DEGRADATION OF POLYMER BLENDS

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TO

THE "I AM"

(in gratitude)

ABSTRACT

Polymers are seldom used in the pure state, various additives may be present of which one category includes a second polymer. In the present study, the author reports the effects on degradation properties of a polymer in the presence of a second polymer in its environment. The effect of degradation of polystyrene (PS) and pbly (vinyl chloride) *(WC)* in the presence of various second polymers has been studied. Polymers are heterogeneous systems and in many cases the observed degradation effects reflect the two phase character. It has been found in the present study that interaction processes result in some cases in destabilisation of the system while in other cases the thermal and weathering stabilities are improved in the blend. The method of study involves the use of infra-red spectrophotometecto follow chemical changes in the micro-structure when films were exposed outdoor and when heated in an air oven at 100 ^{o}C The changes in the mechanical properties were followed by measurement of tensile strength using an instron machine. Cast films have been used for the studies.

In the system containing *PS/ABS* blend it was found that PS has a stabilising effect on ABS when exposed outdoors, the converse is true when the blend was heated in air oven at lOO^{o}C

It was also found that the weatherability of PVC and PB were considerably improved in the presence of PS. The presence of PS in PS/PB blend imparts rigidity to the blend. Similarly from a measurement of carbonyl index it was found that PVC has a

stabilising effect on PB. In all cases the l:l blend gave the best compromise of good mechanical properties, heat stability and outdoor weathering.

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GLOSSARY

PS - Polystyrene

PVC - Poly(vinyl Chloride)

PB - Polybutadiene

ABS - Acrylonitrile butadiene Styrene

TVA - Thermal Volatilization Analysis

DSC - Differential Scanning Calorimetry

TG - Thermogravimetry

UTS - Ultimate Tensile Strength

CHAPTER ONE

1.1 INTRODUCTION

Degradation reactions are important in two phases of the life of a synthetic polymer: first during fabrication when processes like calendering, moulding and extrusion take place and second during their subsequent useful life. It is during fabrication that a great deal of damage is done to the polymer. It is therefore no wonder that a lot of studies made up to date on the degradation of polymer had been at temperatures corresponding to that likely to occur during processing. The deteriorative stresses placed upon polymeric products during their subsequent useful life even though less intense are by no means less important. Long term stability is important and the prolonged effect of light, water, and oxidation cannot be ignored.

There is no doubt, from the commercial point of view, that polymers such as polystyrene, poly (vinyl chloride), polybutadiene, their copolymer and copolymer blends incorporating two or all the three of the monomers acrylonitrile, butadiene and styrene have become very important. It is therefore important to have information about their stability and those of their blends towards the various degradative agencies particularly the changing weather in Nigeria. It is also important to have some ideas about what the effect of heat might have on these polymers and their blends.

1.2 DEGRADATION

In the classical chemical usage the word "degradation" means a breaking down of chemical structure. When applied to polymers "degradation" could imply any of the following:- loss in molecular weight, decolouration and deterioration of some of the mechanical properties. Due to the importance of polymeric products it has become essential to understand the nature of the deteriorative processes and hence find conditions which could enhance the stability of a polymer. Some of the agents of degradation of polymers are oxygen, ozone, water, heat and light. Polymers like polytetra fluoroethylene have been found to be very stable to the factors above.

Since products of degradation could be dangerous to human life, polymer chemists are interested in the ultimate stability of polymeric materials, factors that contribute to their decomposition and also in the kinetics of polymer degradation. This is in order to be able - taking the mechanical properties of the polymer into consideration together with life hazards - to put a particular polymer in its best use. Some specific materials have been found useful in improving the stability of the polymer. These are called in general 'additives. Another way polymer chemists have tried to improve, correct or modify the deficiency of a polymer is by polyblending.

