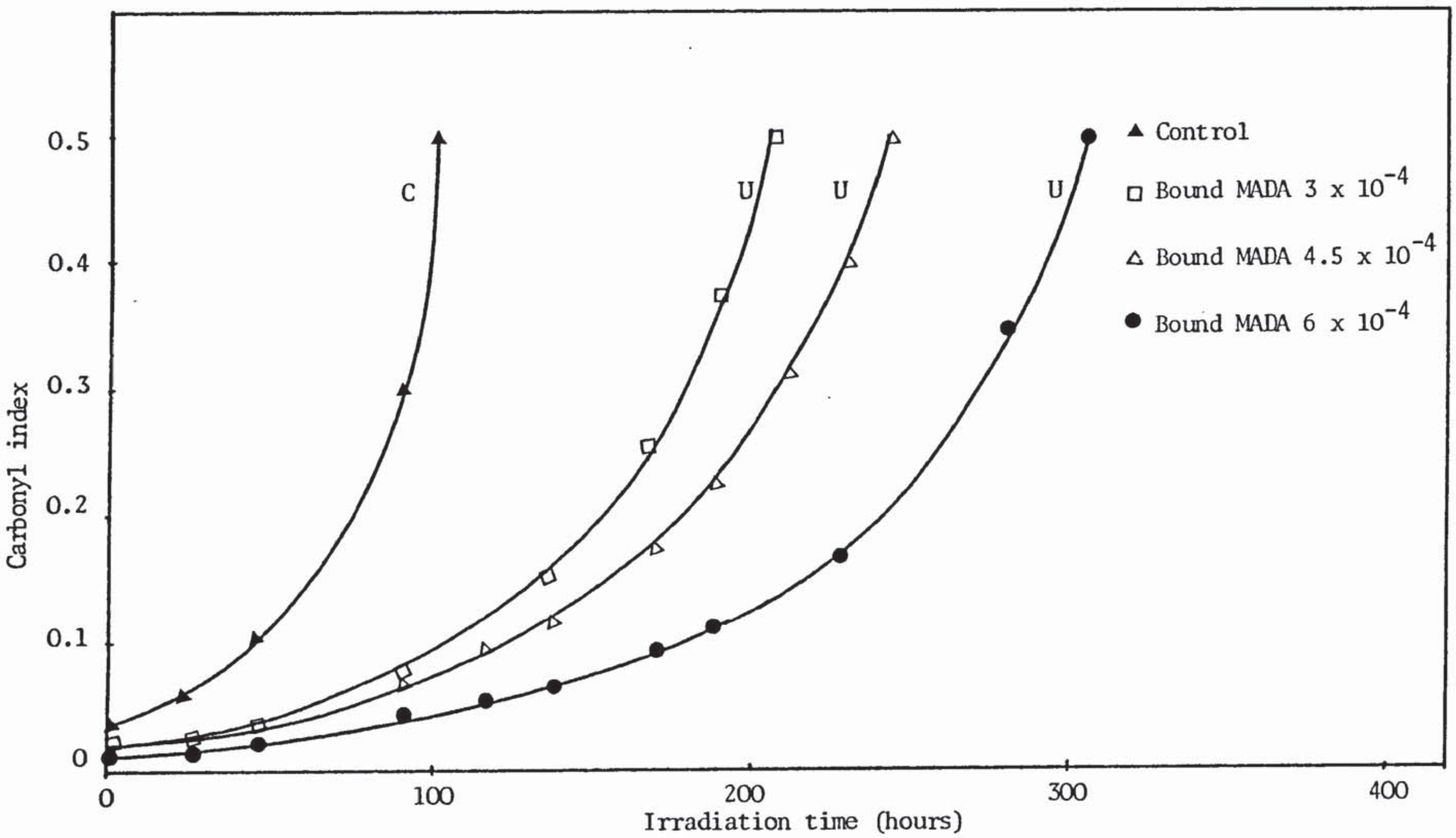


Fig 4.28 Development of carbonyl (1710 cm^{-1}) in PP sample containing MADA bound during ur irradiation (U = unextracted, C = control)

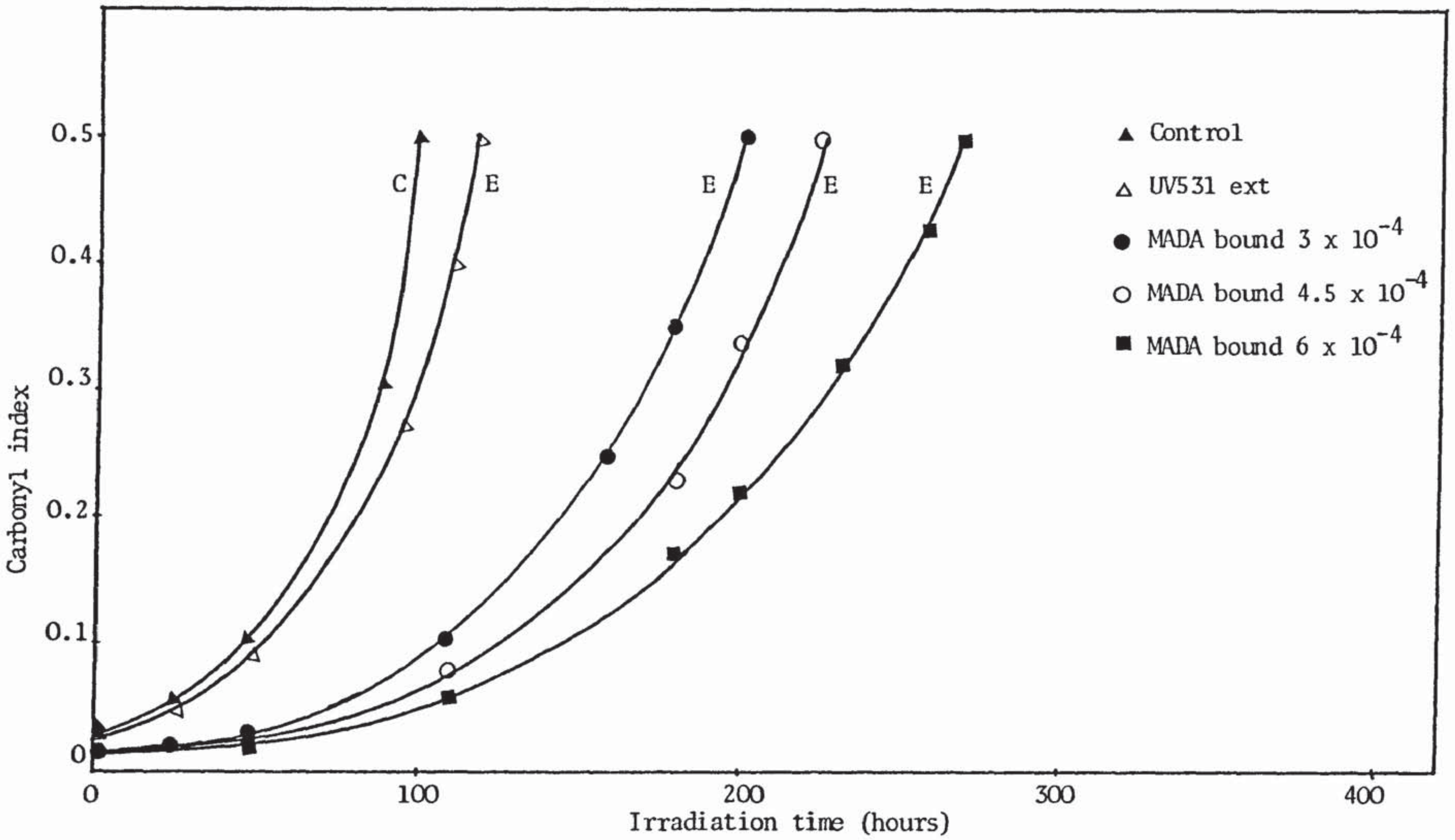


Fig 4.29 Development of carbonyl (1710 cm^{-1}) in PP samples containing MADA bound, processed at 180°C, 10 minutes, closed chamber (E = extracted, C = control)

Table 4.4 Uv embrittlement time of PP films containing MADA bound, all samples are processed at 180°C, closed chamber, 10 minutes

	PP containing bound MADA (3 x 10^{-4}mol or 0.077 g/100 g)		PP containing bound MADA (4.5 x 10^{-4}mol or 0.115 g/100 g)		PP containing bound MADA (6 x 10^{-4}mol or 0.15 g/100 g)		Control
	Unext	Ext	Unext	Ext	Unext	Ext	
Embrittlement time (h)	220	190	280	220	360	300	90

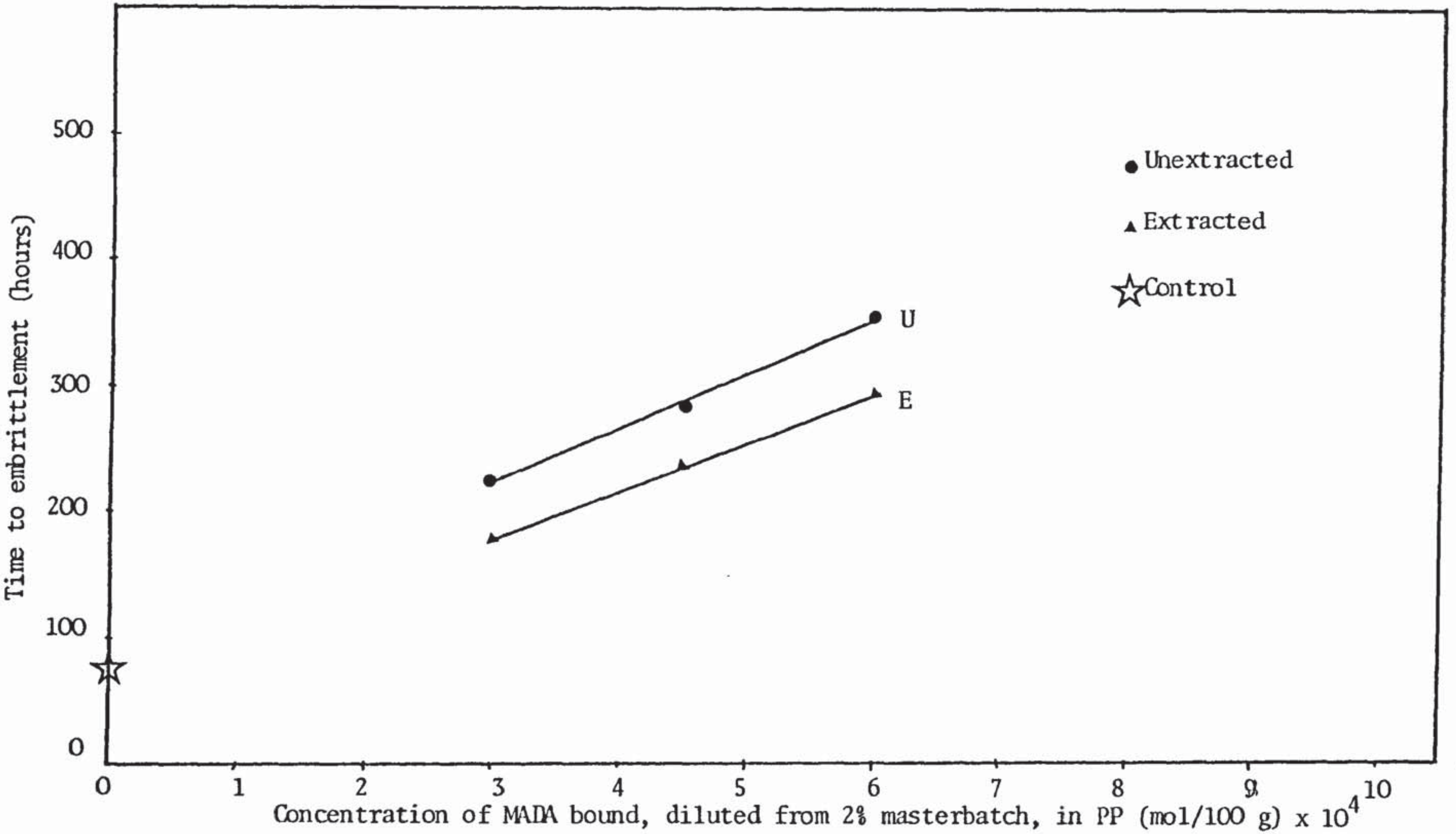


Fig 4.30 Relationship between MADA concentration with embrittlement time in PP. All samples processed at 180°C for 10 minutes, closed chamber (U = unextracted, E = extracted)

the embrittlement time of the PP films containing MADA bound after acetone extraction, compared to the control sample (ie containing no antioxidant).

A major area which polypropylene is being used is in the production of hot water pipes. Additives added conventionally to the pipes which are used at temperatures around 100°C and in the presence of leaching solvent (water) may gradually become lost from the polymer matrix. In order to find out the effectiveness of MADA bound system, polymer films containing MADA bound and commercial antioxidants (ie NiDBC and Irganox 1076) were hot water extracted. Polymer films were placed in a soxhlet and they were extracted using water as a solvent under steady stream of air. The extraction temperature in the soxhlet was around 85-90°C. The tensile strength and elongation at break of the samples were measured (see section 3.12). Results are presented in Figs 4.31 and 4.32.

It can be seem from Fig 4.31 that the tensile properties of the samples containing MADA is superior to the control without additive and commercial stabilisers conventionally added. The tensile properties of the samples containing conventional stabiliser (ie NiDBC and Irganox 1076) drop sharply after 10 days of hot water extraction, whereas samples with MADA bound retain about 80% of the original tensile strength. The change in elongation at break follows the same trend (see Fig 4.32). However, elongation decreases more sharply than tensile strength but it is also clear that samples with MADA bound show much better properties after

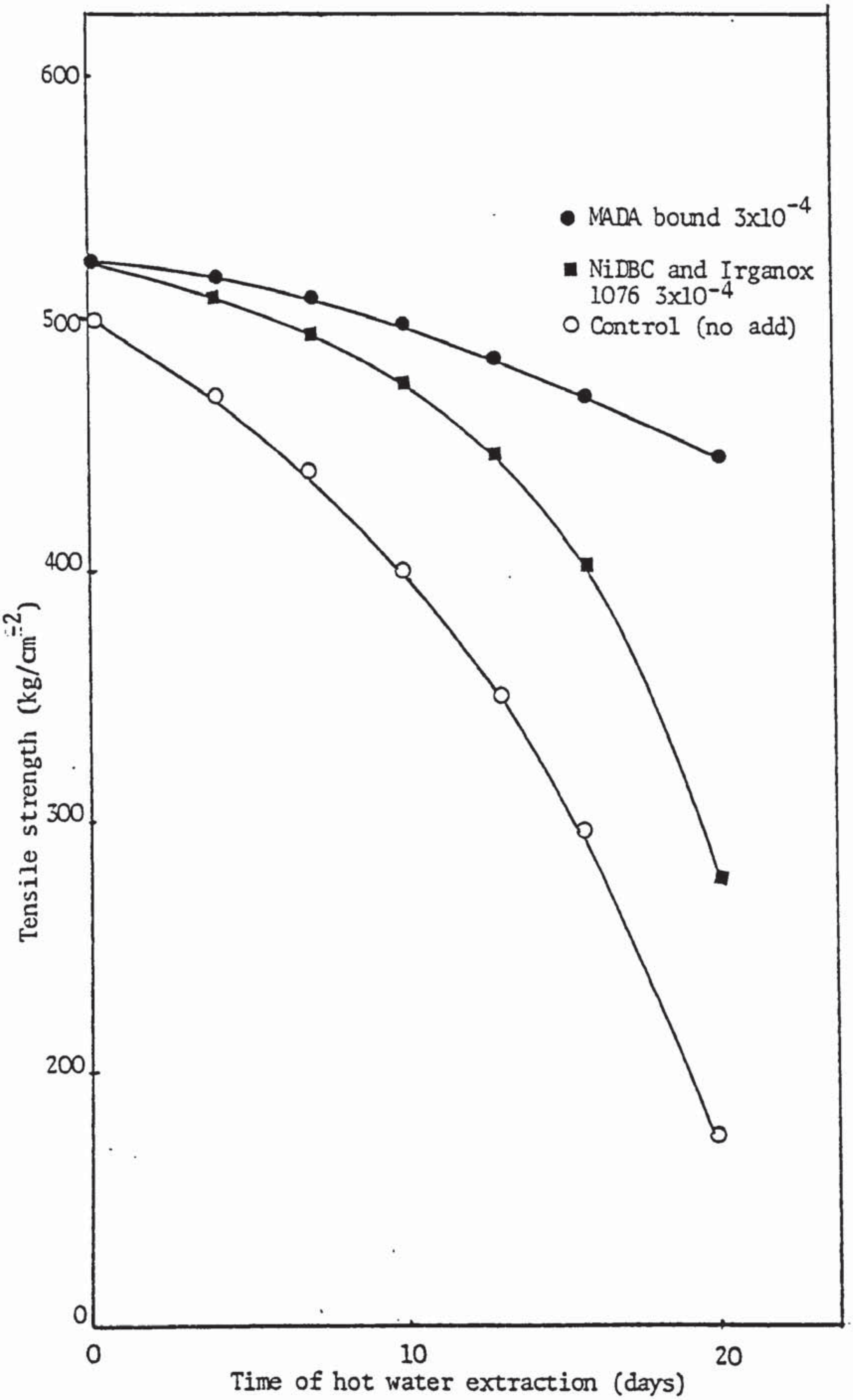


Fig 4.31 Changes in tensile strength of PP film during hot water extraction at 90°C under air stream (additive concentration 3×10^{-4} mol/100 g)

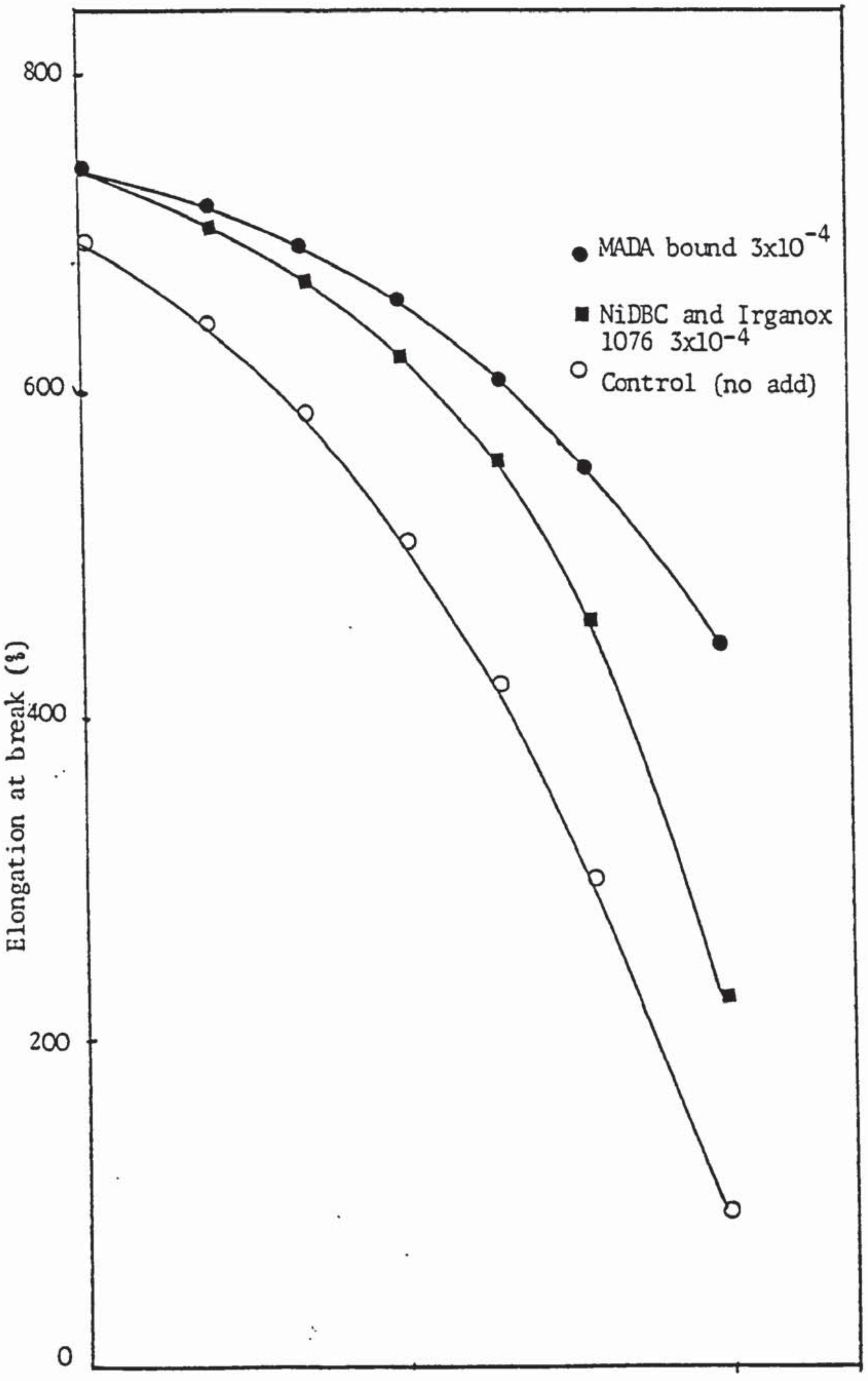


Fig 4.32 Changes in elongation at break (Eb%) of PP films during hot water extraction at 90°C under air stream (additive concentration 3×10^{-4} mol/100 g)

20 days of hot water extraction (ie continuous extraction during day time for 8 hours and left overnight in cold solvent under a stream of air).

The colour of the polypropylene film containing 2% MADA (masterbatch) was yellowish-brown which was turned to greenish-blue after dilution to 3×10^{-4} mol/100 g concentration and processed at 180°C for 10 minutes. This became colourless after 5-10 hours of uv irradiation.

4.3.3 Results of Photo and Thermal Oxidation of Polyethylene Containing MADA Bound

A comparison of the behaviours of stabilisers as additives and MADA and EBHPT bound on uv exposure are shown in Fig 4.33. It is clear that commercial additives such as Tinuvin 770 and NiDBC before solvent extraction are superior to UV531 and bound MADA and EBHPT. However, MADA and EBHPT bound behave quite similarly to UV531. Extraction, however, gives a different result. It can be seen from Fig 4.34 that bound MADA gives much better protection to the films after acetone extraction for a minimum of 48 hours. Even samples containing EBHPT bound (only 20% of EBHPT is bound) were superior to UV531 (commercial uv absorber). The effect of thermal oxidation (oven ageing) at 110°C on LDPE films containing commercial additives and MADA, EBHPT bound at 3×10^{-4} mol/100 g are shown in Figs 4.35 and 4.36. It can be seen from Fig 4.35 that before solvent extraction LDPE films containing Irganox 1076

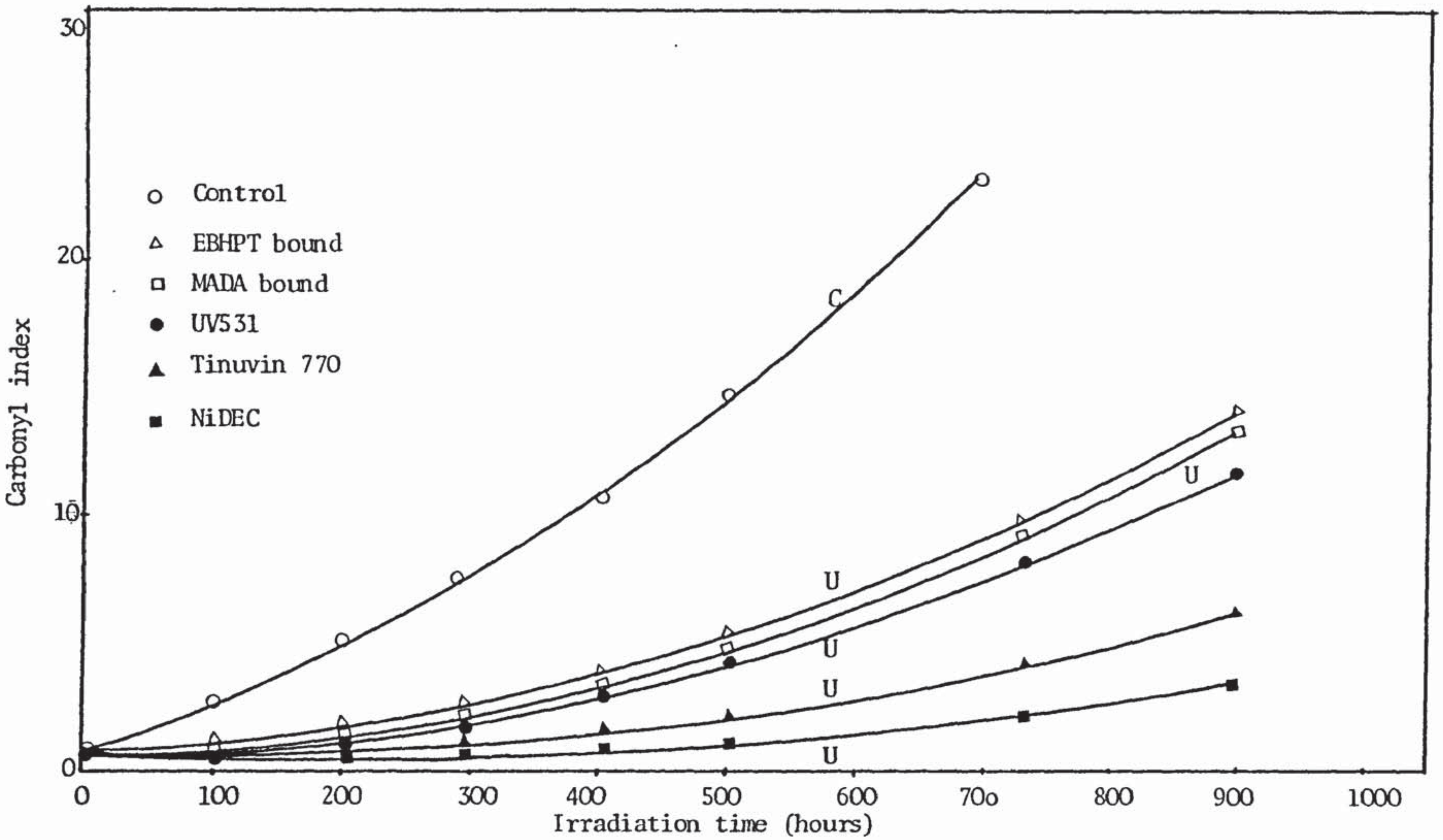


Fig 4.33 Comparison of behaviour of stabilisers as additive in LDPE (all samples processed for 10 minutes at 160°C, closed chamber, concentration 3 x 10^{-4} mol/100 g, C = control, U = unextracted)

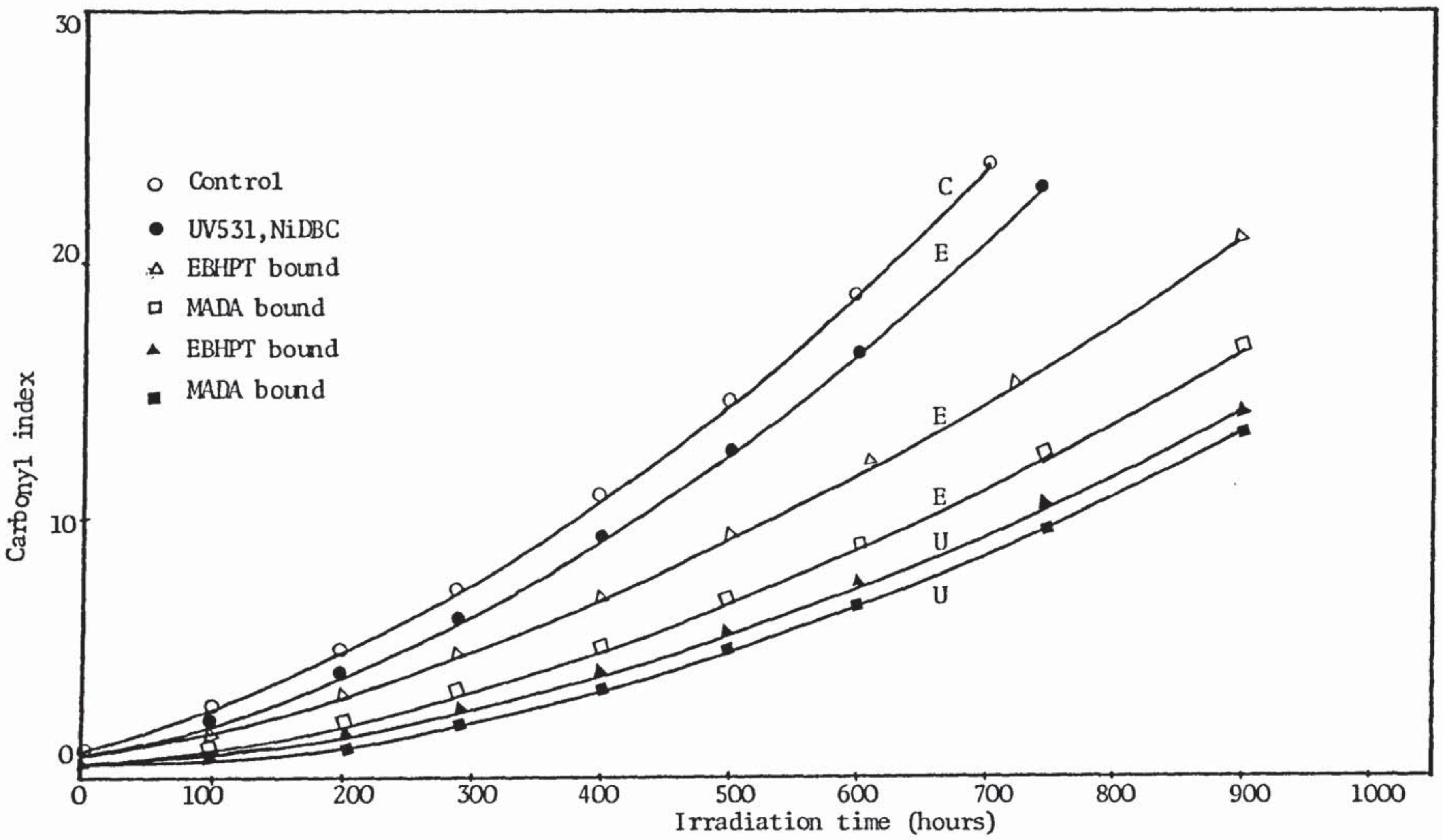


Fig 4.34 Comparison of behaviour of extracted and unextracted stabilisers as additive and bound diluted from masterbatch with concentration of 3 x 10^{-4} mol/100 g. (All samples processed at 160°C, 10 mins, closed chamber) C = control, E = extracted, U = unextracted

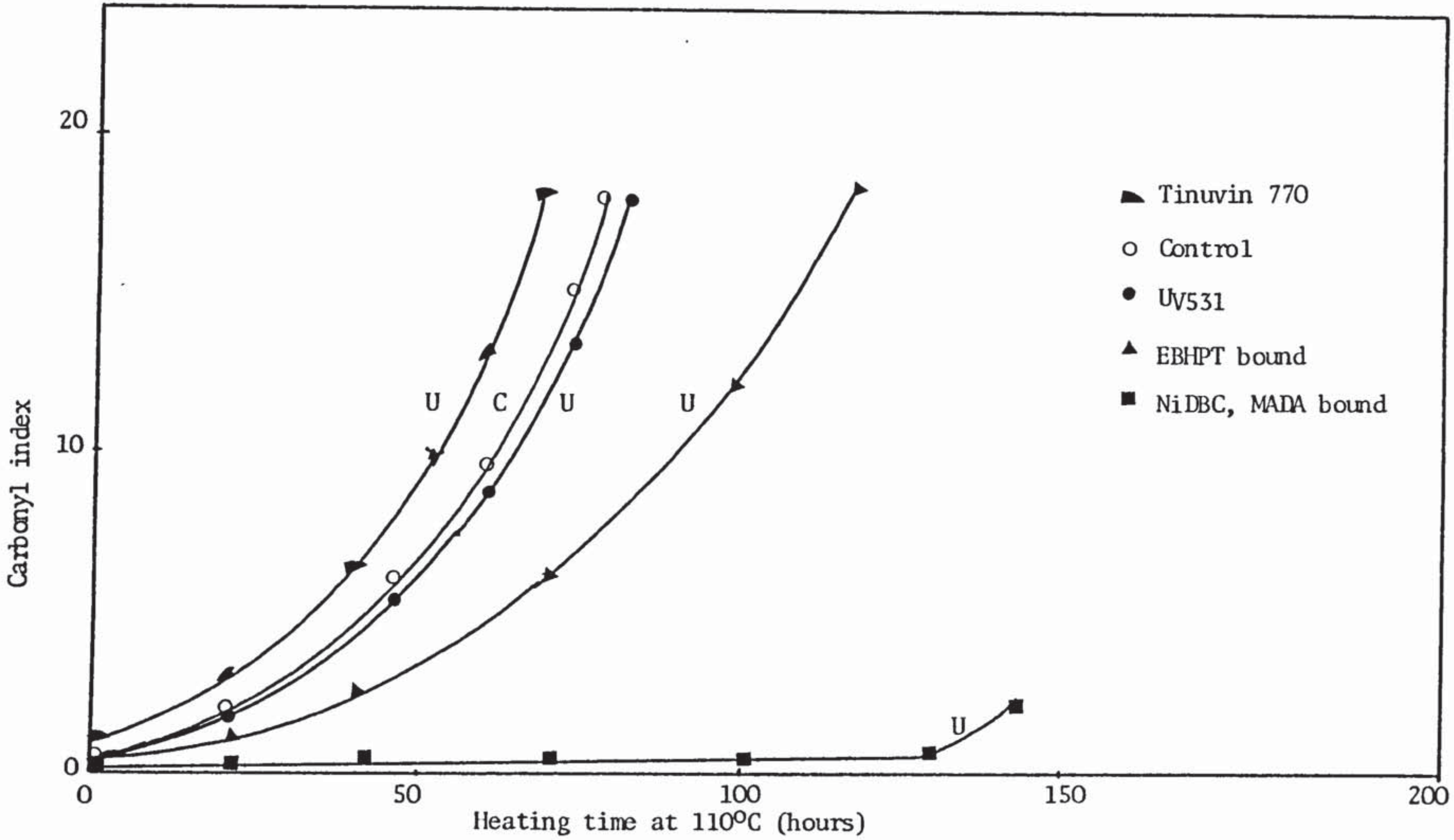


Fig 4.35 Effect of thermal oxidation (oven ageing) at 110°C in air of LDPE films containing antioxidants (3×10^{-4} mol/100 g) unextracted. All samples processed at 160°C/10 mins, open chamber, C = control U = unextracted

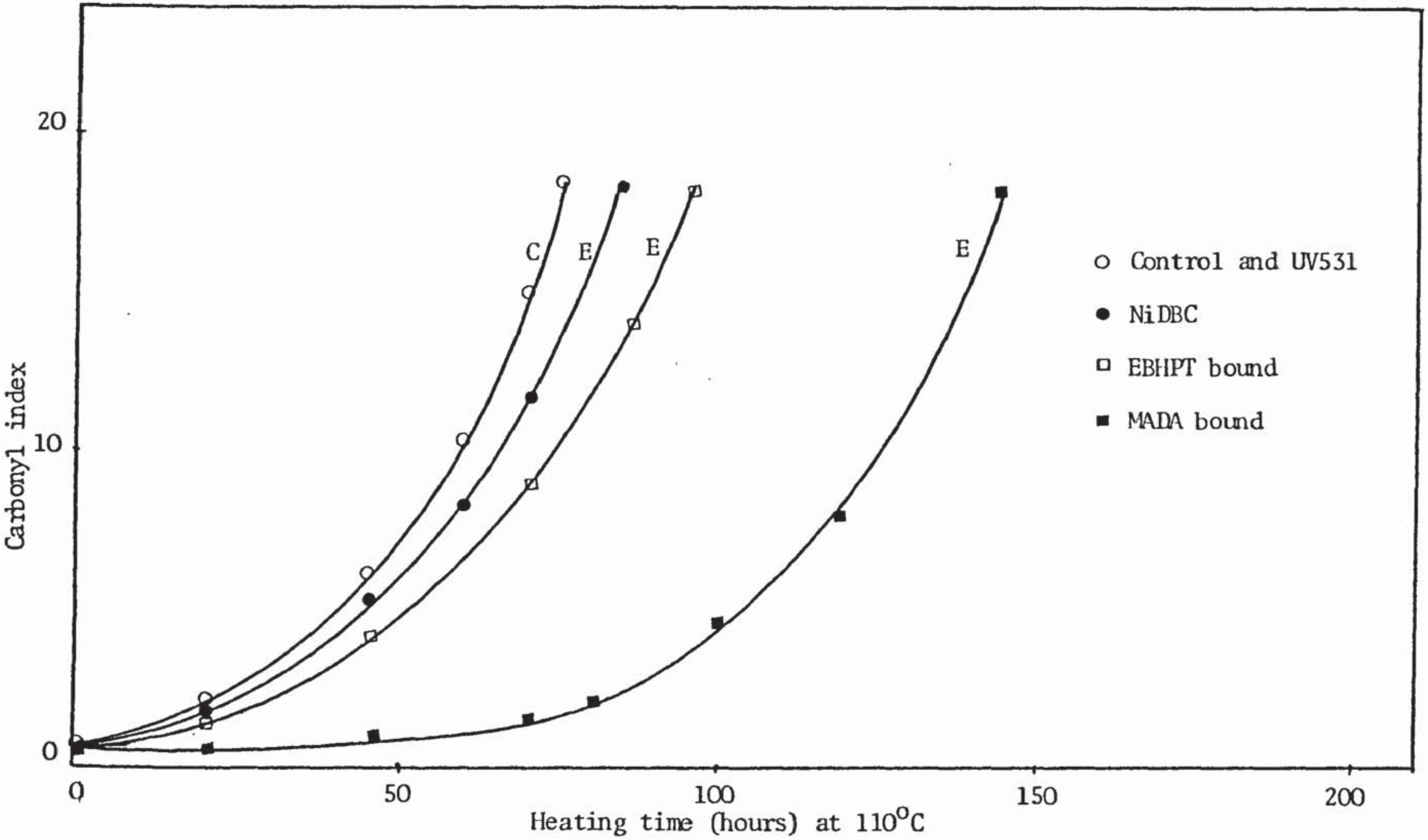


Fig 4.36 Effect of thermal oxidation (oven ageing) at 110°C in air of LDPE films containing antioxidants (3×10^{-4} mol/100 g) extracted. All samples processed at 160°C/10 mins, open chamber, C = control, E = extracted

(CB-A) and NiDBC (PD-C) and MADA bound behave similarly with around 130 hours of induction period. LDPE containing EBHPT bound protects samples better than UV531 and control during thermal oxidation. After acetone extraction, the behaviour of the antioxidants was completely changed and as is seen in Fig 4.36. LDPE films containing MADA are superior in protecting the polymer film against thermal oxidation. However, commercial antioxidants such as NiDBC and Irganox 1076 and UV531 are similar to control with no additive. LDPE films containing EBHPT bound show better protection indicating the presence of bound additive. These results demonstrate the importance of bound antioxidants in the polymers used in close contact with solvent (eg dry cleaning processes etc). Tables 4.5 and 4.6 summarise the embrittlement times and induction periods of the samples on uv exposure and oven ageing respectively.

4.4 Discussion

Oven ageing behaviour of extracted polyethylene and polypropylene films containing bound MADA (at 110 and 140°C respectively for PE and PP), and also photo-oxidation of the extracted films show a remarkable improvement in stability over the conventional phenolic (CB-A) and peroxide decomposer (PD-C) antioxidants.

Scheme 4.2 outlines the chemistry of adduct and by product formation where X· is an initiating radical such as $RO_2^{\bullet}$.

Table 4.5 Embrittlement time of polyethylene films on uv exposure, samples containing 3×10^{-4} mol/100 g of additive (U = unextracted, E = extracted)

Additive type	Control (no additive)	Tin 770	NiDBC		UV531		EBHPT bound*		MADA bound*	
			U	E	U	E	U	E	U	E
Embrittlement time (hours ± 100)	1500	2600	2800	1600	2500	1520	2600	1800	2500	2100

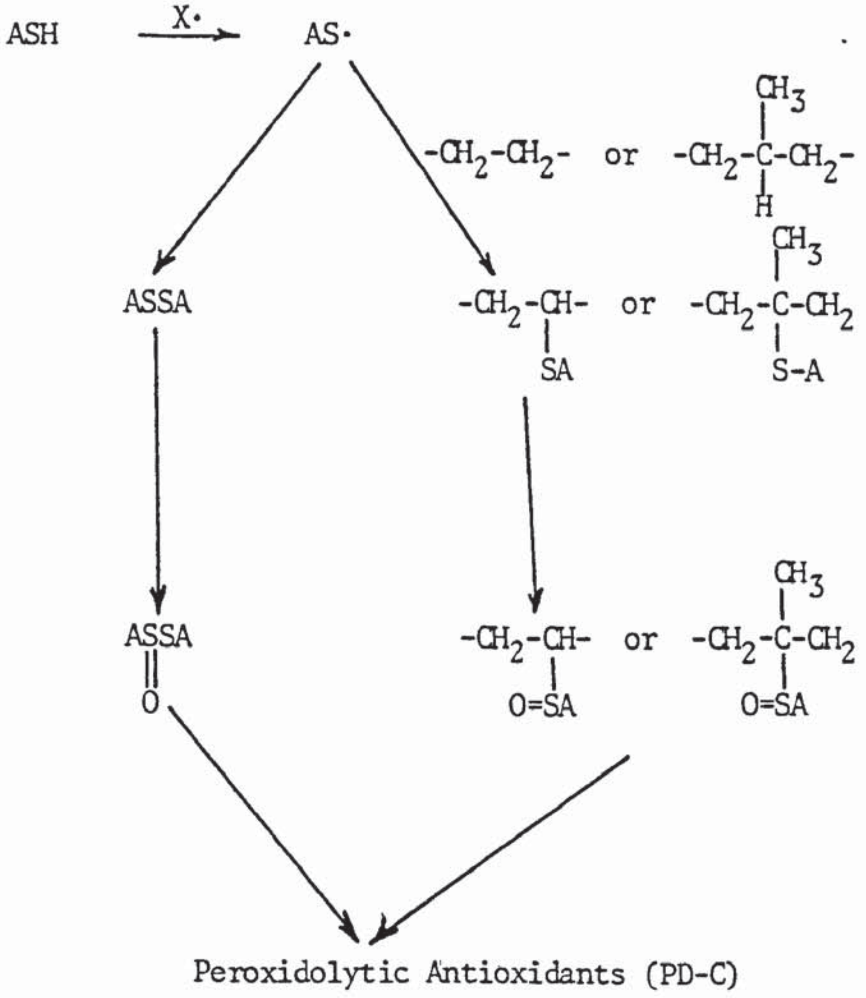
* diluted from 2% masterbatch

Table 4.6 Induction period of polyethylene films containing 3 x 10^{-4} mol/100 g of additive, on oven ageing at 140°C in air (U = unextracted, E = extracted)

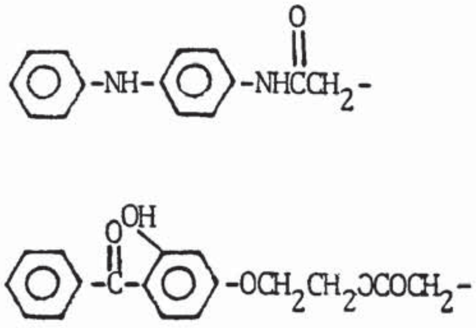
Additive type	Control	UV531		NiDBC		EHBPT bound*		MADA bound*	
		U	E	U	E	U	E	U	E
Induction period / hours	10	15	10	150	20	28	22	140	80

* diluted from 2% masterbatch

Scheme 4.2



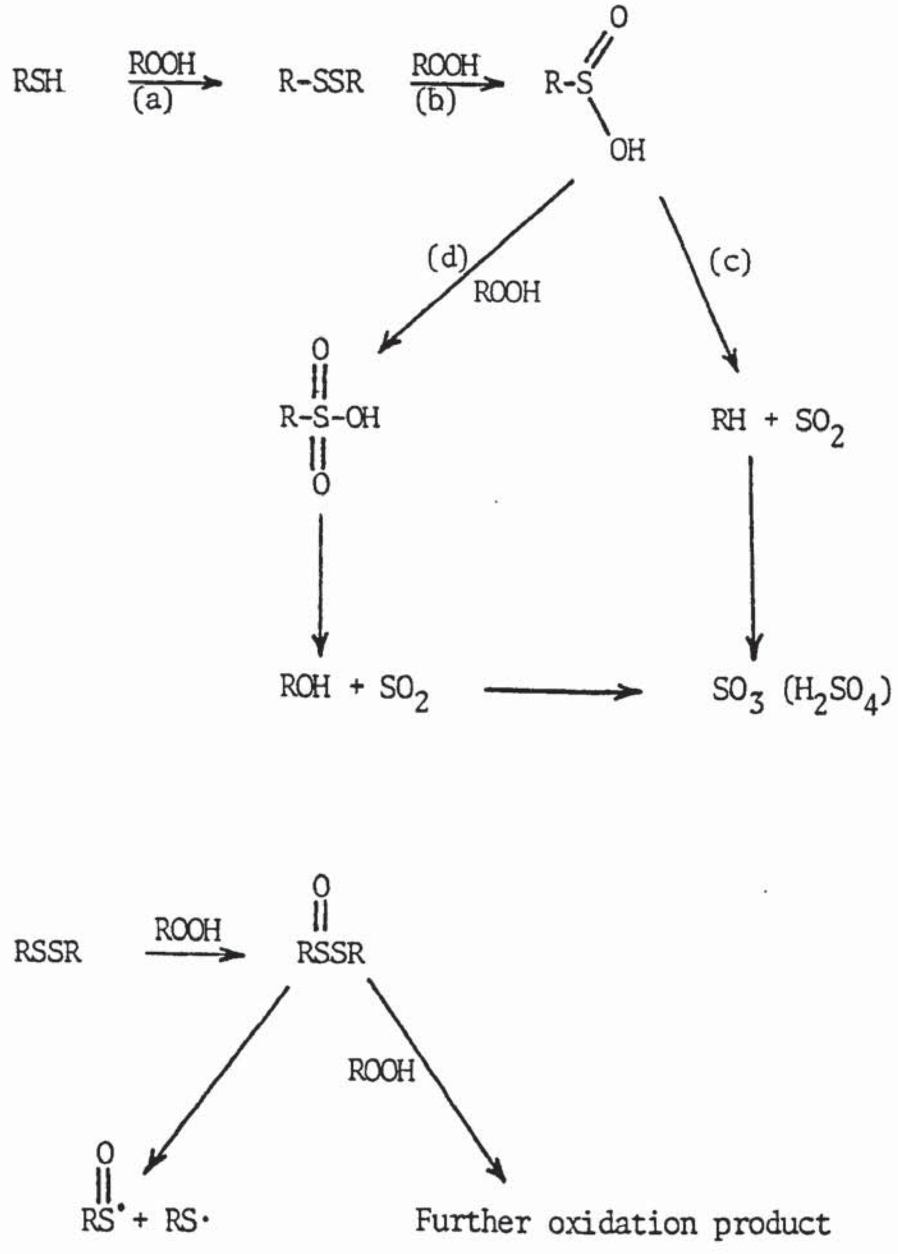
A can be A =



This adduct formation occurs in the presence of a small amount of dissolved oxygen in the mixer along with the high shear forces operating in the polymer. The by products disulphides formed from the initial thiols under these conditions could possibly be converted to thiol sulphinates and related oxygenated species which are precursors of the peroxidolytic antioxidants(145) (see scheme 4.2). The derived sulphur acids are highly effective peroxidolytic antioxidants(146) and the mechanism of their formation has been discussed by Scott et al(145-148). In an investigation for finding the mechanism of antioxidant activity with hydroperoxides by Husbands et al(146), it was reported that two products are responsible for antioxidant behaviour, namely sulphonic acid and inorganic acids (SO_3, H_2SO_4) formed by the decomposition of the unstable intermediate sulphinic acid. At low hydroperoxides to sulphur compounds, disulphide is the exclusive product formed from the sulphur compound. This product consumes hydroperoxides by further oxidation (scheme 4.3). On the other hand, in the presence of excess hydroperoxide, sulphur compound is converted to the sulphonic acid which is a powerful antioxidant which catalyses the decomposition of cumene hydroperoxide to phenol and acetone.

Sulphur dioxide is a powerful hydroperoxide decomposer which leads to the formation of sulphur trioxide which is a trace catalyst for the ionic decomposition of hydroperoxides.

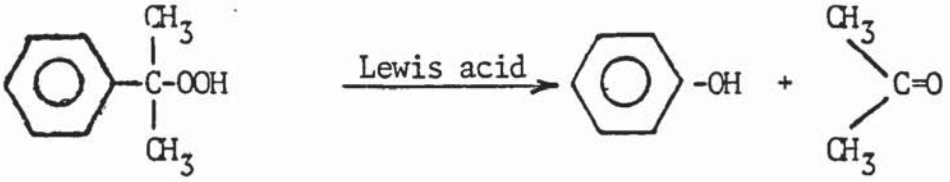
Scheme 4.3



(a) in the presence of low concentration of hydroperoxide

(b) in the presence of excess hydroperoxide

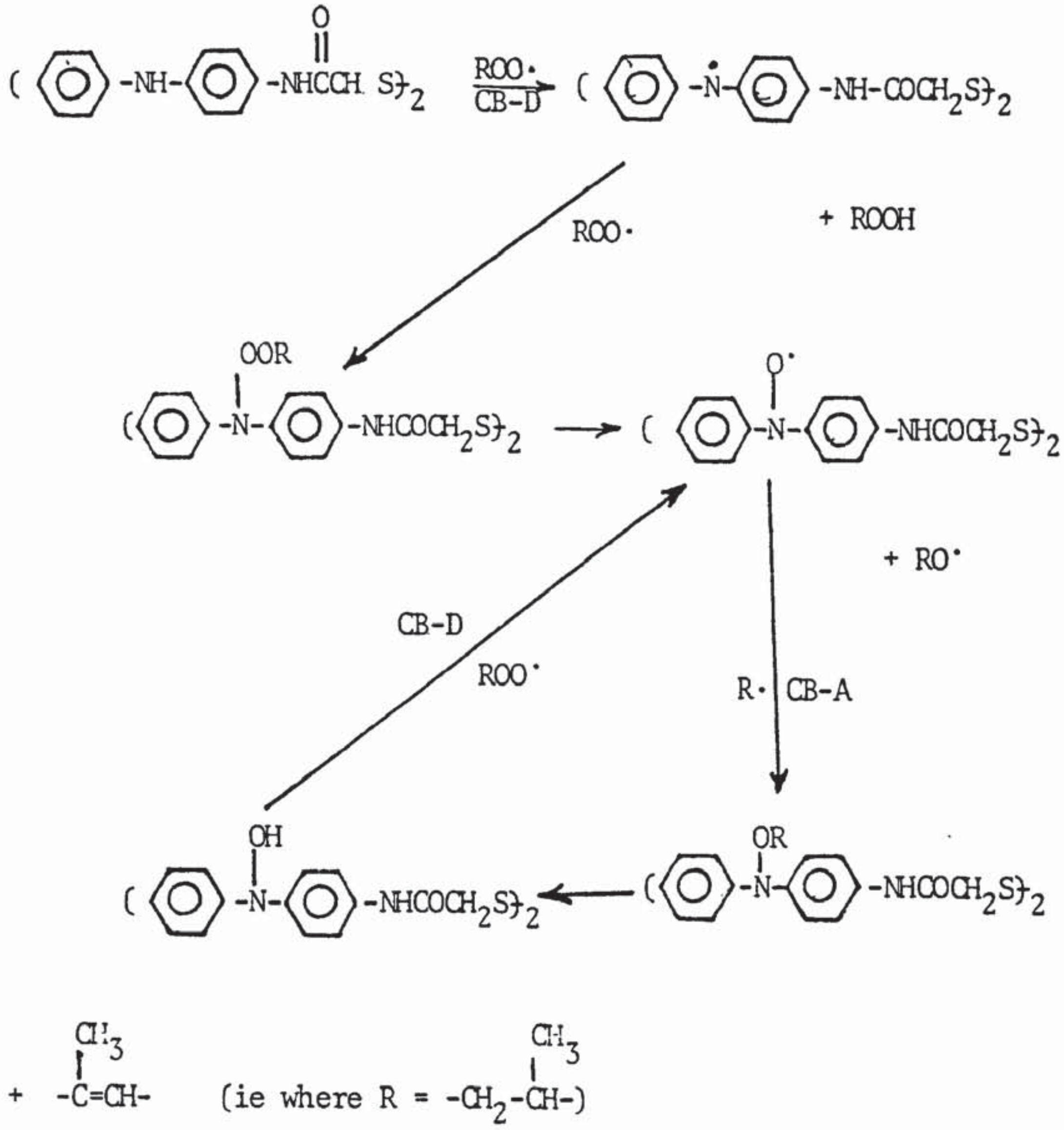
The decomposition of cumene hydroperoxide in the presence of EBHPT was studied by Fernando et al(104). The GLC decomposition products in the presence of the thiol compounds including EBHPT showed a Lewis acid catalysed process leading to the formation of phenol and acetone (in the presence of hydroperoxide).



The oven ageing results of polyethylene samples containing EBHPT and UV531 (Fig 4.35) indicates better thermal stability of the films containing EBHPT which correlates with above mechanism.

The photostabilisation effect of bound MADA might also be due to the formation of nitroxyl radicals formed in the adduct. This is known to operate by the CB-A mechanism in addition to peroxide decomposing activity. The mechanism proposed for the photostabilisation might be a cyclic process as follows:

Scheme 4.4


ROO·
CB-D
+ ROOH
ROO·
OOR
O·
+ RO·
CB-D
ROO·
R·
CB-A
OH
OR
-NHCOCH₂S)₂
+ -C=CH- (ie where R = -CH₂-CH-)
CH₃
CH₃

CHAPTER FIVE

IMPROVEMENT IN MECHANICAL AND LONG TERM PERFORMANCE OF WASTE POLYPROPYLENE (SINGLE COMPONENT)

CHAPTER FIVE

IMPROVEMENT IN MECHANICAL AND LONG TERM PERFORMANCE OF WASTE POLYPROPYLENE (SINGLE COMPONENT)

5.1 General Background

All polyolefins are susceptible to degradation by ultra-violet (uv) light, the rate of degradation increasing with the intensity of the uv light and the temperature of the material during irradiation. Both these factors vary with latitude, altitude and season, while the temperature of the material under given conditions will increase the darker the colour.