1.3 POLYBLENDING:

Polyblends are physical mixtures of structurally different homo - or co-polymers. Polyblends are prepared by mixing polymers. There are different ways of blending polymers. The more important ones are:-

(a) Melt-mixing:- this involves melting both polymers and then allowing them to mix in a rheometer. Melt-mixing of polymers avoids the contamination and removal problems of diluents and assumes a system that will not change in molding operations.

(b) Solution blending:- this involves dissolving the polymers in a given solvent or in a mixture of solvents. In solution blending the presence of the diluent added lowers the temperature and shear force requirements for satisfactory mixing without degradation. However, attempts to remove the diluent can often lead to changes in the domain sizes of the blend and in severe cases complete polymer separation.

(c) Latex mixing:- This is one of the most important techniques for the preparation of commercial polyblends. In latex blending, polymers are present as suspended microspheres. Interaction of neighbouring spheres are prevented by the suspending medium (soap). After thorough blending, a mixture of two latexes with different polymers contains a random suspension of different particles each unaffected by the other.

Coagulation is random since the rate of flocculation is dependent entirely on the soap concentration and not on polymer characteristics. Coagulated material contains an intimate mixture of the polymers. Most polyblends involving rubber are made in this manner e.g. ABS.

1.4 METHODS OF STUDYING POLYMER DEGRADATION

Many different methods are available for studying polymer degradation. The more common ones include the use of:-

(i) Thermal volatilization analysis (TVA)

(ii) Temperature - Programmed Degradation using thermogravimetric (TG) method.

(iii) Differential Scanning Calorimetric (DSC) method.

(iv) Volatile degradation products could be examined using the infrared spectrophotometer and mass spectrometry.

(v) Thermal methods - heating polymer in air at elevated temperatures and measuring the chemical and physical changes.

(vi) Ultra-violet irradiation by exposure to sunlight and following changes occuring by the infrared spectrophotometer.

(vii) Oxygen absorption technique

1.5 DEGRADATION AND STABILIZATION OF POLYSTYRENE

Polystyrene (PS) undergoes both photo and thermal degradation. The volatile products of the thermal degradation of PS are monomer together with progressive decreasing amounts of the dimer, trimer, tetramer and pentamer. Malhotra' and co-workers, by use of differential thermogravimetric and scanning calorimetric techniques, found that when high molecular weight samples of PS undergoes thermal degradation random scission to lower molecular weights was the important process. On reaching molecular weights of $\leq 10^5$ rapid and complete depolymerization became the most important process.

Photodegradation and photooxidation of PS films and PS in solution have been widely studied [2 - 15]

During uv irradiation of PS film in air (or oxygen) a rapid change of mechanical properties is noted [16 - 18] During photooxidation of PS, hydrogen CO, CO_2, H_{20}; methane, benzene, styrene, benzene alcohol and benzophenone are the volatile products liberated from the polymer.[5, 14, 19] PS is unaffected by 3650 A° radiation in the absence of oxygen, but there is a photolytic decomposition threshold somewhat below this wavelength since 2537 A° radiation is strongly active. Three well defined affects have been noted; [3, 4, 5, 14] evolution of gas, development of insolubility and discolouration. Industrially the most important adverse manifestation of PS degradation is the development of yellow colouration

which is associated with oxidation. The presence of nitrogen [14] accelerates the rate of formation of this yellow colouring but the mechanism of this effect is not known.[15] In the opinion of Rabek and Ranby[15] the yellow colouration of PS in a vacuum is due to the photoisomerisation of benzene molecules present in the photodegraded polymer or the benzene rings in the PS to fulvene and benzalvene. The yellow colour of fulvene is due to its conjugated double bond system.

Polystyrene is now believed not to be subject to mechanical degradation. It is reported [20] that even though large amounts of styrene were evolved during mechanical degradation of both as received and out-gased PS, none was observed from reprecipitated samples. This shows that the styrene evolved when PS is subjected to mechanical stress was due to residual monomer present in sample and not mechanical degradation products. Contrary views were however put forward when others [21] found that thin films of PS degrade drastically when subjected to high mechanical shear.