Other variables which affect the rate of degradation are rainfall and atmospheric pollution. Rain slowly leaches out some types of stabiliser from the surface molecular layers and the diffusion of stabiliser from the underlying material to replace this loss can be even slower, leaving the surface open to uv attack. Atmospheric pollution may reduce the rate of attack by screening the surface with layers of grime.

The effect of strong uv light on polypropylene is to degrade the surface layer, first causing crazing and this leads to a chalky powder which is relatively easily removed, the material beneath being virtually unaffected. The effect of these surface changes is to reduce considerably their impact resistance and it is this property that is normally used as a means of monitoring the uv resistance of various formulations.

Increasing quantities of polypropylene (PP) are now appearing in the form of discarded packaging (film, crates, sacks and ropes). They frequently contain a substantial quantitiy of polymer and quite apart from the problem they create in normal waste collection, the polymer content is such as to make the prospect of recycling attractive in principle. These contain a variety of antioxidants, pigments and uv stabilisers which although effective separately, may give rise to antagonism when used in combination(148,149).

The problem of stabilising mixed polypropylene wastes for recycling to secondary products is therefore a complex one. There is, therefore, a requirement for an ideal cheap and effective melt stabiliser which confers good long term stability on the polymer. Since it is possible that a proportion of the polymer may be recycled more than once, good melt and service stability should be retained with repeated processing.

The purpose of the present study is to investigate the improvement in mechanical and long term properties of polypropylene (PP) using ethylene-propylene diene monomer (EPDM) as solid phase dispersants (SPDs). The motivation of the work was based on the recent findings of Scott et al(28) that repeated processing of unstabilised polypropylene leads to inferior mechanical and long term properties.

5.2 Experimental

Materials Unstabilised polypropylene (PP) and ethylene-propylene diene monomer (EPDM) were used as described in section 2.1.

Processing The blends were processed at 180°C in the RAPRA torque rheometer for 10 minutes in a full chamber (ie 35 g). The blends were then compression moulded at 180°C for 3 minutes (1.5 minutes without pressure and 1.5 minutes with pressure) into sheets as described in section 2.2.2.

Table 5.1 shows the formulation with varying proportions of EPDM (0. 5, 10, 15, 20, 25 and 30%). All formulations were based on 35 g of polymer (in a full mixer chamber).

Tensile strength, % elongation and Young's modulus were calculated at the cross-head speed of 2 cm/min at room temperature (21 ± 1°C) (details are given in section 2.12).

Measurement of dynamic mechanical properties The Rheovibron model DDVII (Toyo Measuring Instrument Co Ltd, TMI, Tokyo) was used over a temperature range from -100 to 0°C. All measurements were made at a frequency of 110 Hz. Only one specimen was used for each material throughout the oxidative degradation and the value of tan δ was read directly from the Rheovibron (see also section 2.13).

Table 5.1*

Consumption (%)		Charge weight to mixer (g)	
PP	EPDM	PP	EPDM
100	0	35	0
95	5	33.25	1.75
90	10	31.50	3.50
85	15	28	7
80	20	26.25	8.75
75	25	24.5	10.5
70	30	22.75	12.25

* All samples were processed at 180°C/10 minutes, closed chamber

Impact strength measurement Impact strength was measured by a falling weight tester as previously described in section 2.11. Samples of exactly equal thickness (0.015 - 0.018 cm) were chosen for replicate impact studies and test was started with breaking weight, then reduced until no breaking occurred.

About ten measurements of impact strength were made for evey period of degradation. The impact strength of a film was taken as the energy required to break the film per unit thickness.

Melt flow indes (MFI) Melt flow indices were determined on the processed polymer using a Davenport polyethylene grade at 230°C (details are given in section 2.4).

Microscopy examination Microscopic examination of the films was carried out as described in section 2.14.

Measurement of carbonyl index by infra red spectroscopy A standard procedure was adopted on solid films using Perkin Elmer Spectrophotometer model 599. The peak at 2710 cm^{-1} was taken as the reference peak. The carbonyl index was measured as the ratio of absorbance at 1710 cm^{-1} to that of the reference peak.

5.3 Results

5.3.1 Changes in Mechanical Properties of PP with Addition of EPDM

The dynamic mechanical property, namely tan δ, and complex modulus are shown for PP films and PP films containing different concentrations of EPDM (ie 0 to 30%) over a temperature range of -100 to 0°C in Figs 5.1 and 5.2 respectively. Tan δ for PP/EPDM (ie 70 : 30 ratio) starts at approximately 0.02, with no change up to -65°C and rises rapidly as the temperature is raised reaching a maximum of 0.05 at -46°C, with increasing temperature up to -20°C, tan δ starts to rise and it continues to rise up to room temperature (see Fig 5.2). Complex modulus decreases sharply around -46°C and levels off and decreases again at -20°C. The effect of the concentration of EPDM added on the stage of the tan δ recorded directly from the Rheovibron is shown in Fig 5.1. It can be seen that by increasing the EPDM concentration from 10 to 30%, tan δ peak becomes sharper. There was a direct relationship between the tan δ recorded and the concentration of EPDM added. This linear relationship is shown in Fig 5.3.

The improvement in impact properties of PP films by addition of EPDM is shown in Fig 5.4. This experiment was carried out at room temperature and there was about 300% increase in impact properties of PP by addition of 30% EPDM. However, the increase in low temperature damping (see Figs 5.1 and 5.3), shows a much greater increase with EPDM addition (ie 30%). Correlation between impact

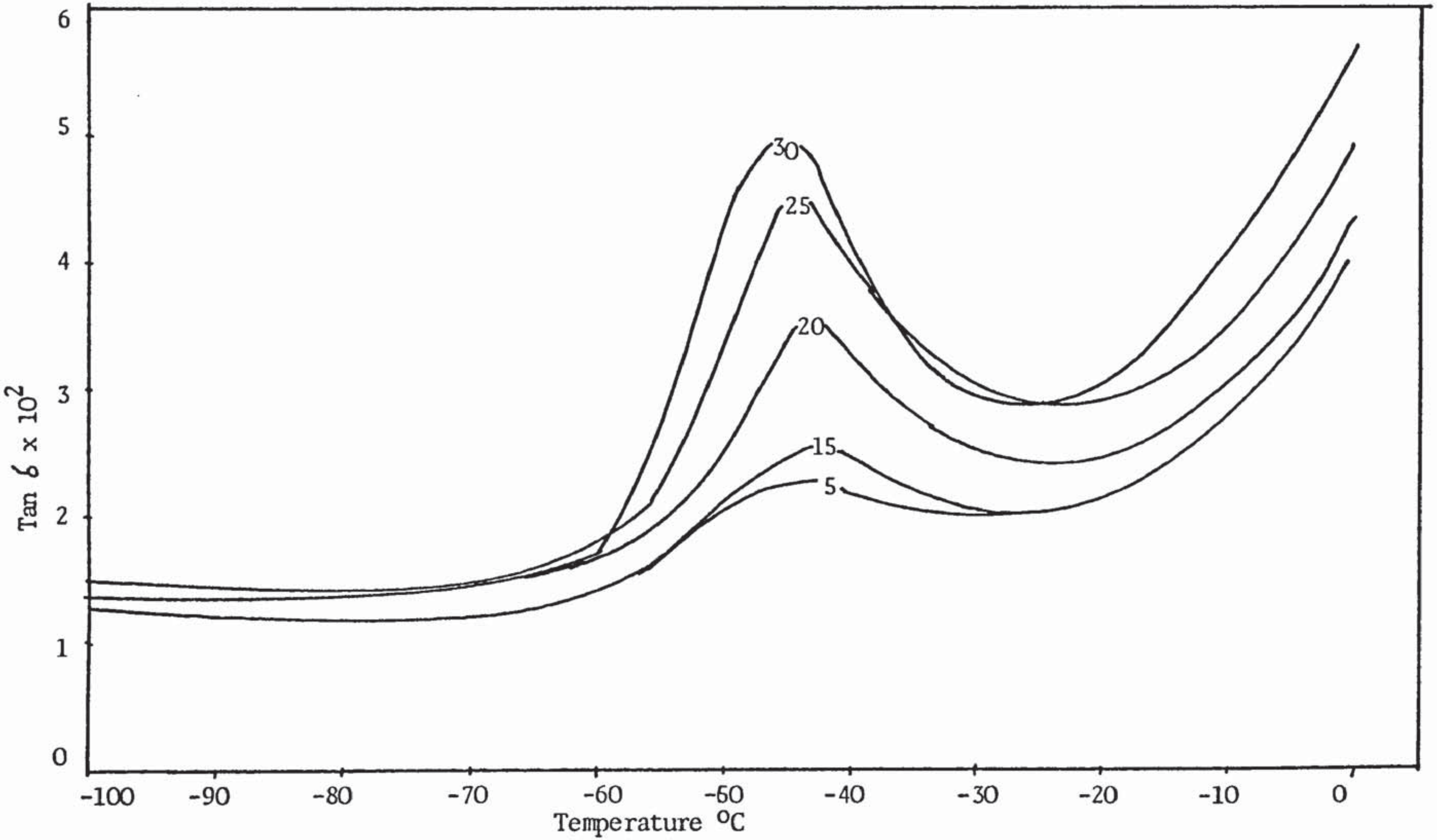


Fig 5.1 Effect of EPDM concentration on low temperature damping (-46°C) of PP films (numbers on curves are EPDM concentration in g/100 g). All samples processed at 180°C/10 mins, closed chamber

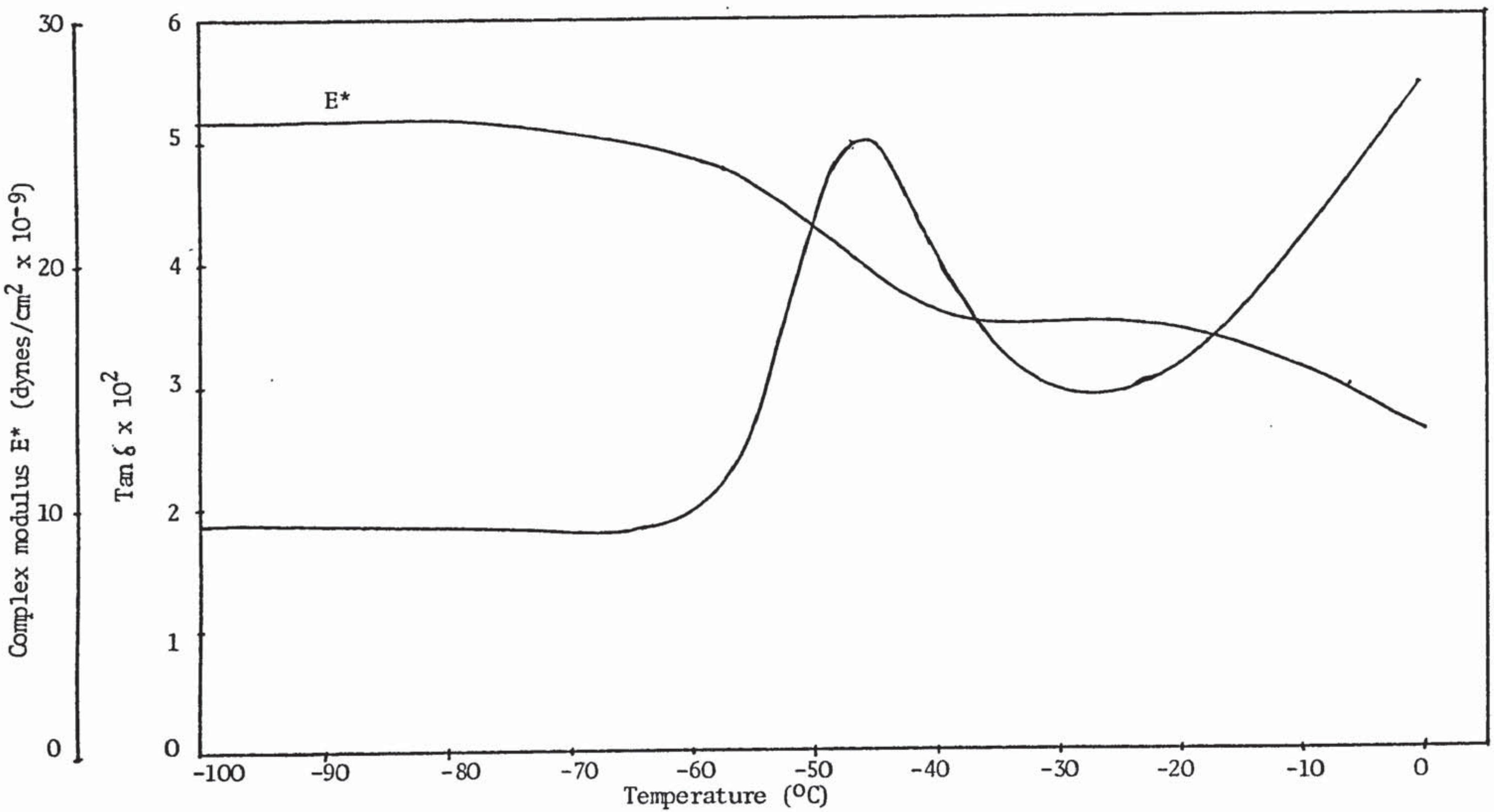


Fig 5.2 Relationship between tan δ and complex modulus of PP:EPDM (70:30), samples processed at 180°C/10 mins closed chamber

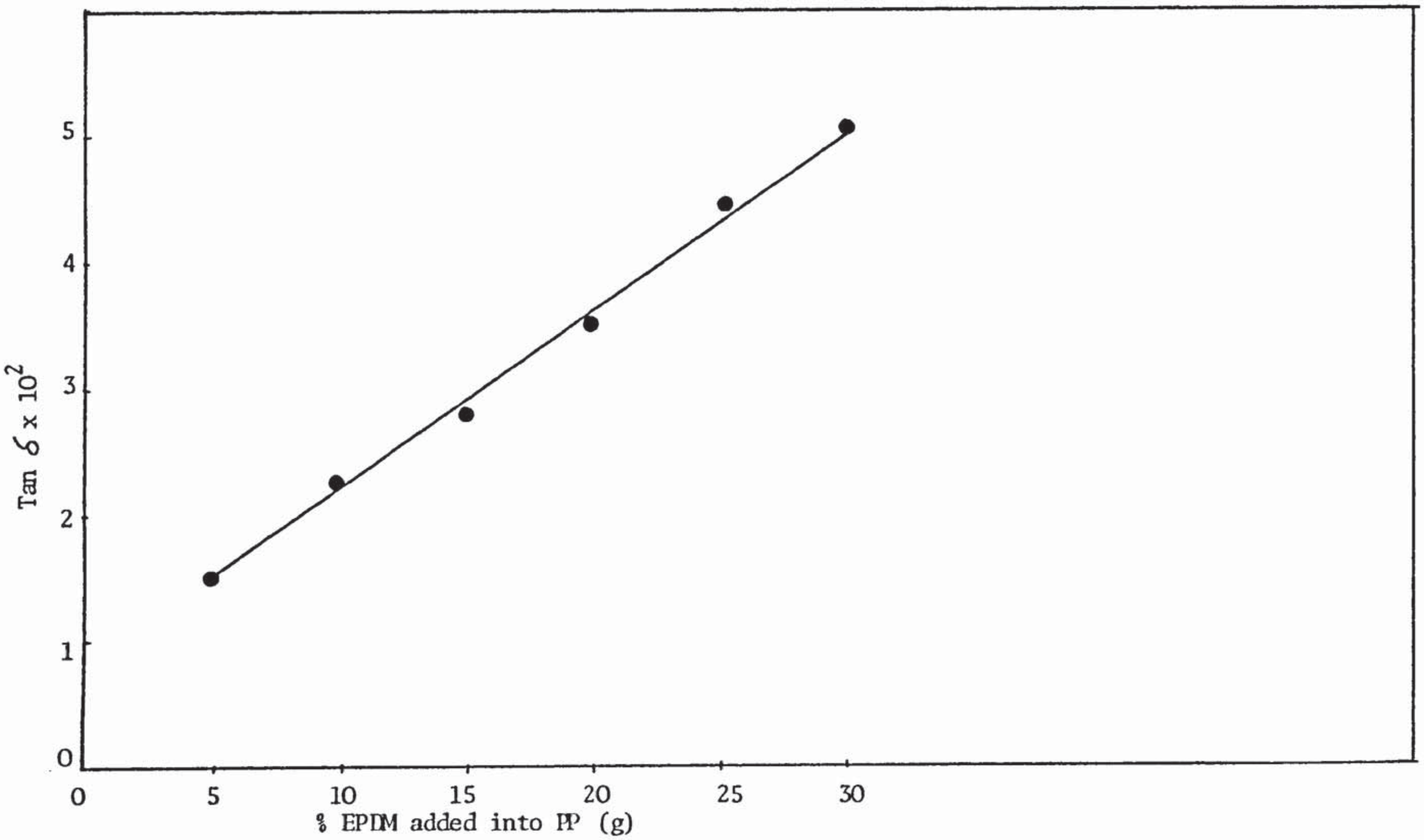


Fig 5.3 Correlation of tan δ' (-46°C) with the concentration of EPDM added to PP. All samples processed at 180°C/10 mins, closed chamber

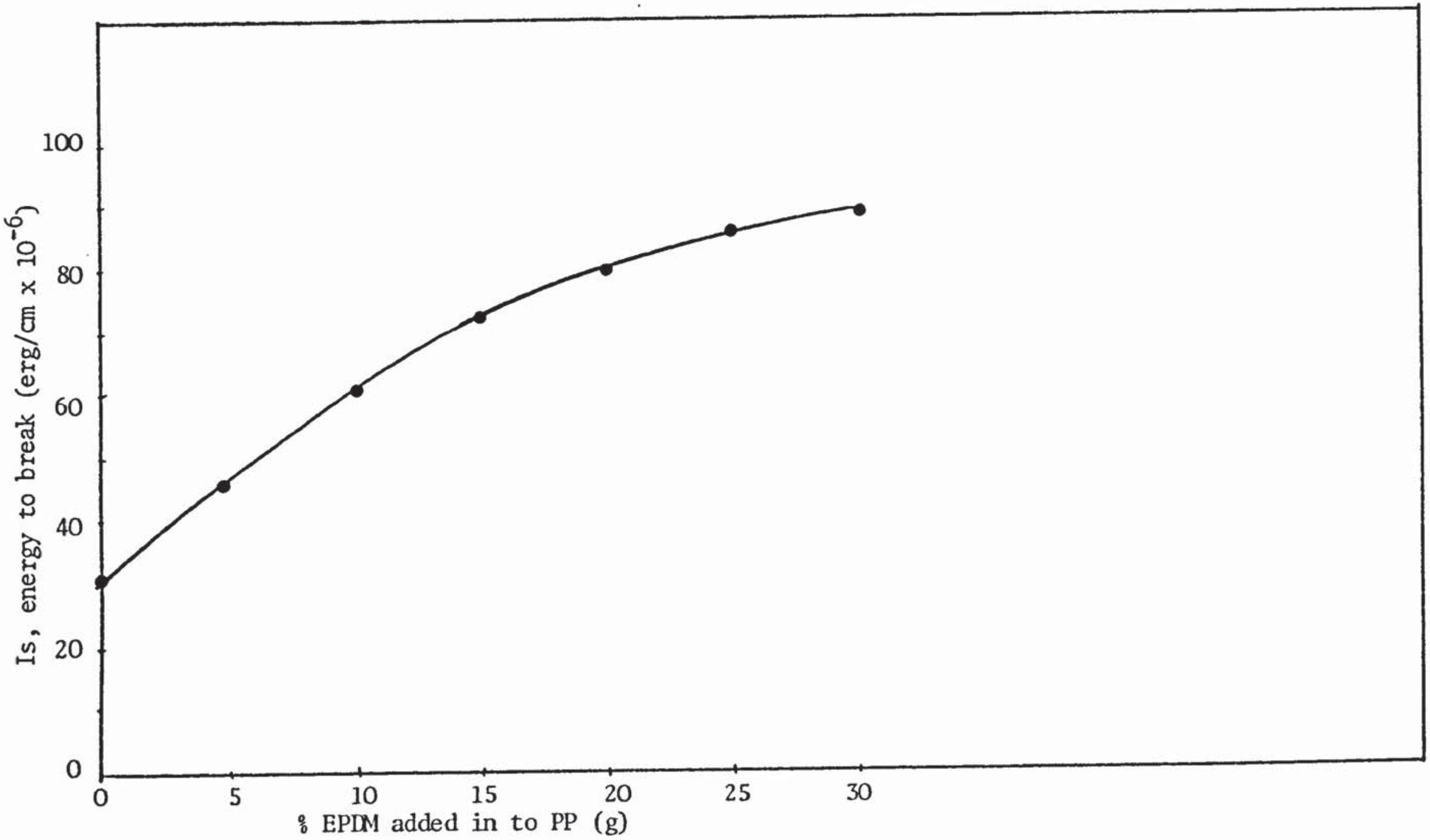


Fig 5.4 Correlation between impact strength (Is) with the concentration of EPDM added to PP. (All samples processed at 180°C/10 mins, closed chamber)

strength (Is) with tan δ (low temperature damping) in polypropylene films containing EPDM (ie 0-30%) is presented in Fig 5.5. There is a linear relationship between these two parameters. A reduction in stiffness is the inevitable penalty for adding rubber to the material and must be weighed against the increased fracture resistance conferred by the rubber. The decrease in tensile strength of polypropylene by addition of EPDM is shown in Fig 5.6. It is also clear from Fig 5.7 that the complex modulus recorded at room temperature decreases with the addition of EPDM rubber into polypropylene films. The changes in melt flow index (MFI) of the samples containing different concentrations of EPDM (ie 0-30%) is shown in Fig 5.8. It clearly demonstrates that the melt flow index decreases as the concentration of EPDM increases.

At low levels of EPDM addition (5% EPDM) MFI decreases very sharply due to the low viscosity of EPDM (ie higher molecular weight distribution), then with further increase in EPDM content, there is a gradual decrease in MFI. Also the microscopic studies of polypropylene films containing 10-30% of EPDM was carried out using optical microscopy and are presented in Plates 5.1, 5.2, 5.3 and 5.4.

5.3.2 Effect of Ethylene-propylene Diene Monomer (EPDM) Concentration on the Photo and Thermal Oxidation of Polypropylene (PP)

Infra-red examination of the unstabilised PP/EPDM blends during uv irradiation shows the effect of EPDM concentration on the rate of

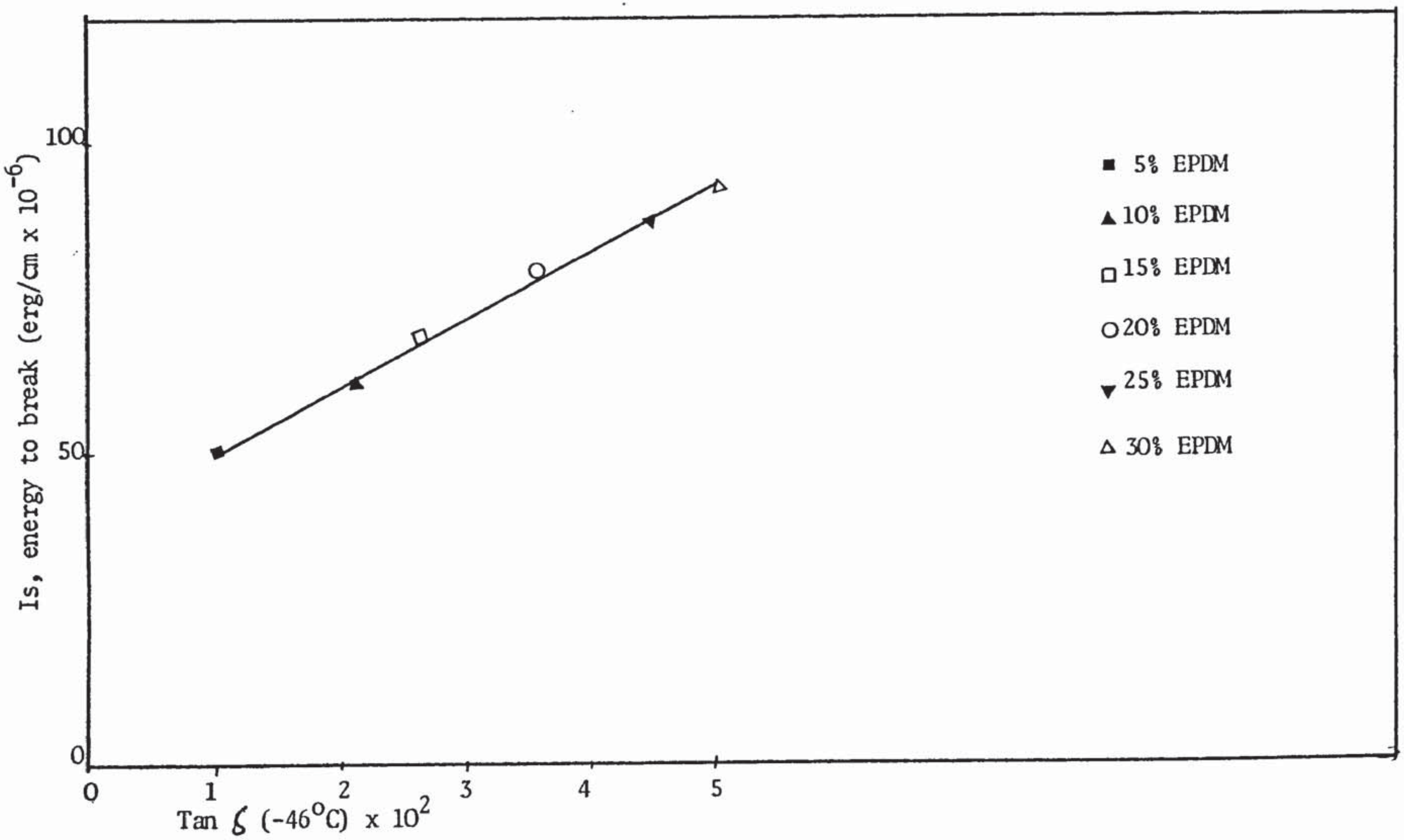


Fig 5.5 Correlation between impact strength (Is) with tan δ (at +46°C) in samples of PP containing EPDM (all samples processed at 180°C/10 mins, closed chamber)

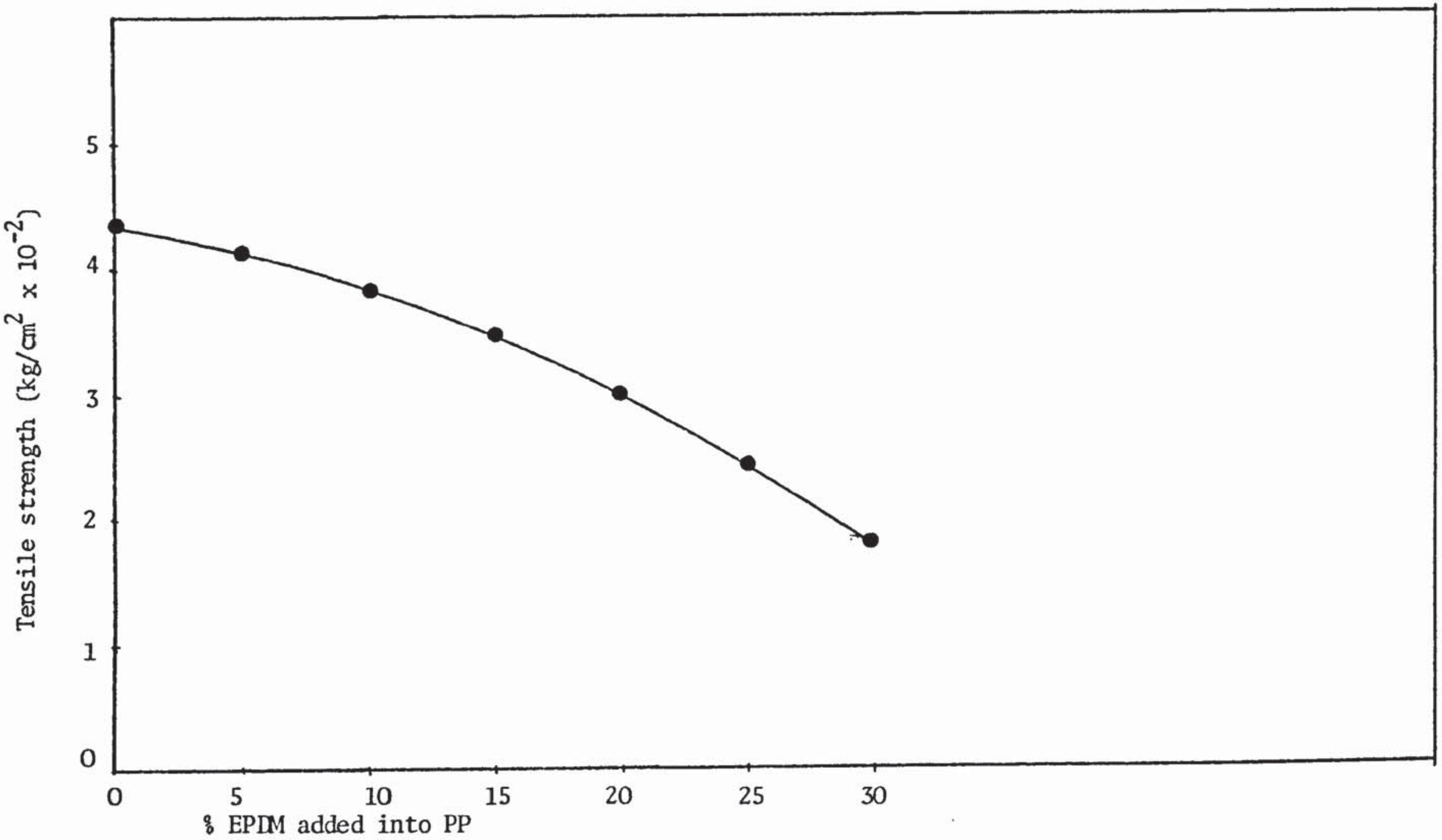


Fig 5.6 Effect of the addition of EPDM on tensile strength of PP films processed at 180^{o}C/10 mins, closed chamber

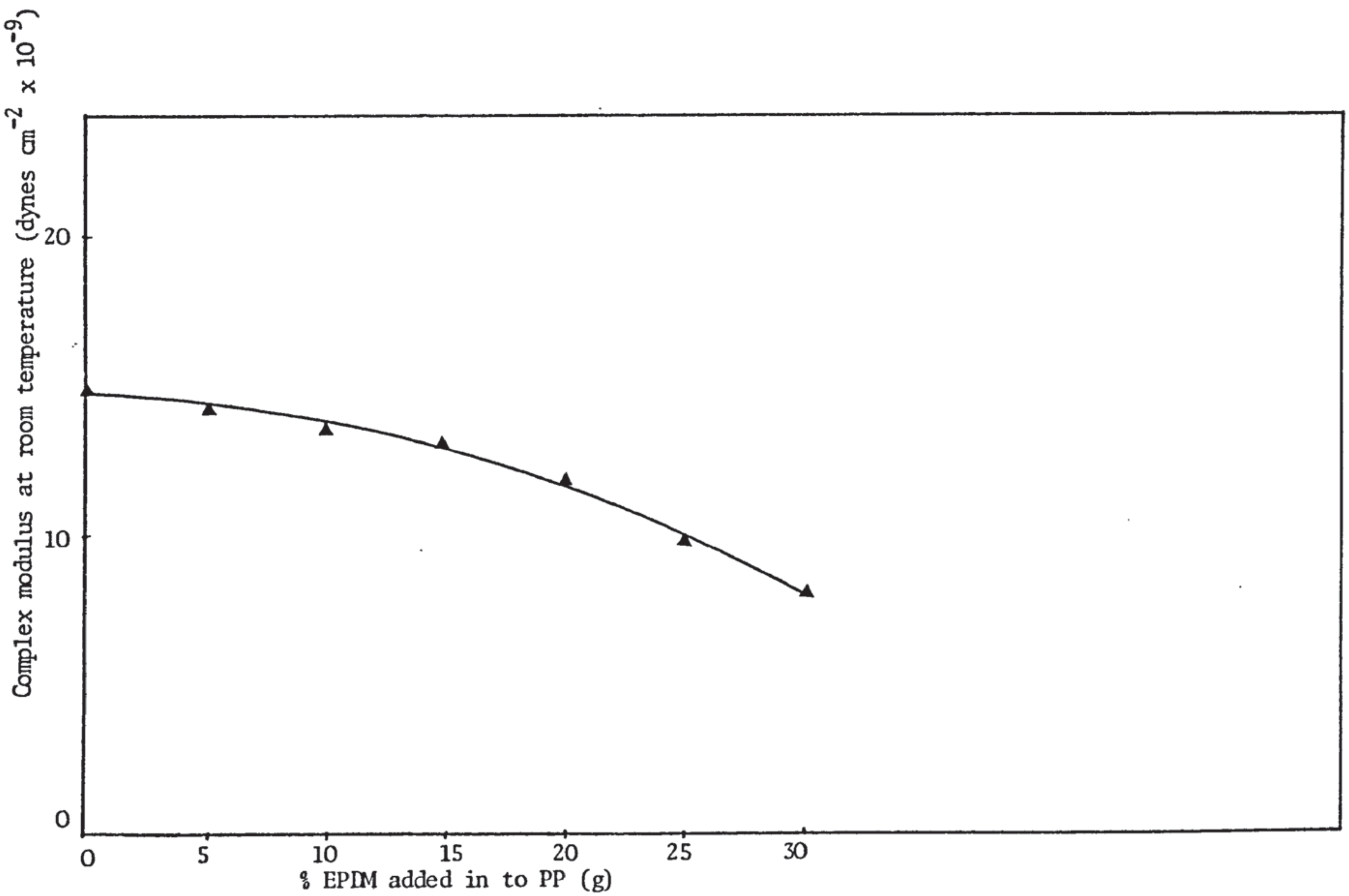


Fig 5.7 Effect of the addition of EPDM on complex modulus of PP films at room temperature (all samples processed at 180°C/10 mins, closed chamber)

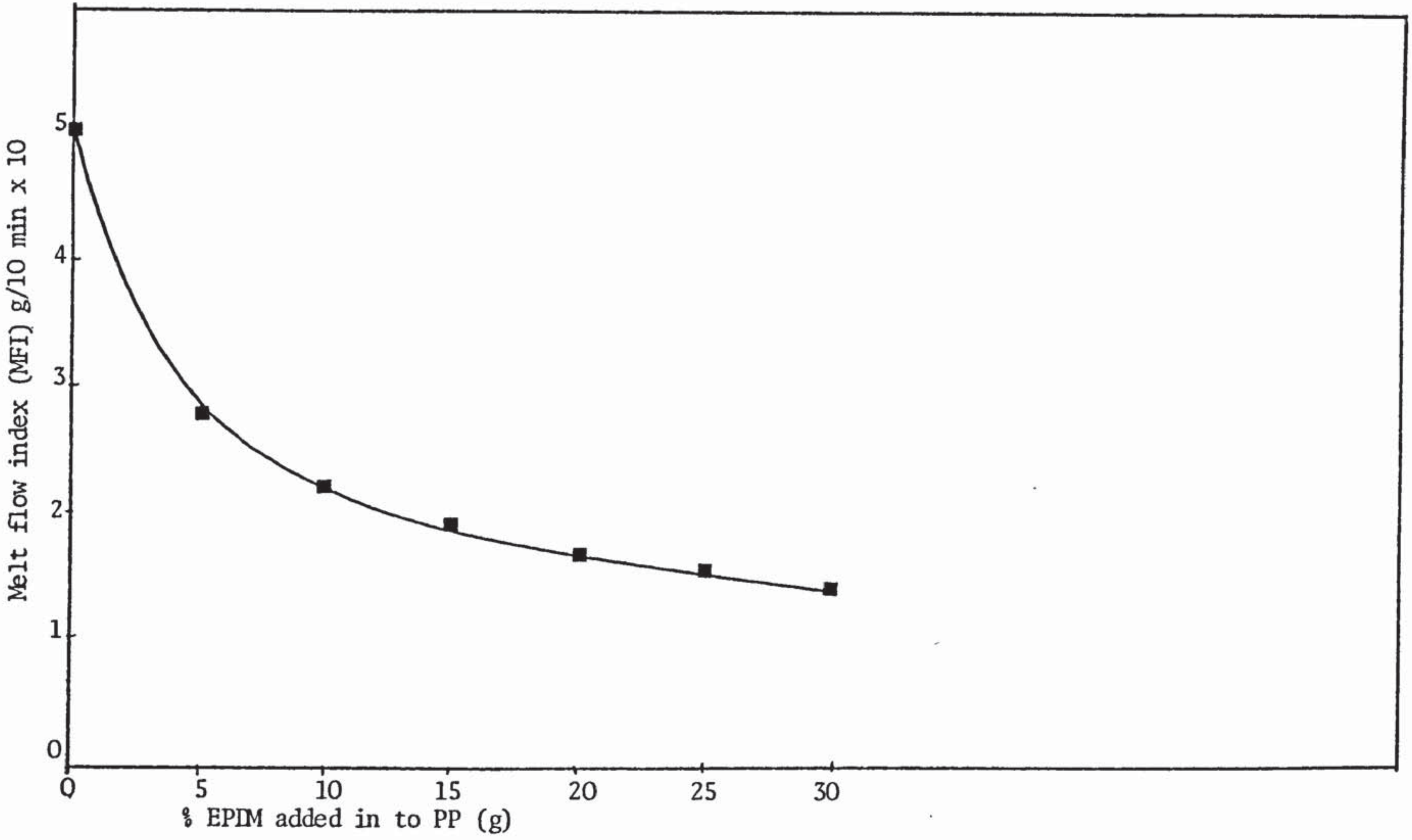


Fig 5.8 Effect of the addition of EPDM on melt flow index (MFI) of PP (all samples processed at 180°C/10 mins, closed chamber)

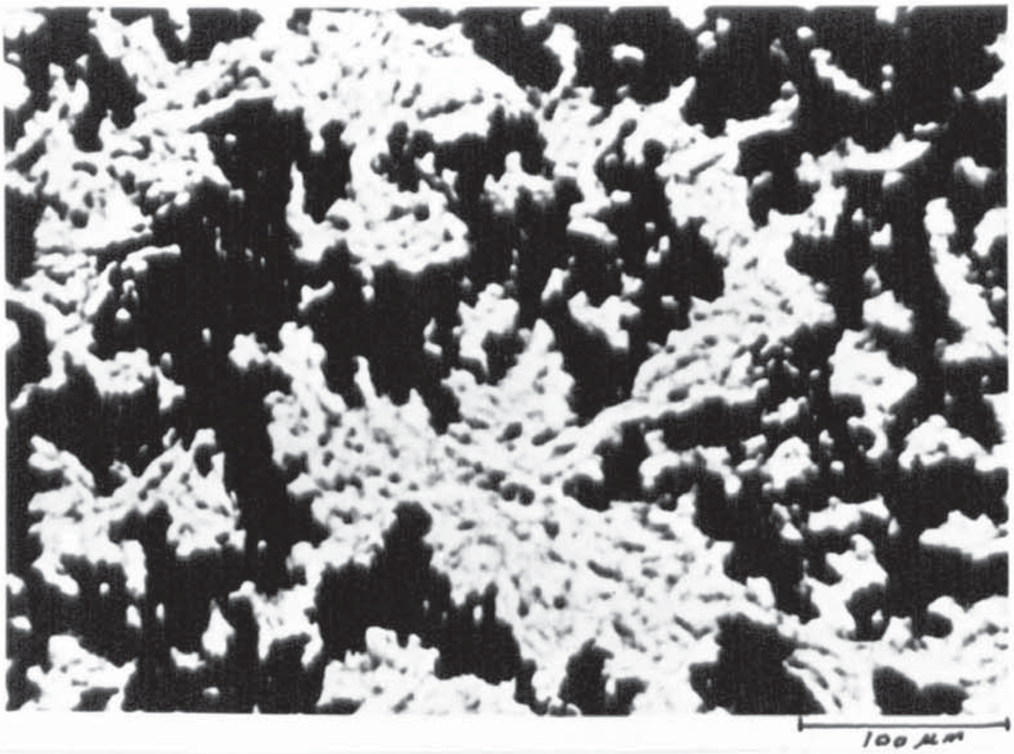


Plate 1 (100% PP) 0.01 cm = 100 micron

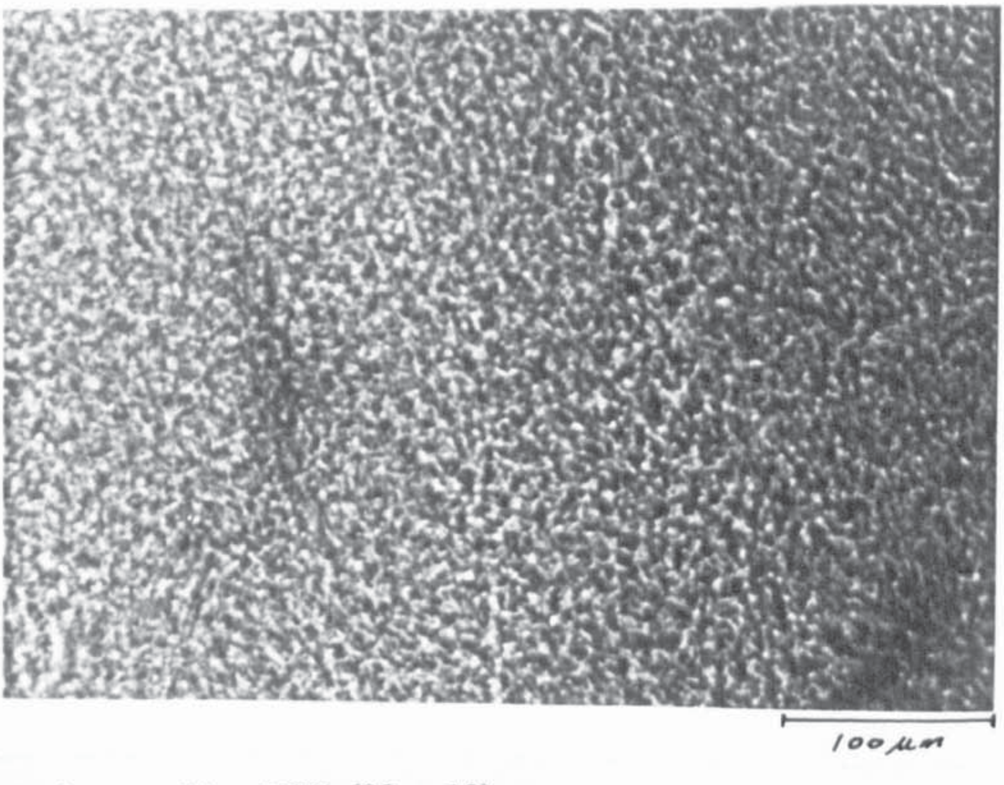


Plate 2 PP : EPDM (90 : 10)

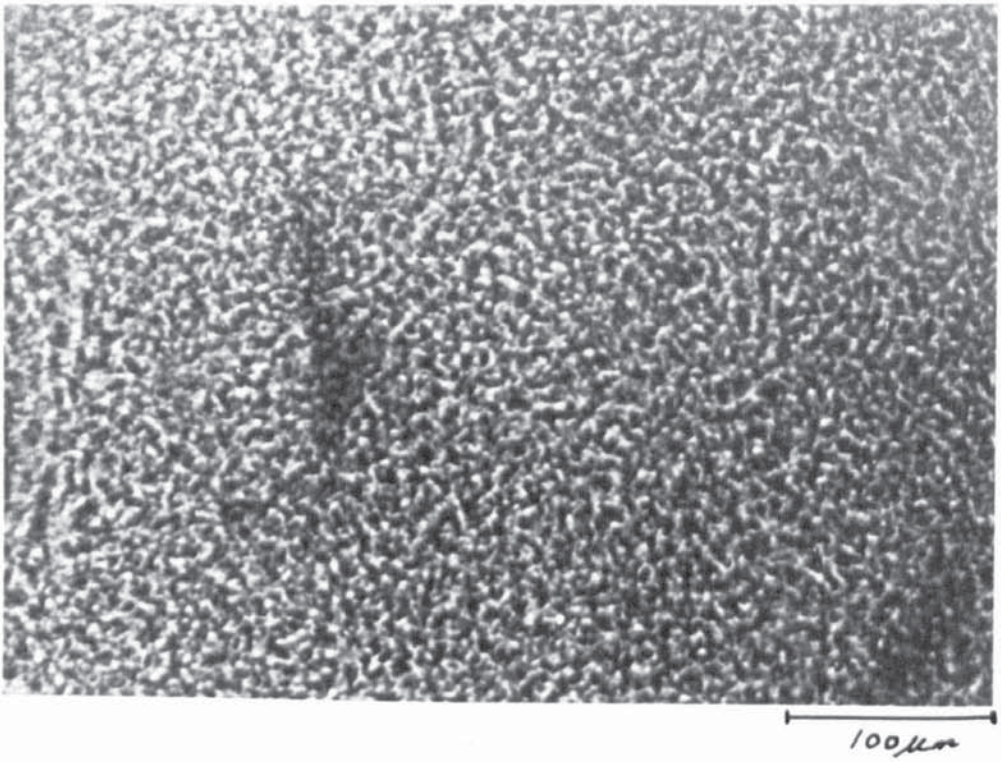


Plate 3 PP : EPDM (80 : 20)

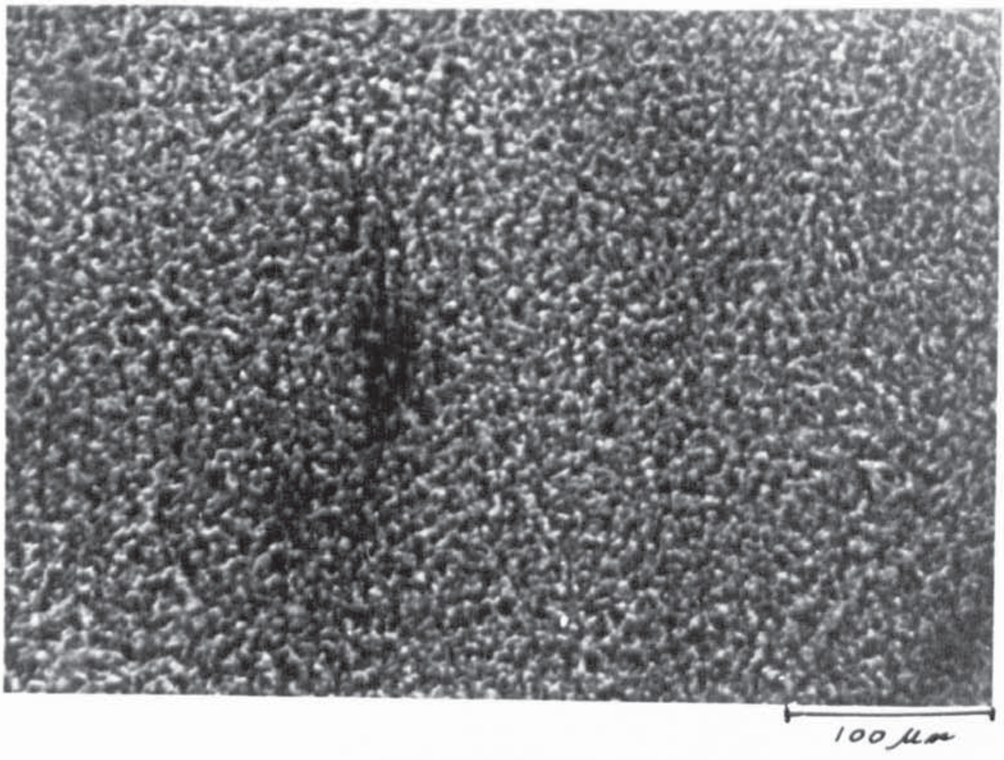


Plate 4 PP : EPDM (70 : 30)

some growing functional groups in the region of 3000-3500 cm^{-1} (OH) and 1700-1715 cm^{-1}(C=O) respectively (Figs 5.9-5.13). Examination of Figs 5.9-5.13 shows that as the concentration of the EPDM is increased, the polyblends show greater susceptibility to ultra-violet light degradation (Fig 5.14). this lower photo-oxidative stability of the polyblends can be attributed to the presence of unsaturation in EPDM. Moreover, the melt processing operation involves a temperature (180°C) under which thermal oxidation of the PP and EPDM would be expected to give hydroperoxides and carbonyl groups which are believed to be the main photo-initiator(151). Although, addition of EPDM into PP increases its photosensitivity to uv light, as measured by carbonyl formation, the embrittlement times of the samples containing EPDM were higher than control polypropylene containing no EPDM (see Table 5.2).

This increase in embrittlement time is due to the diene content of EPDM. The dienes used are selected so that rupture of a double bond on ageing (eg through attack by ozone) does not lead to chain scission (ie the double bond should be part of an in-chain ring or in a pendant grouping). Therefore, the addition of EPDM increases photosensitivity as measured chemically (see Fig 5.14) due to the presence of double bond in the pendant grouping but the embrittlement time is increased due to typical structure of diene which leads to less chain scission(150) (see scheme 5.1). However, on uv exposure of polymers containing polybutadiene segment in which unsaturation is in the main chain such as ABS, SBR, HIPS and impact modified PVC chain scission occurs due to the oxidation of rubber

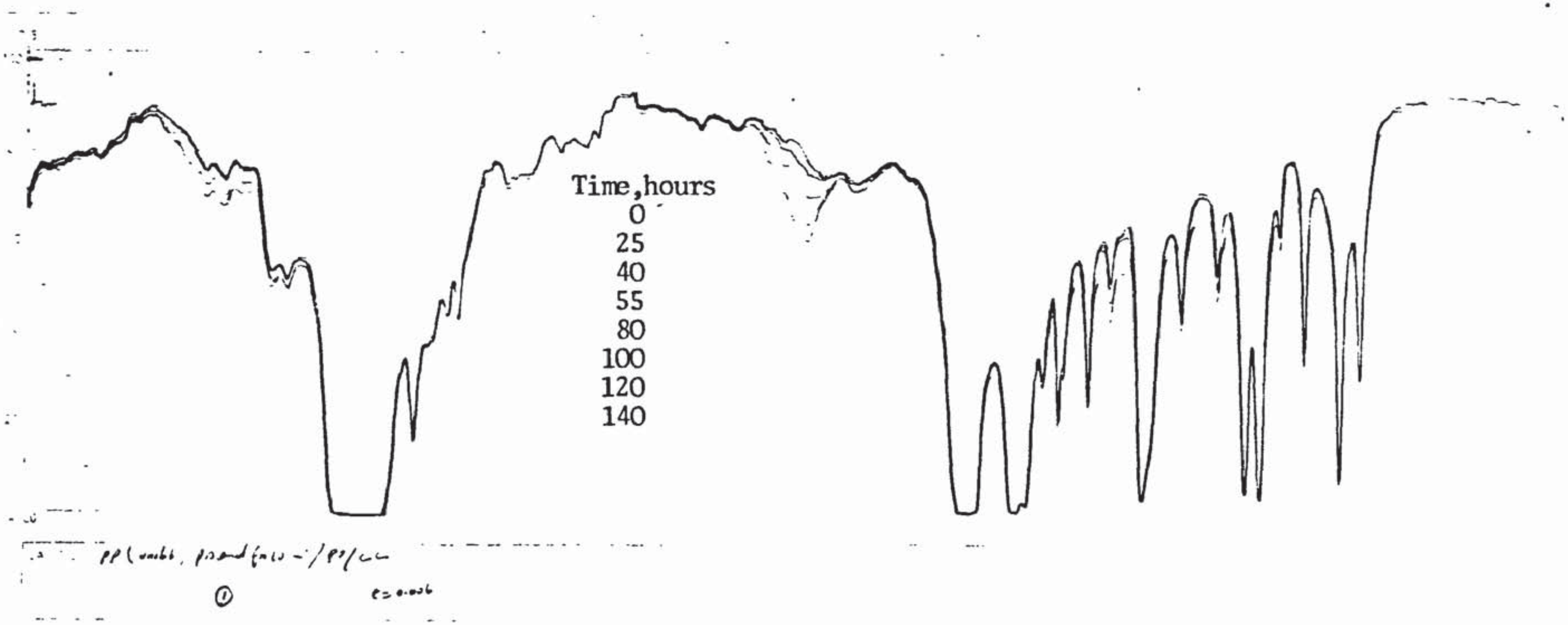


Fig 5.9 Infra-red spectroscopy of PP (100%) film, on uv exposure (numbers on the curve are exposure time in hours)

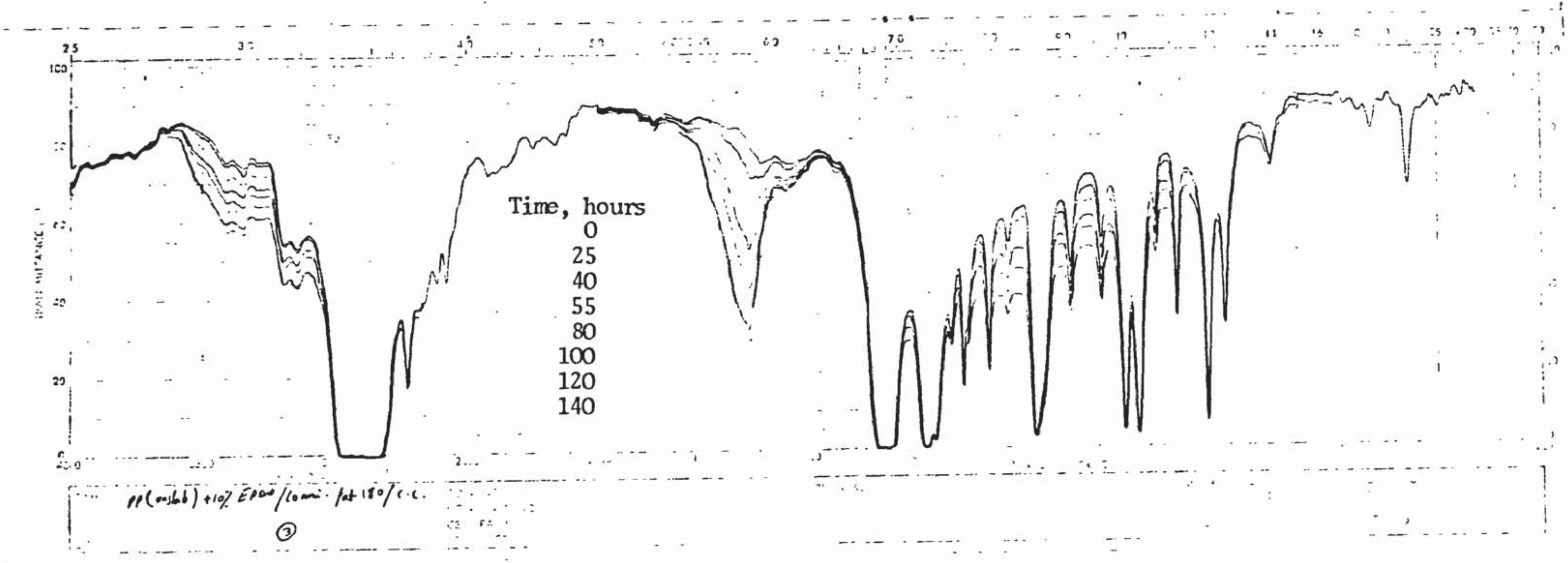


Fig 5.10 Infra-red spectroscopy of PP film containing 10% EPDM on uv exposure (numbers on the curve are exposure time in hours

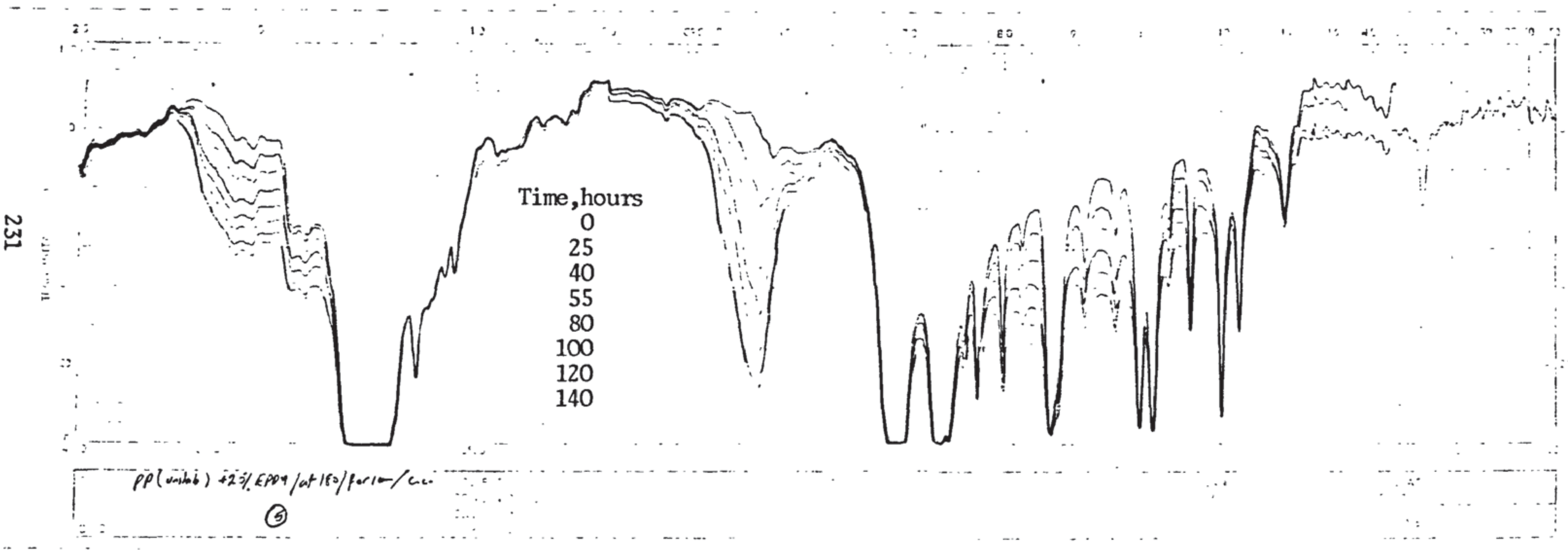


Fig 5.11 Infra-red spectroscopy of PP film containing 20% EPDM on uv exposure (numbers on curve are exposure time in hours)

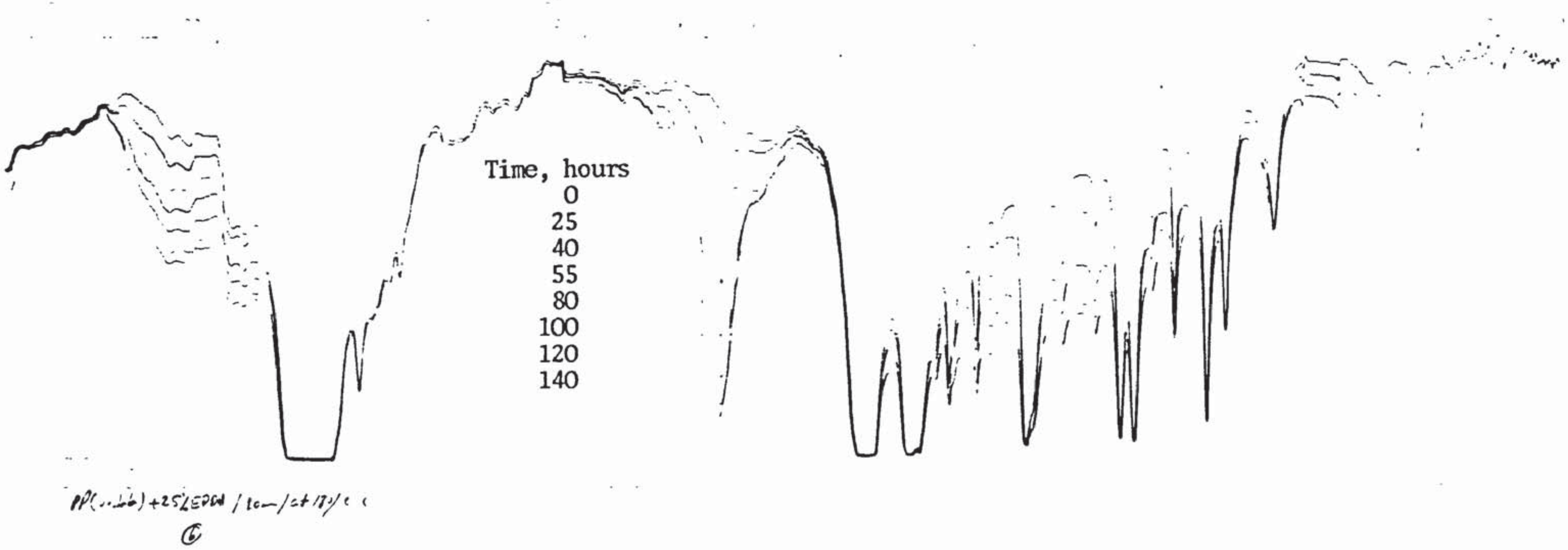


Fig 5.12 Infra-red spectroscopy of PP film containing 25% EPDM on uv exposure (numbers on the curve are exposure time in hours)

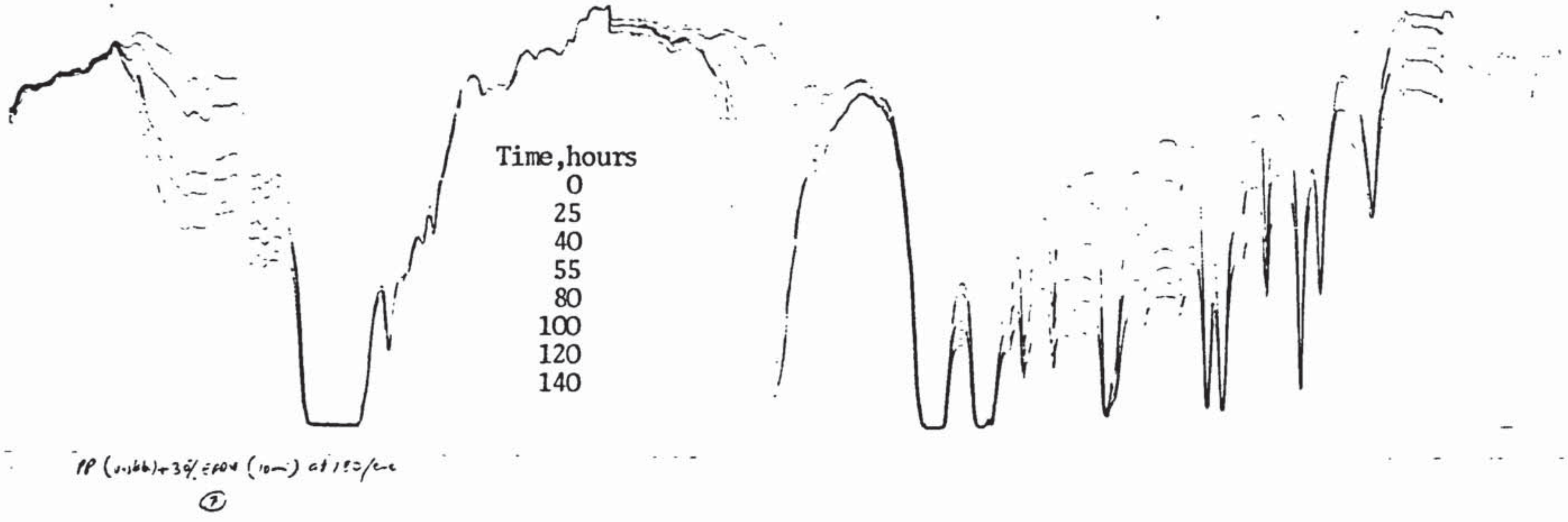


Fig 5.13 Infra-red spectroscopy of PP film containing 30% EPDM on uv exposure (numbers on curve are exposure time in hours)

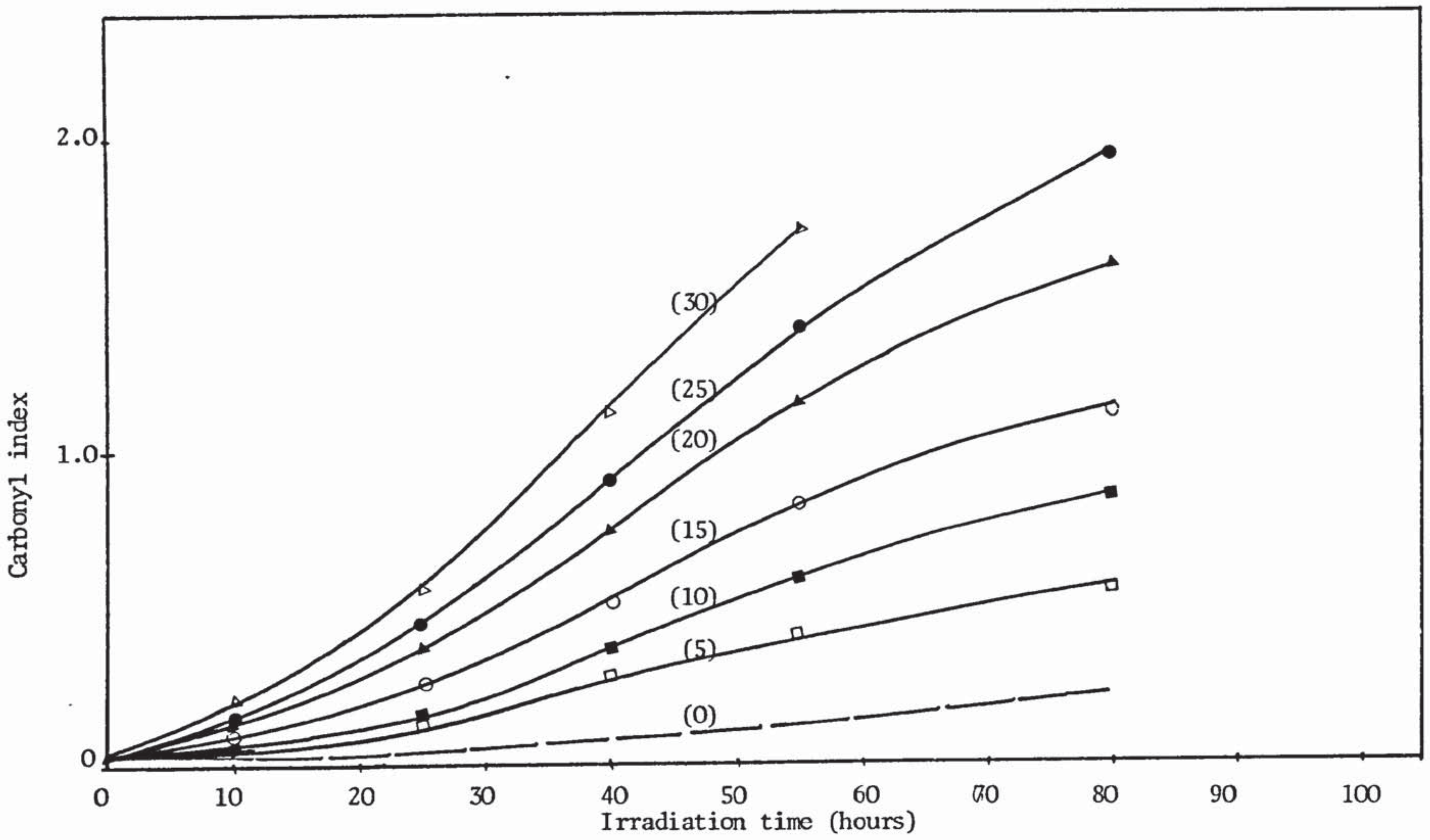


Fig 5.14 Effect of EPDM concentration on carbonyl formation of PP during uv irradiation (numbers on curves are EPDM concentration in percentage)

Table 5.2 Embrittlement time of PP/EPDM blends under uv exposure (hours)

Blend composition PP:EPDM	PP(100%)	95:5	90:10	85:15	80:20	75:25	70:30
Uv exposure embrittlement time (hours)	90	125	135	150	170	190	205

segments leading to loss of useful properties(35,36,104,130). Also the development of carbonyl formation in samples of PP containing different concentrations of EPDM during oven ageing at 140°C is shown in Fig 5.15. Oven ageing embrittlement times are summarised in Table 5.3 which also indicates that the embrittlement time of the PP samples containing EPDM during oven ageing increases as the EPDM concentration is increased (see Fig 5.15). The induction period observed on oven ageing might possibly suggest the presence of a minor amount of antioxidant in commercially supplied EPDM (ie after extraction with acetone).

5.3.3 Photo and Thermal Oxidation of Unstabilised PP/EPDM (75:25) Blend

Non-destructive testing has become increasingly useful for obtaining information about the influence of factors such as molecular composition and molecular weight upon mechanical properties. In a destructive test (impact test) the amount of information available is limited because once an impact test piece is broken, no more information can be obtained on that sample. Dynamic elastic results may be quoted ± 5% with confidence, an accuracy which is not normally associated with standard destructive tests, particularly during degradation, where other factors such as cross-linking are involved. The sample is not broken and repeat results can readily be obtained. This feature represents another advantage of non-destructive testing of the rheovibron type. In this study the carbonyl formation at 1710 cm^{-1}, loss of impact resistance and changes in the height of low demperature damping at

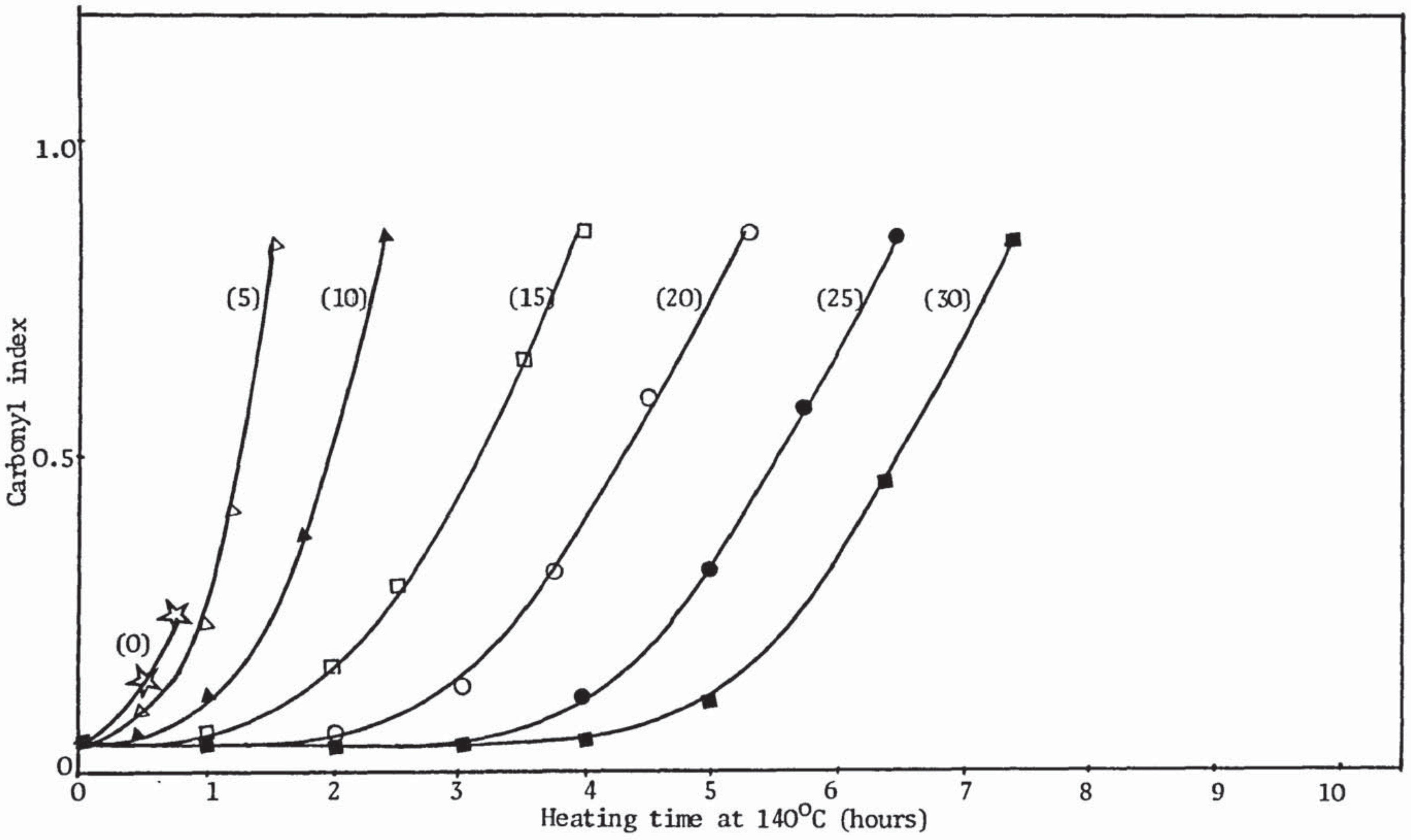


Fig 5.15 Effect of EPDM concentration on carbonyl formation of PP during thermal ageing at 140°C in air (numbers on curves are EPDM concentration in percentage)

Table 5.3 Embrittlement time of PP/EPDM blends during oven ageing at 140°C (hours)

Blend composition PP:EPDM	PP(100%)	95:5	90:10	85:15	80:20	75:25	70:30
Oven ageing embrittlement time, minutes	40	100	150	160	230	480	540

$-46^{o}C$ on uv exposure were studied and their correlation were investigated.

5.3.3a Photo-oxidation of Unstabilised PP/EPDM (75:25) Blend

The changes in height of low temperature damping at $-46^{o}C$ was measured by rheovibron during uv exposure on a sample of polypropylene/EPDM (75:25) blend. Only one sample was used throughout the measurement with thickness identical to those which were used for infra-red and impact strength (0.015 cm). The ageing of this sample was interrupted frequently for low temperature damping measurements. The temperature range was from $-100^{o}C$ to $0^{o}C$ and reading of tan δ was carried out while the temperature of sample was allowed to rise to $0^{o}C$. As it can be seen from Fig 5.16, the change in the height of tan δ and shift to higher temperature during photo-oxidation. There was a sharp decrease in tan δ at first 60 hours of uv irradiation, then with further irradiation, the changes in tan δ was not significant. It was not possible to measure tan δ after 140 hours of uv irradiation and sample broke under stress. The development of carbonyl group at 1710 cm^{-1} was measured in a sample of PP film containing 25% EPDM and it is represented in Fig 5.17 as carbonyl index versus irradiation time. It indicates that the carbonyl groups were produced rapidly during uv irradiation. The changes in impact properties of PP/EPDM (75:25) was measured as a function of uv irradiation time (Fig 5.18). It can be seen that there is a sharp decrease in impact properties of the blend then followed by a gradual decrease and break. The sharp decrease may

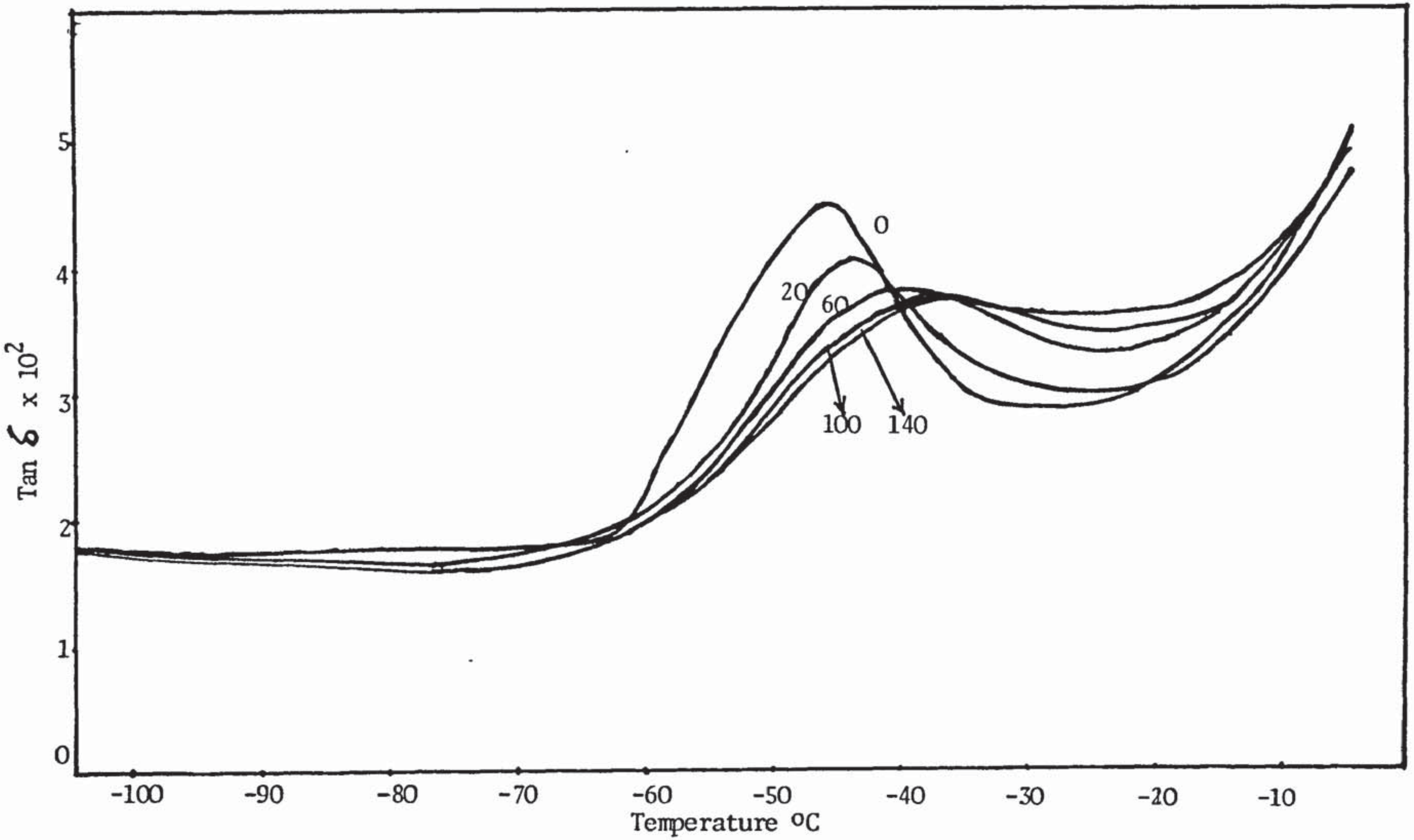


Fig 5.16 Effect of photo-oxidation on low temperature damping (-46°C) of PP/EPDM (75:25) (numbers on curves are hours of uv irradiation)

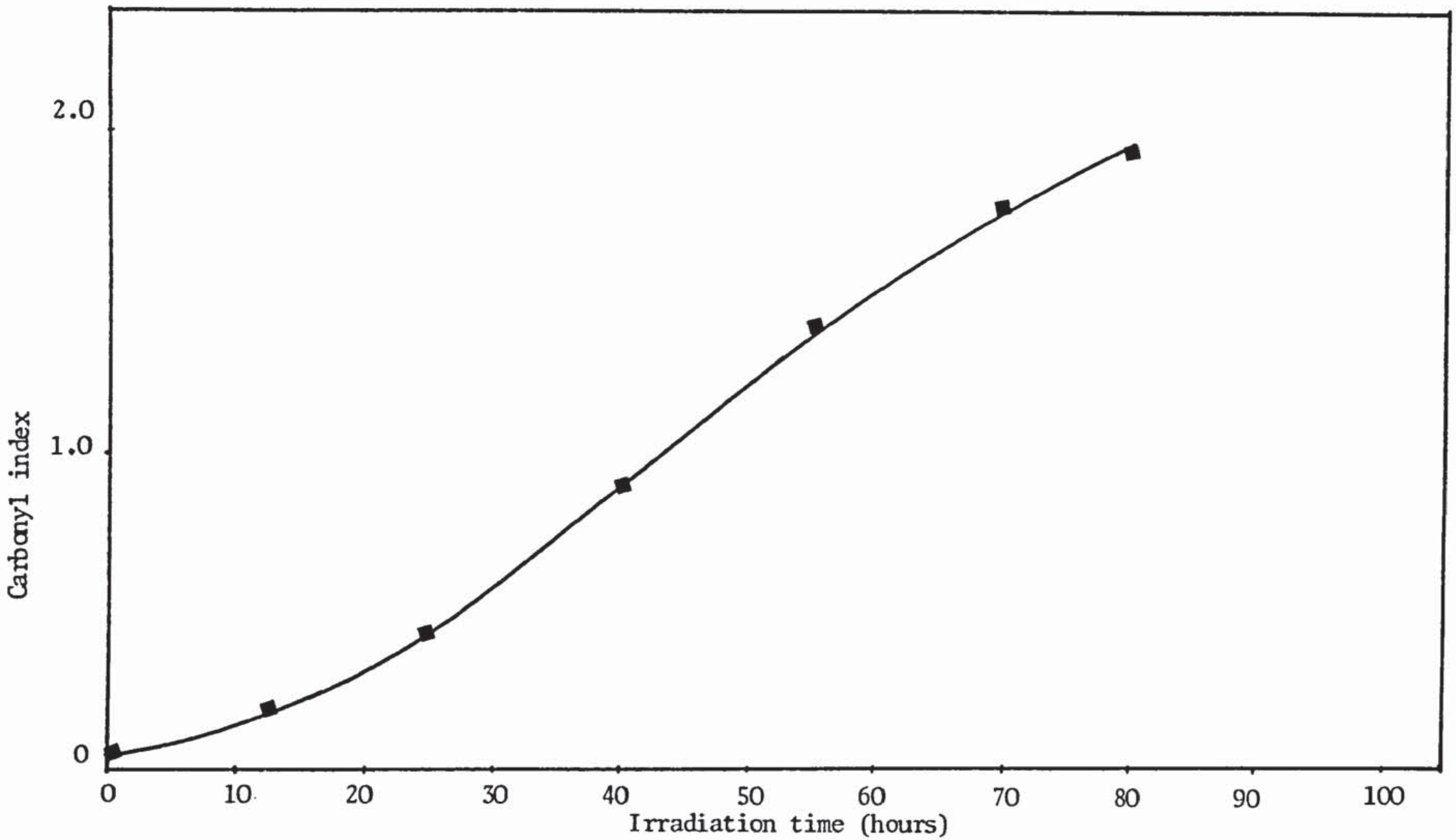


Fig 5.17 Effect of uv irradiation on carbonyl formation of PP/EPDM (75:25) processed at 180°C/10 mins closed chamber

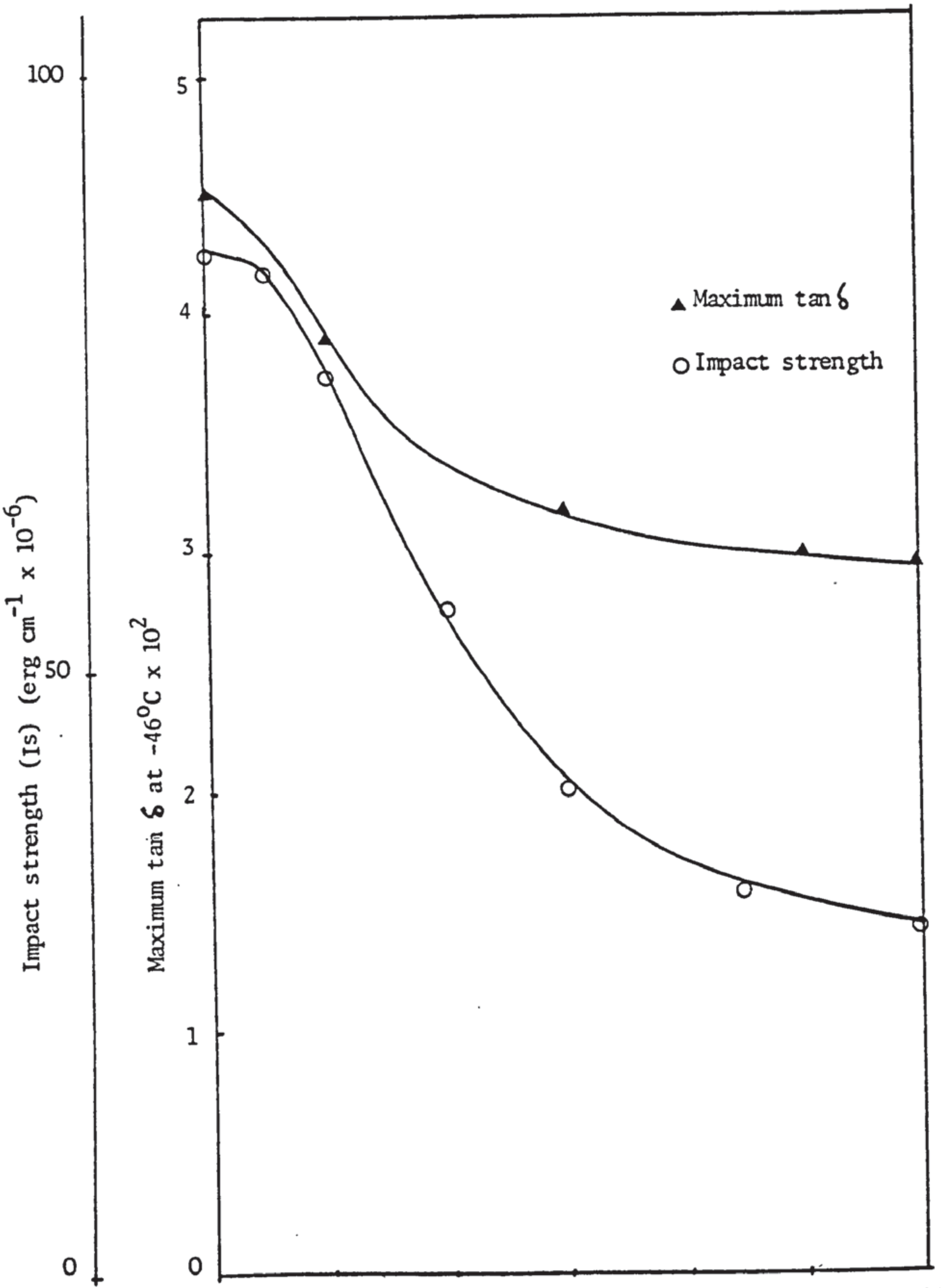


Fig 5.18 Impact strength and maximum height of tan δ peak at -46°C of unstabilised PP:EPDM (75:25) are shown against uv irradiation time (hours)

be due to the oxidation of EPDM part of the blend which is related to the toughening agent, rubber, in the blend. Then polypropylene part degrades until the sample breaks. It is also clear from Fig 5.18 that there is initially a sharp decrease in the height of the damping which is due to the destruction of rubber (EPDM) during uv irradiation (around 100 hours of irradiation), then a gradual decrease up to 140 hours of irradiation. It was not possible to continue the measurement after 140 hours of irradiation and sample broke during the test (under stress).

5.3.3b Thermal-oxidative Degradation of Unstabilised PP:EPDM (75:25) Blend

Compression moulded uv stabilised PP/EPDM (3:1) blends were oven aged at 140°C in air and the changes in the concentration of functional groups were monitored by infra-red spectroscopy, impact strength by falling weight tester and low temperature damping by rheovibron viscoelastometer.

The carbonyl group showed an induction period of 4 hours at 140°C in an air oven. The rapid development of this functional group after the induction period was quite similar to that observed on photo-oxidation. The changes in the carbonyl group is shown as ratio to the absorption at 2710 cm^{-1} against time of heating at 140°C (Fig 5.19).

The change in the height of low temperature damping at -46°C, was

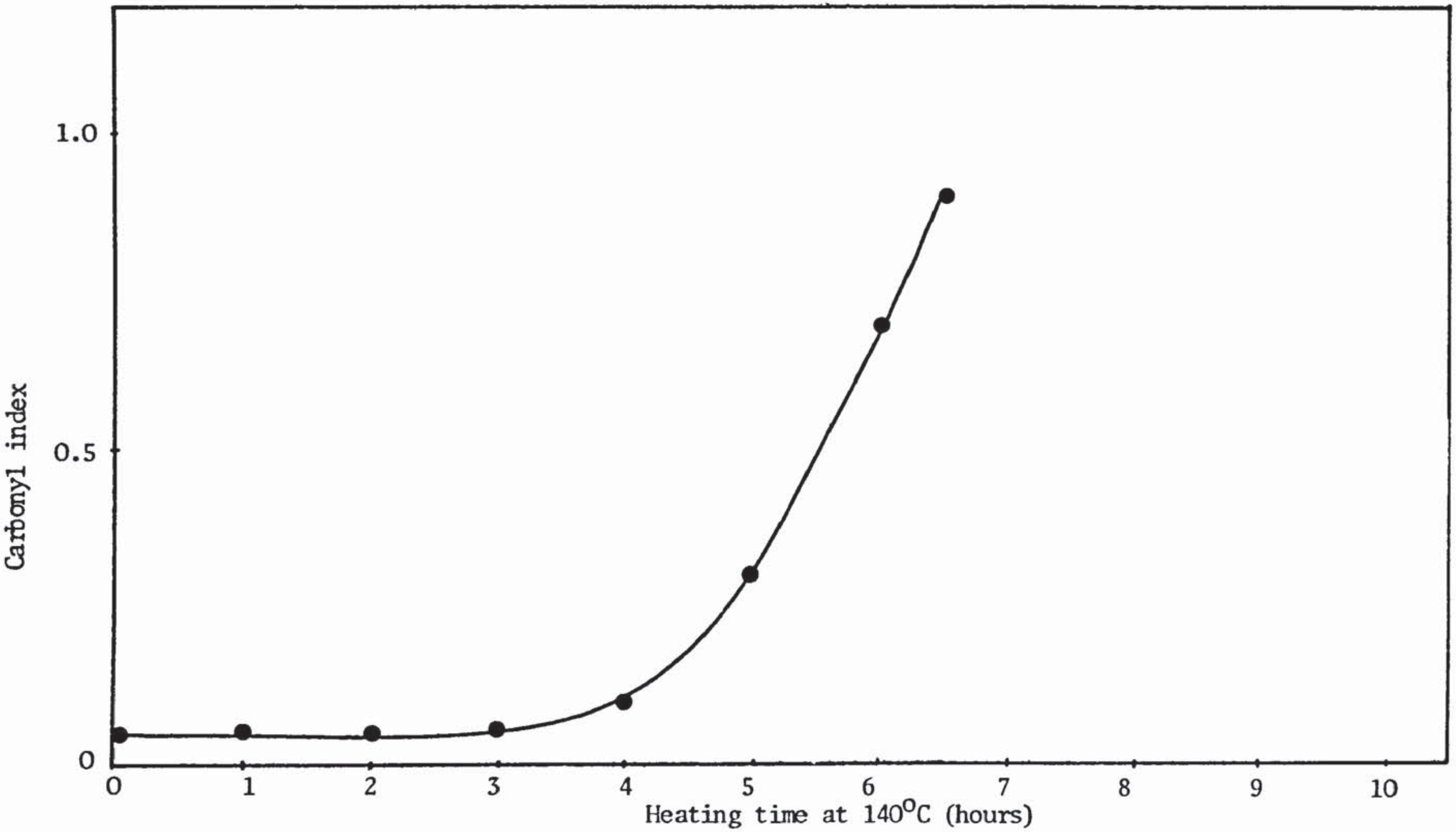


Fig 5.19 Development of carbonyl in PP:EPDM (75:25) during oven ageing at 140°C in air (samples processed at 180°C/10 mins, closed chamber)

measured by rheovibron during oven ageing at 140°C in air. Only one sample was used throughout the measurement with thickness identical to those which were used for infra-red and impact strength (0.015 cm). The ageing of the samples was interrupted frequently for low temperature damping measurements. The method used was similar to that used for photo-oxidation. The temperature range was from -100 to 0°C and the reading of tan δ was carried out while the temperature of the sample was allowed to rise to 0°C. As it can be seen from Fig 5.20, the change in the height of tan δ and shift to higher temperature during thermal oxidation is similar to that observed during photo-oxidation. After 7 hours heating, samples could not normally be tested at low temperature due to fracture. The impact strength of unstabilised PP/EPDM (75:25) blend films of identical thickness were measured during oven ageing at 140°C in air by falling weight impact tester. The impact strength showed an induction period about 3 hours, then a sharp fall and reached the lowest value after 8 hours of ageing (Fig 5.21). It can be seen from Fig 5.21 that the maximum tan δ during oven ageing shows an induction period of 3-4 hours then followed with a sharp decrease and failure.

5.3.4 Stabilisation of PP/EPDM (75:25) Blend During Photo and Thermal Oxidation

Compression moulded PP:EPDM(75:25)films containing different amounts of bound antioxidants (ie EBHPT, MADA and DBCMS) and commercial antioxidants (NiDEC, NiDBC, UV531, Irganox 1076 and Tinuvin 770) were

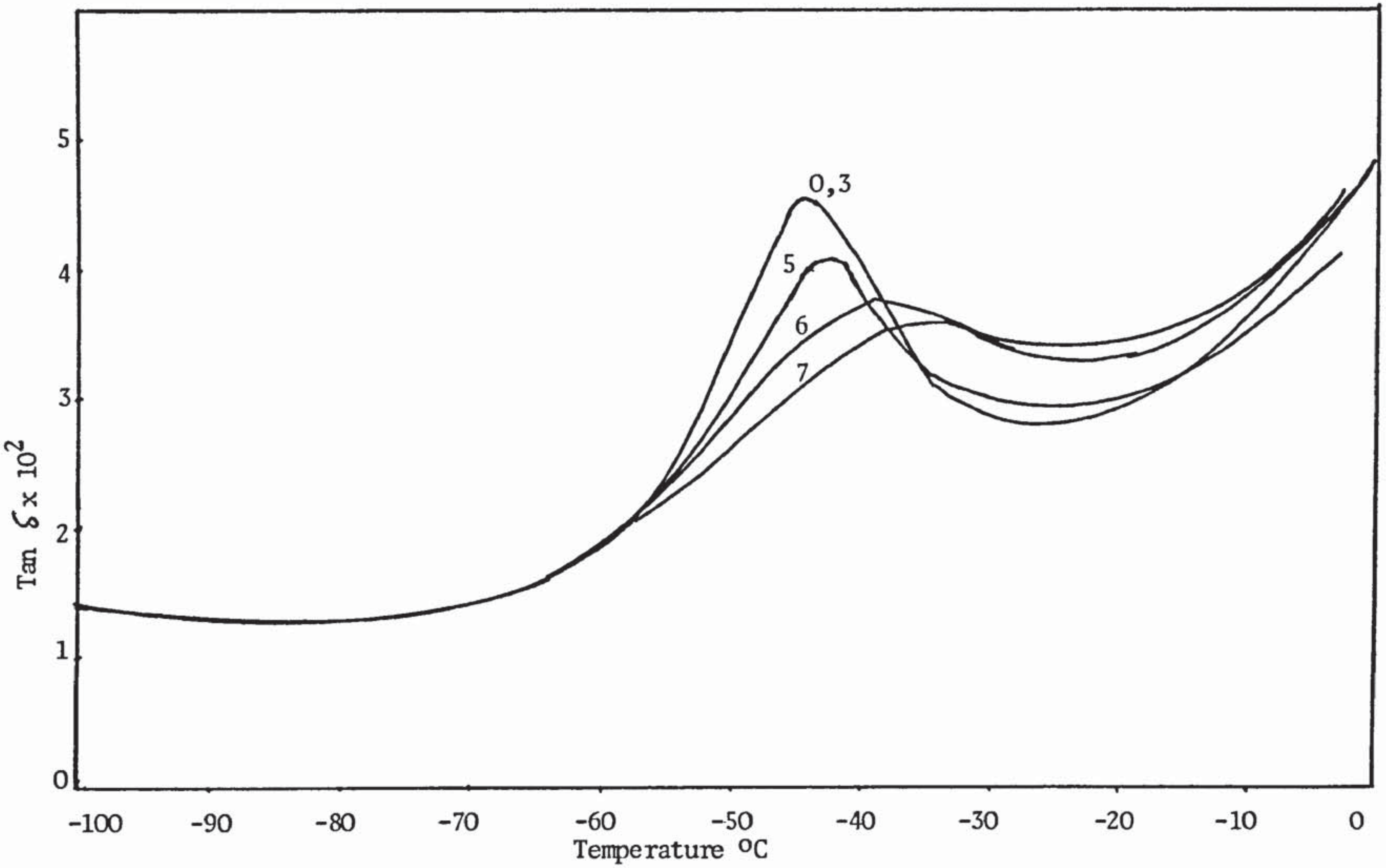


Fig 5.20 Effect of thermal oxidation on low temperature damping (-46°C) of PP/EPDM (75:25) (numbers on curves are hours of oven ageing at 140°C

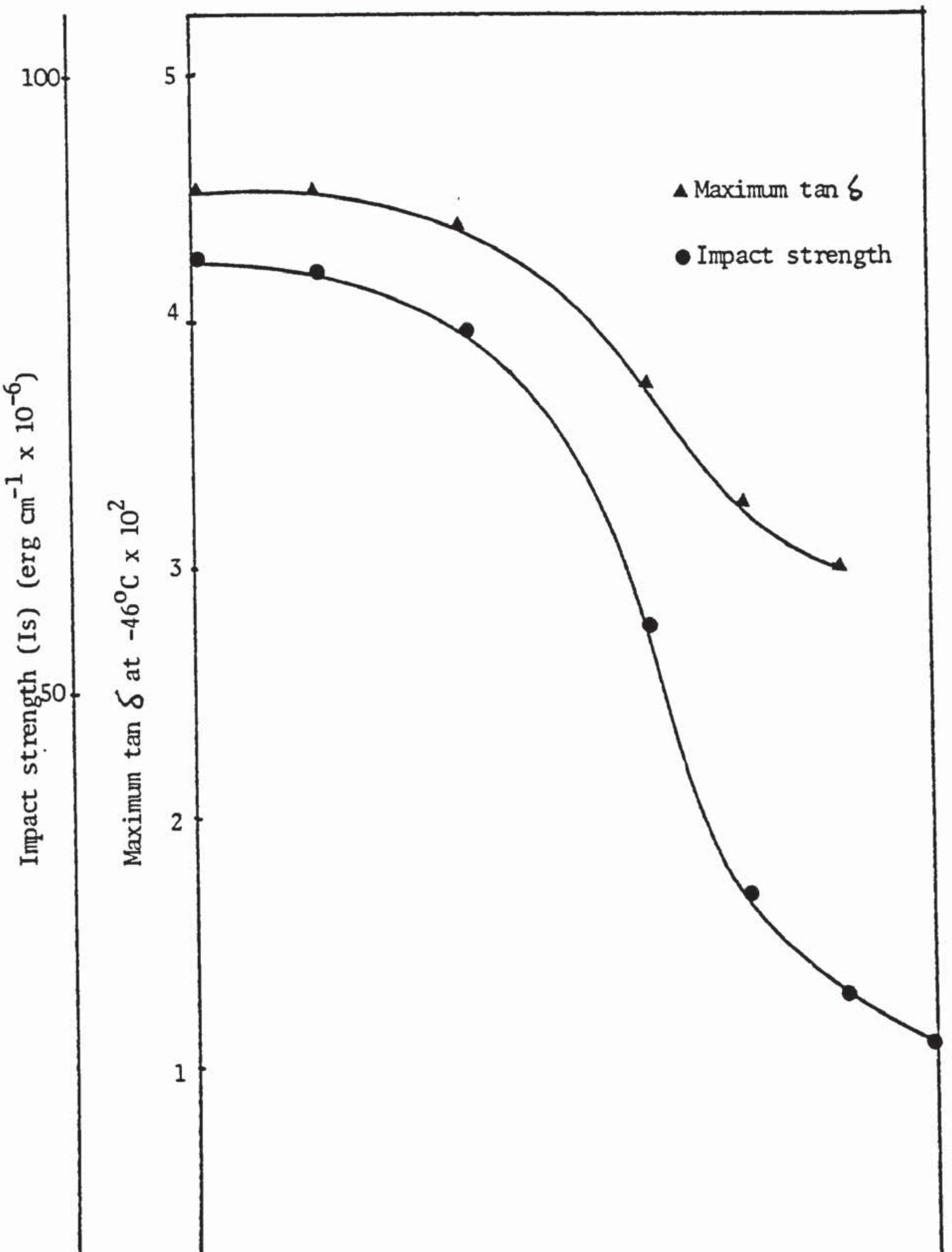


Fig 5.21 Impact strength and maximum height of tan δ at -46°C of unstabilised PP:EPDM (75:25) are shown against thermal ageing at 140°C (hours)

photo and thermo oxidised under identical conditions. Three concentrations of EBHPT and MADA were made from 2, 5 and 10% masterbatches in the solid stage (see sections 4.1.5.1 and 4.1.6.1 for masterbatch preparation). The changes in the functional group, impact strength and dynamic mechanical property of stabilised PP:EPDM (75:25) were measured during photo and thermal degradation.

5.3.4a Photo-oxidation of Stabilised PP:EPDM (75:25) Blend

The infra-red measurements of the functional group (carbonyl group) is plotted against time of exposure for diluted samples made from masterbatches of 2, 5 and 10% (see Table 4.1 for percent binding) in the solid stage and are shown in Figs 5.22, 5.23 and 5.24. The functional group show induction period proportional to the concentration of uv stabiliser. The induction periods and embrittlement times are given in Table 5.4. It is clear from Figs 5.22 and 5.23 that samples containing higher percentage of bound antioxidant after extraction have better photostability. The photostability of PP:EPDM (75:25) films containing different concentrations of unextracted MADA bound (ie 3×10^{-4}, 6×10^{-4}, 9×10^{-4} and 12×10^{-4} mol/100 g of polymer) is shown in Fig 5.24. Increasing bound MADA concentration from 3 to 12×10^{-4} ml/100 g increases induction period and embrittlement time of the samples. The time to embrittlement and induction period of PP:EPDM (75:25) films are given in Table 5.5.