1.6 DEGRADATION AND STABILIZATION OF PVC

(a) Degradation

Photochemical degradation of PVC can be discussed in relation to thermal and high energy degradation. Several fundamental reactions have been found to occur in a similar way.[22 - 40] During u.v. irradiation. degradation and cross-linking processes take place. Also hydrogenchloride and conjugated polyenes are formed, colouration of PVC is also noted. The dehydro chlorination reaction changes the absorption spectrum of PVC. The colouration of PVC results from the formation of polyene structures,[41 - 47] The degradation mechanism of chlorohydrocarbons depends on the Chemical structure and temperature.[48 - 49] It has been found that HCl accelerates the degradation and photodegradation of PVC [50, 51, 52] Dehydrochlorination and oxidation occur simultaneously during the photoinduced degradation processing air.[54, 55, 56] The influence of radiation intensity and radiation wavelength on the photooxidation of PVC have been investigated.[57 - 58] Inspite of all said above, it must be stated that there is no agreement as to the exact mechanism of dehydrochlorination of PVC.[60, 61, 6] Certain workers [63] found that the rates of PVC degradation in solution differ depending on the polarity of the solvent. Others [64] also found that method of polymerization of PVC affects its thermal degradation.

Gibb and his co-workers[65] and others[66, 67], showed that oxygen was essential for photodegradation of PVC.

(b) Stabilization

Mixtures of different stabilizers are normally used, Some are uv stabilizers, thermal stabilizer, etc.

The more common thermal and uv stabilizers used for PVC during processing includes:-

(i) Lead compounds

(ii) Organic salts of barium, cadmium, Zinc, tin and calcium.

(iii) Organic nitro bases.

(iv) Epoxy compounds.

The stabilizing effects of some substances on PVC have been investigated. For example, it is reported that when incorporated singly into PVC lubricants such as calcium stearate and wax E and organotin stabilizer e.g. Ingastab T_{290}, altered the rate but not the mode of degradation whereas when incorporated together, the three additives altered the mode of photooxidation, autoaccelerating to constant rate. Also processing PVC at 170° with the three additives caused an increase in the rate constant.[68] Tsunoda[68] studied by Xray diffraction the products obtained by volatilisation (by heating) of cd from a PVC/cadmiun stearate mixture.

He identified the products as $CdCl_2$ in air and as metallic Cd and $CdCl_2$ in nitrogen. The mechanism of stabilization in hard and impact resistance PVC containing the usual stabilizer system was studied for determining the optimal stabilization for improving the light, weather and wear resistance of PVC compound. It was found[69] that high pigment concentration in impact - resistant PVC led to low weathering resistance as a result of surface degradation. It has also been shown[70] that a tin maleate stabilizer effectively retards the formation of hydro-peroxides in association with unsaturation usually formed during processing of PVC. More recently Scott studied the effects of a tin maleate stabilizer and of typical processing lubricants (Wax E and calcium stearate). They[71] found that tin maleate performs the same function during photooxidation as it does duri thermal degradation i.e. eliminating the formation of polyconjugated unsaturation and peroxides during thermal processing. This function persists to the photooxidation stage.

1.7 DEGRADATION OF POLYBUTADIENE

The photochemistry of polydienes is dependent upon the position of the double bond in the macromolecular chains. For example, cis and trans 1, 4 - polybutadiene have their double bonds in the main chain while 1, 2 polydiene (1, 2 - polybutadiene) have theirs in external side groups.

All these polymers are liable to photo-chemical degradation, crosslinking, cyclization and oxidation. Both isomers of 1, 4 - polybutadiene are isomerised when irradiated by ultraviolet light (2537A°) in a vacuum[72]. It is reported that there is no migration of double bonds in the main chain during uv irradiation of cis 1, 4 - polybutadiene[73]. During uv irradiation of 1, 2 polybutadiene there is no chain scission only photocyclization reactions which lead to the formation of cyclohexane rings[74].