Photo-stability of samples containing conventional antioxidant such

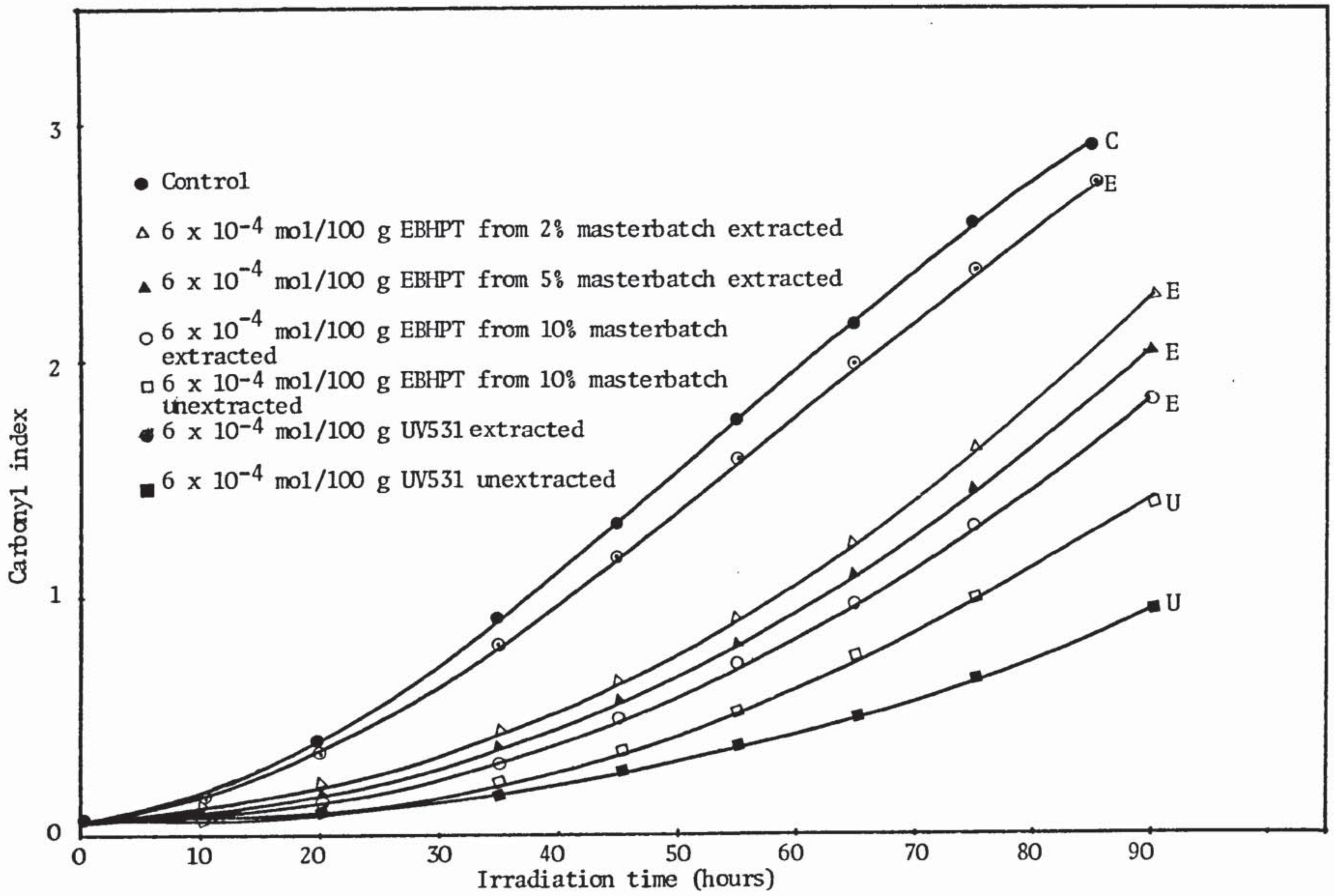


Fig 5.22 Development of carbonyl functional group on uv exposure of PP:EPDM (75:25) film, EBHPT masterbatches were diluted at solid stage (E = extracted, U = unextracted and C = control)

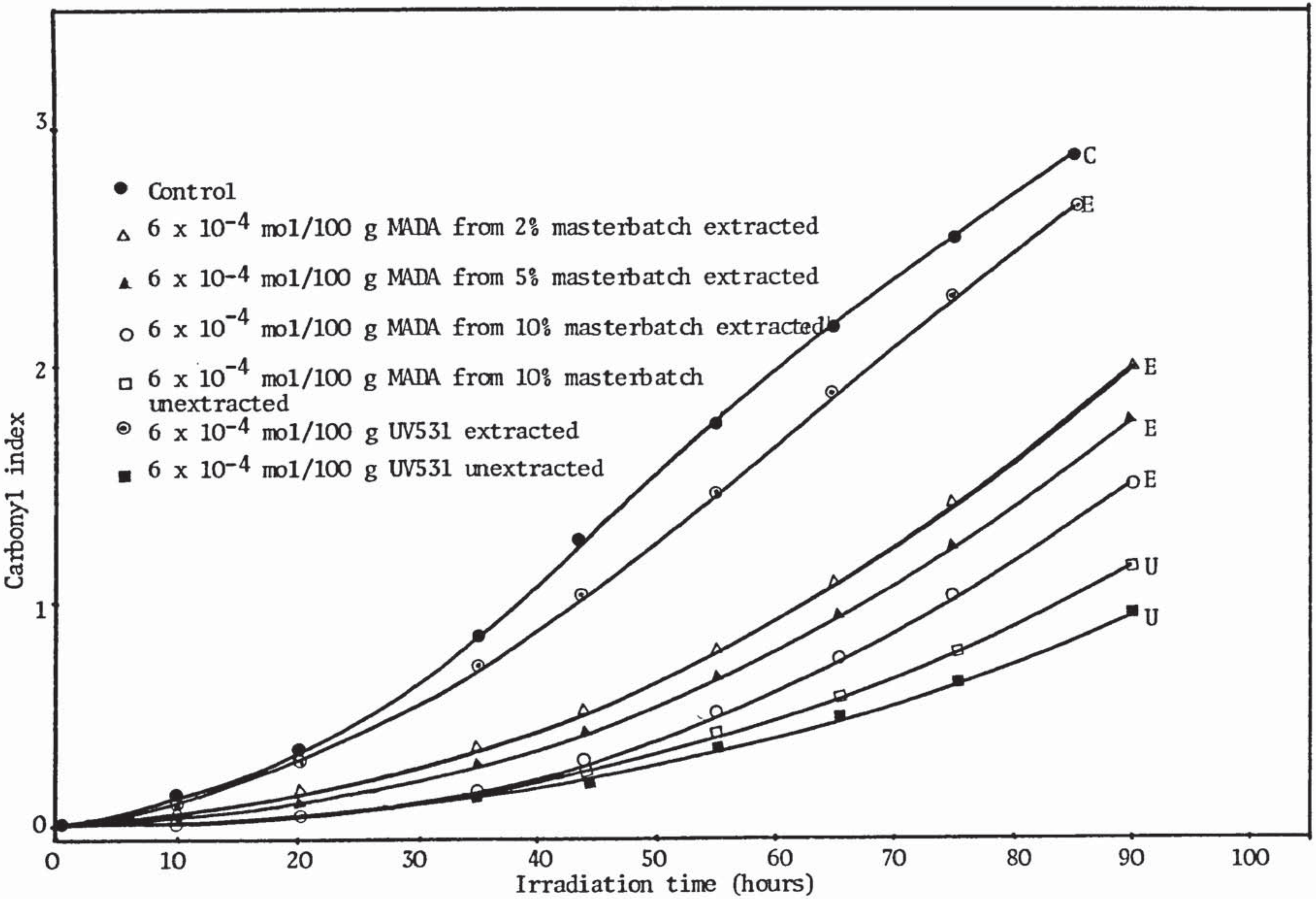


Fig 5.23 Development of carbonyl functional group on uv exposure pf PP:EPDM (75:25) film, MADA masterbatches diluted at solid stage (E = extracted, U = unextracted, C = control)

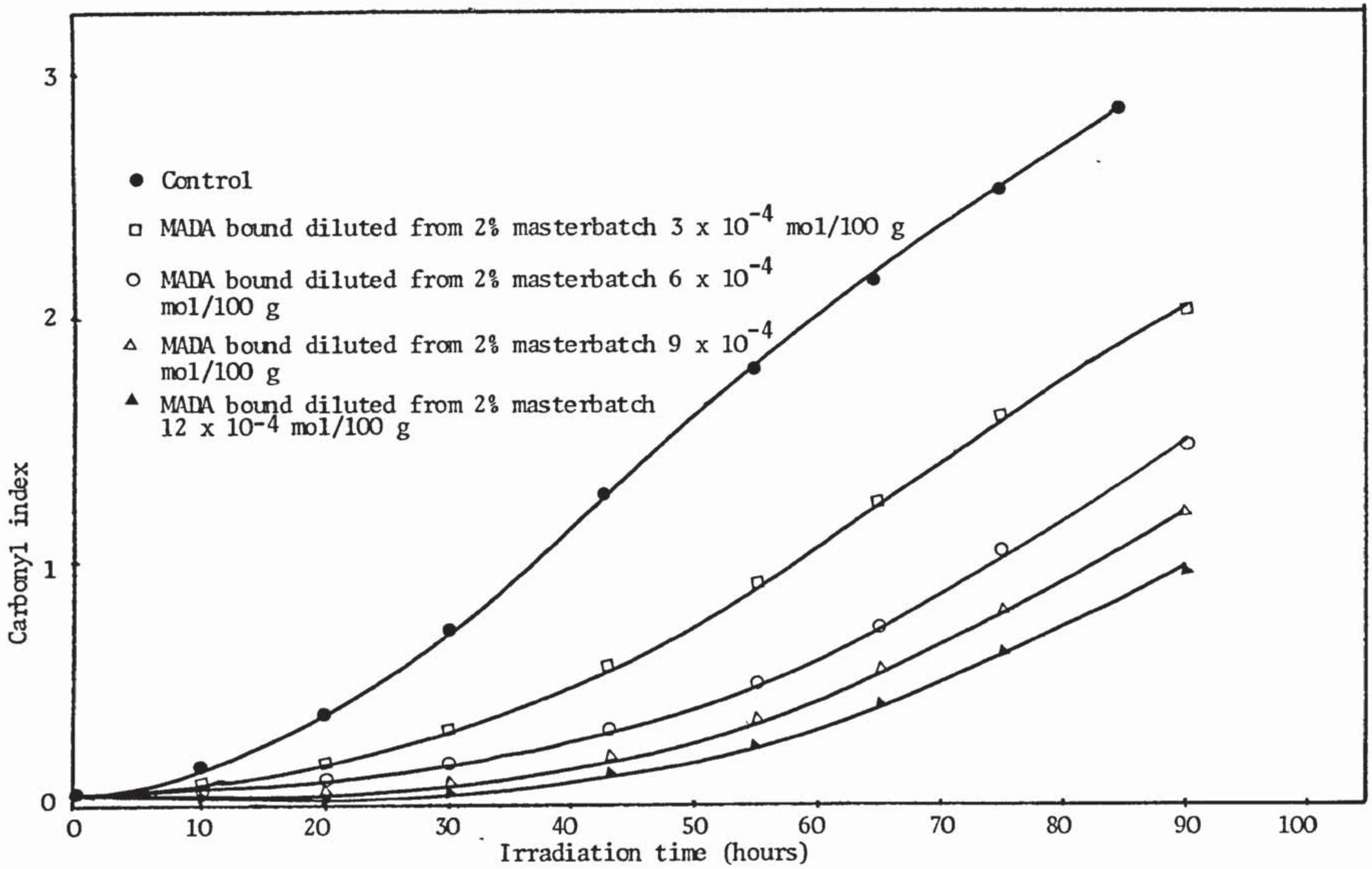


Fig 5.24 Development of carbonyl (1710 cm^{-1}) on uv irradiation of PP:EPDM (75:25) blend, processed at 180°C/10 mins, closed chamber

Table 5.4 Concentration of EBHPT and MADA before and after extraction in the adducts made from masterbatches, their induction periods and embrittlement times, in PP/EPDM (75:25) on uv exposure (U = unextracted, E = extracted)

Stabiliser type	Conc of masterbatch pph	Conc of dilute before extraction		Conc of dilute after extraction	Induction Period after extraction hours	Embrittlement time after extraction hours
		mol/100g	g/100g	g/100g		
Control	-	-	-	-	5-7 5-7	180
EBHPT	2	6x10^{-4}	0.2	0.13	18	290
	5	"	0.2	0.14	20	300
	10	"	0.2	0.155	25	310
	U	"	0.2	-	30	330
MADA	2	6x10^{-4}	0.155	0.116	22	280
	5	"	0.155	0.127	24	300
	10	"	0.155	0.135	29	315
	U	"	0.155	-	35	330
UV531 (HOBP)	U	6x10^{-4}	0.196	-	45-50	400
	E	-	-	-	5-7	200

Table 5.5 Induction period and embrittlement time of PP:EPDM (75:25) films containing MADA bound diluted from 2% masterbatch (unextracted)

Stabiliser type	Concentration of dilute		Induction Period hours	Embrittlement time hours
	mol/100 g	g/100 g		
Control	-	-	5-7	180
MADA	$3x10^{-4}$	0.078	22	260
MADA	$6x10^{-4}$	0.155	35	330
MADA	$9x10^{-4}$	0.232	42	400
MADA	$12x10^{-4}$	0.310	46	430
UV531	$6x10^{-4}$	0.196	45-50	400

as NiDEC, NiDBC, Irganox 1076, UV531 and Tinuvin 770 were measured. Fig 5.25 represents the development of carbonyl group on uv exposure in the samples of PP:EPDM (3:1) containing 3 x 10^{-4} mol of additive per 100 g of blend. As it can be seen, at this concentration, Tinuvin 770 and UV531 retarded the rate of photo-oxidation, whereas NiDEC and NiDBC initially stop photo-oxidation followed by a sharp increase in carbonyl index. At higher concentration (ie 6 x 10^{-4} mol/100 g) NiDBC stability increases and there was 150 hours of induction period. However, the increased stability observed (Fig 5.26) by addition of NiDBC to PP:EPDM (75:25), was accompanied by a green colouration, which is typical of this transition metal complex. It is also clear that by increasing the concentration of UV531, the rate of oxidation of the samples is reduced (see Fig 5.27). Table 5.6 summarises the induction periods and embrittlement times of the PP:EPDM (75:25) samples containing conventional additives.

The impact measurements of PP:EPDM (75:25) samples containing bound MADA diluted from 2% masterbatch were carried out during exposure to uv light. The results are shown in Fig 5.28. All PP:EPDM (75:25) samples containing different concentrations of bound MADA (unextracted) show induction periods proportional to the amount of MADA and their impact strength drops sharply to the lowest value. Also Figs 5.29 and 5.30 indicate the effectiveness of conventional antioxidants such as NiDBC, Tinuvin 770 and UV531 during photodegradation on impact properties of the PP:EPDM (75:25) blends. NiDBC at concentration of 6 x 10^{-4} mol percent shows the

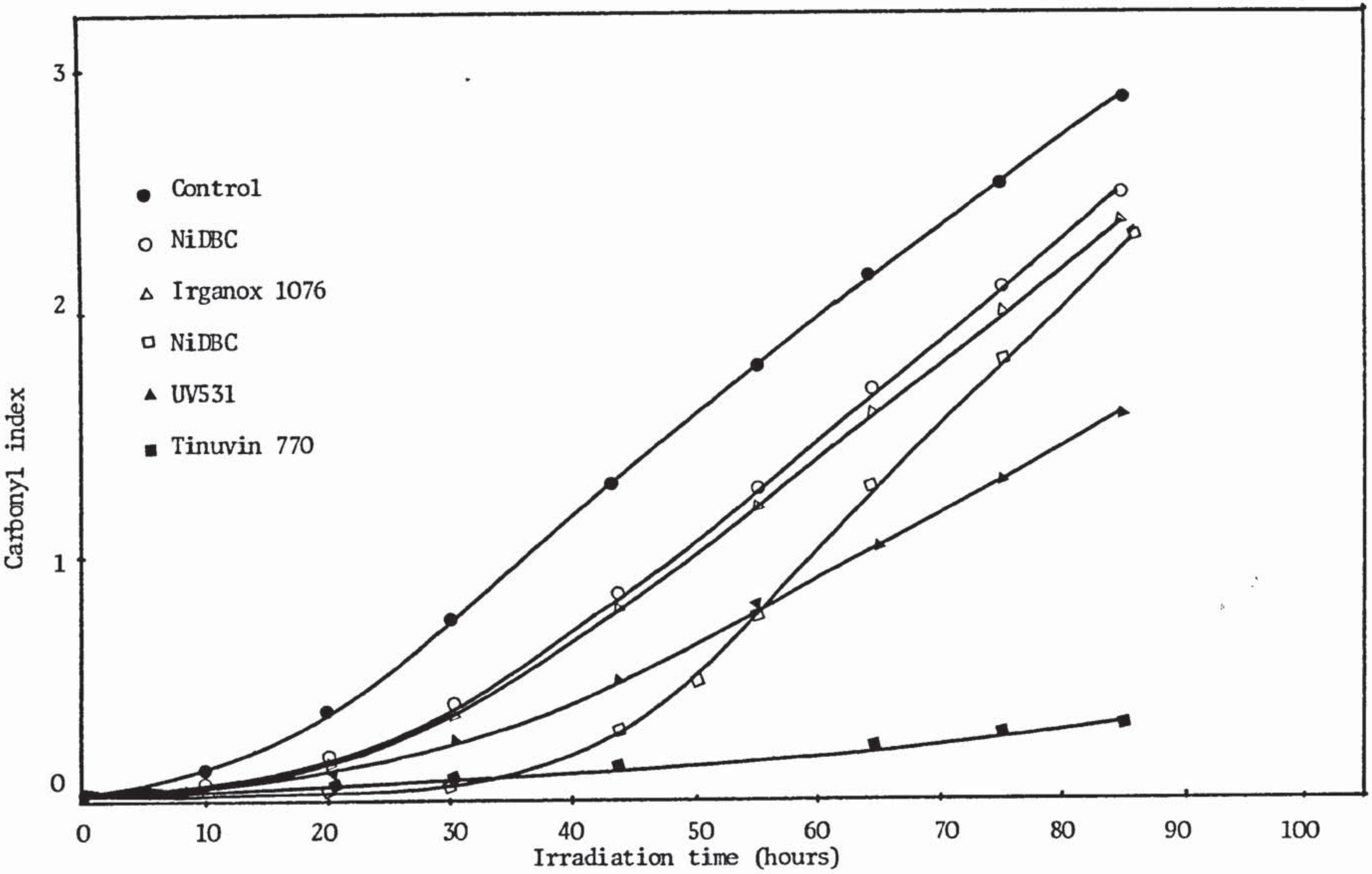


Fig 5.25 Development of carbonyl (1710 cm^{-1}) on uv exposure of PP/EPDM (75:25) containing 3×10^{-4} mole of additive in 100 g of polymer (all samples processed at 180°C/10 mins, closed chamber)

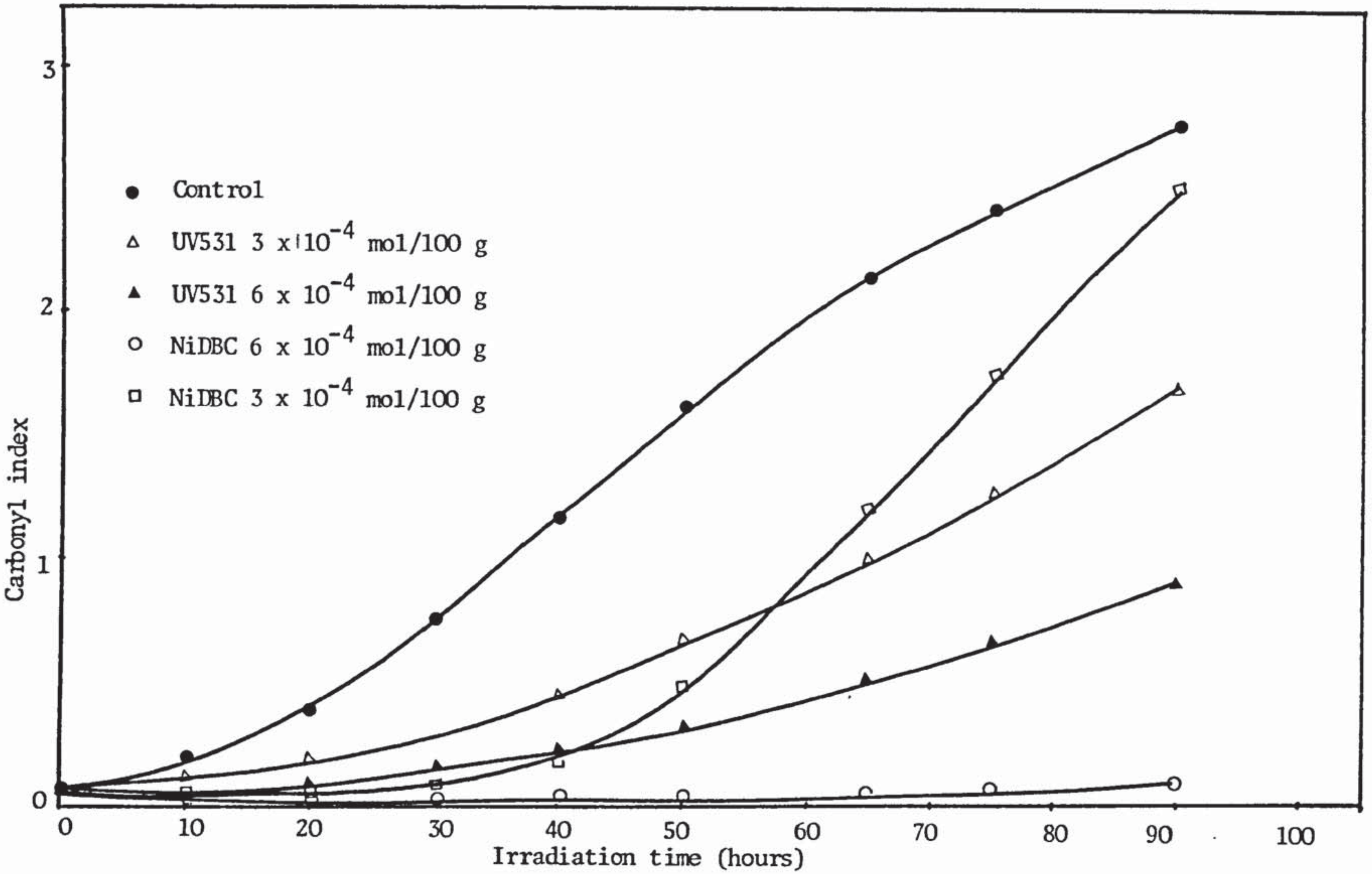


Fig 5.26 Development of carbonyl (1710 cm^{-1}) on uv exposure of PP/EPDM (75:25) (all samples are processed at 180°C/10 mins, closed chamber)

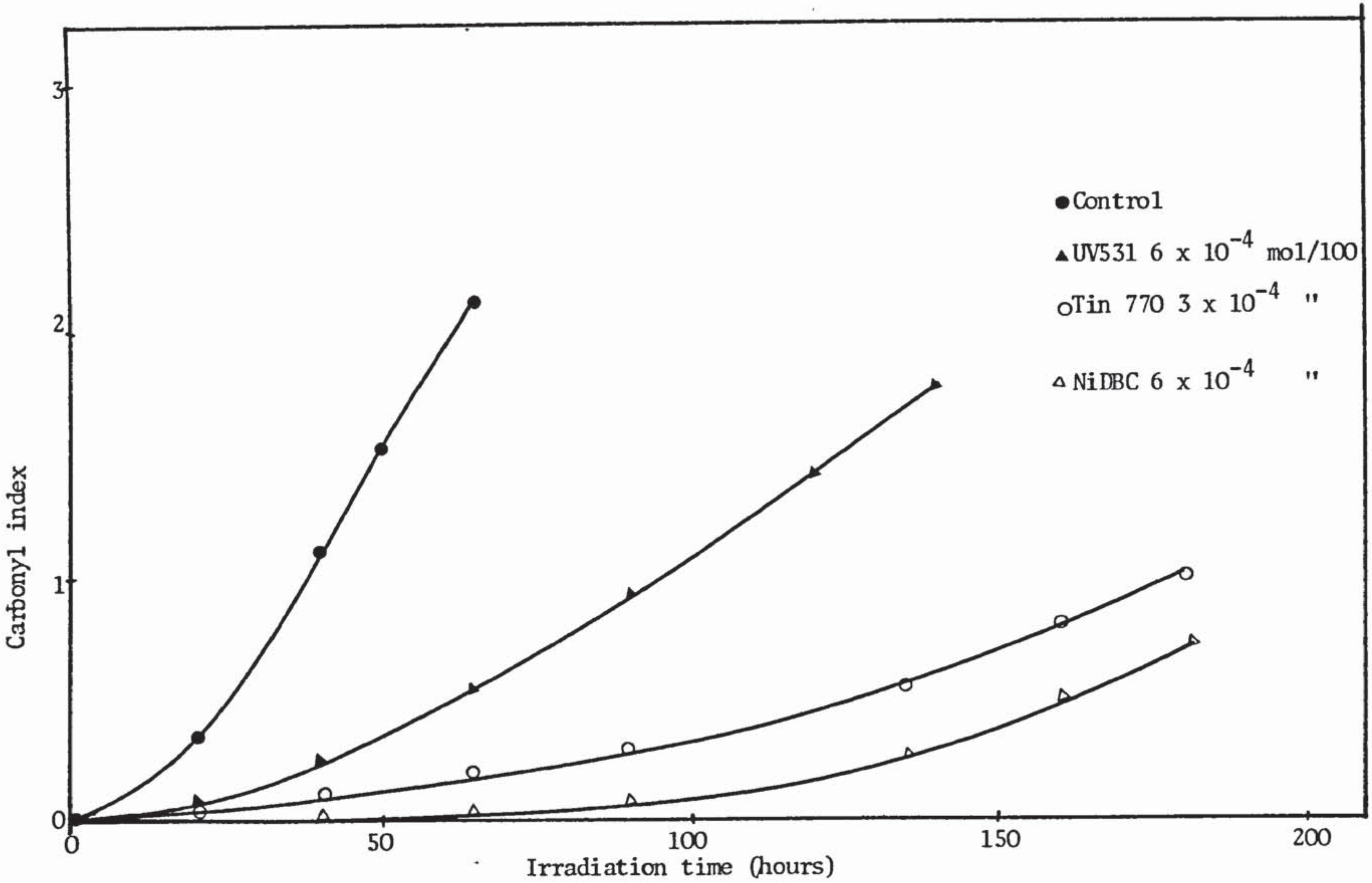


Fig 5.27 Development of carbonyl (1710 cm^{-1}) on uv exposure of PP/EPDM (75:25) (all samples processed at 180°C/10 mins, closed chamber)

<u>Table 5.6</u> Induction period and embrittlement time of PP:EPDM (75:25) films containing conventional additives, all samples processed for 10 mins at 180°C in closed chamber

Stabiliser type	Concentration of additive mol/100 g	g/100 g	Induction period hours	Embrittlement time hours ± 10
Control	-	-	5-7	180
Irganox 1076	3×10^{-4}	0.159	20	240
NiDEC	3×10^{-4}	0.106	22	250
NiDBC	3×10^{-4}	0.141	50	290
NiDBC	6×10^{-4}	0.282	150	510
UV531	3×10^{-4}	0.098	27	240
UV531	6×10^{-4}	0.196	45-50	400
Tin 770	3×10^{-4}	0.144	110	700

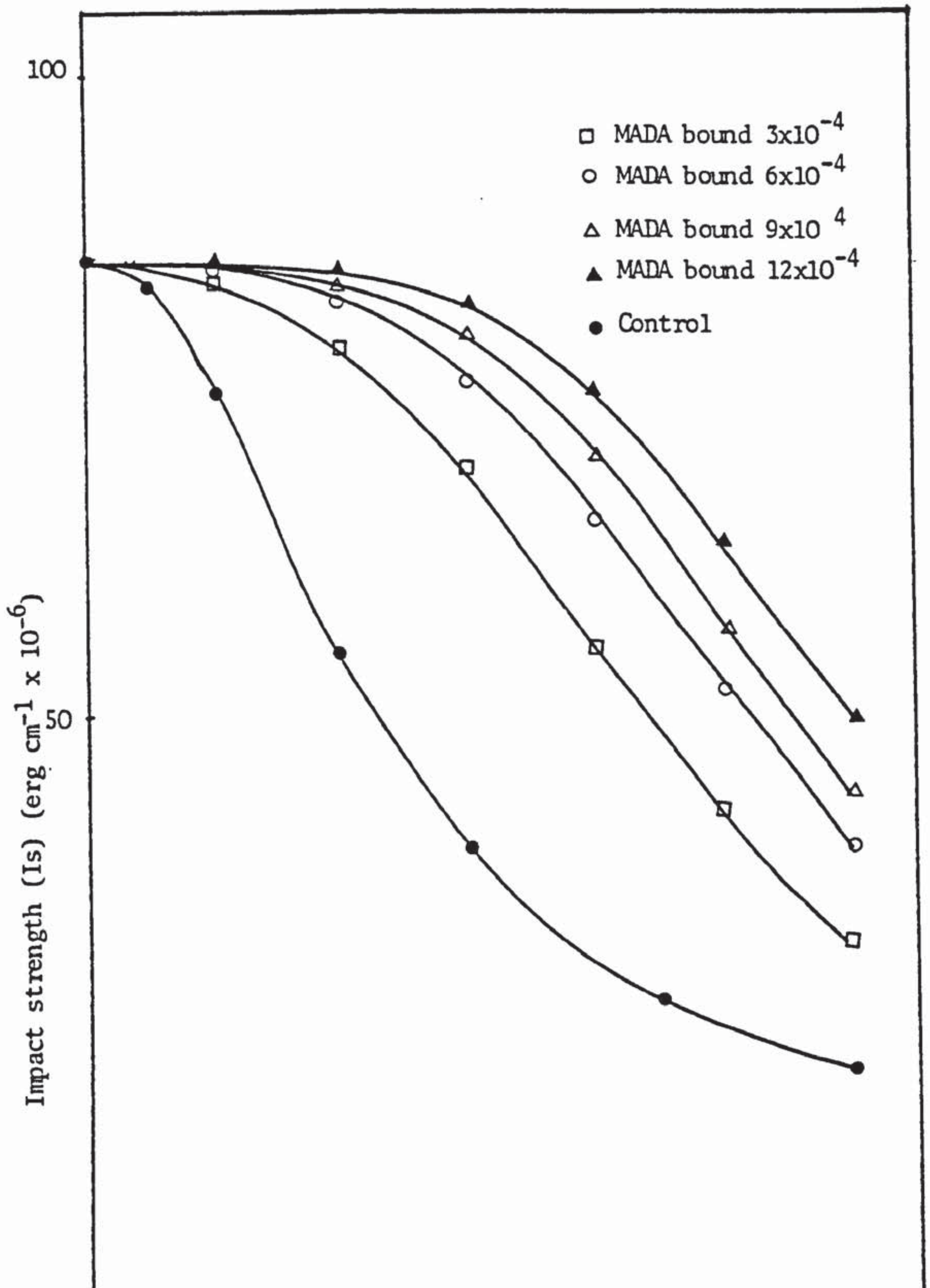


Fig 5.28 Decay of impact resistance on uv exposure of PP/EPDM (75:25) blend films (concentration in mol/100 g)

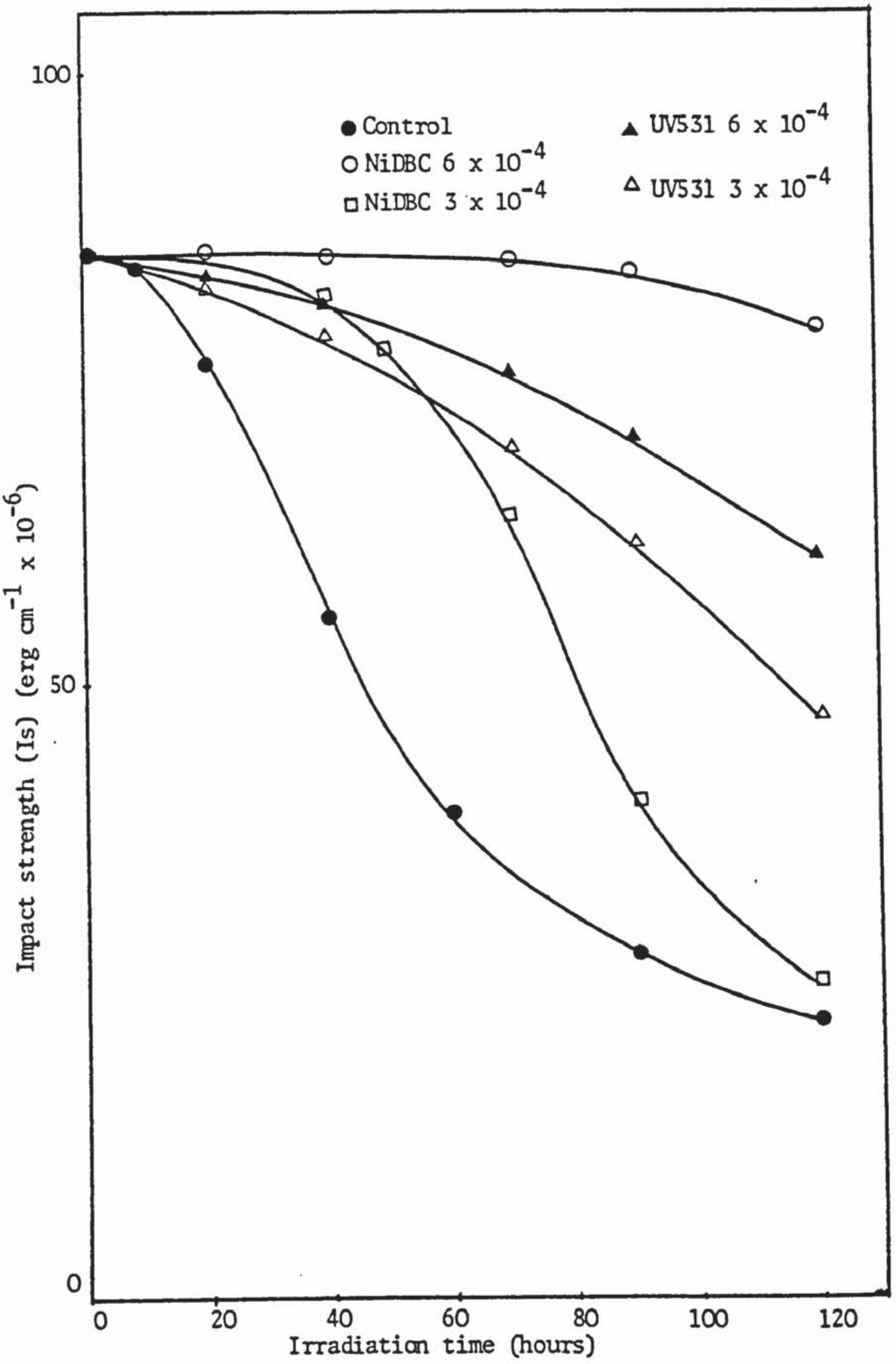


Fig 5.29 Decay of impact resistance on uv irradiation of PP/EPDM (75:25) blend films (concentration mol/100 g)

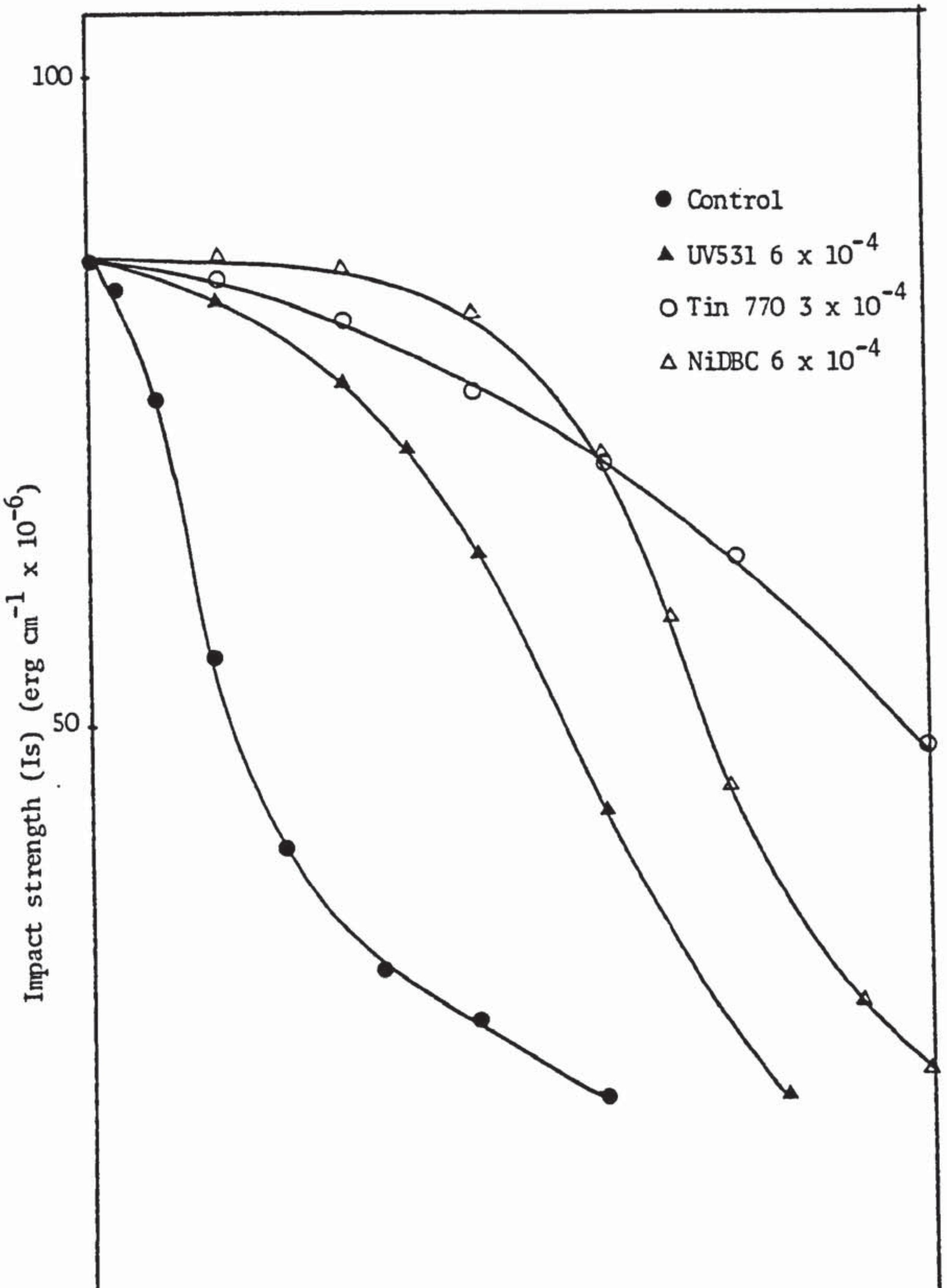


Fig 5.30 Decay of impact resistance on uv exposure of PP/EPDM (75:25) blend films processed at 180°C/10 mins, closed chamber (concentration mol/100 g)

best photostabilising effect.

Dynamic mechanical properties of stabilised PP:EPDM (75:25) samples containing NiDBC (6 x 10^{-4} mol/100 g) was measured at the Tg of rubber component. Only one sample was used throughout the measurement. The sample was uv exposed and exposure was interrupted for measurement. The effect of photo-oxidation on low temperature damping of PP:EPDM (75:25) containing NiDBC (6 x 10^{-4} mol/100 g) is shown in Fig 5.31. The dynamic spectra of specimen was observed from -100 to 0°C. Tan δ at -46°C reached the maximum 0.045 for uv exposed sample and then started to decrease during uv irradiation. Fig 5.32 shows changes in tan δ peak at -46°C for control (no additive) and NiDBC samples containing 6 x 10^{-4} mole percent.

5.3.4b Thermal Oxidation of Stabilised PP/EPDM (75:25) Blend

Thermal oxidation of the PP:EPDM (75:25) containing MADA and DBCMS bound masterbatches (see sections 4.1.6.1 and 4.1.7 respectively) which were diluted to required concentrations along with samples containing conventional antioxidants (ie NiDEC, NiDBC and UV531) were carried out at 140°C in air. Thermal oxidation was followed by measuring the changes in the concentration of functional group (C=O), impact strength and changes in height of tan δ at -46°C. Samples with thickness 0.015 cm were used for all measurements. The changes in concentration of functional group (carbonyl at 1710 cm^{-1}) as a function of heating time at 140°C in air are shown in Figs 5.33, 5.34 and 5.35. It is clear from

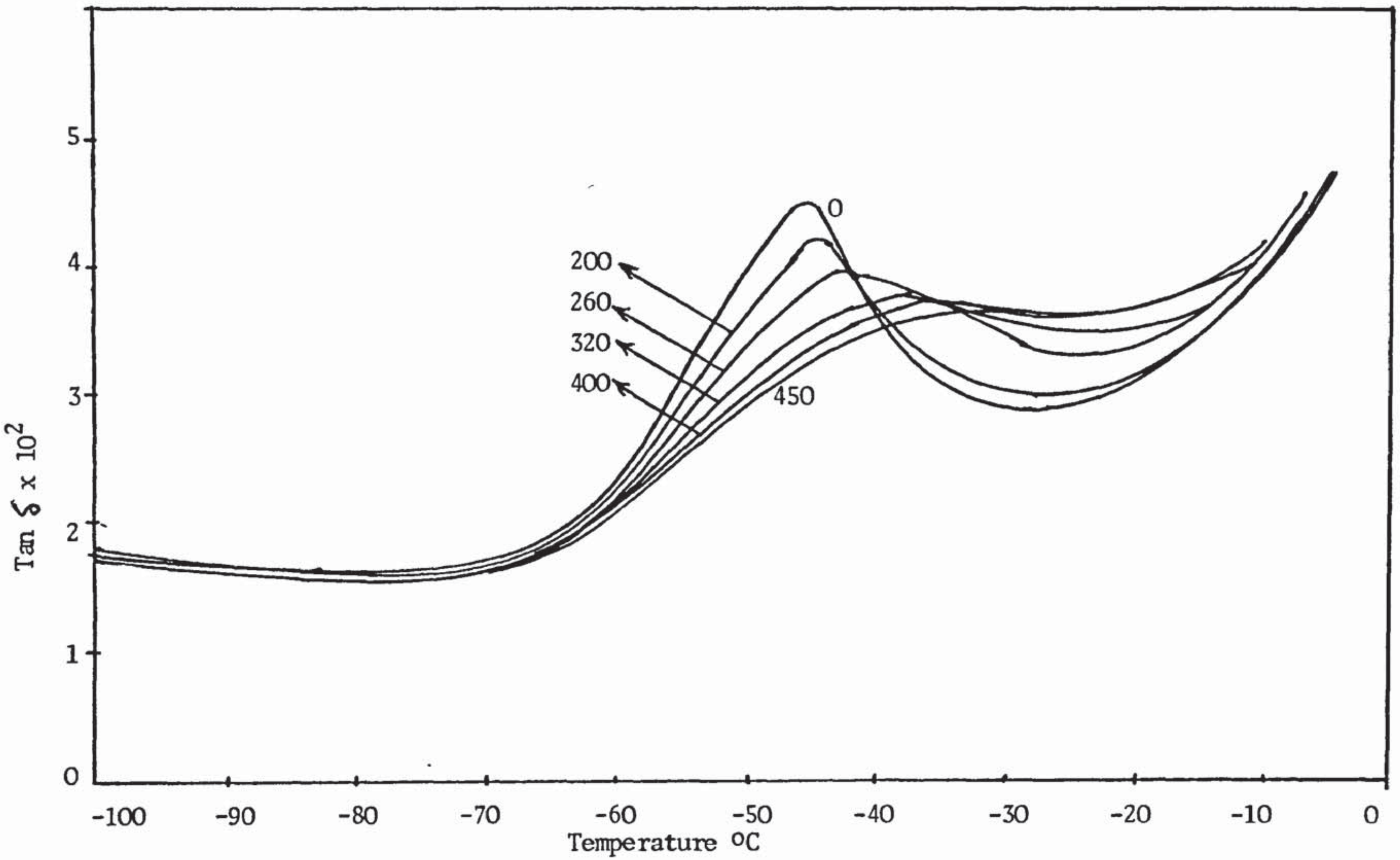


Fig 5.31 Effect of photo-oxidation on low temperature damping (-46°C) of PP:EPDM (75:25) containing NiDBC (6×10^{-4} mol/100 g) (numbers on curves are hours of irradiation)

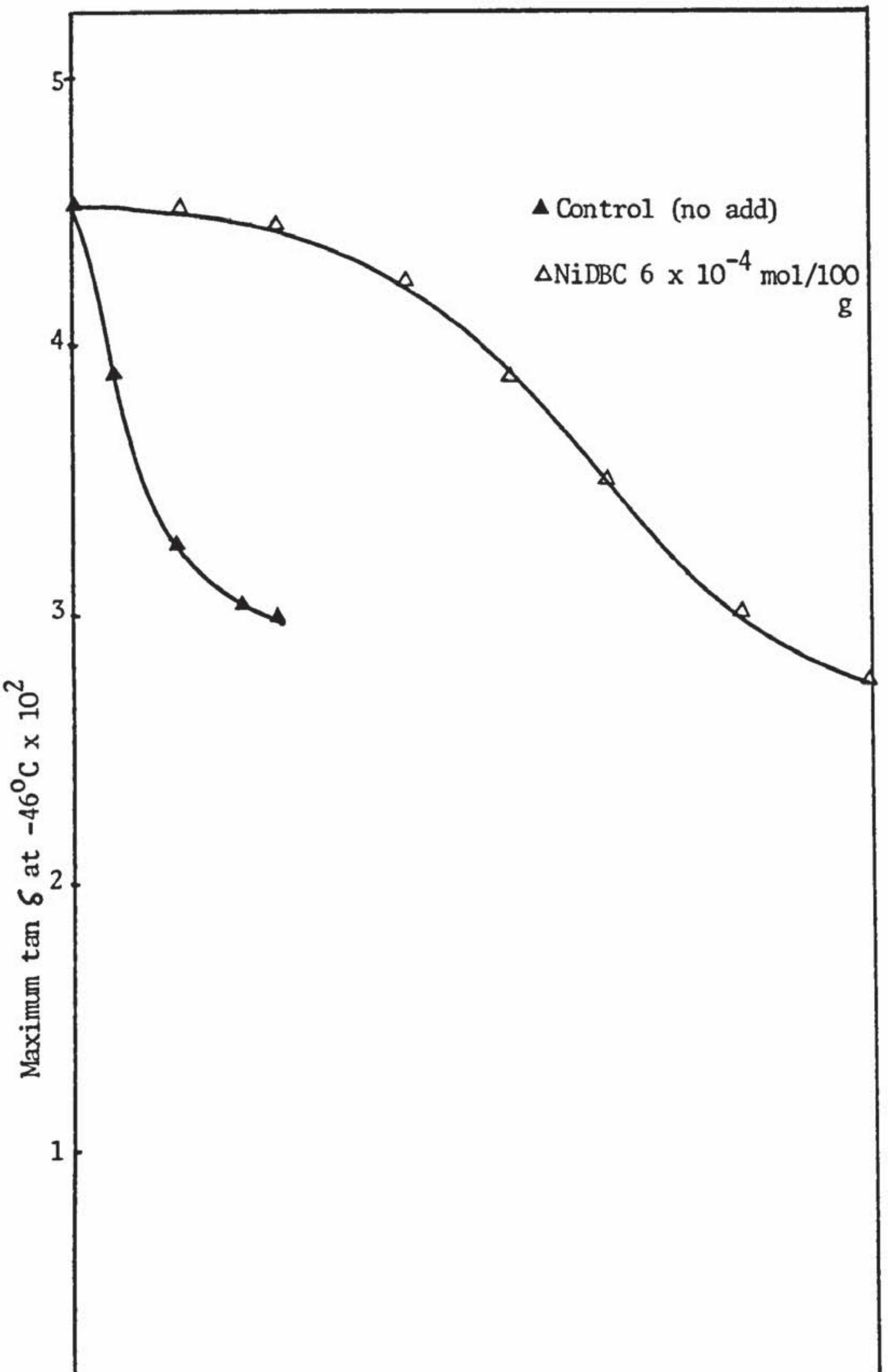


Fig 5.32 Changes in the maximum height of tan δ peak at -46°C of PP:EPDM (75:25) blend on uv exposure

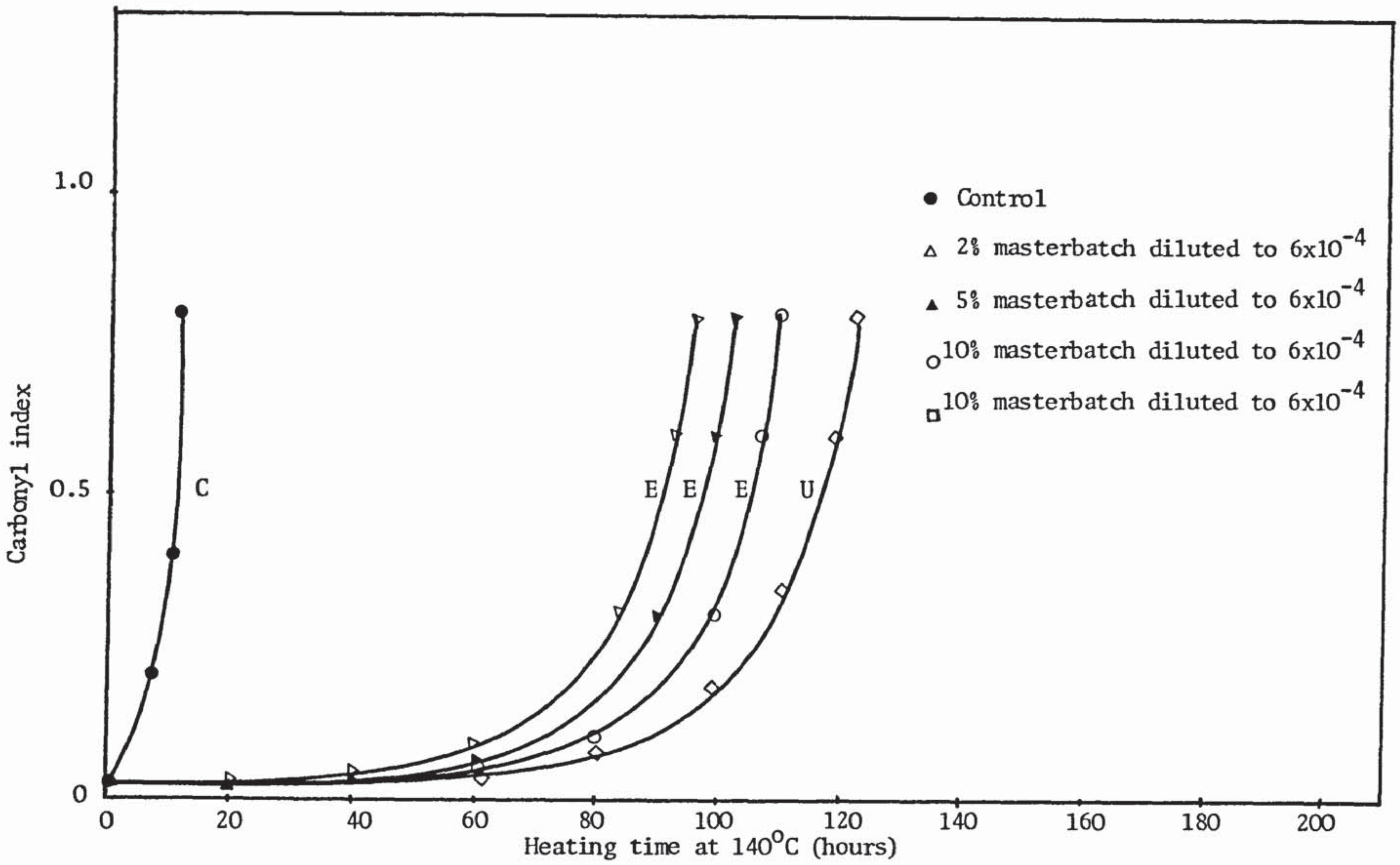


Fig 5.33 Development of carbonyl in PP/EPDM (75:25) blends containing bound MADA on oven ageing at 140°C in air (concentration mol/100 g, C = control, E = extracted, U = unextracted)

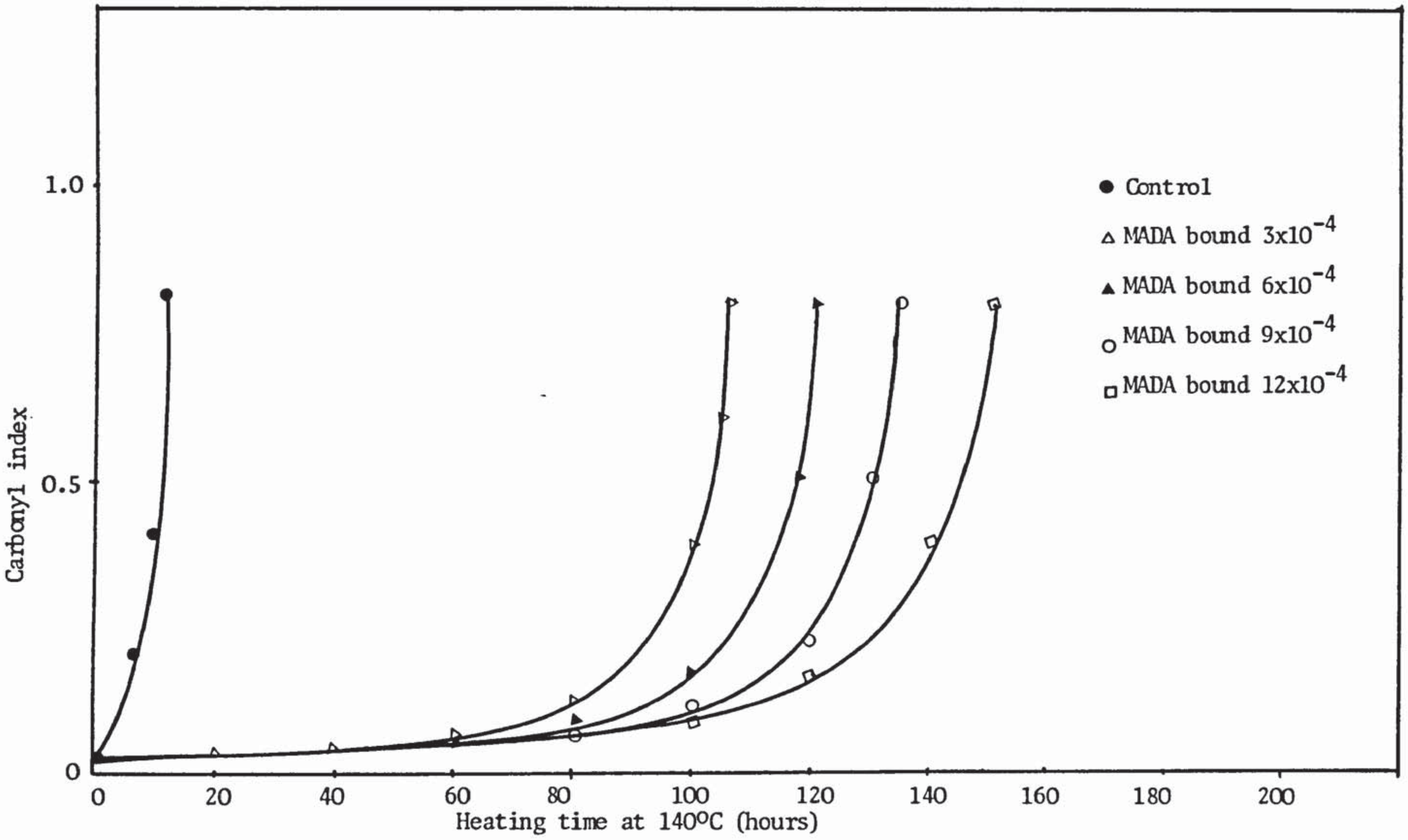


Fig 5.34 Development of carbonyl in PP:EPDM (75:25) blends containing bound MADA during oven ageing at 140°C in air (concentration mol/100 g)

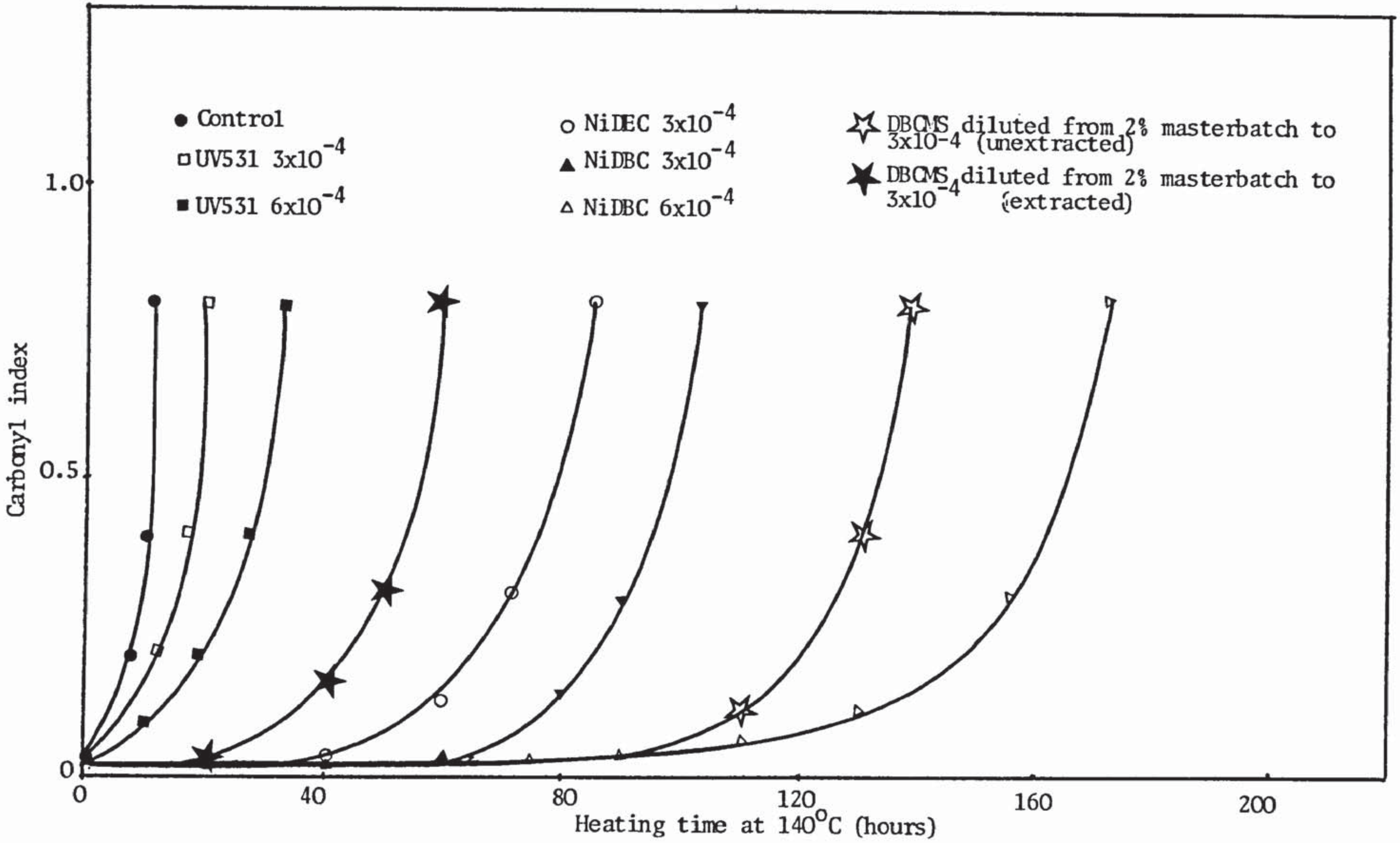


Fig 5.35 Development of carbonyl in PP:EPDM (75:25) blends containing additives during oven ageing at 140°C in air (concentration mol/100 g)

Fig 5.33 that extracted samples containing 6 x 10^{-4} mol percent of MADA bound diluted from 2, 5 and 10% masterbatch, show different induction periods confirming that the amount of bound MADA is increased by increasing masterbatch concentration (see also Fig 4.7). Table 5.7 shows the induction period and embrittlement time of the sample containing MADA bound before and after extraction.

Fig 5.34 also indicates that with increasing MADA concentration in unextracted samples of PP:EPDM (75:25), diluted from 2% masterbatch the induction period and embrittlement time increases (see Table 4.1 for extent of binding). Table 5.8 summarises their induction periods and embrittlement times.

Also in Fig 5.35 the development of carbonyl group in PP:EPDM (75:25) samples containing conventional antioxidant and DBCMS (see Table 4.1 for extent of binding) diluted from 2% masterbatch to 3 x 10^{-4} mol/100 g are shown. The induction periods and embrittlement times of the samples are presented in Table 5.9.

The impact strengths of PP:EPDM (75:25) containing bound antioxidant (DBCMS) and conventional antioxidants were measured by falling weight tester during thermal oxidation (see Fig 5.36).

5.4 Discussion

The impact resistance of polypropylene has been improved through copolymerising and blending with EPDM rubbers. Improvement in the

Table 5.7 Concentration of MADA before and after extraction in the adduct made from masterbatches. Their induction periods and embrittlement times in PP/EPDM (75:25) blend processed at 180oC, 10 minutes, closed chamber (U = unextracted)

Stabiliser type	Concentration of masterbatch pph	Conc of dilute before ext		Conc of dilute after ext g/100g	Induction Period hours	Embrittlement time hours
		mol/100 g	g/100 g			
MADA	2	$6x10^{-4}$	0.155	0.116	60	95
MADA	5	"	"	0.127	70	100
MADA	10	"	"	0.135	80	115
MADA	U	"	"	-	100	150
Control	-	-	-	-	4	7-8

Table 5.8 Induction period and embrittlement time of PP:EPDM (75:25) blend samples containing MADA bound during oven ageing at 140°C diluted from 2% masterbatch

Stabiliser type	Concentration of dilute mol/100 g	g/100 g	Induction period hours	Embrittlement time hours
Control	-	-	4	7-8
MADA	$3x10^{-4}$	0.078	70	100
MADA	$6x10^{-4}$	0.155	90	130
MADA	$9x10^{-4}$	0.282	105	150
MADA	$12x10^{-4}$	0.310	120	165

Table 5.9 Induction period and embrittlement time of PP:EPDM (75:25) containing conventional additives during oven ageing at 140°C (U = unextracted, E = extracted)

Stabiliser type	Concentration of additive		Induction period hours	Embrittlement time hours
	mol/100 g	g/100 g		
Control	-	-	4	7-8
UV531	$3x10^{-4}$	0.098	4-5	15
UV531	$6x10^{-4}$	0.196	8	20
NiDEC	$3x10^{-4}$	0.106	45	100
NiDBC	$3x10^{-4}$	0.141	75	130
NiDBC	$6x10^{-4}$	0.282	140	200
DBCMS U	$3x10^{-4}$	0.093	100-110	140
DBCMS E	-	0.028	30	45

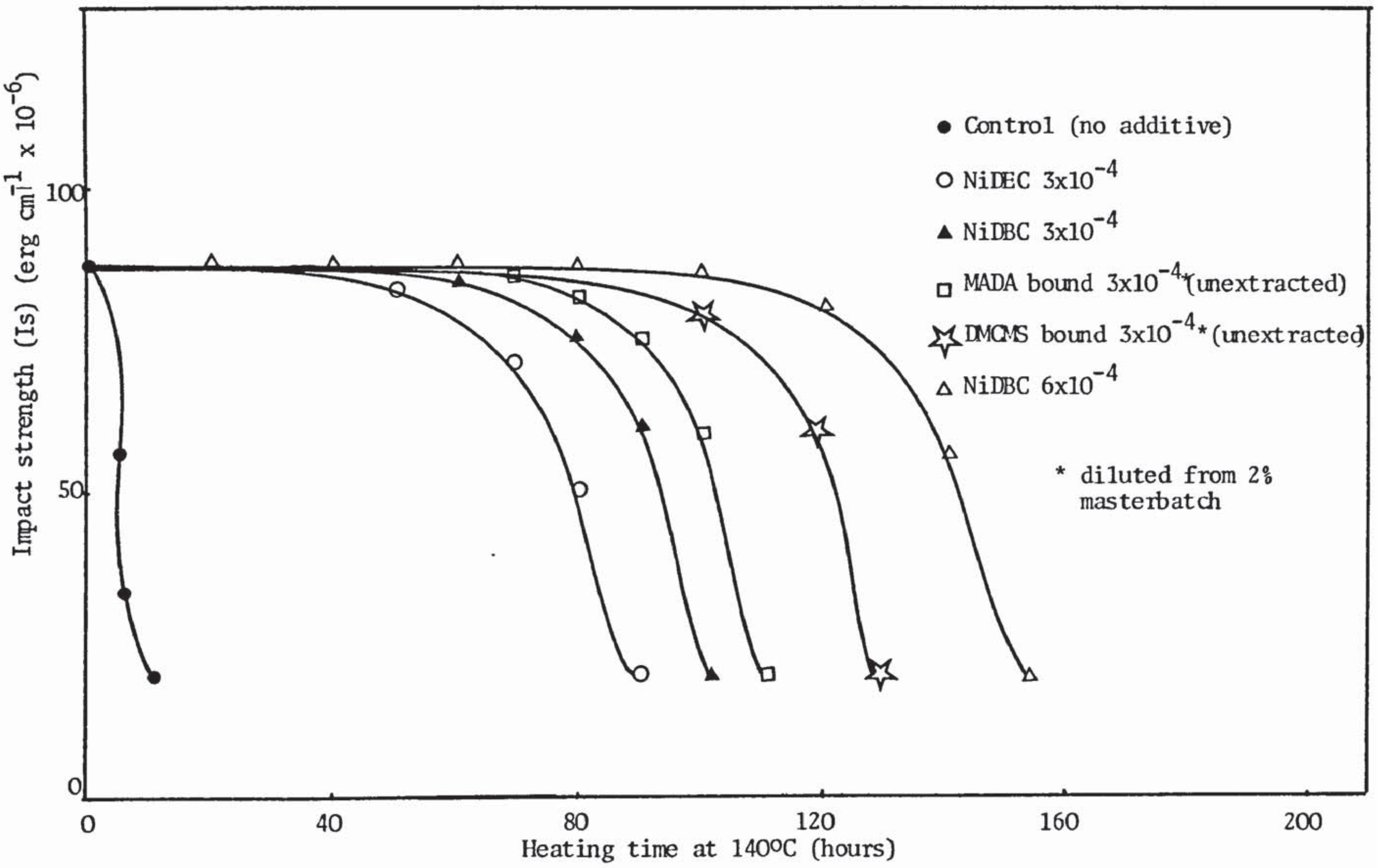


Fig 5.36 Decay of impact strength during oven ageing at 140°C in air of PP/EPDM (75:25) samples, processed at 180°C/10 mins, closed chamber, concentration mol/100 g

impact resistance of polypropylene generally results in a reduction in modulus, strength and high temperature properties. It can be seen from Figs 5.1 and 5.4 that the low temperature damping and impact at room temperature of polypropylene has increased and there was a straight line relationship between impact strength at room temperature and low temperature damping (tan δ) at -46°C due to the presence of EPDM (see Fig 5.5). This increase in impact was accompanied with reduction in tensile properties (see Fig 5.6). These property reductions can be tolerated in many applications because impact resistance is of primary concern. Speri and Patrick(152) have concluded that the optimum particle size may be near 0.5 μm, but they point out that this is achievable only under conditions of high shear when bulk viscosities of the continuous and disperse phases are most closely matched.

Infra-red spectroscopy is a useful non-destructive method which can be used to follow degradation of a polymer film by measuring changes in the funcitonal groups. Examination of thin film by transmission spectroscopy permits the course of the degradation reaction to be followed without damage and the same area of the film can be used repeatedly for test.

It can be seen from the infra-red spectra of unstabilised PP:EPDM (containing 5-30% EPDM) blends (see Figs 5.10, 5.11, 5.12, and 5.13) that the absorption at 3450 cm^{-1} and 1710 cm^{-1} changes during uv irradiation due to the increase in the hydroxyl and carbonyl group concentrations.

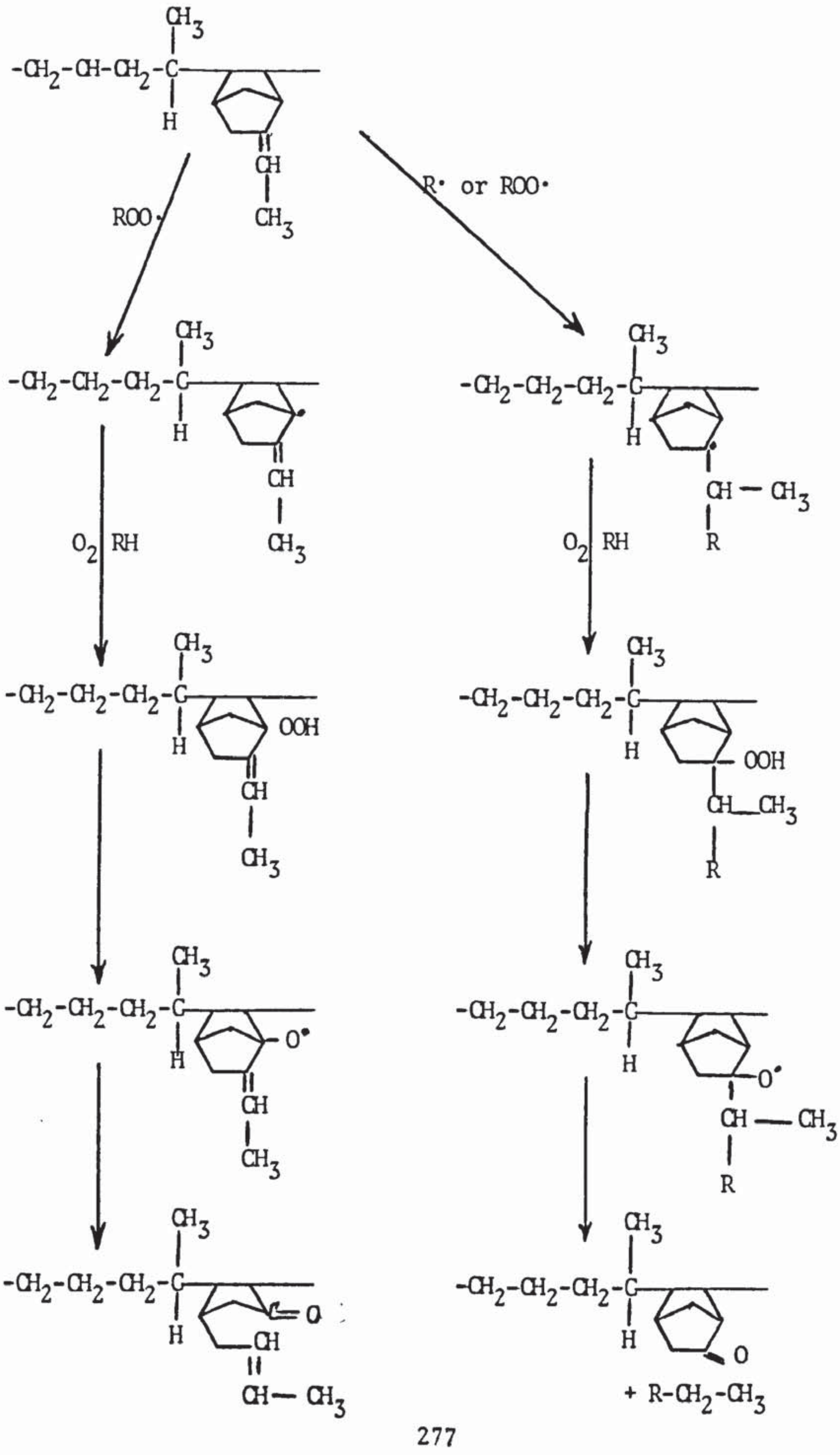
Similar changes in the polybutadiene (PBD) component were observed by Scott et al(101) in HIPS and also in ABS(104,130). There is general agreement(104,153,37) that the polybutadiene component of ABS is the only moiety which is affected during exposure to uv light and that its destruction is accompanied by a rapid loss of physical properties such as impact strength. Also the photo-oxidation of polypropylene containing different concentration of diene (EPDM) indicates that as the concentration of diene increases the photosensitivity of the blend increases and this leads to the fast build up of carbonyl group at 1710 cm^{-1} (see Fig 5.14).

The impact properties of PP:EPDM (75:25) blends was measured during uv exposure (see Fig 5.18) and it indicates that after around 5-8 hours of induction period, then it is followed by a sharp decrease in impact strength until it reaches the value of polypropylene (impact strength) and decreases gradually. It seems clear that the loss in toughness is due to an embrittlement in the surface. Oxidation starts from the surface of the film and the weight falling tester, the weight strikes on the surface of the film at a high speed and cracks propagate from the brittle surface of the film to inner part of the film which there is still some rubber. Therefore, because of the fast crack formation in the surface of the film, which in turn initiates crack propagation throughout the polymer film, a rapid loss in the impact strength is observed during the early stages of photodegradation.

Dynamic mechanical measurements have been used to study the structural changes in ABS during photo-oxidation(104,130). Dynamic mechanical properties were measured by means of the rheovibron for studying photo-oxidation of PP:EPDM (75:25) blends and only one sample was used throughout photo-oxidation measurements. The damping behaviour of PP:EPDM (75:25) blend during photo-oxidation is shown in Fig 5.16. Reduction in the concentration of rubber during photo-oxidation is accompanied by a decrease in the height of the low temperature damping peak. The damping at low temperature (Tg of PBD) goes through a maximum and then a minimum for a material containing rubber component such as ABS polymer(104,130). At low temperature, there is no molecular motion of the chain segments (stiff spring) because the chain segments are completely frozen in, damping is low. At temperatures above glass transition region, the chain segments are completely free to move, (elastic material) damping is low. In the transition region, the damping is high because some of the molecular chain segments are free to move while others are not. Thus, every time a stressed, frozen in segment becomes free to move, its excess energy is dissipated as heat. It is characteristic of the transition region that only part of the molecular segments are free to move. The low temperature damping (tan δ) cannot be measured when the concentration of rubber is very low because the samples brittle at low temperature. The shift of the rubber peak (at low temperature) to higher temperature during exposure to uv light could possibly be due to introduction of more polar groups in to the polymer chain. The increase of the damping above Tg is suggested to be a result of a further decrease in the molecular weight of the polymer(154). The maximum height of low temperature damping peak were plotted against time of uv exposure (Fig 5.18). The height of the damping peak drops sharply after 60 hours of uv exposure and then decreases gradually with further uv exposure. Dynamic mechanical analysis of PVC containing 10% MBS has been studied by Scott et al(40) and a prominent rubber transition between -50 and -55 due to the polybutadiene moiety was formed. They have also concluded that the rubber transition disappeared rapidly on photo-oxidation. This behaviour closely resembles the decay of the rubber transition at -80°C previously reported for the polybutadiene-modified polystyrene and ABS which was clearly identified with the decay of the 1,2- and 1,4-polybutadiene structure(35,111,112). The possible photo-oxidation mechanism for PP:EPDM blends may possibly be shown as scheme 5.1.

The results show that the bound antioxidant, MADA and EBHPT, behave as photo-stabilisers in PP:EPDM (75:25) blend (see Figs 5.22 and 5.23). Although they are not as effective as conventional antioxidants, such as NiDBC (peroxide decomposer) and UV531 (conventional uv absorber) on a molar basis (before extraction) but after solvent extraction they are superior to conventional antioxidants. The former could be due to low dispersibility in the blend system. However, samples containing bound MADA show very good thermal stability (see Fig 5.34). The mechanism of the effectiveness of thiol adducts formed from MADA and EBHPT are discussed in section 4.4 (see schemes 4.2, 4.3 and 4.4).

Scheme 5.1 Possible mechanism for unstabilised PP:EPDM blends



Figs 5.25, 5.26 and 5.27 show the typical behaviour of a number of commercial antioxidants in unstabilised PP:EPDM (75:25) blend incorporated by a normal compounding procedure at the same molar concentration. It is clear from Figs 5.25 and 5.27 that Tinuvin 770 has a very good photostabilising effect. The mechanism of the photostability of hindered piperidine has been found(155) to be due to the formation of nitroxyl radicals which are effective traps for alkyl and macroalkyl radicals.

Typical chain breaking antioxidants (Irganox 1076) and peroxide decomposer (NiDEC) behaved very similarly but NiDBC was found to be more efficient, possibly due to its high molecular weight and compatiblity. The very good uv and thermal stability of samples containing higher concentrations of NiDBC (ie 6 x 10^{-4} mol/100 g) indicates that in reprocessing of polypropylene into secondary products, this additive could be used, because the ideal requirement is for a cheap and effective melt stabiliser which confers good long term stability on the polymer. Since it is possible that a proportion of the polymer may be recycled more than once, good melt and service stability should be retained with repeated processing.

The transition metal dithiocarbamates are very much more effective broad spectrum stabilisers. They are known to function primarily by a peroxide decomposition mechanism(155-159) and it is found(28) that hydroperoxide formed during processing is the photo-initiator primarily responsible for change in melt flow index (MFI) during reprocessing and loss of useful properties during thermal and photo-oxidation of reprocessed films. In view of the ready accessibility of a range of PD-C antioxidants containing sulphur (which include the dithiophosphate(159,160), the xanthate(160) and the mercaptobenzthiazolates(161)), these would be stabilisers of choice for reprocessed polypropylene where colour is less important than in initial use.

CHAPTER SIX

IMPROVEMENT IN MECHANICAL PROPERTIES AND LONG TERM PERFORMANCE OF MIXED PLASTICS WASTE (BINARY BLENDS OF POLYETHYLENE-POLYPROPYLENE AND POLYETHYLENE-POLYSTYRENE)

CHAPTER SIX

IMPROVEMENT IN MECHANICAL PROPERTIES AND LONG TERM PERFORMANCE OF MIXED PLASTICS WASTE (BINARY BLENDS OF POLYETHYLENE-POLYPROPYLENE AND POLYETHYLENE-POLYSTYRENE)

6.1 General Background

Solid wastes represent a potential source for raw materials in a world confronted with increasing difficulties in the proper utilisation of depleting resources. The proportion of plastic materials in domestic wastes is as yet low (4-6%); however, it is forecasted that this is likely to increase significantly (see section 2.2.3). In addition to domestic wastes, which consist mainly of packaging materials, there exists large quantities of industrial wastes, which are relatively easier to handle in recycling operations. However, whether we are dealing with mixtures of polymeric or single plastics species, both are contaminated with foreign materials. A typical estimated composition of plastics is found in domestic wastes is as follows: polyethylene 50-60%, polystyrene 20-25%, PVC 5-10%, polypropylene 5-10% and other minor compounds (see also Table 2.2).

Recycling of waste plastics as a blend of generic types is attractive since a difficult separation problem would thus be avoided. However, blends of incompatible polymers are frequently very brittle and cannot be considered for many applications.

Additives which modify the blend to give it ductility may provide a solution to this problem.

Chlorinated polyethylene (CPE) made by a slurry process has been suggested for this application by Schramor and Blanchard(62). Paul et al(61) have found that the poorest mechanical properties of ternary blends of incompatible polymers generally occur when all three components are present in equal amounts. They have also found that along the binary legs of the triangular diagram for PE-PVC-PS that the 50/50 point generally exhibited the poorest mechanical properties. Addition of CPE to blends with such a composition generally increases the elongation at break and the energy to break very dramatically with ordinarily some loss in strength and modulus. This approach works most effectively in blends of high polyethylene and poly(vinyl chloride) content.

Scott et al(54) have also found that the mechanical properties of three binary mixtures of incompatible polymers (LDPE/PP, LDPE/PS and LDPE/PVC) exhibited poorest properties in the ratio of 50/50 of each component. They have also studied the mechanical properties of such blends (1:1 ratio) in the presence of potential solid phase dispersants (SPDs) and have concluded that:

(i) the addition of a styrene-butadiene block copolymer (SBS) in a PE/PS (1:1) blend improves the impact resistance of the blend, and

(ii) the addition of an ethylene-propylene terpolymer (EPDM) in a PE/PP (1:1) blend improves the impact resistance of the blend.

The purpose of the present study is to extend the above findings in a more detailed investigation of mechanical improvement and long term performance of the PE/PP and PE/PS blends.

6.2 Experimental

Materials Unstabilised polypropylene (PP), polyethylene, polystyrene, ethylene-propylene diene monomer (EPDM) and styrene-butadiene block copolymer (SBS) were used as described in section 2.1.

Processing The blends were processed at 180°C in the RAPRA torque rheometer for 5 minutes in a full, closed chamber (ie 35 g). The blends were then compression moulded at 180°C for 3 minutes (1.5 minutes without pressure and 1.5 minutes with pressure) into sheets as described in section 2.2.2.

Table 6.1 shows the formulation with varying proportions of PP or PS (0, 20, 40, 60, 80, 100%). All formulations were based on 35 g of polymer (in a full mixer chamber). Also Table 6.2 represents the composition of ternary blends of PE/PP/EPDM and PE/PS/SBS.

Tensile strength, % elongation, Young's modulus were calculated

Table 6.1*

Composition (%)		Charge weight to mixer (g)	
PE	PP or PS	PE	PP or PS
100	0	35	0
80	20	28	7
60	40	21	14
50	50	17.5	17.5
40	60	14	21
20	80	7	28
0	100	0	35

* All samples processed at 180°C, 5 minutes, closed chamber

Table 6.2

Composition (%)			Charge weight to mixer g		
PE	PP or PS	EPDM or SBS	PE	PP or PS	EPDM or SBS
50	50	0	17.5	17.5	0
45	45	10	15.75	15.75	3.5
40	40	20	14	14	7
35	35	30	12.25	12.25	10.5

at room temperature ($21 \pm 1^{\circ}C$) as described in section 2.12.

Measurement of dynamic mechanical properties The rheovibron model DDVII (Toyo Measuring Instrument Co Ltd, TMI, Tokyo) was used at room temperature. All measurements were made at a frequency of 110 Hz and the value of tan δ was read directly from the rheovibron (see also section 2.13).

Impact strength measurement Impact strength was measured by falling weight tester as previously described in section 2.11. Samples of exactly equal thickness (0.015-0.018 cm) were chosen for replicate impact studies. About 10 measurements of the impact strength were made for every period of degradation. The impact strength of a film was taken as the energy required to break the film per unit thickness.

Measurement of carbonyl index by infra-red spectroscopy A standard procedure was adapted on solid films using Perkin Elmer spectrometer model 599. The peak at 2710 cm^{-1} and 1940 cm^{-1} were taken respectively for blends of PE/PP containing EPDM and PE/PS containing SBS as solid phase dispersants. The carbonyl index was measured as the ratio of absorbance at 1710 cm^{-1} to that of the reference peak.

Measurement of trans-1,4-polybutadiene index by infra-red spectroscopy A standard procedure was adoped on solid films of PE/PS blends containing SBS using Perkin Elmer spectrometer model 599. The peak at 1940 cm^{-1} was taken as the reference peak. The trans-1,4-polybutadiene index was measured as the ratio of absorbances at 965 cm^{-1} to that of the reference peak.

6.3 Results and Discussion

6.3.A.1 The Effect of Polypropylene Concentration on Mechanical and Long Term Performance of LDPE/PP Blend

The changes in tensile strength, elongation at break, tensile at yield and complex modulus of LDPE are plotted against PP composition in Figs 6.1, 6.2, 6.3 and 6.4. The results indicate the incompatibility of the blends and this is reflected much more strongly in the elongation at break (Eb%) of all blends. Scott et al(54) have found that LDPE/PP blends show evidence of limited compatibility (up to 5% PP) but all fall away to less than 10% of the Eb of pure polyethylene at 20% of second component (PP). They have also found that impact strength (Is) shows a parallel behaviour to elongation at break. The changes in impact strength and elongation at break may be due to the increased viscoelasticity as a result of addition of PP. Since polypropylene is more susceptible to photo-oxidation than LDPE, it might be anticipated that even a small proportion of PP would sensitise LDPE to photo-oxidation. Since reprocessed waste polyethylene packaging is likely to have polypropylene as a contaminant, infra-red spectroscopy was used to follow degradation of polymer blend film by measuring changes in functional groups.

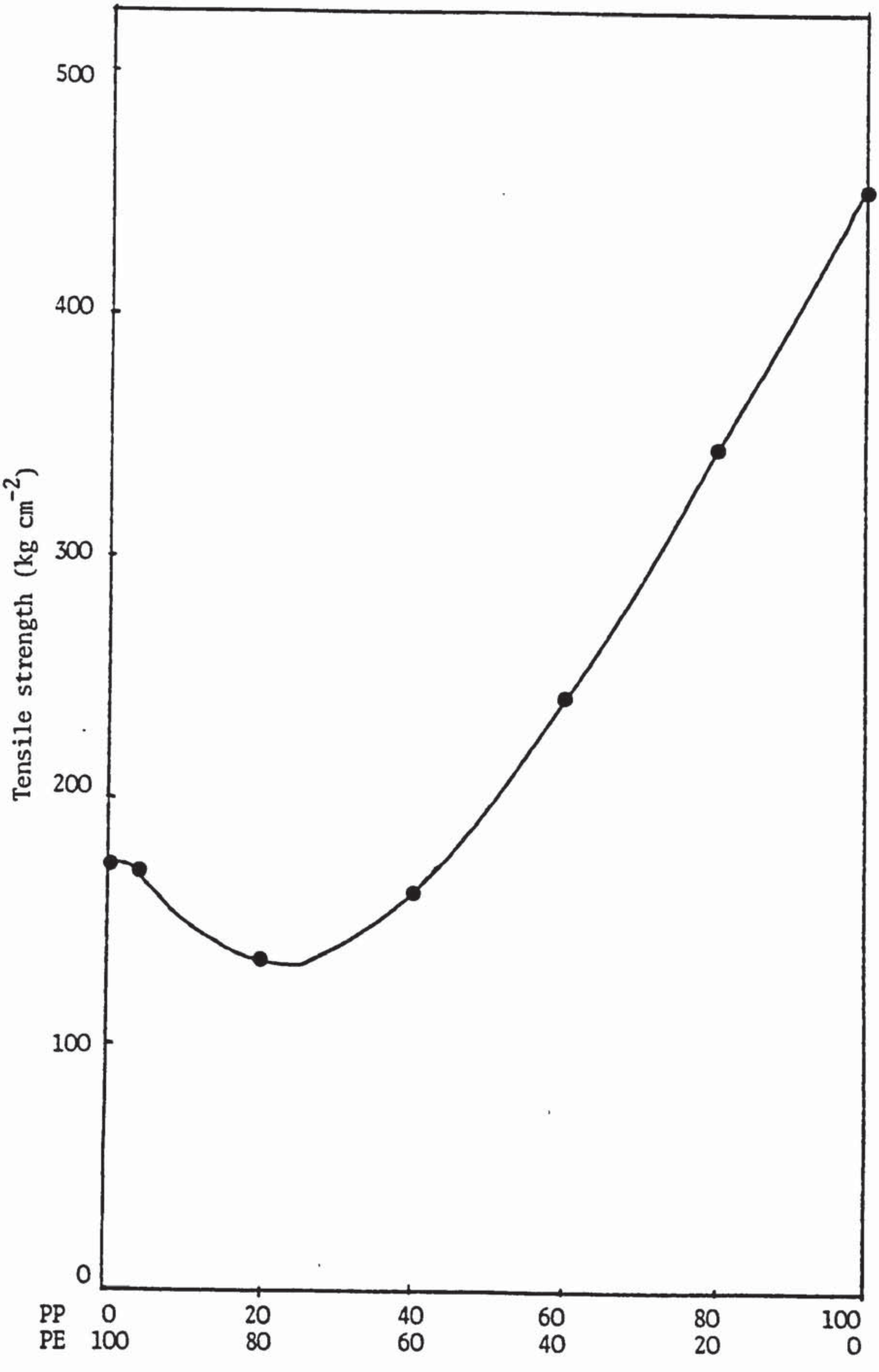


Fig 6.1 Change in tensile strength with composition for PE/PP blends

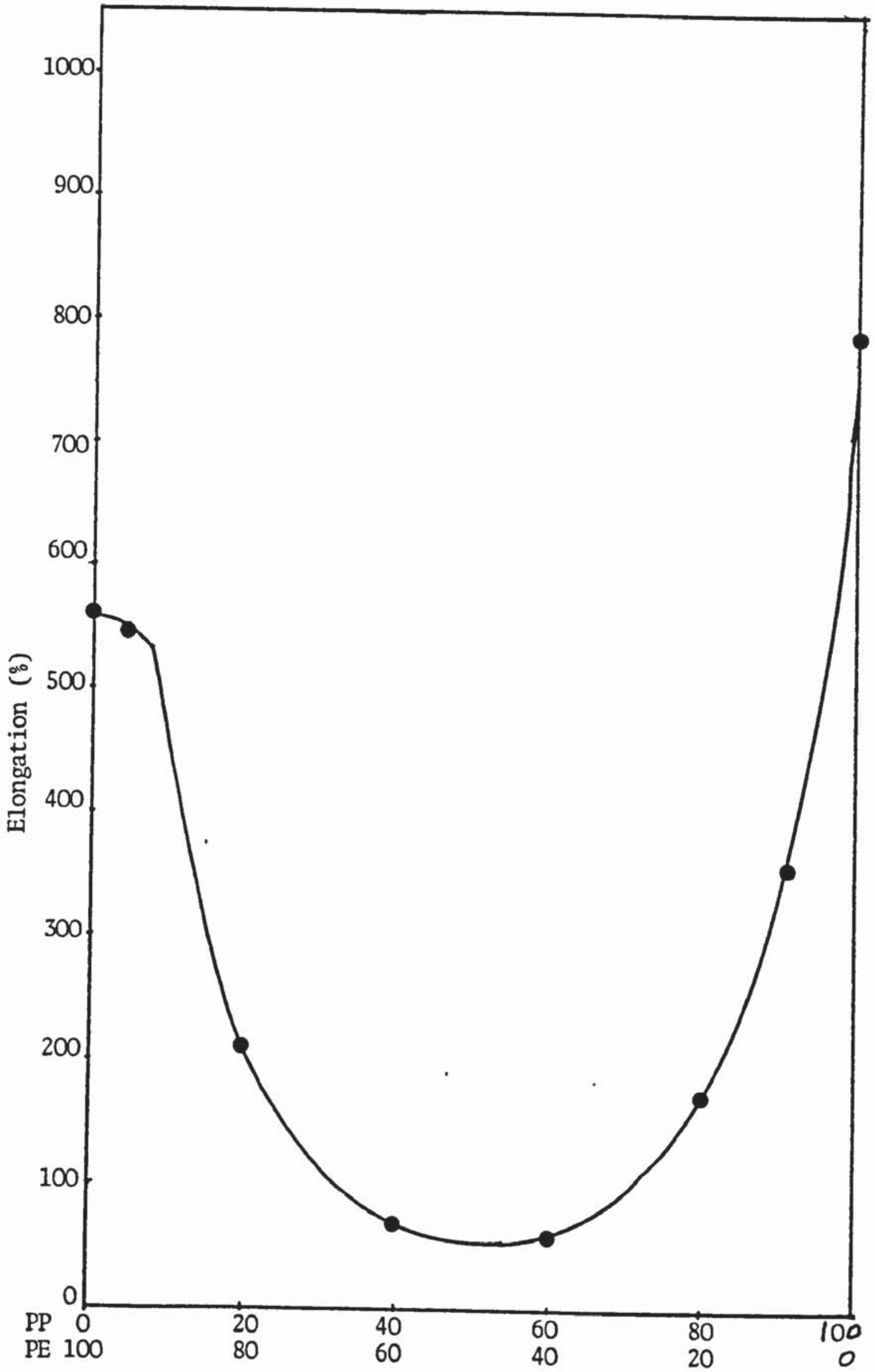


Fig 6.2 Change in elongation at break with composition for PE/PP blends

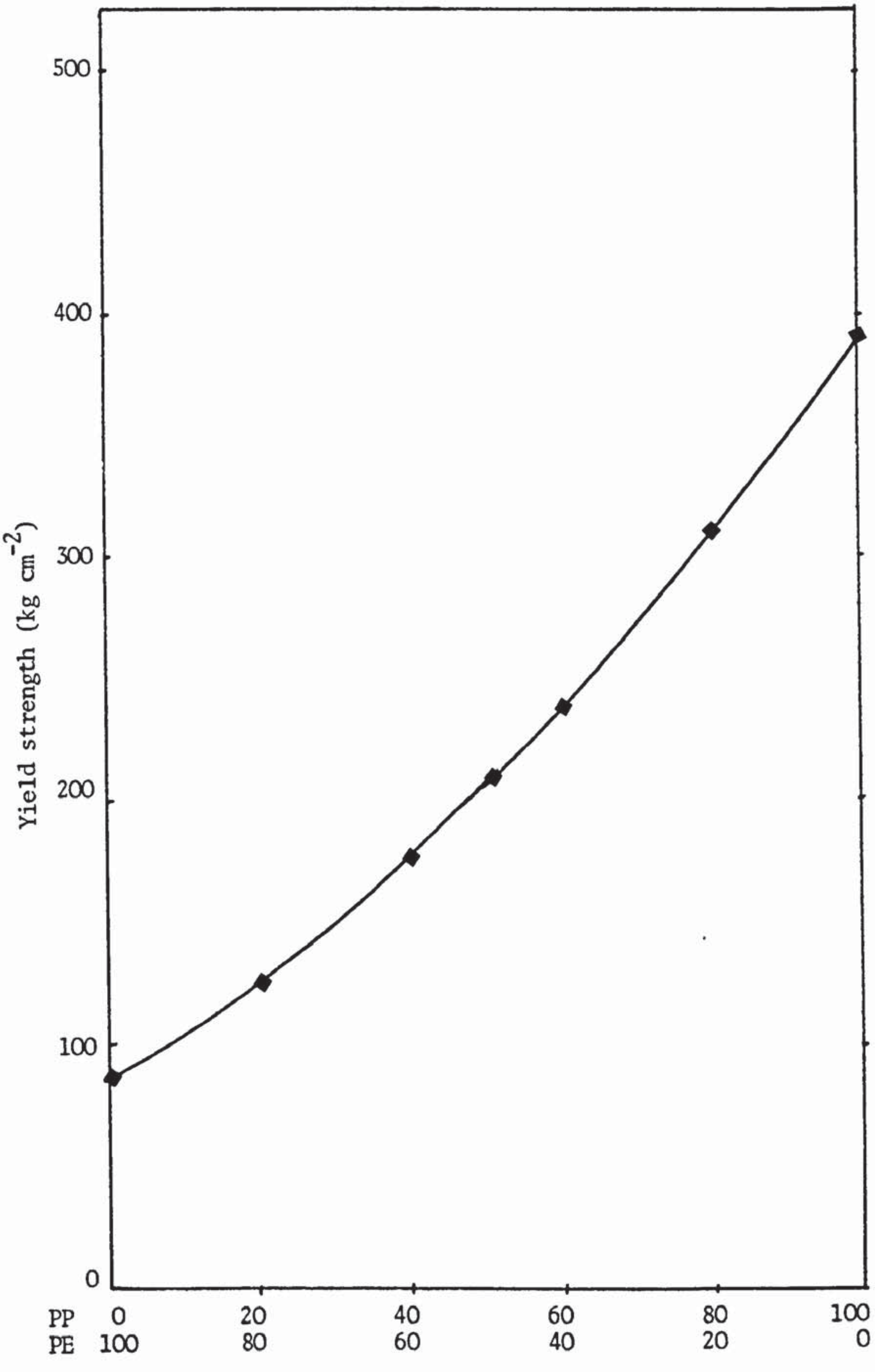


Fig 6.3 Change in yieldstrength with composition for PE/PP blends

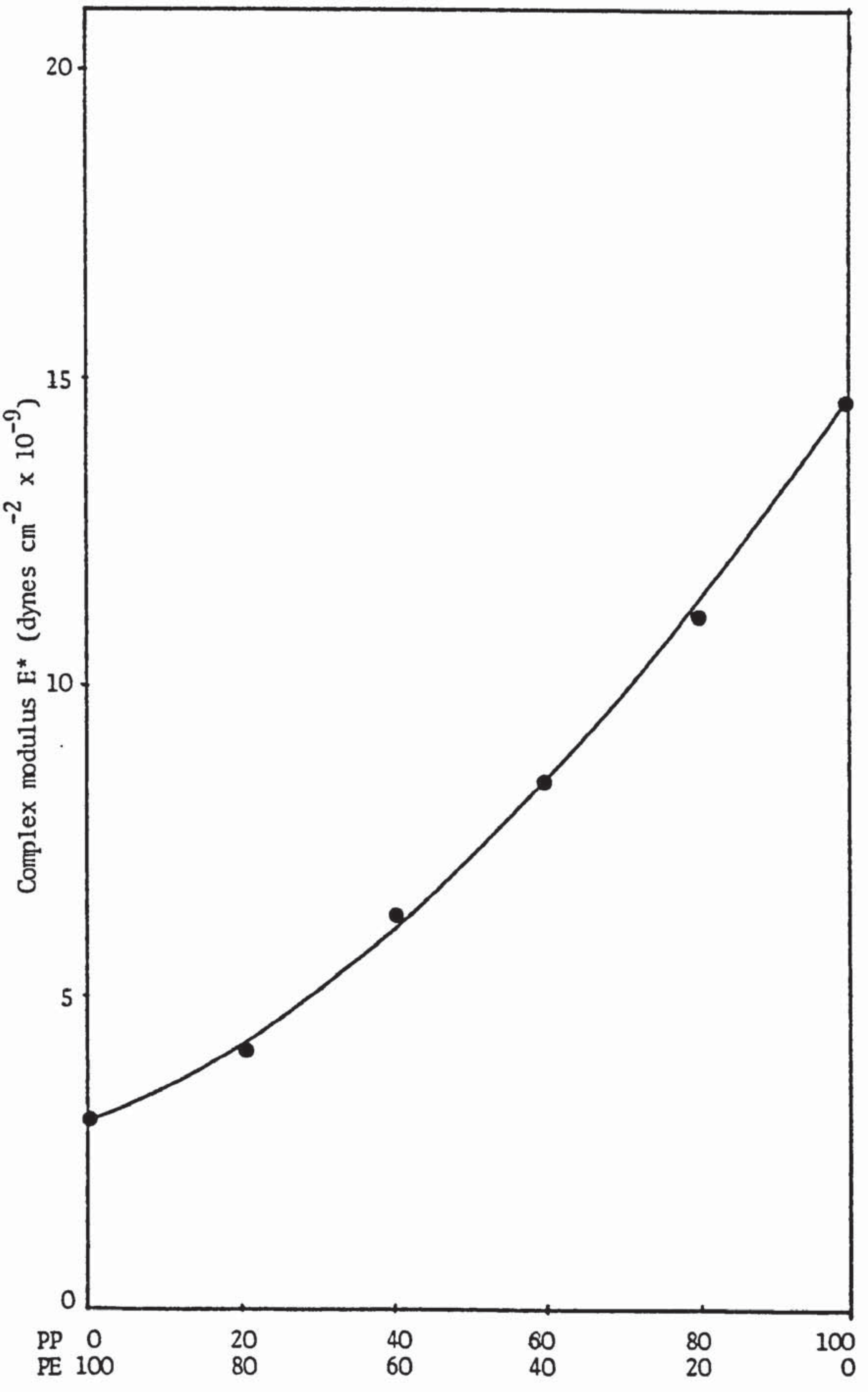


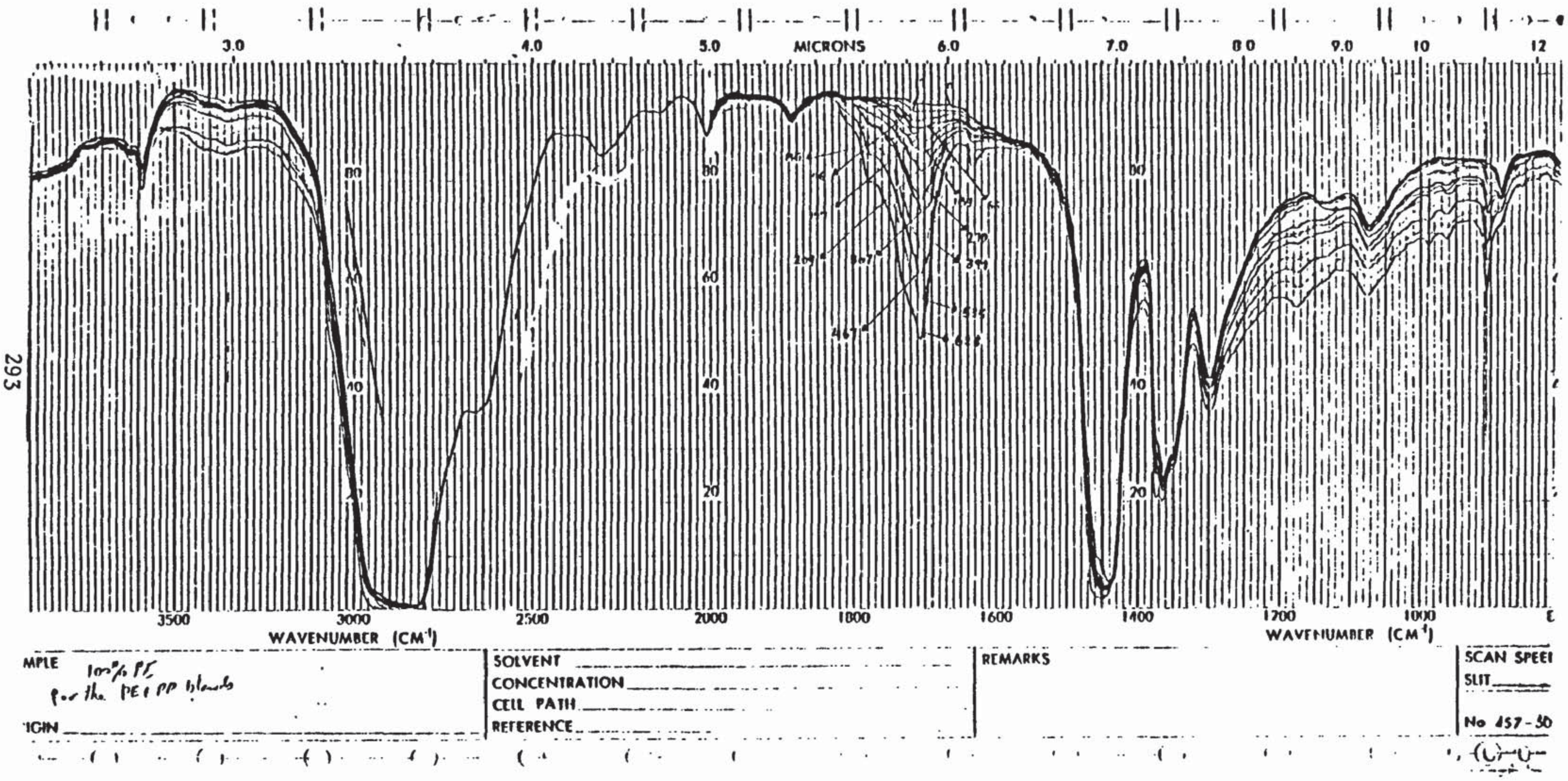
Fig 6.4 Change in complex modulus with composition for PE/PP blends

It can be seen from infra-red spectroscopy of unstabilised PP and unstabilised PE/PP (50:50) blend (Figs 6.5 and 6.6) that the absorption at 3300-3500 cm^{-1} and 1710 cm^{-1} change during uv irradiation due to the increase in hydroxyl and carbonyl concentration respectively. It is clear from the infra-red spectra that the addition of polypropylene photosensitised LDPE as measured by the growth of carbonyl in LDPE containing 50% PP. Sadrmohaghegh(41,42) has also studied the changes in carbonyl group of low density polyethylene with varying concentrations of polypropylene (see Fig 6.7). It can be seen from Fig 6.7 that the rate of photodegradation of polyethylene increases as polypropylene concentration is increased. The embrittlement time of polyethylene (100%) decreased from 900 hours to 180 hours by addition of 50% polypropylene (ie PE/PP (1:1) ratio). The present and previous studies confirm this conclusion; as little as 5% of PP has a very significant effect on changes in mechanical properties of LDPE during photo-oxidation. This is not a morphological effect since the polymers are completely compatible at this ratio.

6.3.A.2 The Effect of EPDM Concentration on Mechanical and Long Term Performance of LDPE/PP (50:50) Blend

It has been shown previously(54,65) that the toughness of PE/PP blends can be very considerably improved by the incorporation of minor proportions of an ethylene-propylene diene terpolymer (EPDM). The improvement in impact resistance of this polyblend is due to

Fig 6.5 Infra-red spectra of photo-oxidised LDPE film (numbers on curves are exposure time in hours)



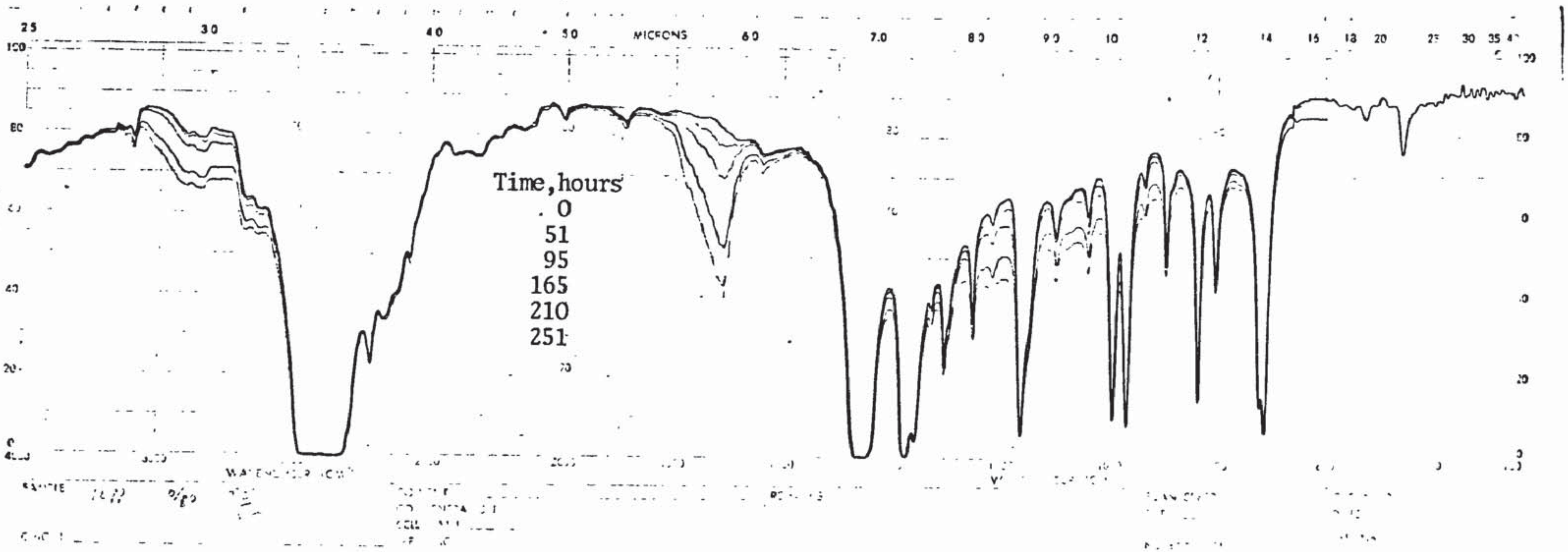


Fig 6.6 Infra-red spectra of photo-oxidised LDPE/PP (50:50) blend film (numbers on curve are exposure times)

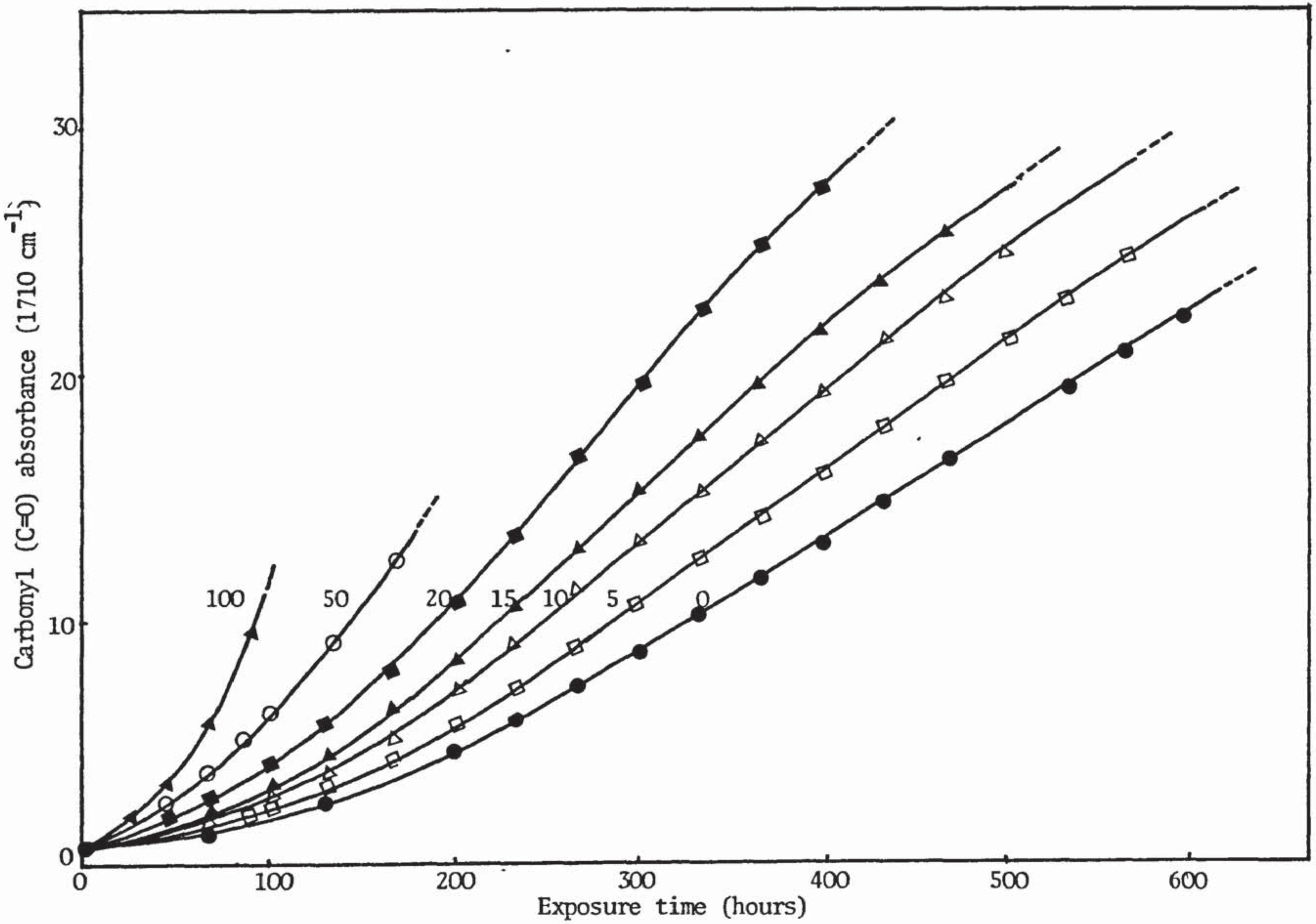


Fig 6.7 Effect of PP concentration on carbonyl formation of PE/PP blends during uv irradiation (numbers on curves are PP concentration in percentage) (Reproduced from C Sadrmohaghegh's Thesis)

the ability of the elastomer to behave on the one hand as a solid phase dispersant (SPD) and on the other hand as an impact modifier$^{(54)}$. The effect of the addition of EPDM on the impact strength, elongation at break and tensile strength of PE/PP (1:1) ratio are shown in Figs 6.8, 6.9 and 6.10. It is clear that the addition of 10-20% of EPDM to a weak LDPE/PP (1:1) blend leads to a remarkable improvement in impact resistance (Is) and elongation at break. The addition of rubbery EPDM reduces the tensile strength of PE/PP (1:1) and the complex modulus (E*) at room temperature was decreased half its value by addition of 20% EPDM (see Figs 6.10 and 6.11). Tan δ at room temperature shows a gradual increase by increasing EPDM concentration. However, the fact that EPDM actually increases the impact resistance of 1:1 blend of LDPE/PP suggests that as in the case of other impact modified polymers$^{(36)}$ the rubber forms as an energy absorbing interphase between the continuous (LDPE) and the dispersed phase (PP). However, the tensile strength of the polymer blend is substantially decreased by this treatment to about 50% of that of LDPE itself and it appears that separation of the two phases may occur relatively easily. EPDM is being increasingly used as an impact modifier for PP. Speri and Patrick$^{(152)}$ have recently reported that the optimum particle size of the dispersed phase is in the region of 0.5 nm. However, they point out that this is achievable only under conditions of high shear and when the bulk viscosity of the continuous phase and dispersed phase are closely matched. These conditions are satisfied only by polypropylene of such high molecular weight that it cannot conveniently be injection