1.8 DEGRADATION OF COPOLYMERS OF BUTADIENE, STYRENE AND ACRYLONITRILE

Polybutadiene will undergo thermal degradation giving mainly hydro-carbons[75] while acrylonitrile will give both anmonia[3] and hydrogen cyanide. Thermal degradation of copolyme of butadiene and acrylonitrile prepared by bulk polymerisation has been studied[76]. Samples containing 100 - 25 mole % butadie gave the same products as did the constituent homopolymers. Thre different methods were used TVA, TGA and DTA. Grassie and Heaney noted that over coplymer composition range with the possible exception of the 80% butadiene copolymer the molar ratio NH_3/HCN is 2.

When ABS undergoes oxidative decomposition CO_2 evolves. It has been noted[77] that the evolution of CO_2 during the treatment of ABS, by etching solution, was controlled by the acrylonitrile - styrene phase.

Oxidative degradation of ABS was thus followed by etching solutions by measuring the amount of CO_2 and the results were compared with those obtained in a similar degradation of acrylonitrile-styrene copolymer and butadiene. The degradation was noted to have followed a zero order kinetics typical for diffusion controlled processes in the saturation range.

Work has also been done on effects[78] and ageing[79] and stabilization of ABS polymers. The ABS polymer was studied by determining the impact resistance of weathered unpigmented common samples. The values of S after the weathering were reported higher, the higher the polybutadiene content in the original sample. In contrast, the photooxidation of thin films of ABS were faster the higher the polybutadiene content. The mechanism of the photodegradation of ABS has also been examined.[80 - 85] Scott[86] found that the rate of photodegradation of ABS was determined primarily by the initial concentration of unsaturated groups. Processed ABS[86] was also observed to undergo photooxidation with little or no induction period.

1.9 ON BLENDS

Polybends involving PS have been made and many of these have been investigated regarding their ability to give the required necessary properties to PS.

Oxidative thermal degradation of ABS and styrene copolymers was reported[87] to show a dependence of the changes in impact strength on changes in C-C double bond and the concentration of the polymer. The oxidative rate and intrinsic viscosity of acrylonitrile - styrene polymer were found to be 2 - 3 fold lower than that of PS. Butadiene - styrene polymer had a low oxidative thermal stability and ABS containing 28% polybutadiene degraded at 60°. ABS and Butadiene - styrene polymer showed a linear relationship between C-C double bond and CO group concentration and impact strength. Photodegradation of styrene polymer was increased by copolymerisation with photosensitive benzalacetone and acrolein.[88] A higher rate of phtodegradation was observed for acrolein-styrene copolymer than for benzalacetone styrene copolymer film containing 1 - 9% of the photosensitive monomer. It is also known that in linear butadiene - styrene rubber, the degree of workability is dependent on the combined styrene content. Increased amounts of the combined styrene content increased the degree of degradability but decrease abrasion resistance. Its ageing resistance[79] was found dependent not only upon the amount of combined styrene but also on the distribution of these combined styrene within the macromolecule. The degradability of benzalaceto - phenon-styrene copolymer was found[89] to be than that of styrene alkyl styryl ketone copolymers under irradiation from a high pressure Hg lamp in an investigation of a series of photodegradable polymers having pendant CO groups attached.

directly to the polymer chain. The quantum yield for bond scission along the main chain of the copolymer was established to be $\simeq 5 \times 10^{-3}$ by 325 nm irradiation in C_6H_6.