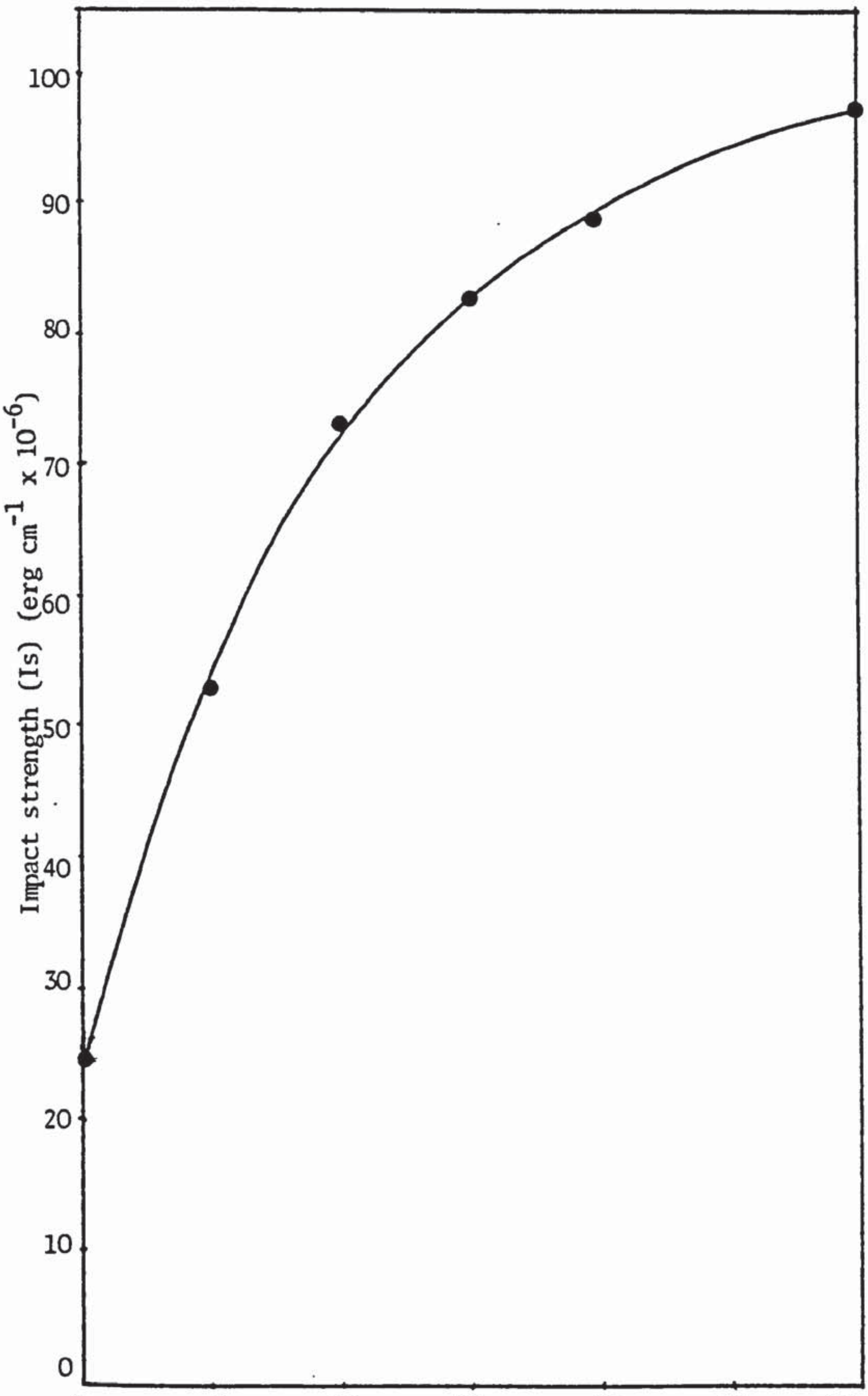


Fig 6.8 Change in impact strength (Is) of PE/PP (1:1) blend as a function of EPDM content

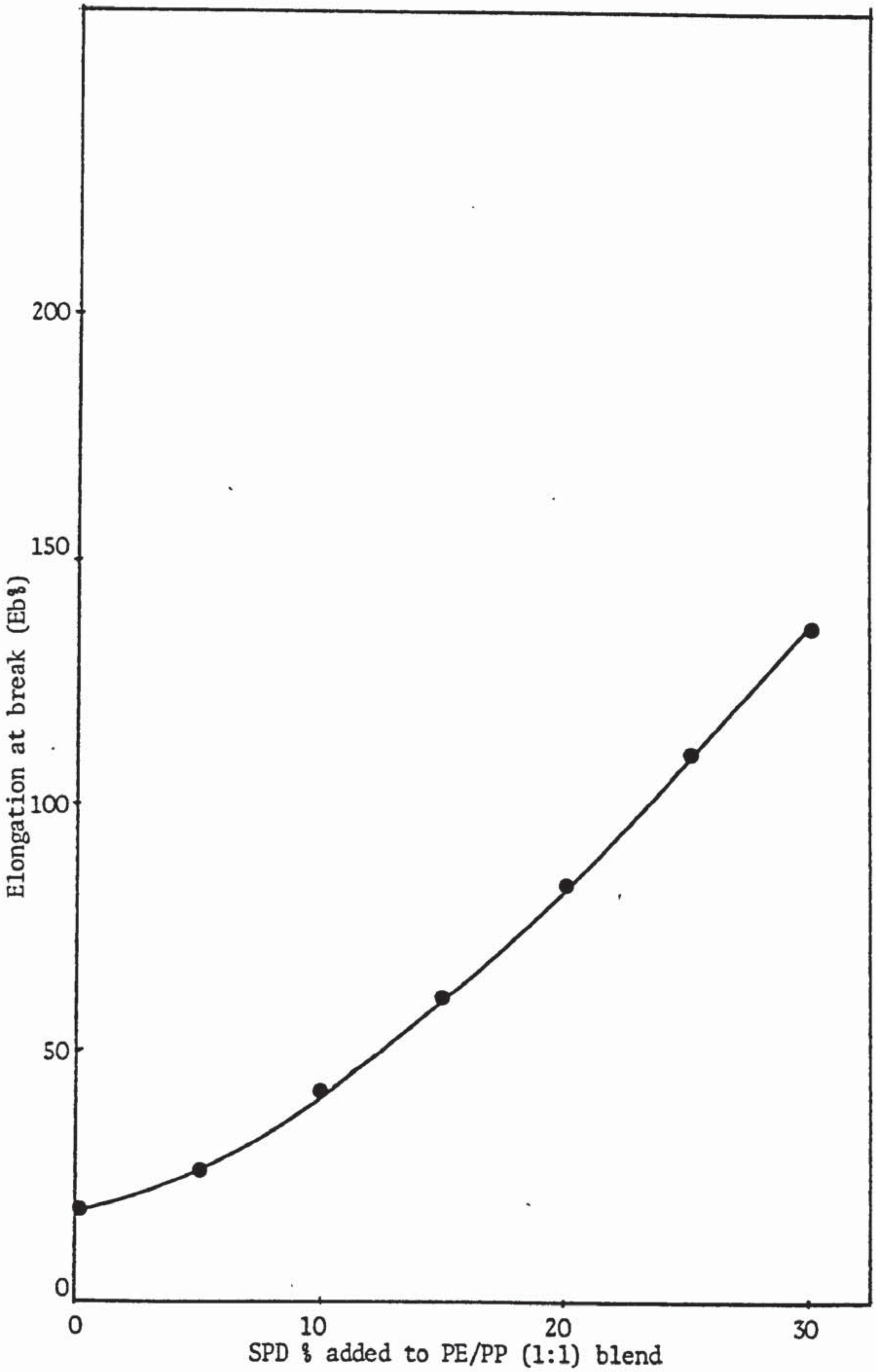


Fig 6.9 Change in elongation at break (Eb%) of PE/PP (1:1) blend as a function of EPDM content

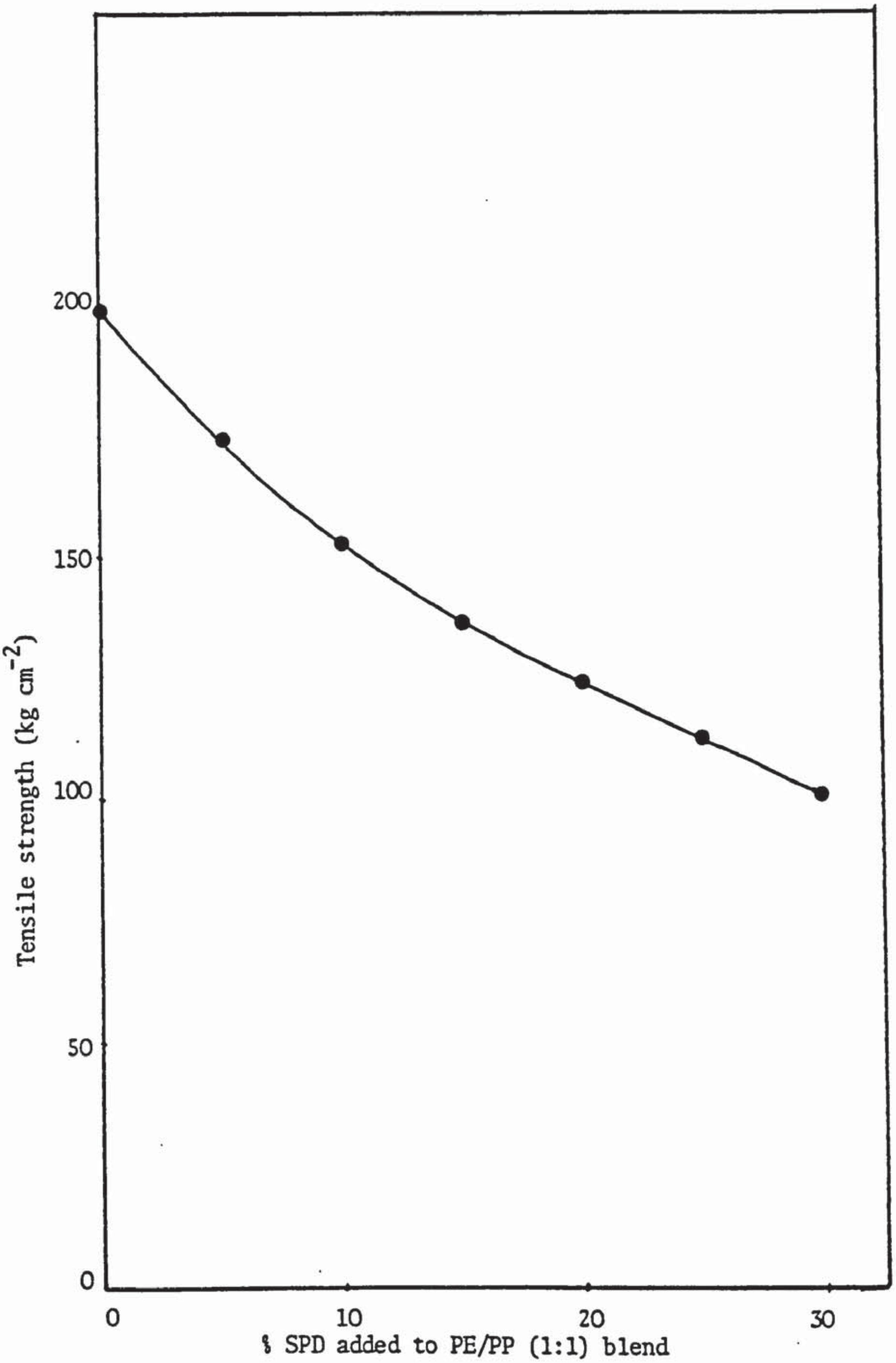


Fig 6.10 Change in tensile strength (Ts) of PE/PP (1:1) blend as a function of EPDM content

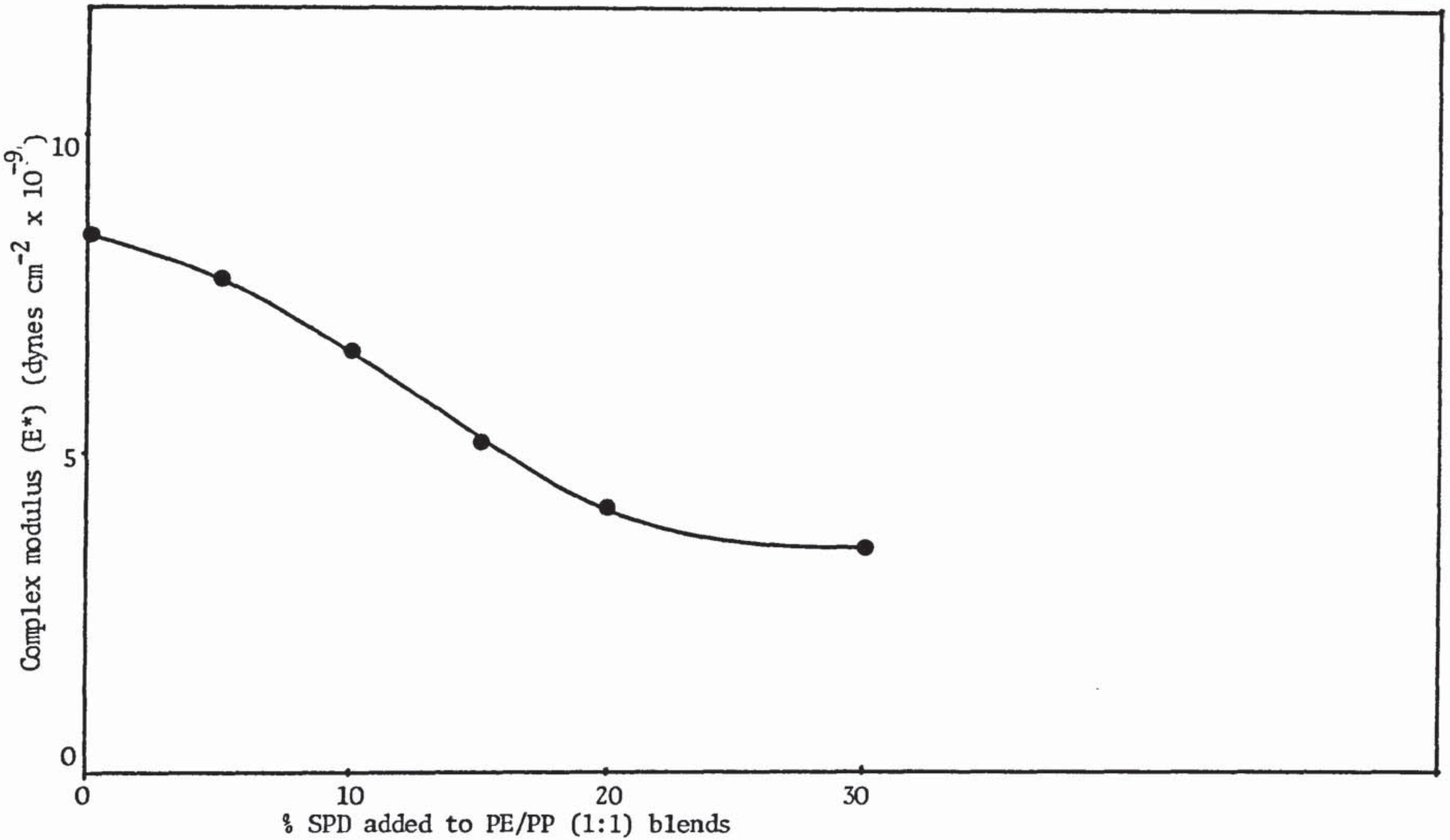


Fig 6.11 Change in complex modulus (E*) of PE/PP (1:1) blend as a function of EPDM content (room temperature)

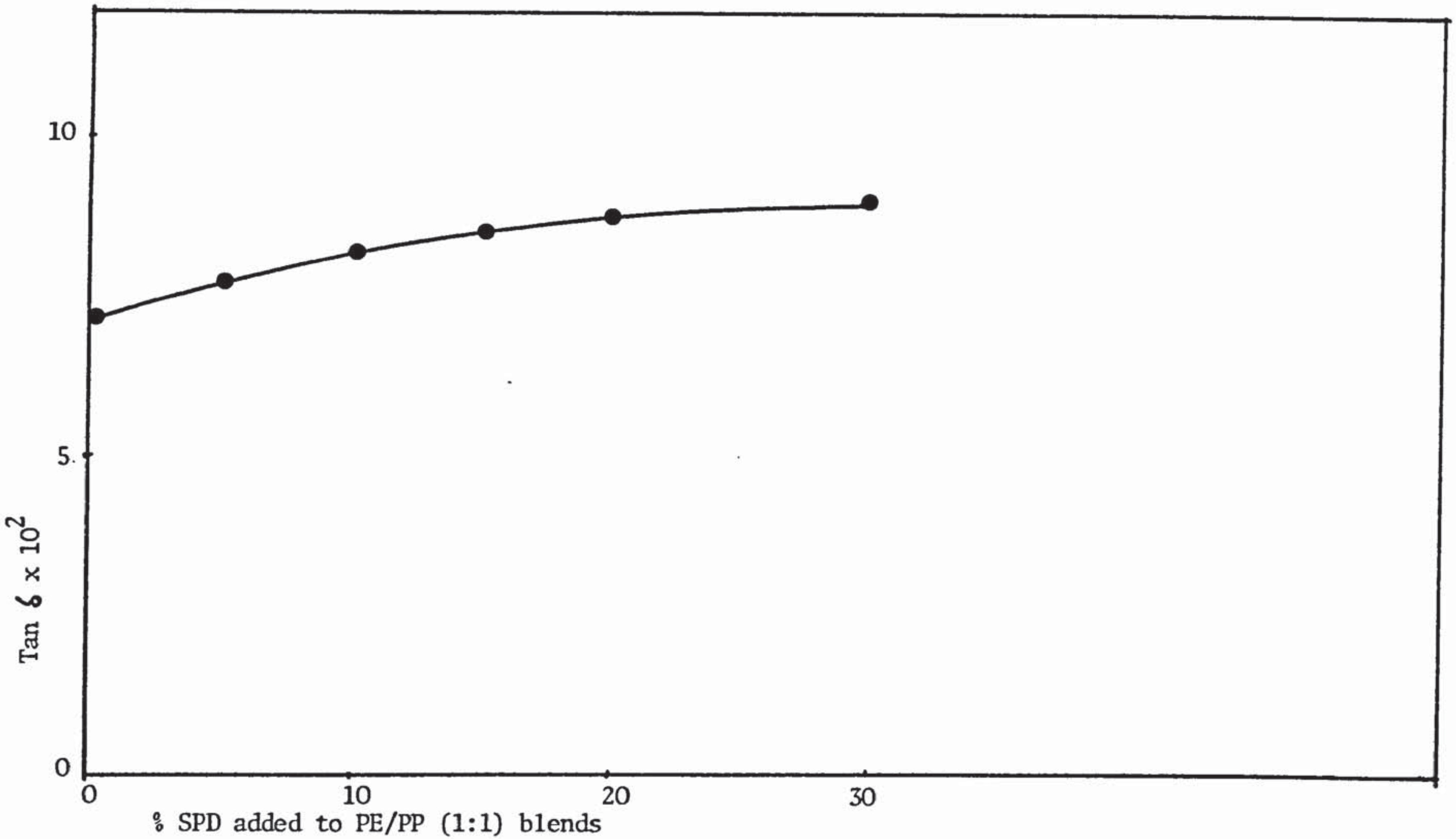


Fig 6.12 Change in tan δ of PE/PP (1:1) blend at room temperature as a function of EPDM content

moulded. The addition of HDPE was found to increase the dispersibility of EPDM in PP and gave a high flexural modulus in the toughened PP.

It is well established that oxidisable polymers can act as photosensitisers for photostable polymers(162). Chain-branching and unsaturation are particularly effective photo-pro-oxidants even when present in very minor proportions(38,39,156,162,163). This has been shown(39,163) to be due to the formation of hydroperoxides at the oxidatively susceptible sites during thermal processing. Although the addition of EPDM to PE/PP (1:1) blend improves its mechanical properties (particularly impact strength) the presence of an additional centre of photo-oxidative instability by the introduction of ethylenic unsaturation, might be expected to lead to more rapid loss of impact resistance under photo-oxidative conditions. Figs 6.13 and 6.14 show that as anticipated, the rate of carbonyl formation is higher the higher the concentration of EPDM and all tertiary blends give a higher rate of photo-oxidation than LDPE/PP (1:1) blend alone. A study of the loss of impact resistance under the same conditions confirms this conclusion. Fig 6.15 shows that the impact resistance of the ternary blends are not substantially less than that of pure LDPE, but that their rate of loss of impact strength on uv irradiation is considerably higher for the ternary blends than for the binary blend. However, Table 6.3 shows that the embrittlement times of all the ternary blends are considerably longer than that of LDPE/PP (1:1) which is in turn more oxidatively stable than unstabilised PP itself,

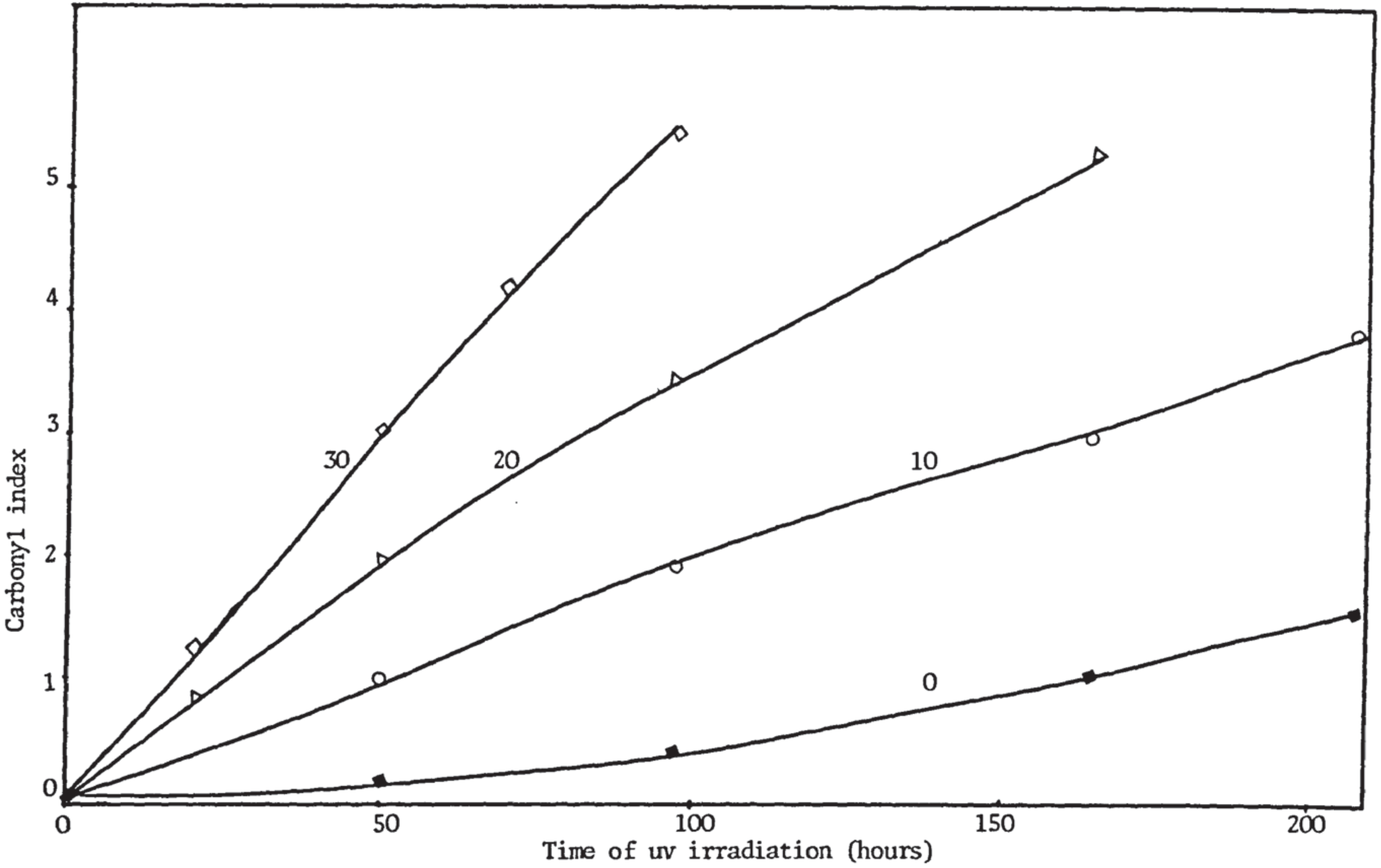


Fig 6.13 Effect of EPDM concentration on carbonyl formation in PE/PP (1:1) blends during uv irradiation (numbers on curves are EPDM concentrations in g/100 g)

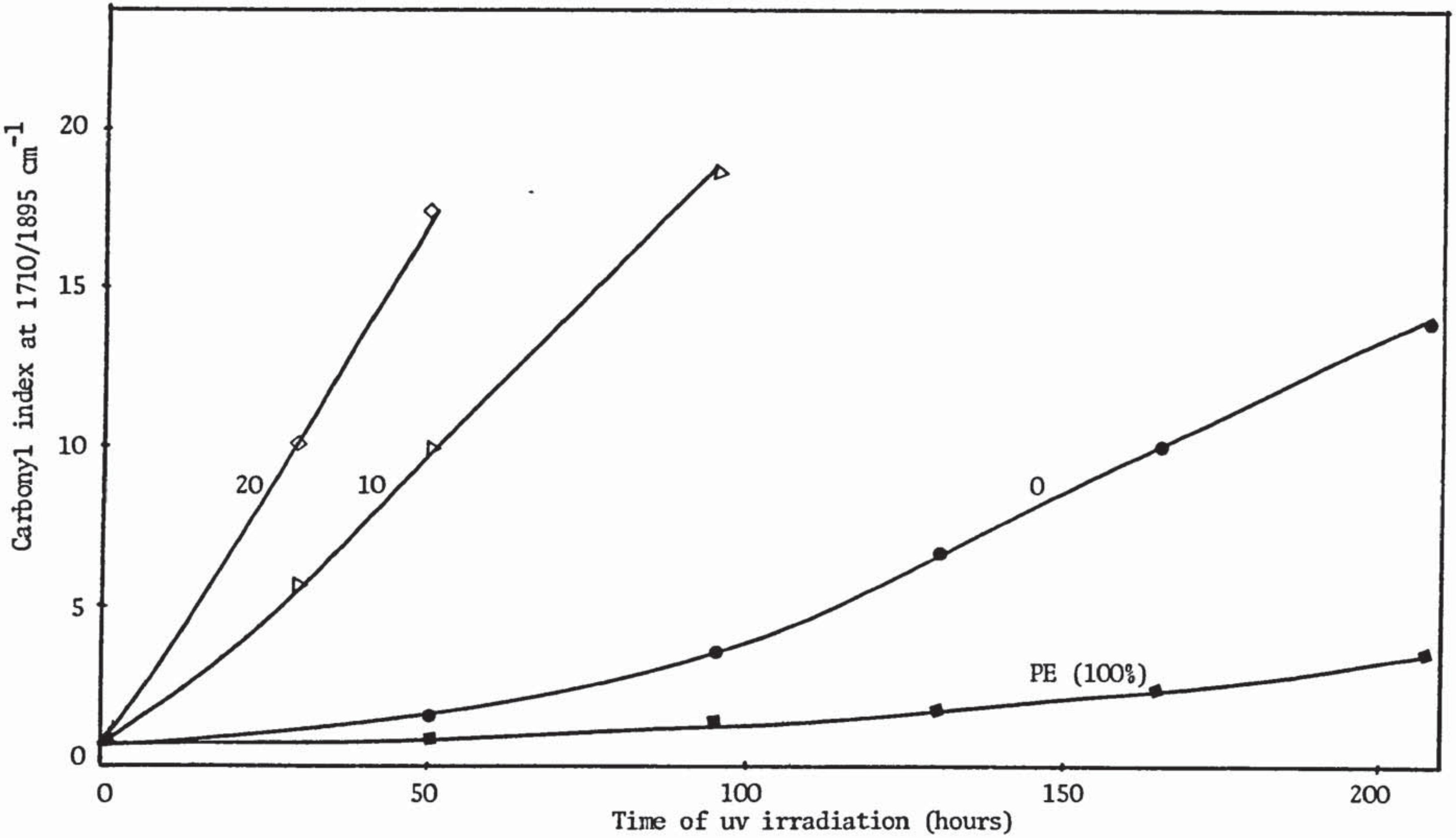


Fig 6.14 Effect of EPDM concentration on carbonyl formation in PE/PP (1:1) blends during uv irradiation (numbers on curves are EPDM concentration in g/100 g)

Table 6.3 Embrittlement time of PE/PP blends

Blend composition	PE(100%)	PP(100%)	PE/PP 50:50	PE/PP/EPDM 45:45:10	PE/PP/EPDM 40:40:20	PE/PP/EPDM 35:35:30
Embrittlement time (hrs ±20)	900	90	180	210	260	320

although none of the blends compare with unstabilised LDPE in stability. This increase in embrittlement times of ternary blends (ie with different concentrations of EPDM) could possibly be due to the particular structure of the diene used which does not lead to chain-scission, with rupture of the double bond (see also scheme 5.1). The increase in impact strength observed in binary LDPE/PP and ternary PE/PP/EPDM blends in initial stages on uv irradiation (Fig 6.15) is evidence for a chemical interaction between the phases. It has been shown previously(151) that LDPE undergoes a cross-linking process involving the oxidatively susceptible vinylidene groups present in the polymer under the same conditions and it seems likely that the formation of interfacial grafting may occur at the boundaries of the PP domains under photo-oxidative conditions, leading to better interphase adhesion. Fig 6.15 indicates the increase in impact strength of polyethylene 100% at around 100 hours of uv irradiation.

6.3.A.3 Stabilisation of LDPE/PP (1:1) Blend Containing 20% EPDM as Solid Phase Dispersant

Ternary blends containing LDPE/PP/EPDM with the ratio of 40/40/20 were taken respectively and were stabilised using conventional stabilisers such as NiDEC, NiDBC, UV531, Tinuvin 770 and Irganox 1076 as well as bound MADA diluted from 2% masterbatch (see section 4.1.6.1 for masterbatch preparation). The photo and thermal degradation of the polymer blends were carried out by measuring carbonyl formation at 1710 cm^{-1} and the absorbance at 2710 cm^{-1}

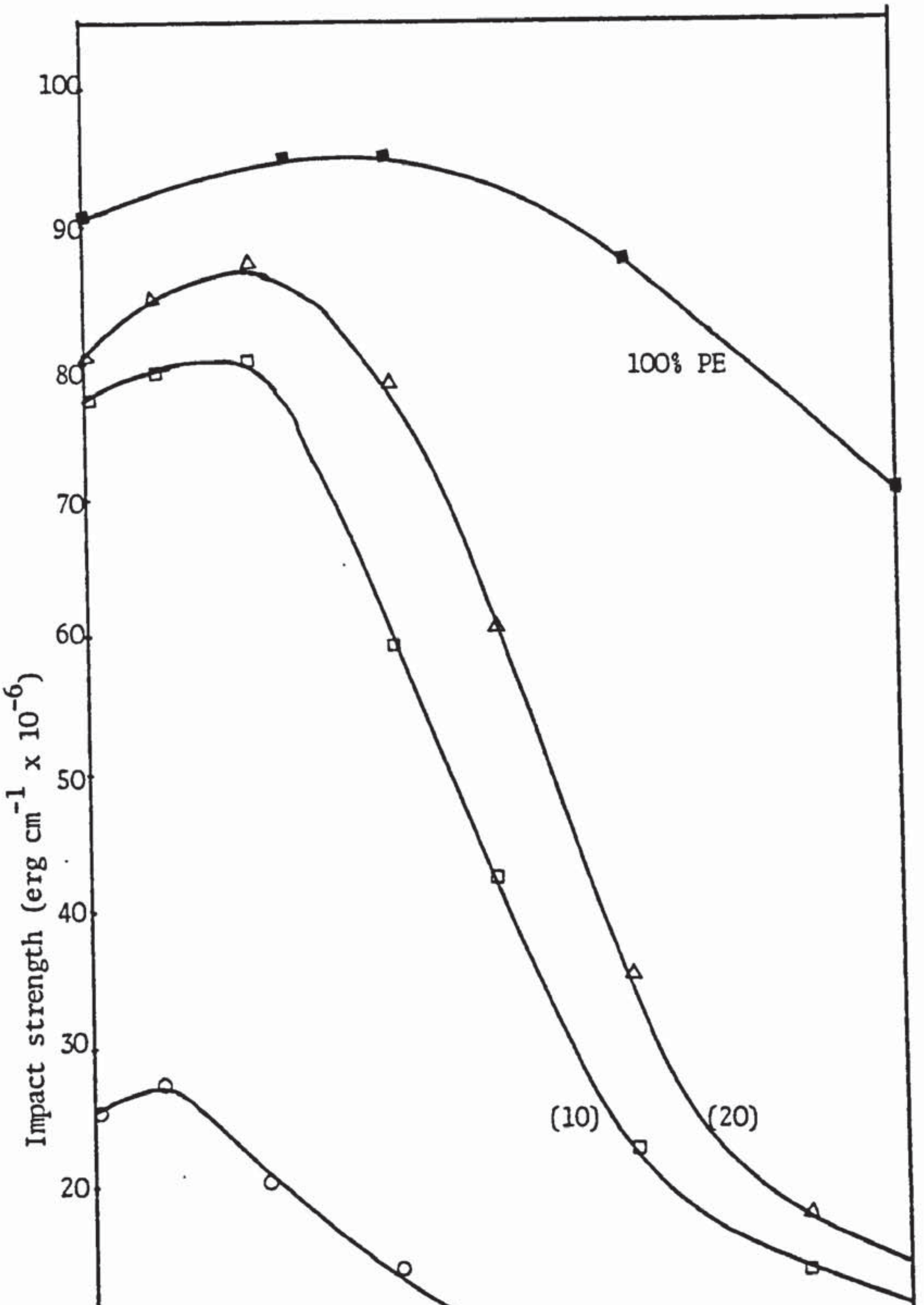


Fig 6.15 Effect of EPDM concentration on impact strength (Is) of PE/PP (1:1) blends during uv irradiation (numbers on curves are EPDM concentration in g/100 g)

was taken as reference peak in PE/PP/EPDM blends. The carbonyl index was measured as the ratio of absorbance at 1710 cm^{-1} to that of the reference peak. Also the loss in mechanical properties (ie impact strength) of the blends was carried out using the falling weight impact tester (see section 2.11). Compression moulded films of stabilised and unstabilised ternary blends were uv exposed and also heated at 110°C and the change in impact was measured by the falling weight tester. The development of carbonyl in ternary blends of PE/PP/EPDM containing 3×10^{-4} mole percent of conventional additives are shown in Fig 6.16. As it can be seen, Irganox 1076 (CB-A) and UV531 (uv absorber) retard the rate of photodegradation and NiDBC (PD-C) was much more effective than UV531 and induction period of 100 hours was observed. Tinuvin 770 with the same molar ratio showed better stabilising effect. By increasing the concentration of the additives to 6×10^{-4} mole percent, NiDBC was found to operate better than other additives with 210 hours of induction period. The effect of additives concentration on carbonyl formation are shown in Fig 6.17. The decay of impact resistance of samples containing NiDBC, UV531 and Tinuvin 770 with different concentrations were studied and are shown in Fig 6.18. As it can be seen, the loss of impact strength correlates with carbonyl formation after induction periods observed. The importance of hydroperoxides as initiators for the photo-oxidation of the polyolefins is now well established(20,157,148,164) and the rate of photo-oxidation is found(20,164) to be a direct function of the initial (thermally produced) hydroperoxide concentration. The 'uv absorber' is

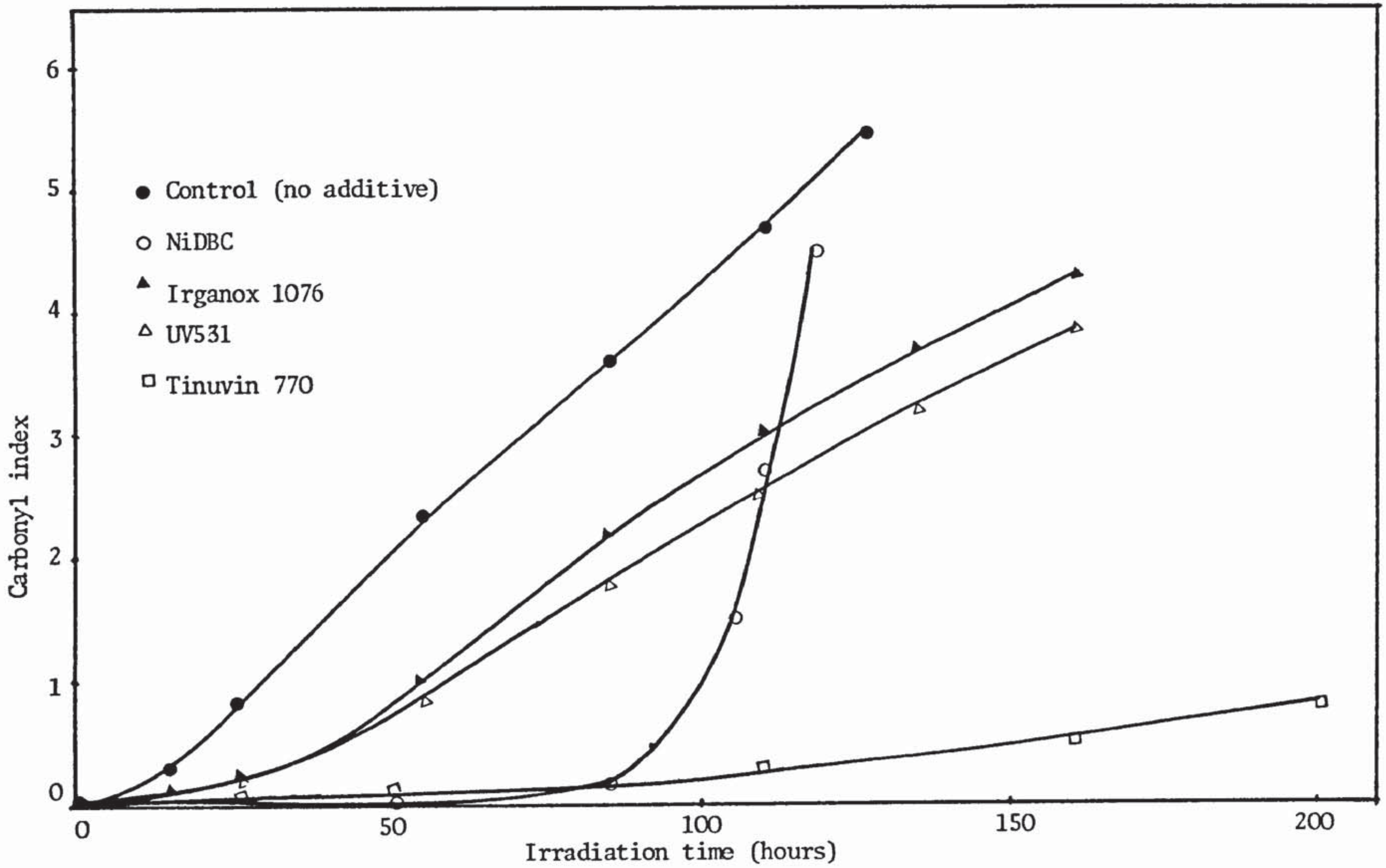


Fig 6.16 Development of carbonyl (1710 cm^{-1}) on uv exposure of PE/PP blends containing 20% EPDM (additive concentration 3 x 10^{-4} mol/100 g, processed at 180°C/10 mins, closed chamber)

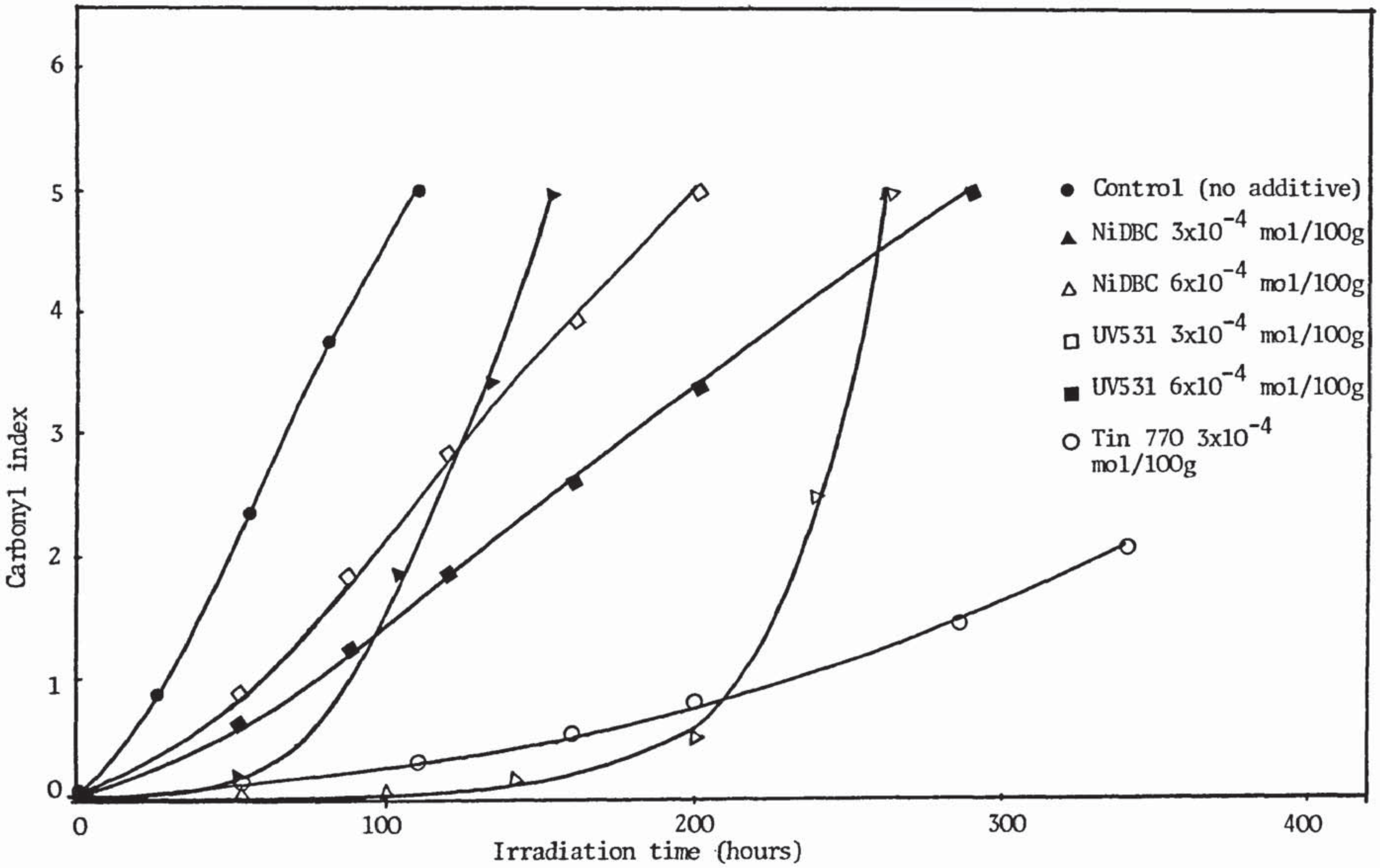


Fig 6.17 Development of carbonyl (1710 cm^{-1}) on uv exposure of PE/PP blends containing 20% EPDM (samples containing conventional antioxidants)

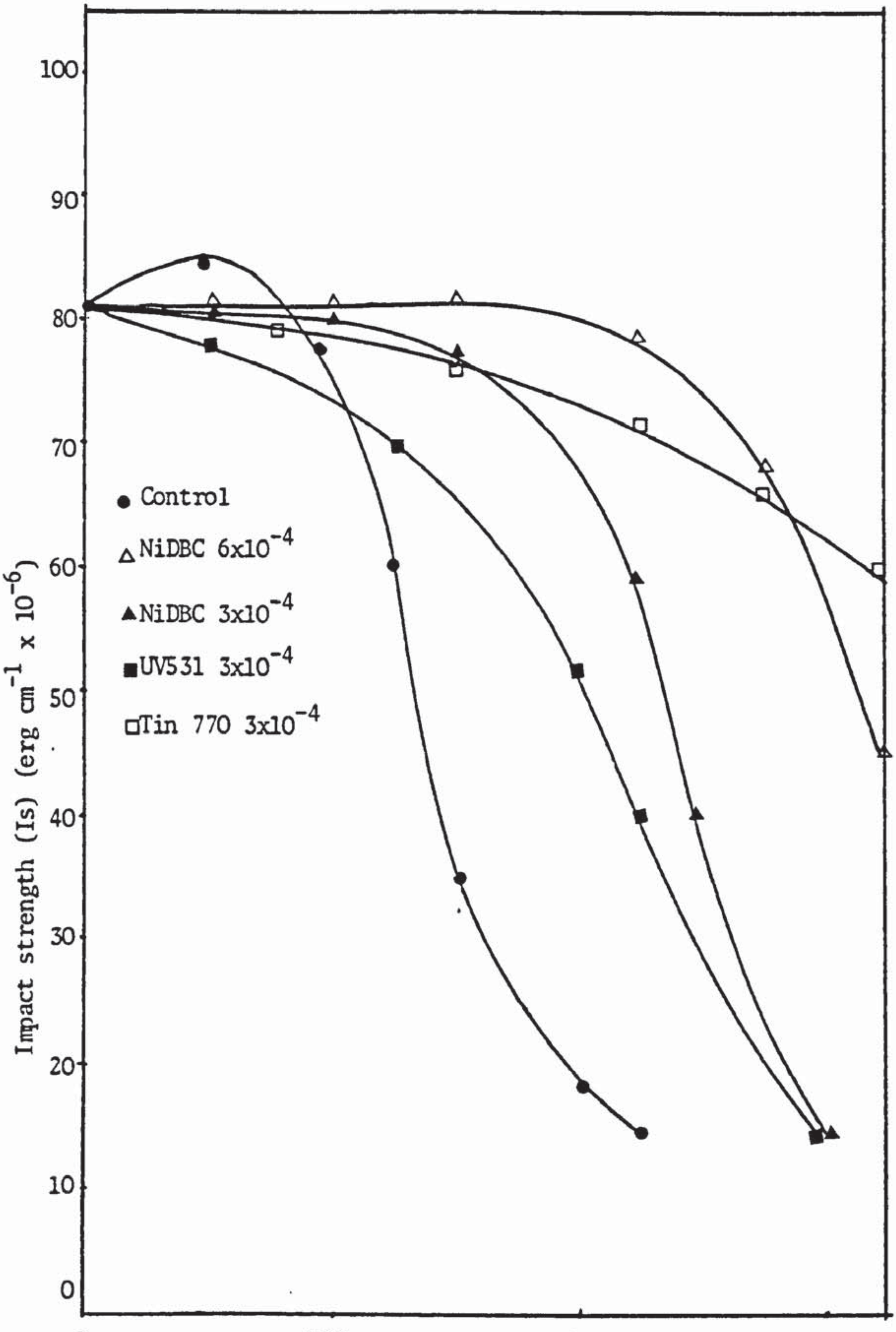


Fig 6.18 Decay of impact resistance of PE/PP blends containing 20% EPDM on uv exposure. All samples processed at 180°C/10 mins, closed chamber, concentration mol/100 g

unable to inhbiit the formation of hydroperoxide in this system during processing and does not destroy it during photo-oxidation and it is found to be rapidly destroyed by hydroperoxides(165). UV531 (HBOP), is, therefore, an indifferent antioxidant during processing (Figs 6.16 and 6.17) and appears to behave essentially as a screen during the early stages of photo-oxidation when hydroperoxides are the primary photo-initiators(166). NiDEC and NiDBC were found to operate as a very good uv stabiliser and it is in accordance with their known ability to catalytically destroy hydroperoxides into non-radical reaction both thermally(47,166) and in the presence of light(47). Tinuvin 770 has been found to operate by(155) its formation into nitroxyl radical through a regenerative mechanism. The development of carbonyl at 1710 cm^{-1} and loss of impact properties of samples containing different concentrations of bound MADA diluted from 2% masterbatch are shown in Figs 6.19 and 6.20. It is clear from Fig 6.19 that bound MADA retards the rate of photo-oxidation of the samples after an induction period. It is also found that increasing MADA concentration increases induction period and embrittlement times of the samples (see Table 6.4). Induction period and embrittlement time of the samples containing different additives are given in Table 6.4. The photostabilising effect of MADA might possibly be due to the formation of nitroxyl radical through a regenerative mechanism (see scheme 4.4, section 4.4).

Thermal ageing of the samples containing NiDEC, NiDBC and UV531 and bound MADA were carried out and the carbonyl formation and

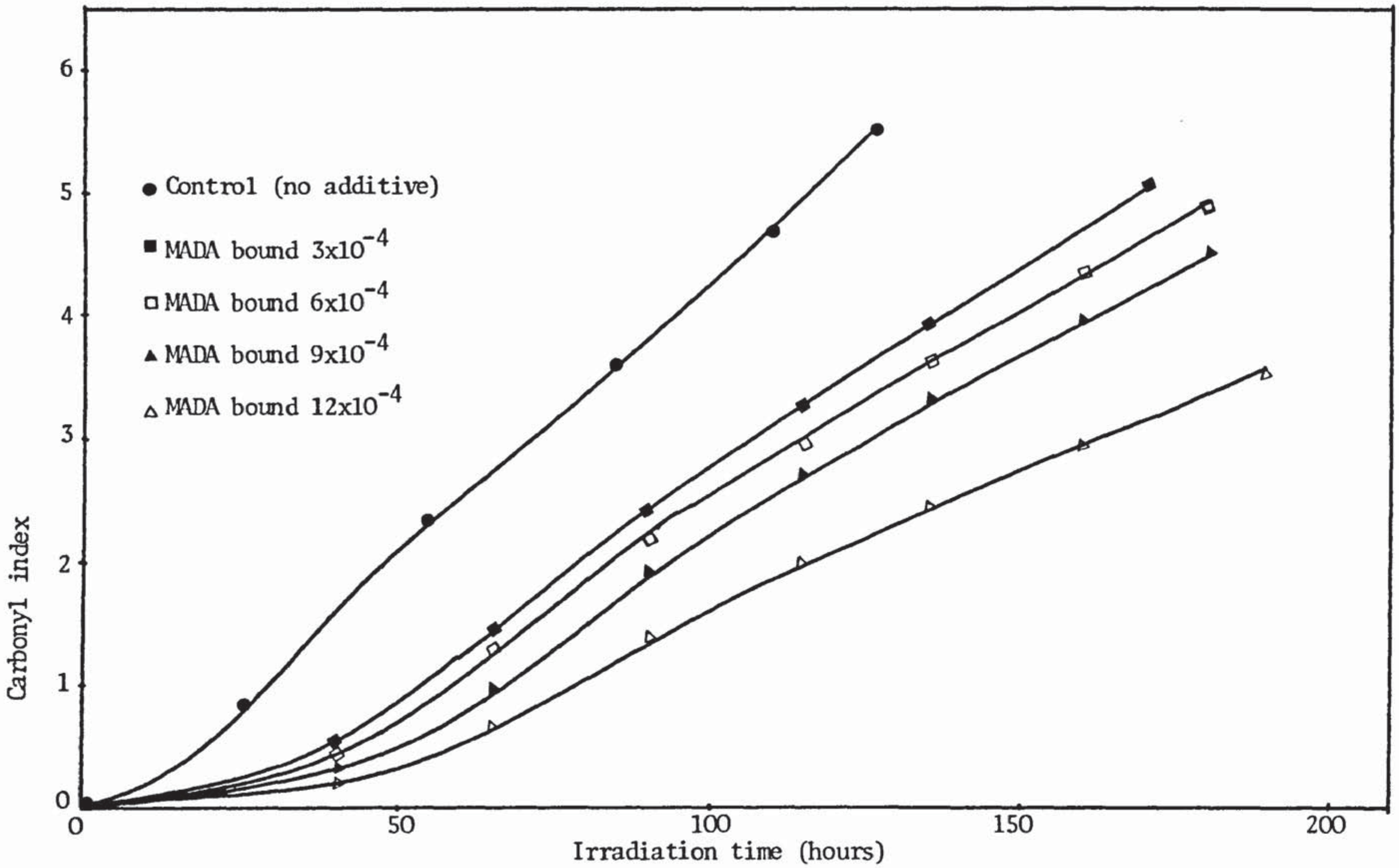


Fig 6.19 Development of carbonyl (1710 cm^{-1}) on uv exposure of PE/PP blends containing 20% EPDM (samples containing bound MADA diluted from 2% masterbatch)

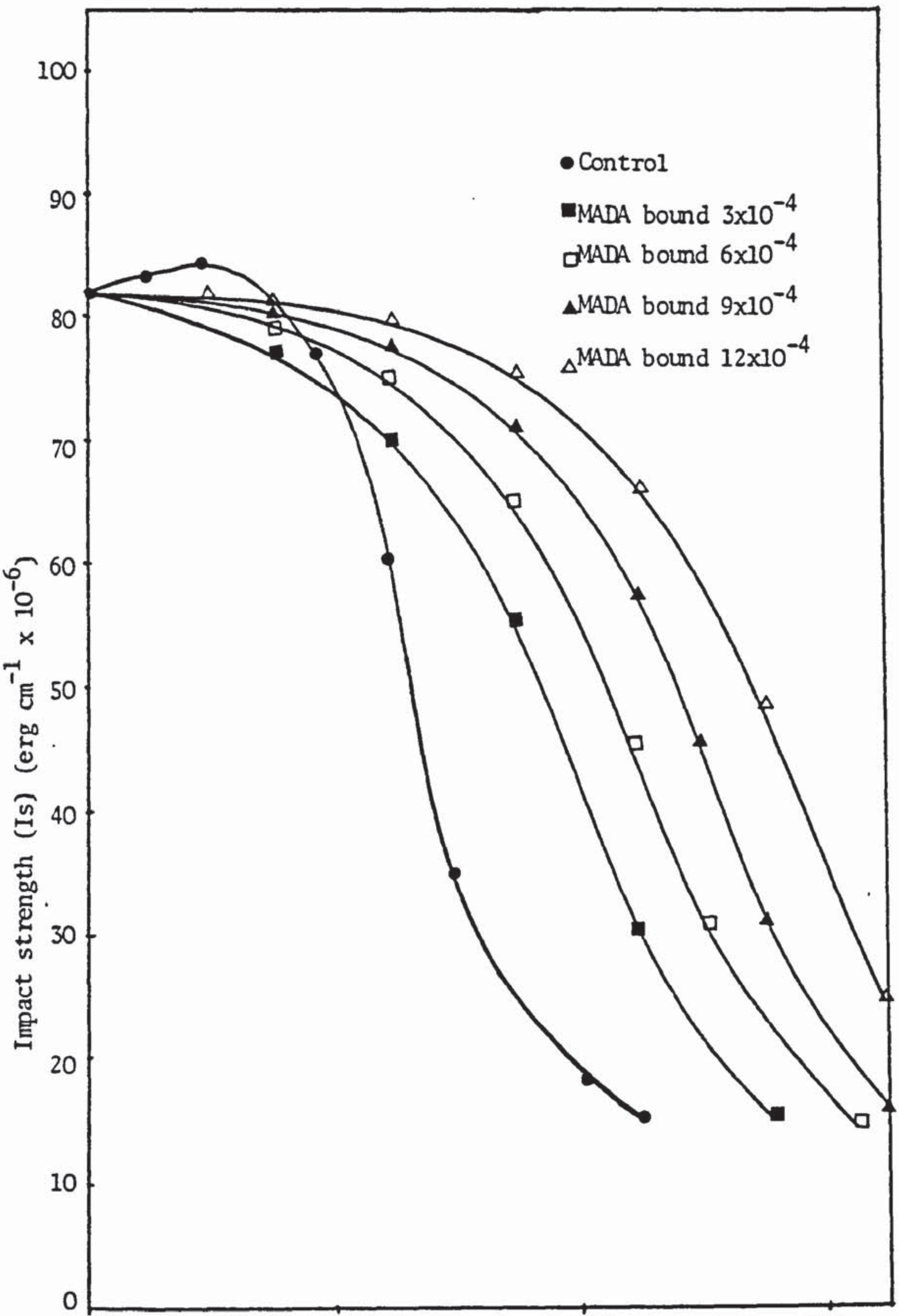


Fig 6.20 Decay of impact resistance of ternary PE/PP/EPDM (20%) containing MADA bound diluted from 2% masterbatch on uv exposure (concentration mol/100 g)

Table 6.4 Induction period and embrittlement times of PE/PP blend containing 20% EPDM as solid phase dispersants during uv irradiation

Antioxidant type	Conc of additive mol/100 g	Conc of additive g/100 g	Induction period hours	Embrittlement time hours ±50
Control (no add)	-	-	10	260
UV531	3×10^{-4}	0.098	30	450
UV531	6×10^{-4}	0.196	40	600
Irganox 1076	3×10^{-4}	0.159	30	330
NiDBC	3×10^{-4}	0.141	100	430
NiDBC	6×10^{-4}	0.282	210	650
NiDEC	3×10^{-4}	0.106	30	400
Tinuvin 770	3×10^{-4}	0.144	-	950
Bound MADA*	3×10^{-4}	0.077	30	330
Bound MADA*	6×10^{-4}	0.155	35	480
Bound MADA*	9×10^{-4}	0.232	43	540
Bound MADA*	12×10^{-4}	0.310	50	640

* diluted from 2% masterbatch

loss of impact from samples were measured. Fig 6.21 shows the formation of carbonyl group at 1710 cm^{-1}. Loss of impact strength with oven ageing at 110°C correlates with the development of carbonyl and impact of the blends is lost rapidly after an induction period (see Fig 6.22). Induction period and embrittlement time of the samples during oven ageing at 110°C are given in Table 6.5. As it can be seen from Fig 6.21, NiDEC and NiDBC are shown to be very good thermal stabilisers by destroying hydroperoxides through a non-radical mechanism. UV531 does not stop thermal degradation of the blends and is similar to the control with no additive (see Fig 6.21). Carbonyl formation of blends containing different concentrations of MADA indicates a very good thermal stabilising effect (see Fig 6.23), and it is found that this is due to the formation of by products disulphides formed from the initial thiol under processing conditions which could possibly be converted to thiol sulphinates and related oxygenated species which are precursors of the peroxidolytic antioxidants(145) (see schemes 4.2 and 4.3, section 4.4).