Apart from the studies on the degradation of block copolymer containing PS as seen above a lot of investigation has been carried out on the blends where PS or PVC are component. For instance, the degradation of films containing both PS and PVC has been examined by TVA and TG. McNeill[90] and Coworkers observed stabilization of both polymers more notably that of PS. The degradation products are the same as when the polymers are degraded alone. Molecular weight measurements indicate a more rapid decrease in molecular weight of PS when PVC is present. The results of another investigation[91] demonstrate a close similarity in degradation behaviour of polyvinyl acetate (PVA)/PS blends to that already mentioned for PVC/PS. The main effect observed is a stabilization of the PS shown by a delay in styrene production under programmed heating conditions. Although stabilization of PVC by the presence of PS was clearly evident in PVC/PS blends stabilization of PVA in the PVA/PS blends was not noticeable. The possibility of interaction between a polymer or its degradation products and a second polymer in the same environment, as in the case of polymer blends or graft copolymers has been examined in a number of degradation studies. PS and poly(methyl methacrylate)(PMMA) show no evidence of interaction in the degradation of a blend[92].

In other cases it has been found that the product of degradation of one polymer greatly influences the degradation behaviour of the other. Thus PMMA depolymerises much more readily in the presence of degrading PVC and this effect has been used as evidence in favour of a radial mechanism for PVC dehydrochlorination in a bulk system[93, 94, 9]. The presence of degrading poly - methyl styrene (PAMS)[95] or poly (oxyethyleneglycol) (POEG)[96] causes PS to depolymerise more readily. Also the degradation behaviour of PMMA is considerably modified by the presence of degrading polychloroprene.[97]

In attempts to improve impact strength and stability to heat and light, many PVC blends have been studied to find the effect of the second polymer or monomer as the case may be on the PVC. Reports[98] on thermal degradation of radially grafted vinyl compound - grafted (30 - 200%) PVC in air showed that the thermal stability of the graft varied in order ethyl acrylate $\geq$ Butyl acrylate $\geq$ vinyl acetate/styrene. Unlike the case of PVC/PS, blends of PVC with purified commercial chlorinated rubbers were reported[99] to be substantially less stable than would be predicted from a comparison of the degradation of the constituent polymers. By use of PVC labelled with ^{36}Cl together with inactivated chlorinated rubber it was found that the greater amount of HCl was from PVC.

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It was therefore suggested that the destabilization of PVC by the presence of chlorinated rubber was first due to the catalytic effect by the HCl produced at lower temperature by the chlorinated rubber destabilizing the PVC. The second reason suggested, concerned the role of free radicals as intermediates in PVC dehydrogenation. This has however been a subject of controversy for many years and strong evidence may be presented both for and against[61, 62, 65]

For many applications (e.g. building) the greatest disadvantages of PVC are its brittleness at low temperatures, its sensitivity towards notch and its poor resistance to impact[100]. It is reported[101, 102] that improvement in resilience, transparency and heat resistance of rigid PVC compounds are observed on addition of polymeric modifiers - usually polybutadiene based materials - the more important of which are acrylonitrile - butadiene - styrene (ABS), methyl methacrylate - butadiene styrene (MBS) and methylacrylate butadiene-styrene (MABS). An improved heat resistance and notch impact strength of PVC was reported[103] on addition of acrylonitrile - styrene polymer and butadiene - methyl methacrylate styrene polymer as modifiers.

When polybutadiene based polyblends (ABS, MBS and MABS) were used as impact modifiers for PVC the rubber phase acted as a photo - activator for functional group formation and colour change in PVC. It has been known that there has been rapid

deterioration of the impact strength of PVC when it photodegrades. This cannot be explained by the known facts:- that the polybutadiene segments on degrading form crosslinks by alkoxy radicals to carbonyl activated and vinyl unsaturation, that polybutadiene - containing polyblends photooxidise much more rapidly than PVC[102 104 108] and that the photooxidation of the PVC is accelerated by the polyblends. Also the polyblends of low density polyethylene (LDPE) and PVC have been investigated[105]. It was found that the elasticity increased steadily from pure LDPE to pure PVC whereas both tensile strength at break and elongation at break passed through a minimum at about 5% PVC[105]. Optical and scanning electron microscope studies have related this mechanical behaviour to morphological changes in the two phases system under stress.

CHAPTER TWO

2) STUDIES ON PS/ABS BLENDS

2.1 Materials.

Commercial samples of the following polymers were used in the preparation of the polyblends. Polystyrene (PS) Acrylonitrilebutadiene-Styrene (ABS)

2.2 Preparation of PS/ABS Cast Films

Polyblends of the following composition were used (a) 90% PS 10% ABS, (b) 75% PS 25% ABS (c) 50% PS 50% ABS (d) 25% PS and 75% ABS. Blends of the different compositions were cast in film form on mercury surface from chloroform Solutions containing both polymers Films of the 100% PS and 100% ABS were similarly obtained from solution.

Observation:

There appears to be no uniform distribution of the polymers in the blends. Probably the polymers were not very compatible. Films from the blends were exposed to electron microscope and results obtained further suggests this incompatibility of PS and ABS. The appearance of the film containing 25% PS 75% ABS was completely different. This appeared to be more uniform but the film did not look as clear as the others. It had some tinge of slight colouration.

2 3 INSTRUMENTATION AND TESTING

2.3.1 (a) Outdoor Exposure

The outdoor weathering of the films were carried out by exposing the films outside the Chemistry Department of the Ahmadu Bello University, Zaria.

Films of average thickness of 0.007cm obtained above were mounted on cardboards and exposed to outside weathering. Degradation of the samples were followed by infrared spectroscopy measurement of the increasing carbonyl absorbance at 1740cm^{-1}, the increasing hydroxyl absorbance at 3450cm^{-1} and the diminishing trans 1,4 - polybutadiene at 912 and 965cm^{-1}. For the above measurements the Perkin-Elmer Model 700 Infrared Spectrometer was used. The spectra from 4000cm^{-1} to 650cm^{-1} were recorded on the chart paper. The peak at about 2200cm^{-1} corresponding to the nitrile group was used as reference. For each of the samples, the observed growth of the carbonyl and hydroxyl absorption peaks and the observed decay of the trans 1, 4 - poly butadiene were expressed as indices. The indices were expressed as the ratio of the absorbance of the growing or decaying peaks to that of the reference peak. From this, the stability of the films to environmental degradation when exposed to sunlight was studied. The average temperature outside at this time was 28^{o}C.

2.3.1 (b) Fresh films of 0.017cm in thickness were again cut into strips of about 0.7cm in width and 5cm in length. The strip were placed centrally over slits on an already prepared plywood. Another plywood with similar slits was placed on top. This system was clamped to hold the strips in position and to prevent their being blown up by the air. Tensile property of strips from each polyblend was measured before and at intervals during exposure using an Instron Tensile Machine Model TM-M. The full scale load used varied with the polyblend composition. For instance for 100% ABS and 75% ABS, 25% PS full scale load was 2000g while that of 100% PS and the other polyblend compositions were 1000g. The same cross head speed and the same chart speed was used for all. The crosshead speed of 10cm/min and a chart speed of 10cm/min were used

2.3.2. Thermal Oxidative Degradation

Films were again mounted on cardboard holders as in 2.3.1 (a). These were suspended by tin wires in an air oven kept at 100°C. The thermal degradation was followed by running the ir spectra at regular intervals.

2.3.3. Embrittlement Test

The embrittlement test was carried out on all the specimens. This test was carried out by bending the specimen twice at 180°. The first bending was performed towards the unirradiated surface and the second was carried out towards the irradiated surface. This procedure was carried out at regular time intervals. The results obtained are shown in table

2.4. RESULTS AND DISCUSSIONS

(1) Outdoor Exposure.

The results obtained from the mechanical and chemical studies of the various compositions of PS and ABS varying from 100% PS to 100% ABS have been presented graphically as shown in Fig 2.1 - 2.12. Some data are also shown in table I.

Fig 2.1 shows the stress-strain behaviour of these polymers. It can be observed from the shapes of the different graphs that 100% PS behaves typically as a hard and brittle polymer while 100% ABS shows the characteristic shape for the soft and tough polymer. There is also a progressive decrease of the area under the curve (at break point) as the amount of the ABS in the blend decreases thus showing that there is decrease in toughness with decrease of ABS. This is expected because the rubber component of ABS impacts toughness.