6.3.B.1 The Effect of Polystyrene Concentration on Mechanical and Long Term Performance of LDPE/PS Binary Blend

Blends that contain roughly equal proportions of PE and PS have the strength of PE and the brittleness of PS(167). This combination of properties is very poor and consequently such blends have little value as structural materials. The change in tensile strength and elongation at break (Eb%) of low density

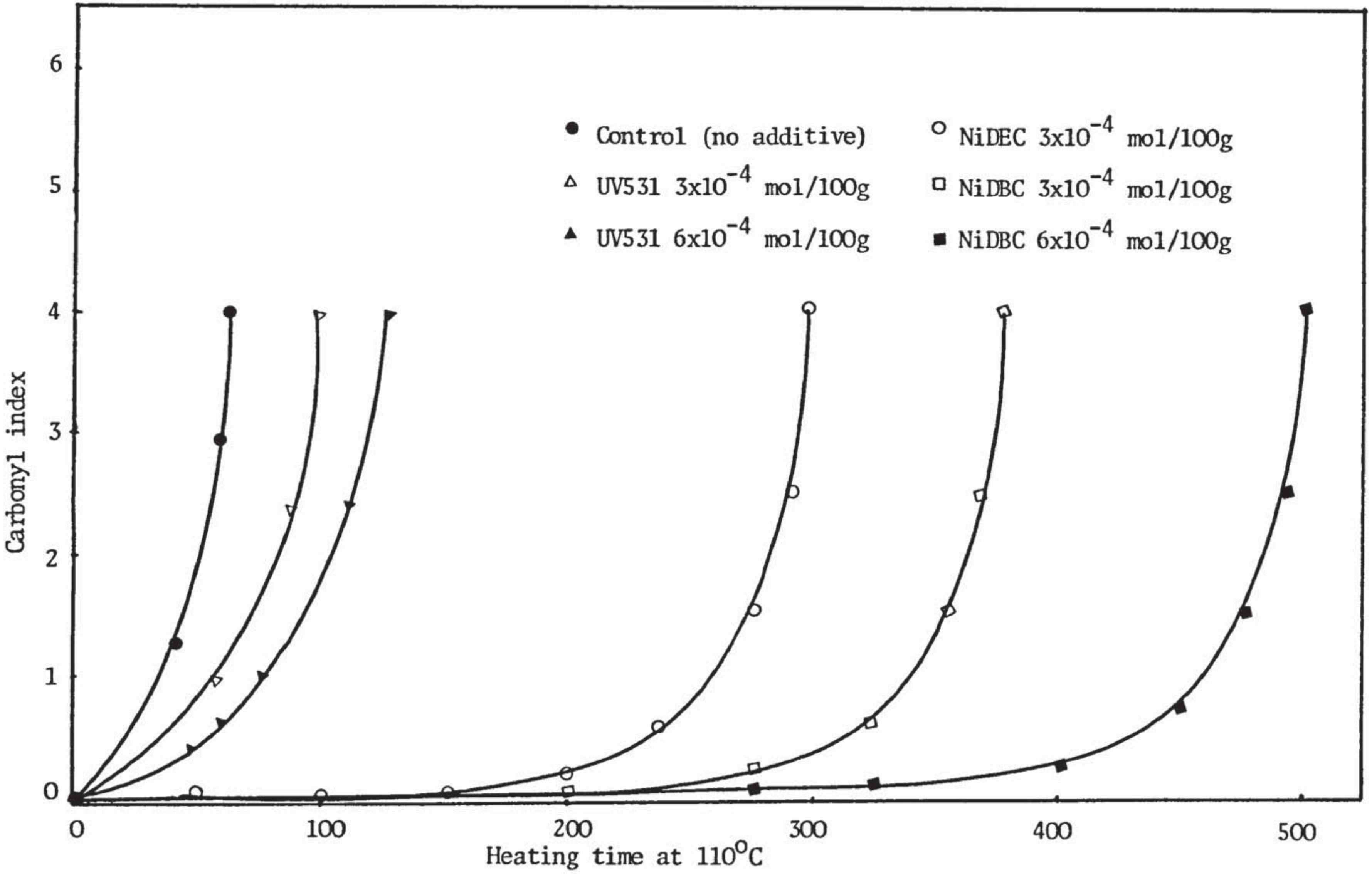


Fig 6.21 Development of carbonyl (1710 cm^{-1}) on thermal ageing at 110^{o}C in air of PE/PP blend containing 20% EPDM

Table 6.5 Induction period and embrittlement time of PE/PP blend containing 20% EPDM as solid phase dispersant during oven ageing at 110^{o}C

Antioxidant type	Concentration of additive mol/100 g	Concentration of additive g/100 g	Induction Period (hours)	Embrittlement time (hours $\pm$ 50)
Control	-	-	20	150
UV531	$3x10^{-4}$	0.098	23	160
UV531	$6x10^{-4}$	0.196	25	200
NiDEC	$3x10^{-4}$	0.106	250	400
NiDBC	$3x10^{-4}$	0.141	330	530
NiDBC	$6x10^{-4}$	0.282	460	750
MADA bound*	$3x10^{-4}$	0.077	200	300
MADA bound*	$6x10^{-4}$	0.155	440	700
MADA bound*	$9x10^{-4}$	0.232	650	850

* diluted from 2% masterbatch

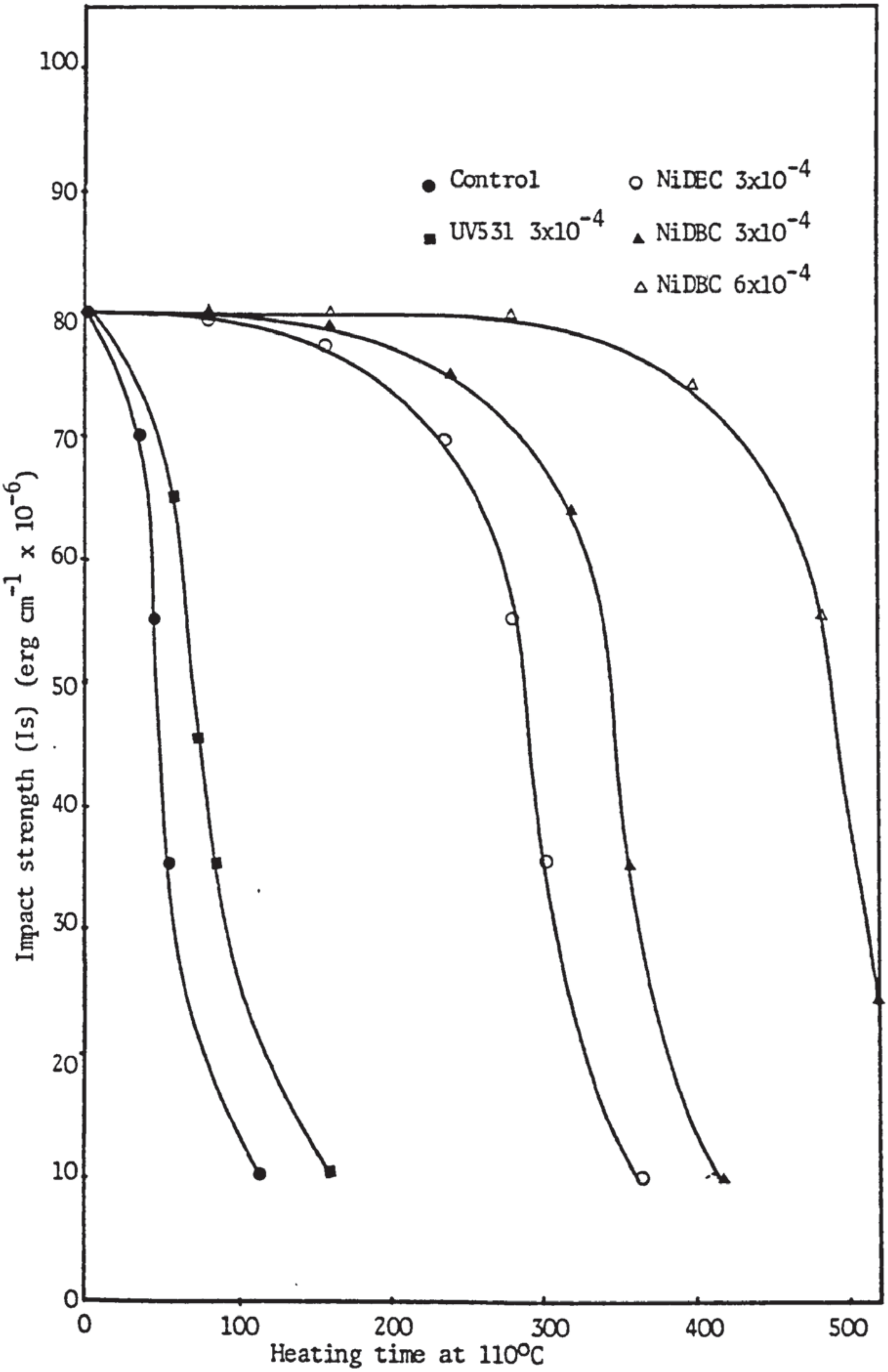


Fig 6.22 Decay of impact resistance of PE/PP blend containing 20% EPDM on oven ageing at 110°C (samples processed at 180°C/5 mins, closed chamber, concentration mol/100 g)

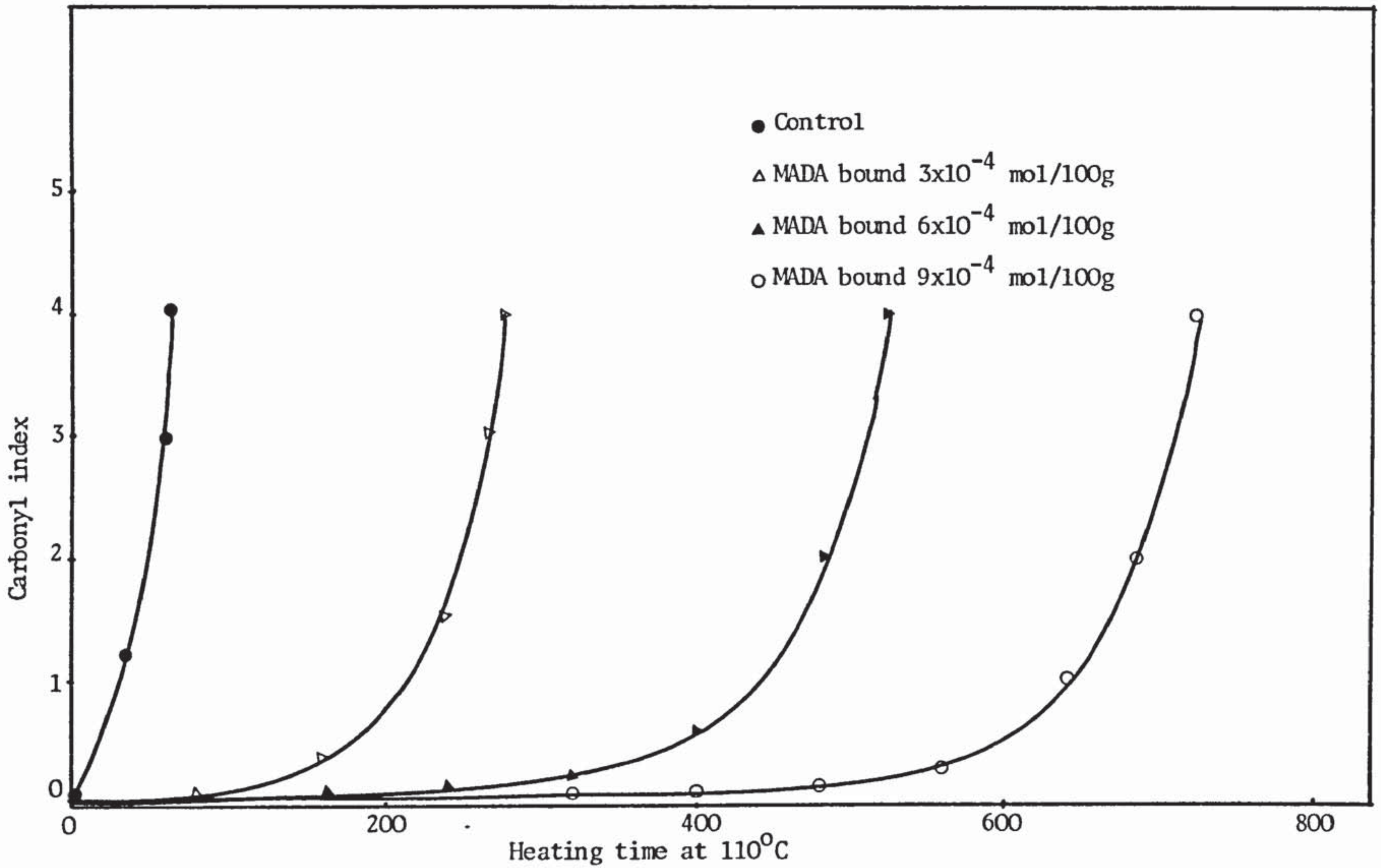


Fig 6.23 Development of carbonyl (1710 cm^{-1}) on thermal ageing at 110°C in air of PE/PP blends containg 20% EPDM (MADA bound diluted from 2% masterbatch)

polyethylene are plotted against polystyrene composition in Figs 6.24 and 6.25. The results indicate the incompatiblity of the blends and this is severe in the elongation at break. PE and PS are quite immiscible and microscopic examination reveals rather large domain structures(54,67,68). Heikens and Baransten(67) have studied the particle size and domains in PE/PS blends as a function of their melt viscosity. Barensten, Heikens and Piet(67,68) concluded from microscopic examination that if the content of one of the polymers in PE/PS blends is less than 40%, this polymer forms a disperse phase.

Infra-red studies of uv irradiated films of PE and PE/PS (1:1) blend are shown in Figs 6.5 and 6.26. Fig 6.26 clearly shows the effect of PS in the blend on the rate of formation of functional group 1700-1725 cm^{-1} (C=O). Sadrmohahgegh(41) has also studied the changes in carbonyl group of low density polyethylene with varying concentration of polystyrene (see Fig 6.27). As it can be seen the rate of photodegradation of LDPE increases as the concentration of PS in the blend of LDPE/PS is increased. This lower photo-oxidative stability of the blends can be attributed to the presence of a labile hydrogen on the tertiary carbon in the polystyrene. Scott et al(101) have studied the photo-oxidation of polystyrene and believe that hydrogen abstraction by an alkoxy radical derived from the decomposition of hydroperoxides produced during thermal processing may occur at either the benzylic or methylenic centre.

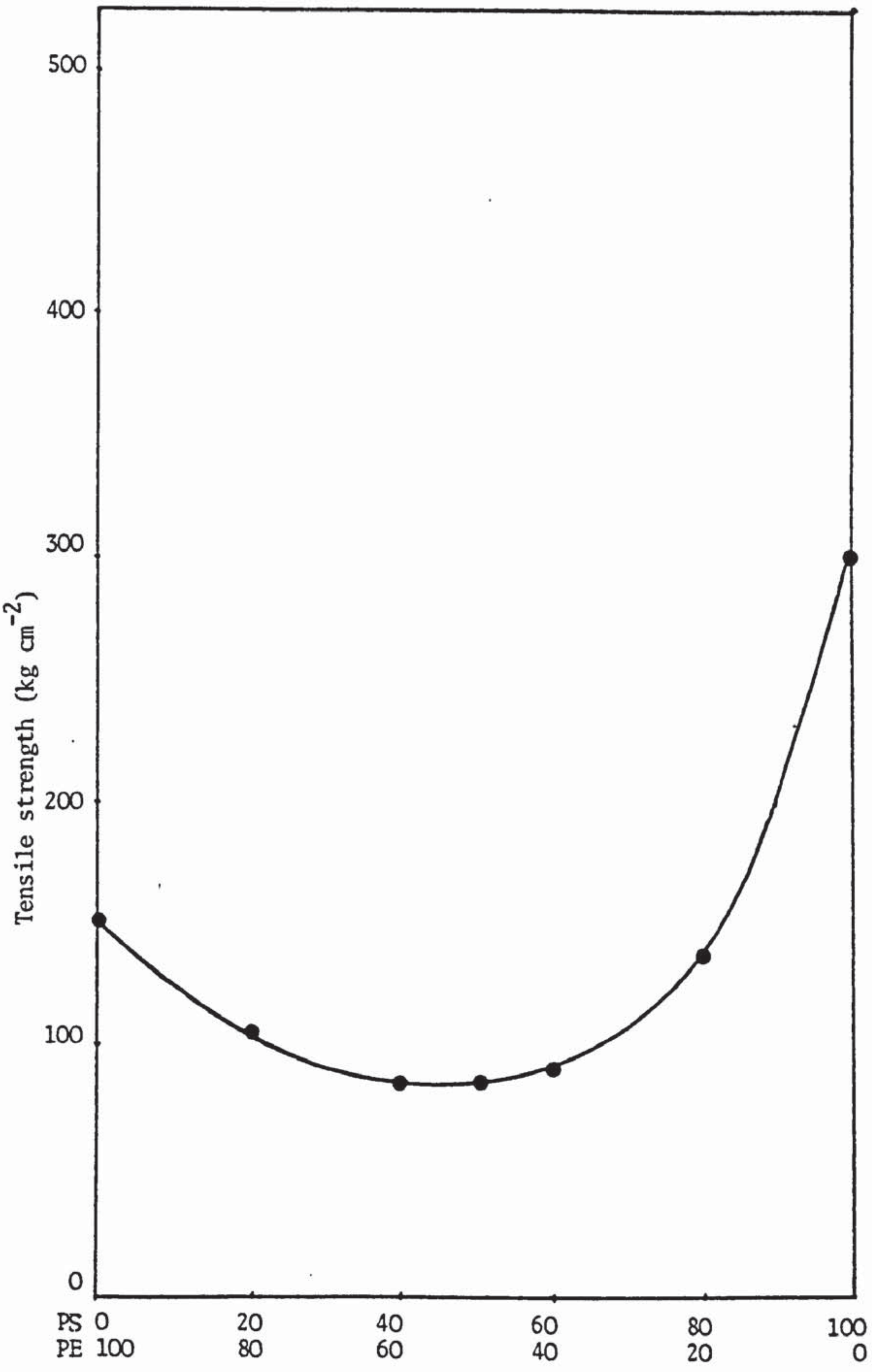


Fig 6.24 Change in tensile strength (Ts) of PE/PS (1:1) blend as a function of composition

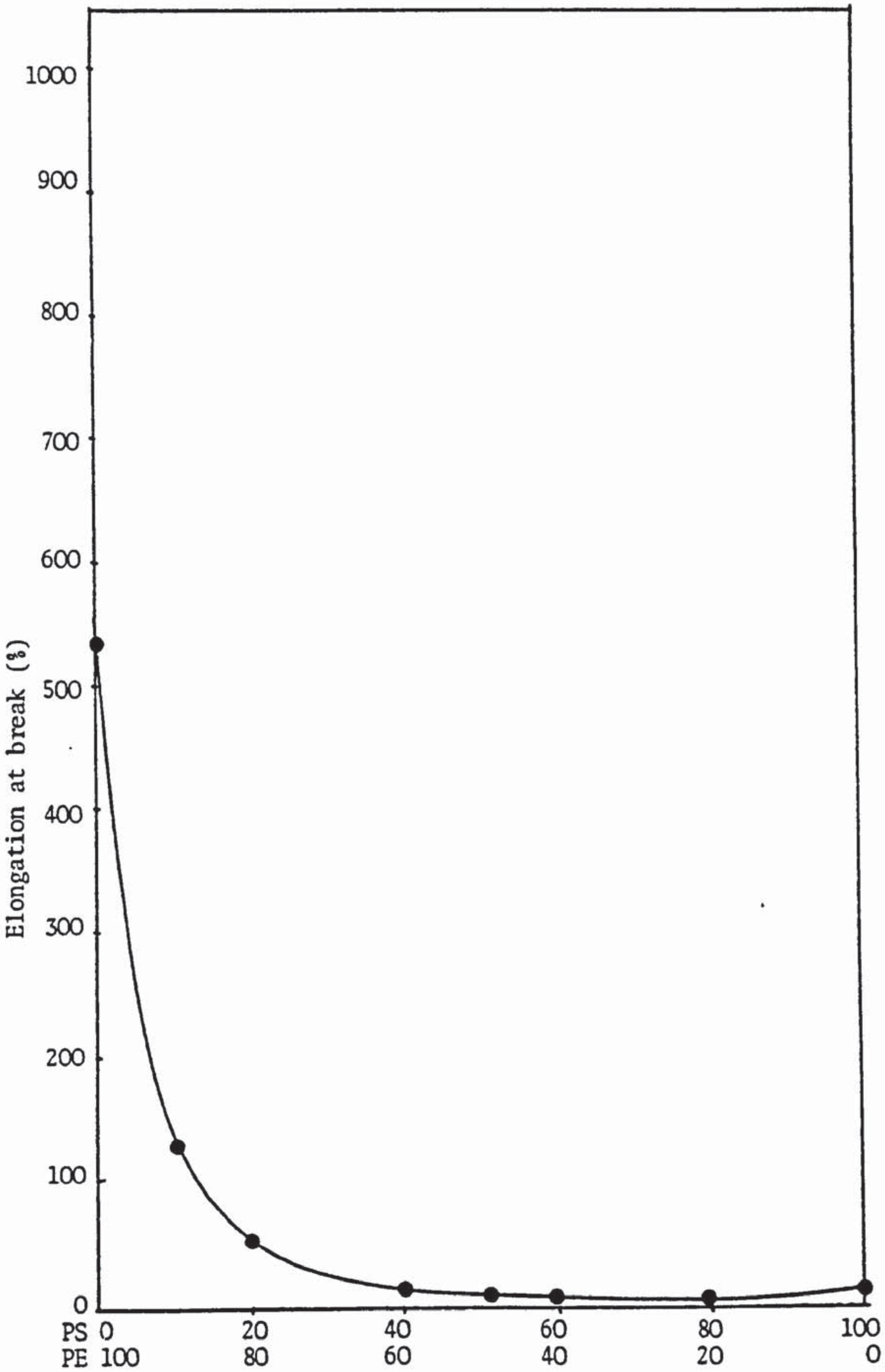


Fig 6.25 Change in elongation at break (Eb%) of PE/PS (1:1) blend as a function of composition

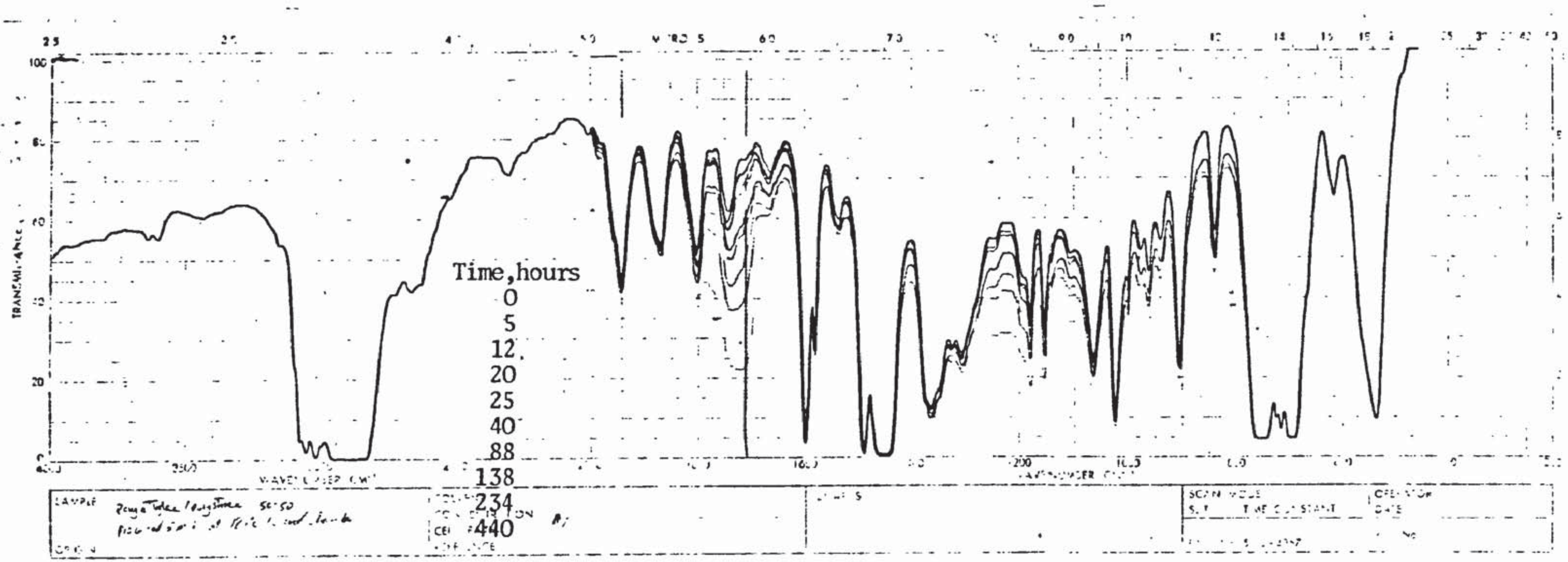


Fig 6.26 Infra-red spectroscopy of PE/PS (1:1) blend on uv exposure (numbers on curve are exposure time in hours)

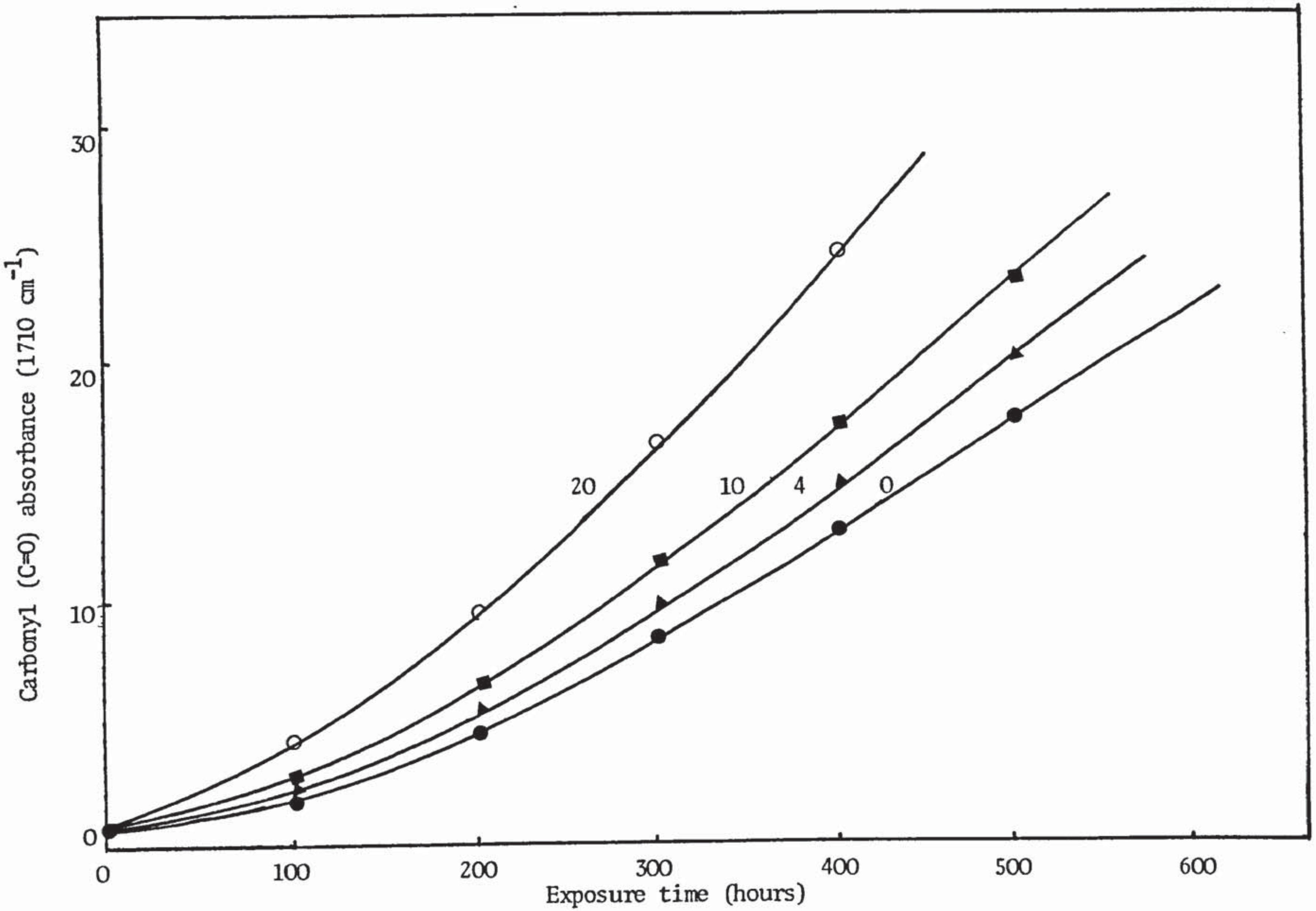


Fig 6.27 Effect of varying concentration of PS on carbonyl formation of PE/PS blends during uv irradiation (numbers on curves are PS concentrations in percentage) (Reproduced from C Sadrmohaghegh's Thesis)

6.3.B.2 The Effect of SBS Concentration on Mechanical and Long Term Performance of PE/PS (1:1) Blend

A potential approach to the problem of incompatibility is to incorporate additives into the blend which will bind together the incompatible polymers. Suitably chosen block or graft copolymers are attractive candidates for this role since they are likely to be located at domain boundaries and provide adhesion between the phases(67,68,167).

It was postulated that the properties of melt blends of polystyrene and polyethylene might be improved by the additives of a graft copolymer of styrene onto a polyethylene backbone(67,71). Such graft copolymers have been studied extensively but no commercial source exists. The addition of graft copolymers into PE/PS (1:1) blend has increased both the yield strength and the elongation at break of the blend.

Scott et al(66) have found that the mechanical properties of PE/PS (1:1) was improved by the addition of PE-g-PS obtained from mechanochemical process of PE and PS using a peroxide as an initiator. Also they found(54) that addition of 20% SBS (styrene-butadiene) block copolymer into blends containing equal proportions of LDPE and PS which represents the poorest balance of properties, increases its mechanical properties (ie elongation and impact strength) to the level of pure polyethylene. The same solid phase dispersant (ie SBS) was used in PE/PS (1:1) blend with varying concentrations (ie 0-30% of SPD) and results of changes in elongation at break, tensile strength and impact strength are shown in Figs 6.28, 6.29 and 6.30. As it can be seen, SBS works as an effective solid phase dispersant in this blend system and improves the mechanical properties dramatically (especially shock resistance). Although the introduction of SBS into PE/PS (1:1) blends improves the blend properties but presence of SBS sensitises the photodegradation of the blend. This photosensitisation effect is due to the presence of butadiene segments in the SBS copolymer. It has previously been reported(35) that the decay of physical properties during the photodegradation of high impact polystyrene (HIPS) is associated with the selective oxidation of the rubber phase. It was also suggested(35) that the oxidative attack occurred at the allylic position in the rubber during thermal processing and that subsequent uv exposure led to photolysis of the hydroperoxide so formed, with initiation of competing cross-linking and chain scission reactions. A comparison of Figs 6.26, 6.31 and 6.32 indicates the fact that introduction of SBS as a solid phase dispersant (SPD) sensitises the photodegradation of PE/PS (1:1) blend. The photodegradation of the polymer blend containing SBS (10;20% of SBS) was studied using the infra-red technique as well as loss of impact strength during the uv irradiation. The development of the carbonyl group at 1710 cm^{-1} and loss of butadiene segment at 965 cm^{-1} was followed as a function of uv irradiation time. The peak at 1948 cm^{-1} was taken as a reference and the carbonyl index and trans-1,4- C=C index were measured as the ratio of absorbances at 1710 and 965 cm^{-1}

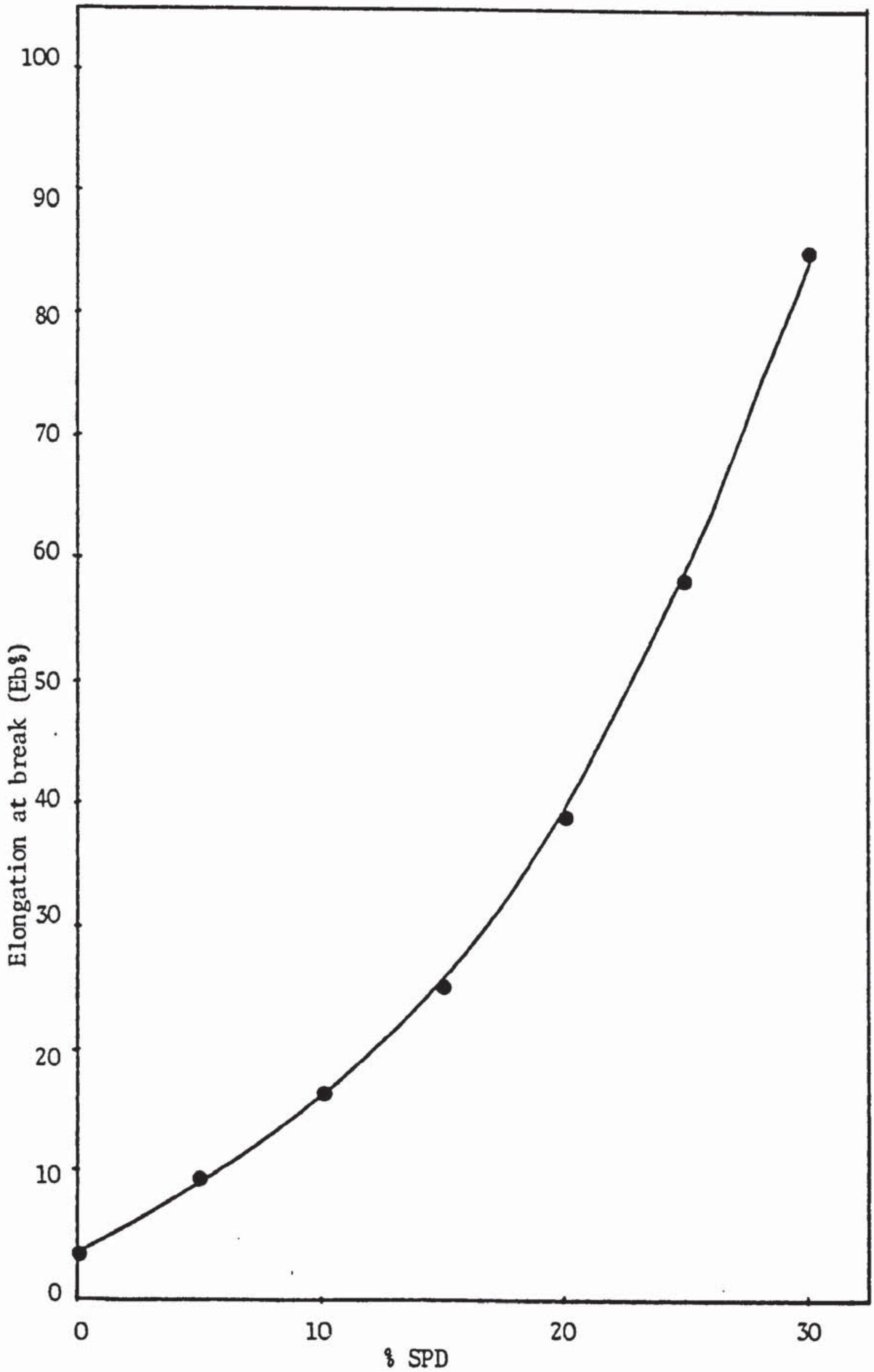


Fig 6.28 Change in elongation at break (Eb%) of PE/PS (1:1) blend as a function of SPD content (SBS)

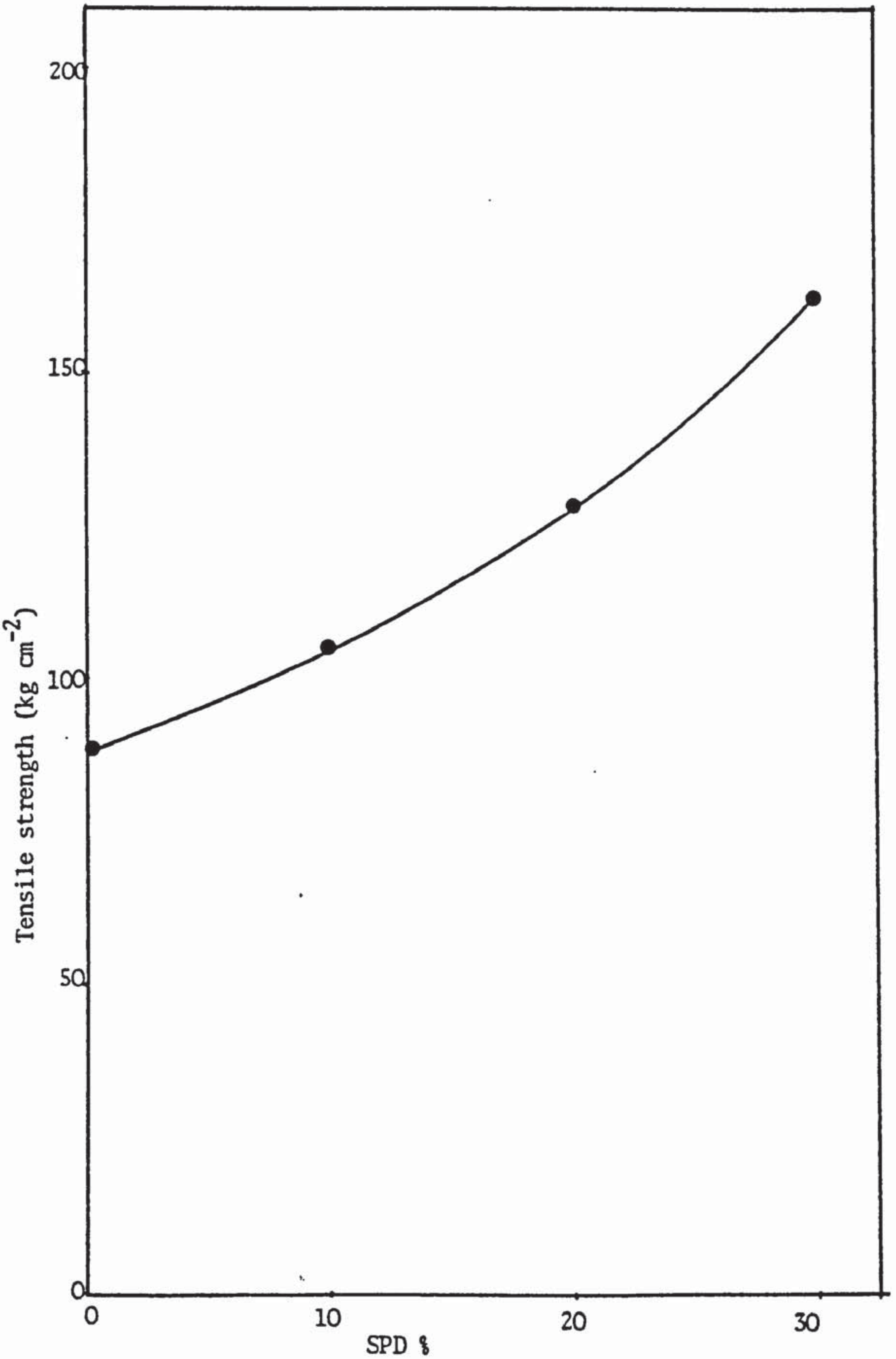


Fig 6.29 Change in tensile strength (Ts) of PE/PS (1:1) blend as a function of SPD content (SBS)

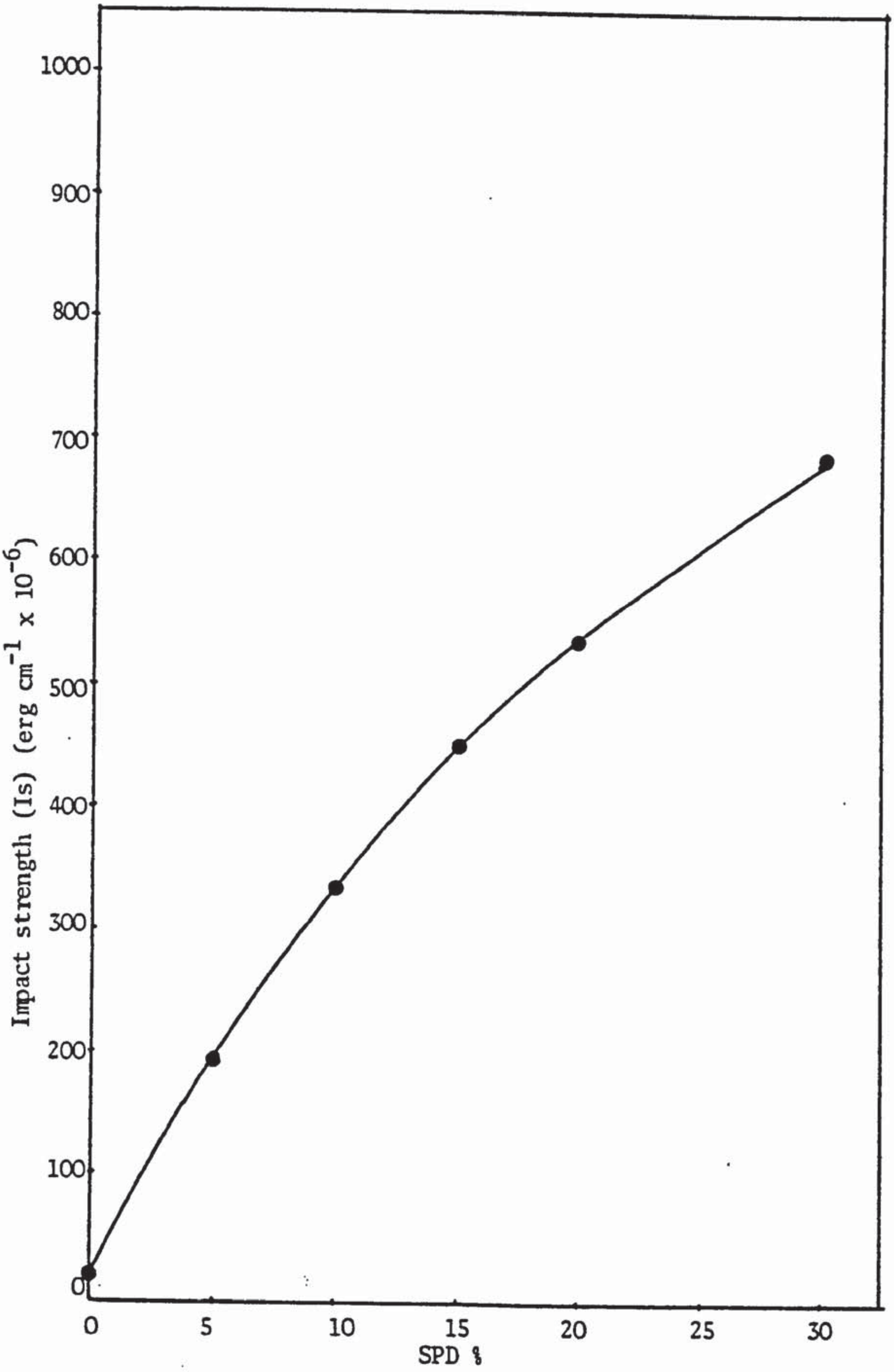


Fig 6.30 Change in impact strength (Is) of PE/PS (1:1) blend as a function of SPD content (SBS)

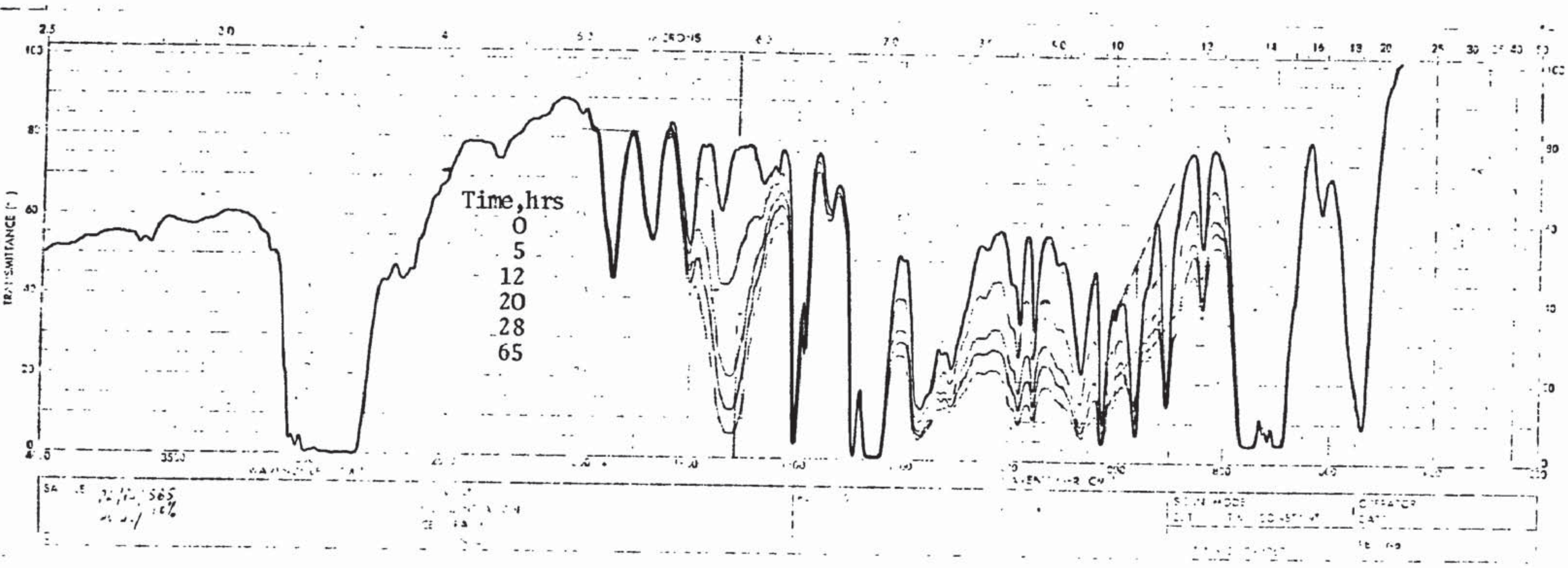


Fig 6.31 Infra-red spectoscopy of PE/PS (1:1) containing 10% SBS on uv exposure (numbers on curves are exposure time in hours)

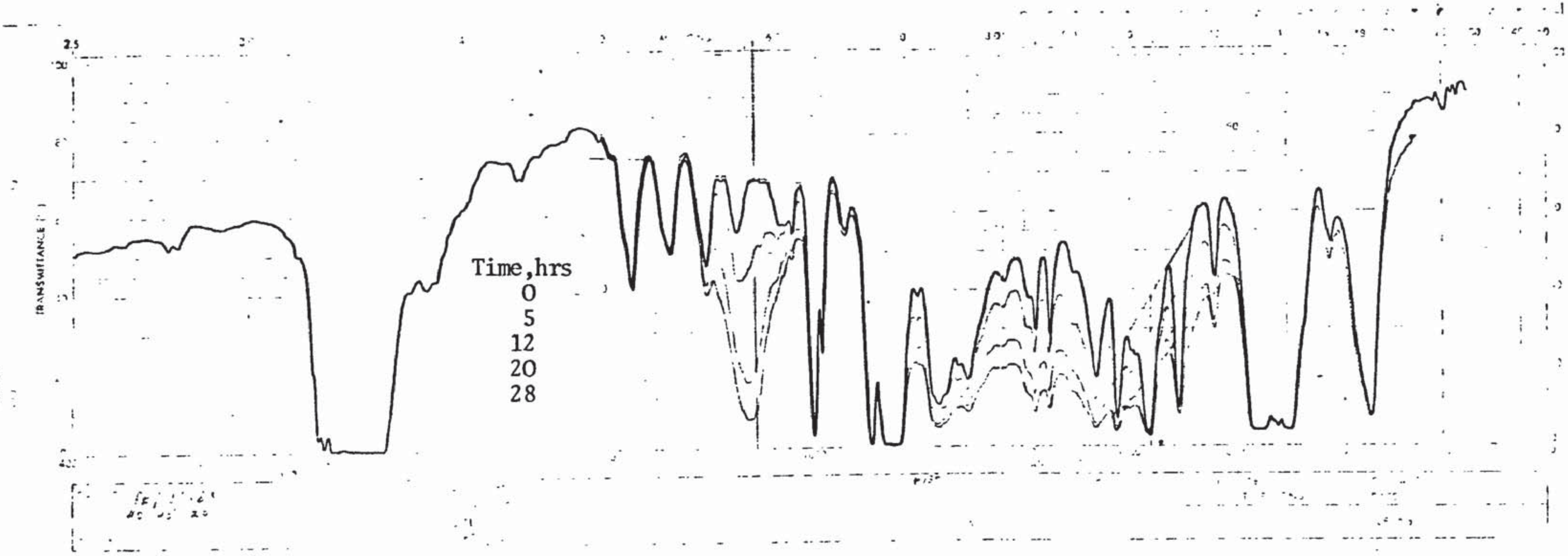


Fig 6.32 Infra-red spectroscopy of PE/PS (1:1) blend containing 20% SBS on uv exposure (numbers on curve are exposure time in hours)

to that of the reference peak (1940 cm^{-1}), respectively. The effect of SBS concentration on carbonyl formation in PE/PS (1:1) blend during uv exposure is shown in Fig 6.33. As it can be seen with increasing SBS concentration the blends become less photostable. Also Fig 6.34 indicates the decrease in trans-1,4-C=C index during uv irradiation which clearly indicates the rate of unsaturation loss after a very short induction period. Furthermore, the unsaturation decay is a first order reaction (see Fig 6.35 for blend containing 10% SBS and decay of impact strength for blends containing 10, 20 and 30% SBS).