Fig 2.2 shows that elongation of ABS at break decreases with increase in time of exposure. This is true for PS also. This is expected for ABS because as ABS undergoes degradation, one of the reaction taking place is crosslinking due to the degradative behaviour of its polybutadiene component. This makes the ter-polymer more rigid but less ductile. The increase in rigidity with exposure time is discussed below.

Elongation also varied with the composition of the blend (Fig 2.3) The % elongation value reaches its minimum with the 15% ABS, 85% PS blend. This composition of the blend has a lower elongation than the pure PS itself.

Within the range of the composition of the blends studied the blend containing 75% ABS 25% PS has the maximum extensibility.

For all the samples studied the ultimate tensile strength increases with time of exposure of the material until the maximum is reached (Fig 2.4). The time required to reach the maximum varied from one composition to another. This was found to have some correlation with the embritilement time of the different compositions.

The graph falls very rapidly once this maximum is reached. Pure ABS has the maximum ultimate tensile stremth after the first 20 hours of exposure. This shows the effect of the rigidity occuring as a result of the degradation of the poly-butadiene component in the ter polymer.

Also in line with the observations above, there is an increase in Young's Modulus with exposure time (Fig 2.5) For pure ABS there is a very rapid increase increase in Young' Modulus is also observed both in the PS and also in the other composition. Fig 2.6 shows variation of modulus with exposure time A very close study of Fig 2.6 shows that even though the Young's Modulus of pure PS increases with time of exposure the presence of even a very small amount of ABS enhances this increase. This shows that the presence of ABS in an exposed PS causes the formation of more crosslinkings than would otherwise be formed in pure PS.

The amount of crosslinks (judged from the Young's Modulus) in general increases with increased amount of ABS in the blend.

Apart from studies made on the mechanical properties with time of exposure the changes occuring in the microstructure were also studied by their spectra. During the photoxidation of PS two characteristic absorption bands were followed the one at 3600 - 3400 cm^{-1} (attributed to the formation of the hydroxyl groups) and the other at 1800 - 1700cm^{-1} attributed to carbonyl groups. This agrees with the spectra obtained by Rabek and Ranby[107] and also by Savides[108] et. al and Fox et. al.[109] There wasn't marked increase in the absorption of these peaks with exposure time. This was found to be true for both the outdoor - exposed sample of PS and also for that undergoing oxidative oven ageing at 100°C. This may not be too surprising because although the mechanism of the photooxidation of PS has been subject of much investigation and speculations, the initiation of the process is not clearly understood. The importance of the polymer sample prehistory[110], the copolymerisation of oxygen and the significance of the singlet oxygen are topics which are relevant to the elucidation of the mechanism of the initiation. The PS sample under study embrittled before it showed any significant changes in the peaks both at the hydroxyl and carbonyl. This might indicate the absence of low concentration phenyl alkyl ketone end groups usually present in commercial PS sample.

These groups are believed[106] to be formed by the scavenging of residual oxygen in the polymerisation process to form a polystyrene - oxygen copoylmer. For the PS sample outside the cracking observed might be due to enviromental stresses which are not surprising because of the weather in Zaria at the time when this study was made. It was during the harmattan.

For ABS and all the different compositions of the blend the general features of all the spectra are similar. In all the spectra in this study the following were observed. The bands relating to the rubber double bonds at 965cm^{-1} and 912cm^{-1} attributed to the poly-trans 1.4 butadiene and cis 1 4 - butadiene respectively decreased. With exposure time A broad hydroxyl band centred at 3450 cm^{-1} and a saturated carbonyl (centred at 1740 cm^{-1}) were formed. During the initial stages of the photoxidation bands at 1665 and 1685cm^{-1} due to unsaturated carbonyl also developed. These species believed[101] to be unsaturated acid ketone and aldehyde respectively accumulated more slowly than saturated carbonyl at 1740cm^{-1}. In ABS the olefinic bands at 912 and 965 disappeared rapidly after an autoaccelerating period while the hydroxyl and carbonyl bands grew.