Scott et al(36) have found that the loss of trans-1,4- polybutadiene and the formation of carbonyl and hydroxyl in HIPS during the initial stage of photo-oxidation plotted as a function of hydroperoxide concentration shows that the reactions occur in the two stages. The first involves little loss in unsaturation and relatively minor formation of carbonyl and hydroxyl for an incremental increase in hydroperoxide formation in the polymer compared with the second stage. This implies that the first stage involves primarily the formation of allylic hydroperoxide from trans-1,4-polybutadiene and the second, the breakdown of peroxides (including peroxy gel) to give carbonyl and hydroxyl and with destruction of the trans-1,4-polybutadiene double bonds. Decay in impact resistance of PE/PS (1:1) blends with different SBS concentration is shown in Fig 6.36. It is clear from Fig 6.36 that with higher concentration of SBS the initial impact is higher but the rate of loss of impact properties is faster. This clearly indicates that during uv irradiation, the rubber

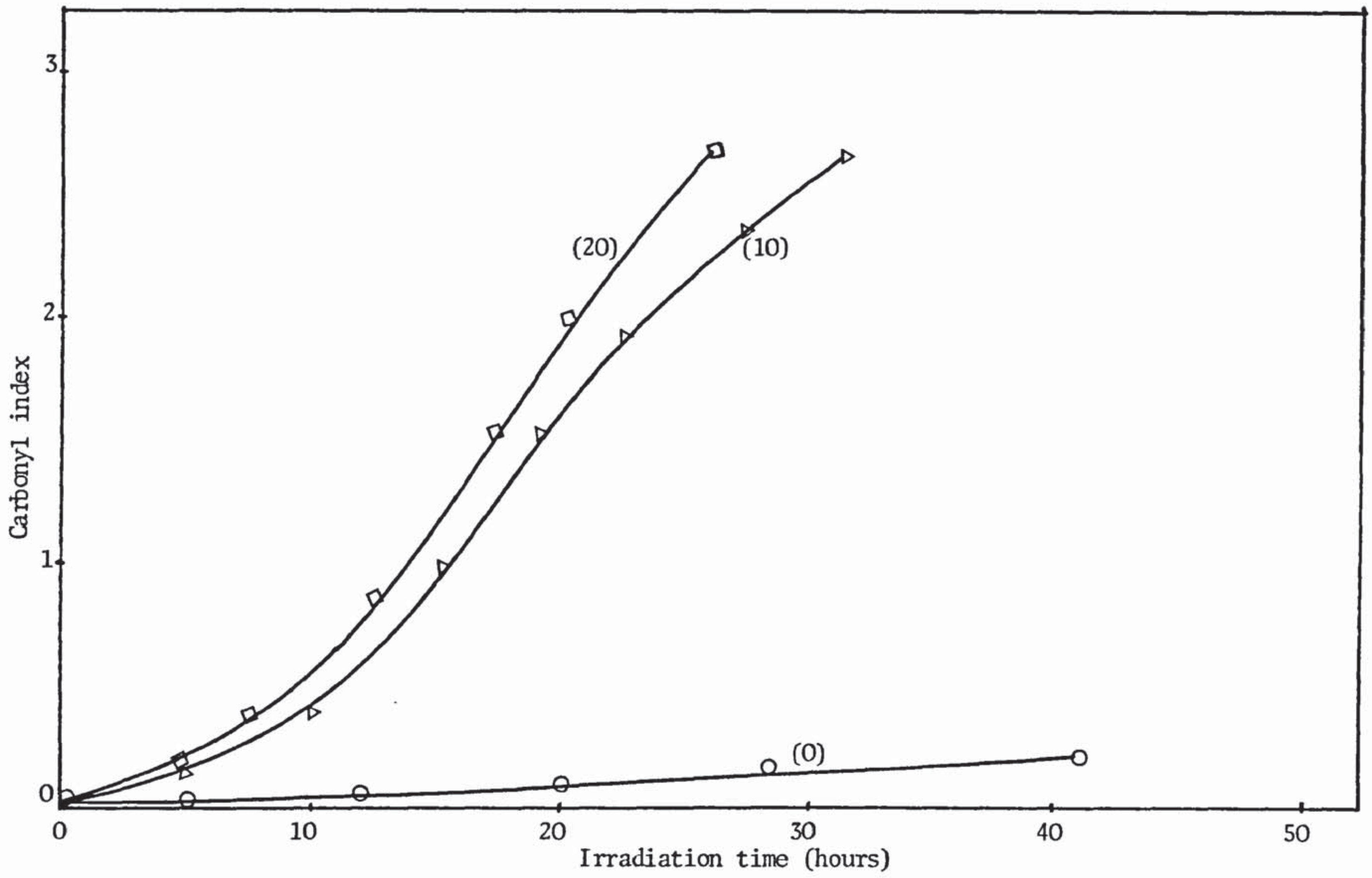


Fig 6.33 Effect of SBS concentration on carbonyl formation in PE/PS (1:1) blends during uv irradiation (numbers on curves are SBS concentration in g/100 g)

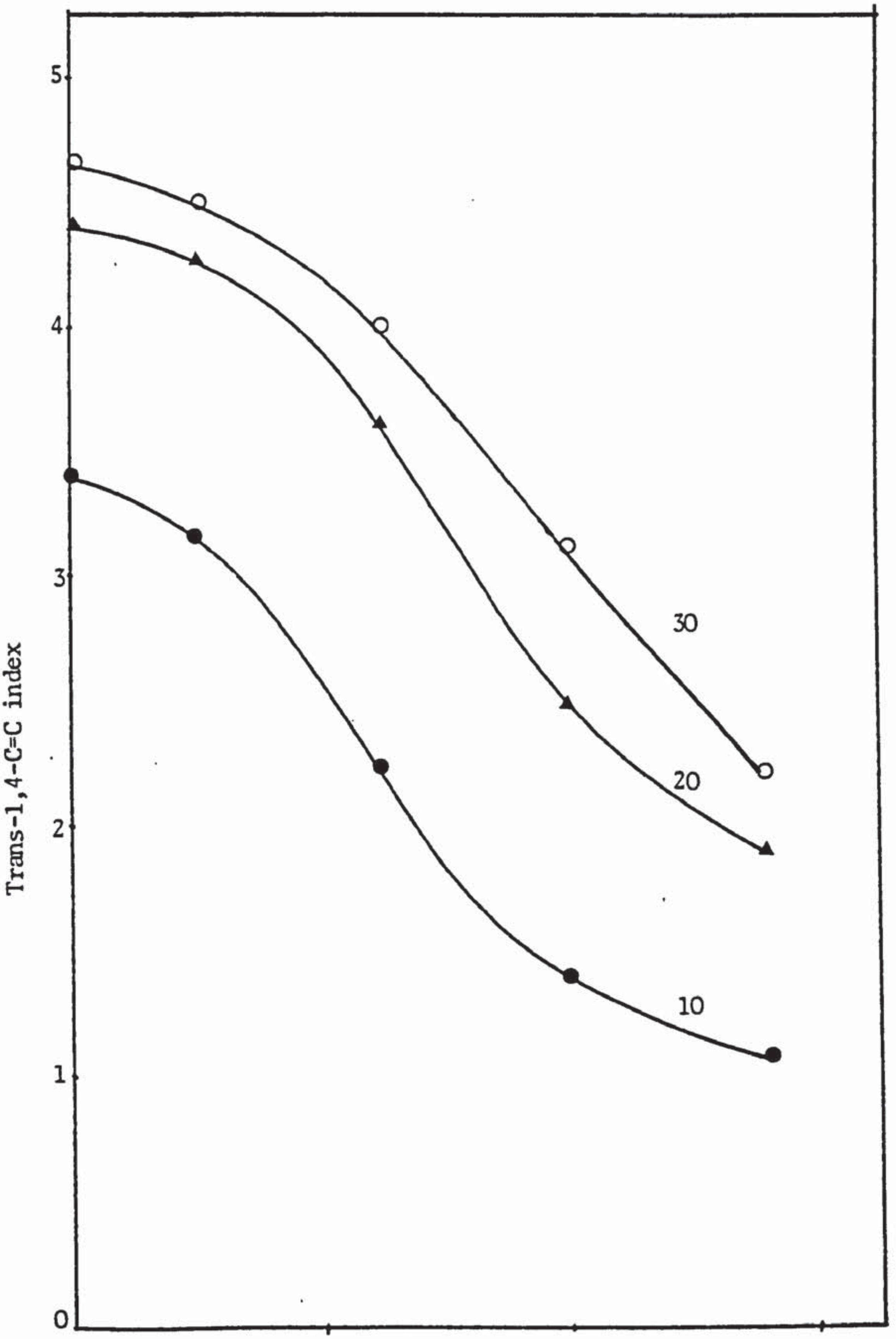


Fig 6.34 Decay of trans-1,4-PB unsaturation (965 cm^{-1}) during the photo-oxidation of PE/PS(1:1) blends (numbers on curves are SBS concentration g/100 g)

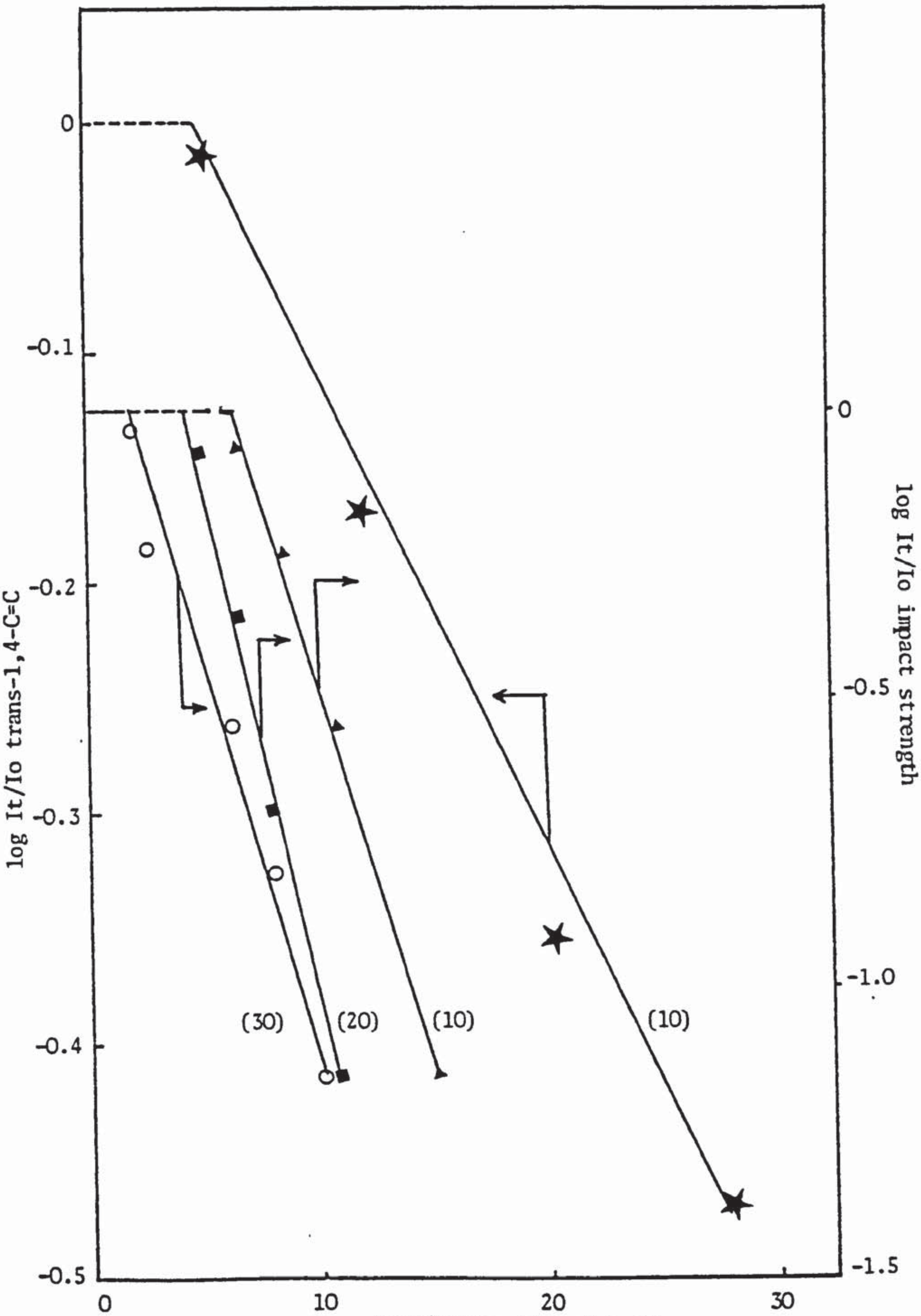


Fig 6.35 Decay of trans-1,4-PB index (PBI) and loss of impact strength plotted as first order in PE/PS (1:1) blend. Data as in Fig 6.33 and Fig 6.35 (numbers on curves represent SBS concentration g/100 g)

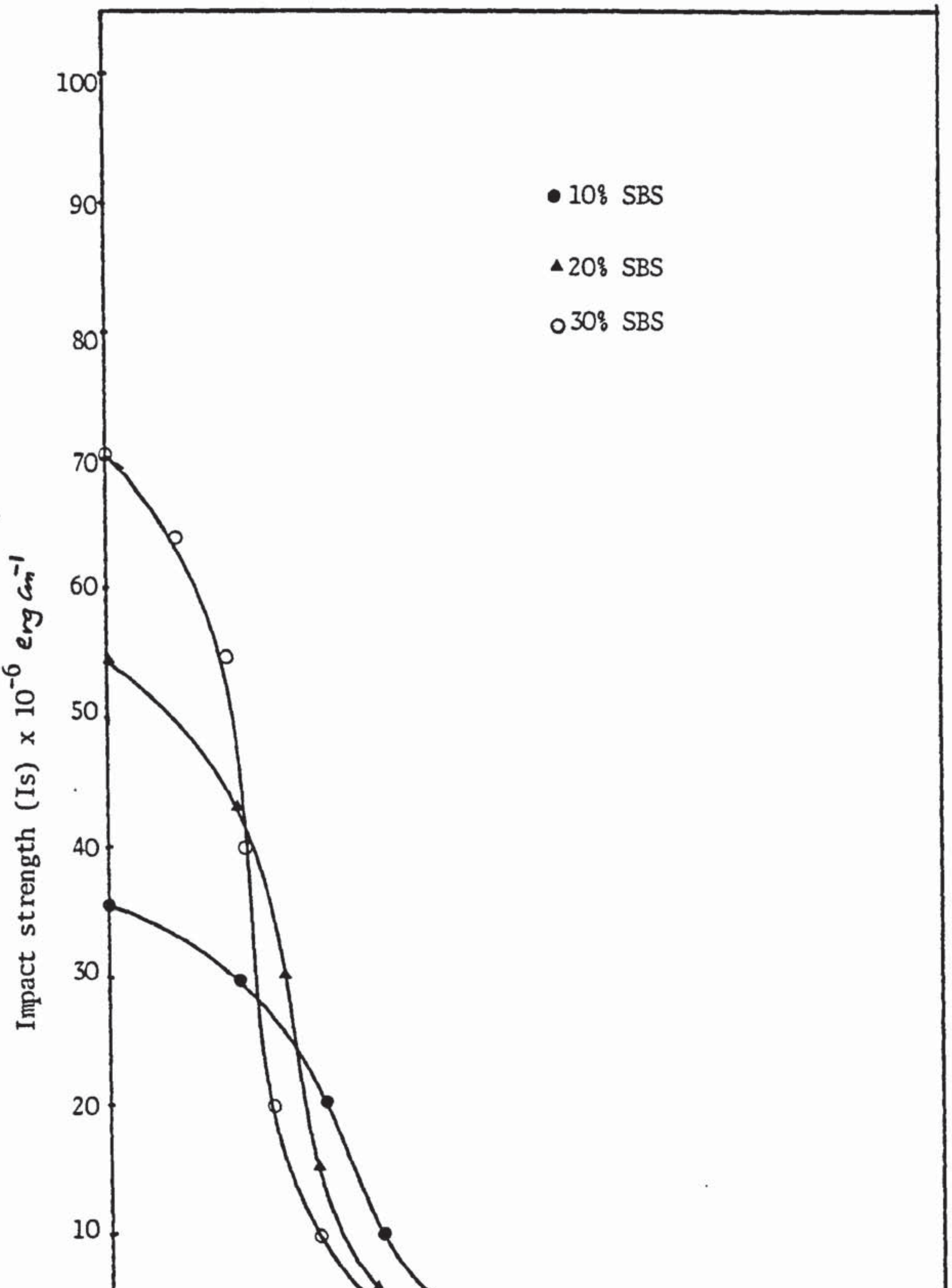


Fig 6.36 Decay of impact strength in PE/PS (1:1) blend during uv exposure

part of the blend which is responsible for the toughness is destroyed very sharply. It has been found(37,153) that the polybutadiene component of ABS is the only moiety which is affected during exposure to uv light and its destruction is accompanied by a rapid loss of physical properties such as impact strength. Under constant incident light intensity, trans-1,4-polybutadiene unsaturation is destroyed at a rate proportional to its concentration(168). The embrittlement time of the PE/PS (1:1) containing 10, 20 and 30% of SBS during photo-oxidation is shown in Table 6.6.

6.3.B.3 Stabilisation of LDPE/PS (1:1) Blend Containing 20% SBS as Solid Phase Dispersant

Ternary blends of LDPE/PS/SBS (40/40/20) containing conventional stabilisers, such as NiDBC (PD-C), UV531 (uv absorber) and Tinuvin 770 (CB-A and CB-D regenerative antioxidant) were processed at 180°C, for 5 minutes under closed chamber conditions. The compression moulded film were uv irradiated and photodegradation was followed by measuring carbonyl index against uv exposure. The carbonyl index was measured as the ratio of absorbance at 1710 cm^{-1} to that of a reference peak at 1940 cm^{-1}. Also the loss of impact resistance during uv irradiation was measured using the falling weight impact tester. The correlation between the disappearance of unsaturation due to the rubber component and impact strength was studied. The change in unsaturation was followed by measuring the changes at 965 cm^{-1} due to trans-1,4-polybutadiene and this

Table 6.6 Embrittlement time of PE/PS (1:1) blend containing 10, 20 and 30% of SBS as solid phase dispersant on uv exposure

Blend composition	PE/PS/SBS 10%	PE/PS/SBS 20%	PE/PS/SBS 30%	PE/PS 1:1
Embrittlement time (hours)	140	110	90	400-500*

* Embrittlement time for PE/PS (1:1) was very difficult to observe due to brittleness of original blend, therefore, the embrittlement was estimated roughly

was plotted as trans-1,4-polybutadiene index (ie the ratio of absorbance at 965/1410 cm^{-1}) against the uv exposure time. Results are shown in Figs 6.37, 6.38 and 6.39.

Fig 6.37 shows the typical behaviour of a number of commercial uv stabilisers in unstabilised PE/PS/SBS (40/40/20) blend incorporated by a normal compounding procedure at the same molar concentration (ie 6 x 10^{-4} mol/100 g). Tinuvin 770, a hindered amine, which is shown to be a very effective stabiliser in polypropylene(155) and also in PE/PP/EPDM (40/40/20) does not show a good stabilising effect in this blend. It is found that Tinuvin 770 is not a good uv stabiliser in ABS even when used alone(110). The photostabilising effect of Tinuvin 770 is found to be due to the formation of the corresponding nitroxyl radical from the parent amine under oxidising conditions(169) which include commercial processing operations(148).

The uv absorber (UV531) is unable to inhibit the formation of hydroperoxide in the blend during processing and does not destroy it during photo-oxidation although it is rapidly destroyed by hydroperoxide (see reference 165). Therefore, HOBP (UV531) is not an effective uv stabiliser in the PE/PS/SBS (40/40/20) blend. On the other hand, NiDBC shows a very good induction period and concentration effect. It can be seen from Fig 6.37 that by increasing the NiDBC concentration from 3 x 10^{-4} to 6 x 10^{-4} mol/100 g, the induction period is increased from 60 hours to 150 hours. It has previously been shown(47) that nickel dialkyl dithiocarbamates in common with other metal dithiocarbamate, are

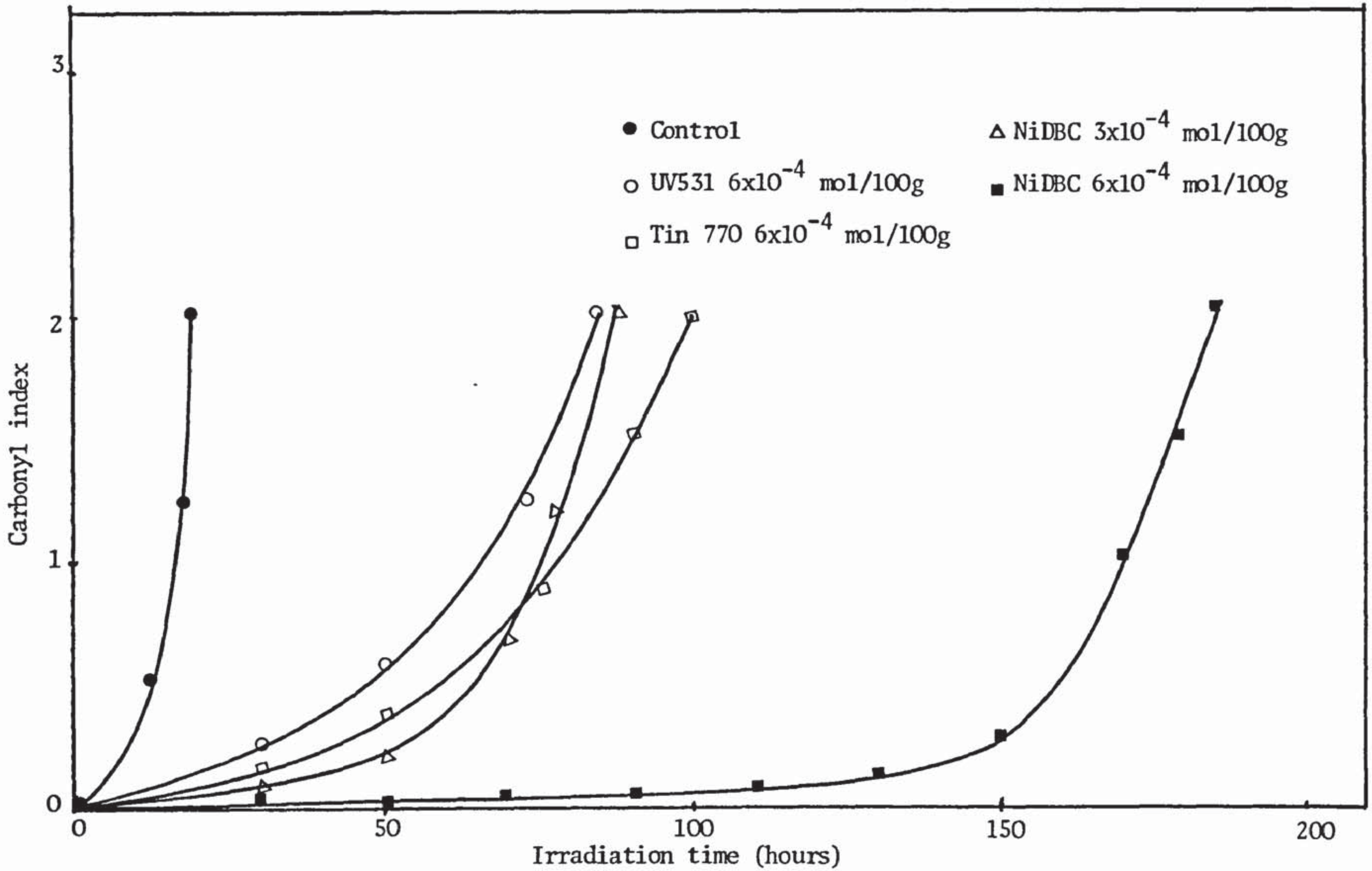


Fig 6.37 Development of carbonyl group at 1710 cm^{-1} on uv exposure of PE/PS (1:1) blend containing 20% SBS as solid phase dispersants

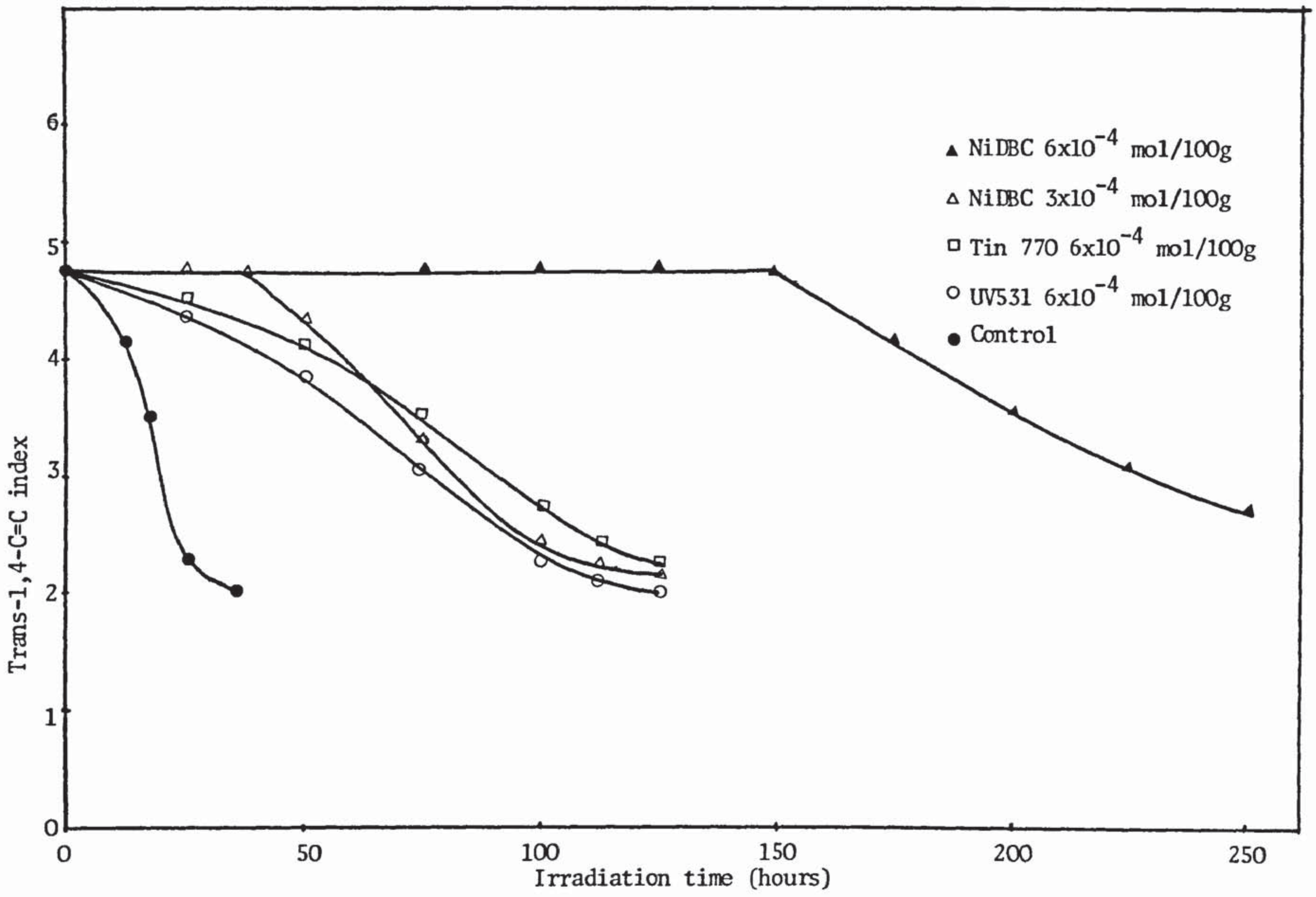


Fig 6.38 Decay of trans-1,4-PB unsaturation (965 cm^{-1}) during the uv exposure of PE/PS (1:1) blend containing 20% SBS as solid phase dispersants

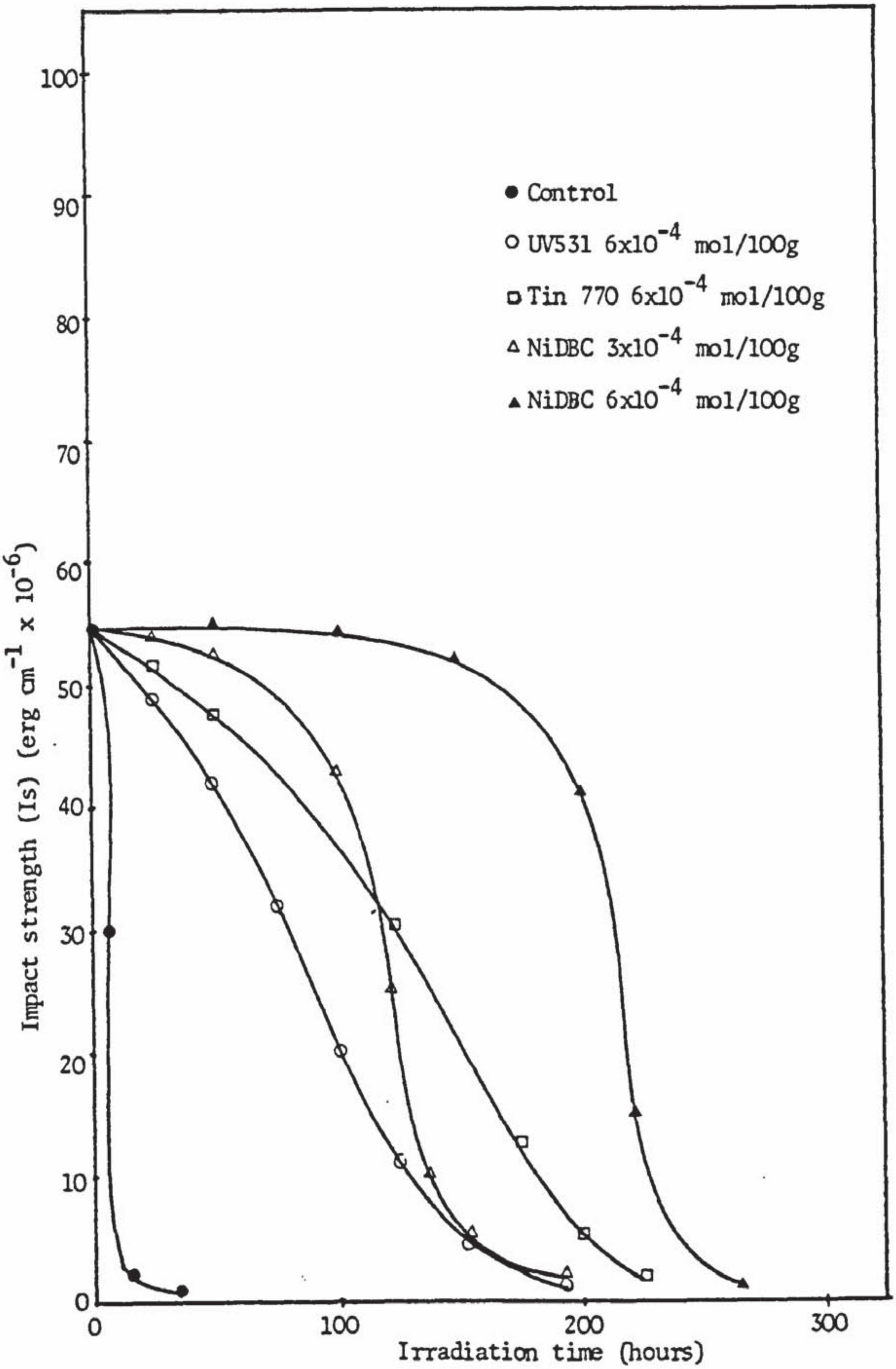


Fig 6.39 Decay of impact resistance of PE/PS (1:1) blend containing 20% SBS as solid phase dispersant on uv exposure

powerful catalysts for the destruction of hydroperoxide through a non-radical mechanism. Also Scott et al(158) have found that the products formed in the catalystic decomposition of cumene hydroperoxide by NiDBC at 29°C in light were identical to those obtained thermally at 60°C (namely phenol and acetone) indicating that the same Lewis acid catalyst (SO_2 or SO_3) must be involved. Husbands et al(170) have concluded that sulphur dioxide is not a catalyst for the decomposition of hydroperoxides. It initially reacts with hydroperoxides stoichiometrically in a homolytic process giving rise to sulphur trioxide, which is a powerful catalyst for hydroperoxide decomposition and is the effective antioxidant principle involved in the action of sulphur containing antioxidants.

The change in trans-1,4-PB unsaturation index against time of uv irradiation (Fig 6.38) clearly demonstrates that in the presence of a peroxide decomposer such as NiDBC, the unsaturation does not change during carbonyl induction period and then it decreases gradually. Whereas in the case of the samples contianing Tinuvin 770 and UV531, the unsaturation decreases gradually with no induction period. Impact studies also indicate the better performance of NiDBC at the same molar concentration than Tinuvin 770 and UV531 (see Fig 6.39).

After the induction period, the impact strength decreases sharply to the lowest value. It is suggested(130) that the loss in toughness is due to embrittlement in the surface. Oxidation starts from the surface of the film and the weight falling tester, the weight strikes on the surface of the film at a high speed and cracks propagate from the brittle surface of the film to the inner part of the film which there is still some rubber. Therefore, because of the fast crack formation in the surface of the film in turn initiates crack propagation throughout the polymer film, a rapid loss in the impact strength is observed during the early stages of photodegradation. In spite of the difference in rate, similarity in the shape of the decay of rubber unsaturation and loss of toughness, confirms the relationship between the loss of elastic properties of the rubber and loss of impact strength of the blend during photodegradation. Induction period and embrittlement time of the samples are shown in Table 6.7.

Table 6.7 Induction period and embrittlement time of PE/PS (1:1) blend containing 20% SBS on uv exposure

Antioxidant type	Conc of additive mol/100 g	Conc of additive g/100 g	Induction Period (hours)	Embrittlement time (hours ± 20)
Control (No additive)	-	-	3-5	110
UV531 (HOBP)	$6x10^{-4}$	0.196	35	150
Tinuvin 770	$6x10^{-4}$	0.288	50	260
NiDBC	$3x10^{-4}$	0.141	60	210
NiDBC	$6x10^{-4}$	0.282	160	440

CHAPTER SEVEN

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

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CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

7.1 Overall Technical Conclusions

(i) The properties of mixed plastics are always inferior to the virgin polymers due to incompatibility. It has previously been shown that the inferior mechanical properties of mixed polymers such as PE/PP and PE/PS can significantly be improved by addition of selected solid phase dispersants (SPDs) containing blocks with physical affinity for each of the heterophases (ie EPDM in former blend and SBS in the latter blend).

(ii) Although the addition of SPDs improve mechanical properties of the mixed plastics (particularly shock resistance), the light stability of the blend decreases leading to a sharp loss of impact resistance. Therefore the stabilisation of SPDs segment was carried out by use of a variety of commercially available antioxidants. Commercial additives were found to be better light and heat stabilisers than antioxidants chemically bound to solid phase dispersants under normal processing conditions. However, in aggressive conditions, such as reprocessing of mixed plastics and in leaching environment, bound antioxidants were found to be superior to commercial additives.

(iii) As a result of the economic survey, it was found that polypropylene used in the packaging industry (eg for crates) frequently end up in the waste stream as a single component item of waste plastics with inferior mechanical properties to that of original polypropylene. Therefore, the impact resistance and low temperature damping of polypropylene was improved significantly by addition of EPDM. However, increase in impact strength and low temperature damping was accompanied by sharp loss of mechanical properties on uv exposure due to the presence of unsaturation. The improvement of light and heat stability of PP/EPDM blends was achieved by use of commercially available antioxidants and it is concluded that under conditions which lead to the loss of conventional additives such as by volatility due to reprocessing and in leaching environments, the SPDs containing bound antioxidants were superior to conventional additives, whereas under normal conditions, conventional additives were found to be better.

7.2 Suggestions for Further Work

(i) Since it has been shown that very considerable quantities of plastics waste are available at the major supermarkets and hypermarkets, recycling systems may be possible involving a three-cornered partnership consisting of a supermarket chain, a recycler and a secondary product manufacturer. Expertise would be available at Aston for the co-ordination of all aspects of the recycling process.

(ii) Although the addition of SPDs such as EPDM and SBS improve the mechanical properties of mixed plastics significantly, (ie PE/PP and PE/PS respectively), this improvement in the quality of the product increases the price of the final product due to the high cost of SPDs. Therefore, the possibility of developing cheap SPDs should be explored (eg by mechanochemical block interchange of rubbers and polypropylene to form block copolymer with SPD and impact modifying properties).

(iii) Past and present investigations confirm that in the photo and thermal oxidation of rubber containing copolymers, the impact modifying rubber segment sensitises both photo and thermal oxidation. The ideal way of stabilising such blends is by chemical binding of antioxidants in to the rubber segments. Therefore, the possibility of binding thiol antioxidants to styrene butadiene block copolymer (SBS) by a mechanochemical process should be investigated and their properties studied.

(iv) An interesting and technologically important point not directly related to the objectives of the present project is the possibility of stabilising EPDM in engineering applications, particularly in vulcanisates, which spend all or part of their service lives immersed in fuel, lubricating oils or hydraulic fluids. Under these conditions, conventional additives are not effective. It has been found however that mechanochemically bound thiol antioxidants improve the oxidative resistance of EPDM under aggressive conditions and this investigation should be extended to the study of antioxidant modified EPDM in engineering applications.

REFERENCES

REFERENCES

1 E S Narrocott, The Impact of plastics on materials resources paper presented at 'Conservation of materials' conference at Harwell, England, March 1974

2 H Teitge, Marl, German Plastics, translated from Kunststoffe 70, 5, 299-302, 1980

3 Anon, Europ Plast News, The UK Consumption of Plastics, Jan edition of each year (1971-1980)

4 C J Burlace, L Whally, Waste Plastics and their Potential for Recycling, Warren Springs Lab, 1977

5 Anon, Plastics and Rubber Weekly, page 24, 25 April 1981

6 J Brydson, Plastics Materials (ed J Brydson) Newres-Butterworth, p112, 1975

7 A V Bridgwater and C J Mumford, 'Waste Recycling and Pollution Handbook', pages 450 and 496, George Goodwin Ltd, Sept 1979

8 Packaging Material and Household Refuse in Europe, Bureau International Technique, Bruxelles, May 1973

9 Royal Commission on Environmental Pollution, 4th Report published by HMSO, London, 1974

10 Department of Environment, Local Authority Waste Disposal Statistics, 1974/5, Waste Management Paper No 10, HMSO, 1976

11 J Milgrom, Conservation and Recycling, 3, 327-335, 1980

12 W Duncan, CBE, Chem and Ind, 311-316, 2 May 1981

13 W L Hawkins in Polymer Stabilisation (ed W L Hawkins), p 3, Wiley Interscience, New York, 1972

14 F H McTigue, M Blumberg, App Polym Symp, 4, 175, 1967

15 F J Golembic, J E Guillet, SPE Journal, 26, 88, 1970

16 H P Frank, H Lehner, J Polym Sci, 31C, 193, 1970

17 E Turi, L G Roldan, H J Oswald, ACS Preprints, 5(2), 538, 1964

18 R J Martinovick, Plast Tech, 9(11), 45, 1963

19 G.Gottfried, M J Cutzer, J App Polym Sci, 5, 612, 1961

20 K B Chakraborty, G Scott, Polymer, 18, 98, 1977

21 J E Guillet, J Dhanly, F J Golembic, G H Hartley, Adv in Chem, 70, 1969

22 G Scott, Macromolecular Chem, IUPAC, 8, 319, 1972

23 C Kujirai, S Hashiya, H Furuno, N Terada, J Polym Sci, A-1, 6, 589, 1968

24 N Uri, Israel J Chem, 8, 125, 1970

25 G Scott, Europ Polym J, Supp, 189, 1969

26 G Scott, Atmospheric Oxidation and Antioxidants, Elsevier, Amsterdam, 1965, chapter 5

27 D C Mellor, A B Moir and G Scott, Europ Polym J, 9, 219, 1973

28 C Sadrmohaghegh and G Scott, Polym Deg and Stab, 3, 333-340, 1981

28a G Scott, Resource, Recovery and Conservation, 1, 381-395, 1976

29 G V Hutson, G Scott, Chem and Ind, 18, 725, 1972; Europ Polym J, 10, 45, 1974

30 M U Amin, G Scott, Europ Polym J, 10, 1019, 1974

31 M U Amin, G Scott and L M K Tillekeratne, Europ Polym J, 11, 85, 1975

32 C Sadrmohaghegh, G Scott, Europ Polym J, 16, 1037, 1980

33 B D Gosner, J App Polym Sci, 9, 3701, 1965

34 T Hirai, J Plast, 22, 4 October 1970

35 A Ghaffar, A Scott, G Scott, Europ Polym J, 11, 271, 1975

36 A Ghaffar, A Scott, G Scott, Europ Polym J, 13, 89, 1977

37 G Scott, M Tahan, Europ Polym J, 13, 981, 1977

38 A Ghaffar, A Scott, G Scott, Europ Polym J, 12, 615, 1976

39 G Scott, M Tahan, Europ Polym J, 13, 989, 1977

40 G Scott, M Tahan, Europ Polym J, 13, 997, 1977

41 C Sadrmohaghegh, PhD Thesis, Aston University, 1979

42 C Sadrmohaghegh, G Scott, E Setoudeh, Polym Deg Stab, in press

43 A Ghaffar, C Sadrmohaghegh, G Scott, Polym Deg Stab, 3, 341, 1981

44 A Holmstron, E M Sorvik, Polym Eng and Sci, 17, no 9, 700, 1977

45 G Scott, P Shearn, J App Polym Sci, 13, 1329, 1969

46 G Scott, Pure and App Chem, 52, 365, 1980

47 J D Holdsworth, G Scott, D Williams, J Chem Soc, 4692, 1964

48 K J Humphries, G Scott, J Chem Soc, Perkin Transactions II, 826, 1973, 831, 1973 and 617, 1974

49 C Armstrong, G Scott, J Chem Soc, 1747, 1971

50 C Armstrong, M A Plant, G Scott, Europ Polym J, 11, 161, 1974

51 T Colclough, J I Cunneen, Chem and Ind, 625, 1960

52 G Scott in Developments in Polymer Stabilisation -4, ed G Scott, p1-22, App Sci Pub

53 A Ghaffar, G Scott, P Crowther, Europ Polym J, 14, 631, 1978

54 A Ghaffar, C Sadrmohaghegh, G Scott, Europ Polym J, 17, 941, 1981

55 E Martuscelli, M Pracella, M Avella, R Grelo, R Royosla Macromol Chem, 181, 957, 1980

56 O F Noel, III, J F Carley, Polym Eng and Sci, 15, 2, 1975 (Feb)

57 R E Robertson and D R Paul, J App Polym Sci, 17, 2579, 1973

58 A J Lovinger, M L Williams, J App Polym Sci, 25, 1703, 1980

59 R Greco, G Mucciarillo, G Rogosla, E Matuscelli, J Material Sci, 15, 845, 1980

60 E Nolley, J W Barlow, D R Paul, Polym Eng and Sci, 20, 364, March 1980

61 D R Paul, E Vinson and L E Locke, Polym Eng and Sci, 12, no 3, 157, 1972 (May)

62 J N Schramm and R R Blanchard 'The use of CPE as a compatibiliser for reclamation of waste plastics materials' presented at Palisades Section SPE RETEC Cherry Hill, New Jersey, 1970

63 D R Paul, C E Locke and C E Vinson, Polym Eng and Sci, 13, 3, 202-208, 1973

64 D R Paul and C E Locke, Polym Eng and Sci, 13, 4, 308-318, 1973

65 E Nolley, J W Barlow, D R Paul, Polym Eng and Sci, 20, no 5, 363-369, 1980

66 M Hajian, PhD Thesis, Aston University, 1980

67 D Heikens, W M Barenston, Polymer, 18, 69, 1977

68 W M Barenston, D Heinkens, P P et, Polymer, 15, 119, 1974

69 W M Barenston, D Heinkens, Polymer, 14, 579, 1973

70 D Heikens, N Hoen, W Barenston, P Piet, H Ludon, J Polym Sci, Polym Symp, 62, 309, 1978

71 C E Locke, D R Paul, J App Polym Sci, 17, 2597, 1973

72 C E Locke, D R Paul, J App Polym Sci, 17, 2791, 1973

73 F Wallrab, J Dumoulin, P Declerck, M Obsomer, P Obsoner, Am Chem Soc, Polym Div Prep, 13, 499, 1972

74 P H Rothschild, Soc of Plast Engineers, 37th Tech Ann Conf, 882-884, 1979

75 J Leidner, Recycling of Postconsumer Plastics, Presented at 35th Ann Tech Conf (SPE), Montreal, Canada, 1977

76 J Leidner, Utilisation of recycled postconsumer plastics, project report, prepared by Ontario Research Foundation for the Ontario Ministry of the Environment, April 1976

77 M J Bevis, Shell Polymers, 5, no 2, 50, 1981

78 Computer Search, PIRA, Leatherhead, Feb 1980

79 M Sittig, Pollution Control in the Plastics and Rubber Industry, Noyes Data Corp, Park Ridge, N J 134-163, 1975

80 D W Buttery, Recycling of Polymers, paper to University of Nottingham Course, Recycling and Disposal of Solid Waste, March 1975

81 A V Bridgwater, Resource, Recovery and Conservation, 5, 51, 1980

82 Oxfam Wastesaver, Analysis of the operating costs, March-May 1976, Sept 1976

83 A cost benefit analysis of the Oxfam Wastesaver Scheme, R Blackmore and R K Turner, M R P Discussion Paper no 78-02, 1979

84 M J Bevis, A J Ham, Plastics Waste Arisings in the Agricultural Horticultural and Product Distribution Industries, Brunel University Internal Report, 1980

85 M J Bevis, J Bromley, Plastics Waste Arisings in the Carpet, Coating and Related Industries, Brunel University Internal Report, Jan 1980

86 Retail Trade Int, vol 1, UK, p49, 1980

87 Private Commication with Hintons Limited

88 R J Taylor, A Lord, Recycling and Waste Disposal, 1, no 3, March 1976

89 H Verity Smith, Polymer Plast Tech Eng, 12, no 2, 141, 1979

90 W Kaminsky, J Mansled, H Sinn, Conservation and Recycling, 1, 91, 1976

91 Anon, British Plastics and Rubb, 6, 51-53, June 1979

92 K T Paul, RAPRA Bull, 2, 29, 1972

93 K T Paul, RAPRA Members J, p 273-281, Nov 1963

94 British Standard, 2782, 105C, Pt I, 1965

95 Plastics Films, ed J H Briston, p 21

96 Renfrew, Morgan, Polyethylene, London, 169, 1975

97 F M Rugg, J J Smith, R C Bacon, J Polym Sci, 13, 535, 1954

98 F H Lohmann, J Chem Ed, 32, 155, 1955

99 Ewing Instrumetal Methods of Chemical Analysis, McGraw Hill, 82, 1960

100 Instruction Manual for Rheovibron, DDVII, Toyo Measuring Instrument Co Ltd, Tokyo, 1969

101 A Scott, PhD Thesis, University of Aston, 1976

102 D J Mussa, J App Phys, 44, no 6, June 1963

103 M Yoshino, M Takayanagi, Jap Soc Testing Materials, 8, 330, 1959

104 W S E Fernando, PhD Thesis, University of Aston, 1977

105 US Patent, 3391,110

106 A H Weinstein, Rubb Chem Tech, 50, 650, 1977

107 R T Stiechl, J Brit, Patent, 1226685, 1971

108 R Dyke, Diamond Shamrock Europe Ltd, unpublished work

109 M R N Fernando, G Scott, J E Stuckey, J Rubb Res Inst Sri Lanka, 54, 531, 1977

110 W S E Fernando, G Scott, Europ Polym J, 16, 971, 1980

111 M Ghaemy, G Scott, Polym Deg Stab, 3, no 4, 253, 1981

112 M Ghaemy, G Scott, Polym Deg Stab, 3, no 3, 233, 1981

113 A A Katbab, G Scott, Polym Deg Stab, 3, no 3, 221, 1981

114 G Scott, Plastics and Rubber: Processing, 41, June 1977

115 G Scott in Developments in Polymer Stabilisation -1, ed G Scott, App Sci Pub, 1981, p 309

116 G Scott in Developments in Polymer Stabilisation -4, ed G Scott, App Sci Pub, 1981, p 121

117 W Kawzmann, H Eyring, J Am Chem Soc, 62, 3113, 1940

118 M Pike, W F Watson, J Polym Sci, 9, 229, 1952

119 D J Angier, W F Watson, Trans IRI, 33, 22, 1957

120 R J Ceresa, W F Watson, Trans IRI, 35, 19, 1959

121 R J Ceresa, Trans IRI, 36, no 2, 45, 1960

122 R J Ceresa, Plast Inst Trans, 28, 178, 1960

123 G Scott, M Tahan, J Vyvoda, Europ Polym J, 14, 377, 1978

124 B B Cooray, G Scott, Europ Polym J, 16, 1145, 1980

125 P Yu Butugin, V F Drozdovskii, D R Razgon, J V Kolbanev, Sov Phys, Solid State, 7, 757, 1965

126 Ye V Reztsova, G V Chubarova, Polym Sci, USSR, no 7, 1481, 1965

127 W D Potter, G Scott, Europ Polym J, 7, 489, 1971

128 A M A Amarapathy, PhD Thesis, University of Aston, 1975

129 K W S Kularatne, PhD Thesis, University of Aston, 1976

130 M Ghaemy, PhD Thesis, University of Aston, 1980

131 H Staudinger, H F Bondy, Ann Div Chem, 1931, 488, 153;

Rubb Chem Tech, 1932, 5, 278

133 Ref 13, p 89 et seq

134 M A Plant, G Scott, Europ Polym J, 7, 1173, 1971

135 D Bailey, D Vogl, J Macromol Sci, Rev Macromol Chem, C14, 267, 1976

136 L E Neilsen, Mechanical Properties of Polymers, New York, Reinhold Pub Corp, 1962

137 D K Hodgeman, Polym Deg Stab, 1, 155, 1979

138 P J Burchill, D M Pinkerton, Polym Deg Stab, 2, 239, 1980

139 D Adams, D Braun, J Polym Sci, Polym Lett Ed, 18, 625, 1980

140 B W Evans, G Scott, Europ Polym J, 10, 453, 1974

141 G Scott, M F Yusoff, Polym Deg Stab, 3, 53, 1980-81

142 G Scott, Polym Plast Tech Eng, 11(1), 535, 1978

143 G Scott, M Tahan, Europ Polym J, 11, 535, 1975

144 J Sohma, M Sakaguchi, Adv Polym Sci, 20, 111, 1976;
E A Andrews, P E Read, Adv Polym Sci, 27, 1, 1978

145 G Scott in Developments in Polymer Stabilisation -7, ed G Scott, App Sci Pub, in press

146 V M Farzaliev, W S E Fernando, G Scott, Europ Polym J, 14, 785, 1978

147 B B Cooray, G Scott, R Suharto, unpublished work

148 K B Chakraborty, G Scott, Chem and Ind, 237, 1979

149 N S Allen, J F McKellar, Europ Polym J, 16, 549, 1980

150 J A Brydson in Rubber Chemistry ed J A Brydson, p 326, App Sci Pub, 1980

151 G Scott in Developments in Polymer Degradation -1 (ed N Grassie), App Sci Pub, 205, 1977

152 W M Speri, G R Patrick, Polym Eng Sci, 15, 668, 1975

153 B D Gesner, SPE Tech Papers, XLV, 178

154 W P Coh, R A Isaksen, E H Merz, J Polym Sci, XLIV, 149, 1960

155 K B Chakraborty, G Scott, Polymer, 21, 252, 1980

156 K B Chakraborty, G Scott, Polym Deg Stab, 1, 37, 1979

157 K B Chakraborty, G Scott, Europ Polym J, 13, 1007, 1977

158 R P R Ranaweera, G Scott, Europ Polym J, 12, 825, 1976

159 G Scott, Pure and App Chem, 52, 365, 1980

160 S Al-Malaika, G Scott, Europ Polym J, 16, 706, 1980

161 M J Husbands, G Scott, Europ Polym J, 15 , 879, 1979

162 Ref 13, p7 et seq

163 G Scott, Adv in Chem Series, 169, 30, 1978

164 K B Chakraborty, G Scott, Europ Polym J, 13, 731, 1977

165 K B Chakraborty, PhD Thesis, University of Aston, 1975

166 R P R Ranaweera, G Scott, Europ Polym J, 12, 591, 1976

167 R A M Arie Moshe, Narkis, J Kost, Polym Eng Sci, 17, No 4, April 1977

168 A Davies, D Gordon, J App Polym Sci, 18, 1159, 1974

169 D J Carlsson, D W Grattan, T Suprunchuck, D M Wiles, J App Polym Sci, 22, 2217, 1978

170 M J Husbands, G Scott, Europ Polym J, 15, 249 , 1979

APPENDIX I

QUESTIONNAIRE 'A'

Please tick appropriate box

1 How much plastics waste do you produce per week?

(a) less than 100 kg ☐ (b) 100-500 kg ☐
(b) 500-1000 kg (d) 1000-200 kg ☐
(e) over 2000 kg ☐

2 How many locations would this involve?

(a) below 5 ☐ (b) 1-10 ☐
(c) 10-50 ☐ (d) above 50 ☐

3 Indicate in which category your waste arises?

(a) wrapping films ☐ (b) hygienic films ☐
(c) protective/plastic bags ☐ (d) polydrums/containers ☐
(e) tank liners ☐ (f) crates/trays ☐
(g) other (please specify) ☐ ....

4 State condition of waste

(a) clean ☐ (b) contaminated ☐

5 Do you at present

(a) receive money for your plastics waste? yes/no (b) give it away? yes/no
(c) pay to have it collected? yes/no

6 Is your waste at present disposed of

(a) recycler ☐ (b) waste merchant ☐
(c) local authority ☐ (d) own incineration ☐

7 If the answer to question 5a is NO would you be interested in selling your waste plastic if a market was available for it?

Yes ☐ No ☐

PLEASE RETURN THIS QUESTIONNAIRE TO:

MR E SETOUDEH
UNIVERSITY OF ASTON IN BIRMINGHAM
DEPARTMENT OF CHEMISTRY
GOSTA GREEN
BIRMINGHAM
B4 7ET

QUESTIONNAIRE 'B'

Please tick appropriate box

1 How much plastics waste do you produce per week?

(a) less than 100 kg ☐ (b) 100-500 kg ☐
(c) 500-1000 kg ☐ (d) 1000-2000 kg ☐
(e) over 2000 kg ☐

2 How many locations would this involve?

(a) below 5 ☐ (b) 1-10 ☐
(c) 10-50 ☐ (d) above 50 ☐

3 Indicate in which category your waste arises.

(a) wrapping films ☐ (b) polydrums/containers ☐
(c) protective/plastic bags ☐ (d) crates/trays ☐
(e) tank liners ☐ (g) others (please specify) ☐

....

4 State condition of waste.

(a) clean ☐ (b) contaminated ☐

5 Do you are present

(a) receive money for your waste plastics ☐ (b) give it away

YES / NO YES / NO

6 Is your waste at present disposed of via

(a) recycler ☐ (b) waste merchant ☐
(c) local authority ☐ (d) own incineration ☐

7 If the answer to question 5a is NO would you be interested in selling your waste plastic if a market was available for it?

YES / NO

8 If you are not interested in completing this questionnaire, please tick box. ☐

PLEASE RETURN THIS QUESTIONNAIRE TO:

MR E SETOUDEH
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