Figs 2.7 and 2.8 show the variation of the -C=C- index at 912 and 965 cm^{-1} respectively with time of outdoor exposure. This index in both cases decreases and falls off after a certain time. The rate of decrease appears to be highest for the blend containing 10% ABS 90% PS and least for the 100% ABS sample. Fig 2.9 shows the dependence of the hydroxyl index of the different compositions on exposure time. The rate of production is highest for ABS and this rate decreases as the amount of ABS in the blend decreases.

Fig 2.10 compares the carbonyl indices of PS, ABS and the different compositions of the blend. All of them show an increase in carbonyl index on exposure. The rate of increase being greatest for 100% ABS and least for 100% PS. None but pure polystyrene has an induction period of 175 hours. The graph also shows that the rate of carbonyl production increased with increase in the amount of ABS in PS/ABS blend. This shows an increase in the stability of ABS as the amount of PS in the blend increases.

(ii) Thermal Oxidative Ageing.

Fig 2.11 shows the dependence of carbonyl index on heating of PS/ABS blend. Under thermal oxidation ABS degrades very rapidly even more rapidly than that of outdoor exposure (c.f. Fig 2.10; see table I) At a glance, one can see that the presence of ABS has a stabilising effect on the PS. When ABS is present in PS an induction period is introduced.

This value is about 230 hours (table I) for the 90% PS 10% ABS. This value of induction period increases as the amount of PS in the PS/ABS blend decreases. The most stable of the different compositions of the blend is that containing 75% ABS 25% PS which has an induction period of about 450 hours. In general ABS has some stabilising effect on PS. PS also helps to stabilise ABS by introducing some induction period and decreasing the rate of its degradation. However, PS has a greater stability to both thermal and photooxidation (Figs 2.10 and 2.11) than ABS. In the presence of 10% ABS, PS undergoes photooxidation without any induction period (Fig 2.10) This might be explained by the fact that PS and ABS are not very compatible polymers (photograph). Thus the ABS in the 90% PS 10% ABS blend undergoes very rapid degradation and the production of the hydroperoxides is facilitated and thus the ABS acts as a destabilising agent for PS and thereby enchances its degradation pattern.

The embrittlement time gives some idea of the length of time that a polymer sample can be exposed under a given condition before it fails i.e. the useful life of a polymer sample under a given condition. From a study of the embrittlement time (Table I) 100% ABS has the least value (96 hours) for the photo-oxidation. This is followed by 10% ABS 90% PS. The others embrittle at about the same time. In the case of the thermal oxidation again 100% ABS degrades first followed by 10% ABS 90% PS. The PS degrades after 548 hours while the others

decompose after over 1000 hours. Thus it appears that ABS has some stabilising effect on PS when the blend undergoes thermal oxidative ageing. This is in agreement with results[112] obtained in thermal oxidation of PS/PB using TVA. Gupta[112] found that the rate of degradation of the PS component is markedly reduced in the PS/PB blend. They found that during the period when PB is breaking down the PS degradation is apparently inhibited. One explanation[112] of the stabilization of the PS during the period when PB is breaking down is that several of the volatile products of PB degradation (propene-pentene, 4 vinylcyclohexene) if they diffuse into the PS phase could act as radical inhibitors by losing H atoms to the PS radicals with the formation of allylic-type radicals of relative ly low reactivity[112]. The 4 - vinylcyclohexene being both of lower volatility and present in greater quantity appears most likely to be effective in this respect: there are five reactive H atoms in the molecule in the position & to a double bond. Even though this present work was carried out at 100°C it is not unlikely that the behaviour of PB at 200°C is not much different from that of ABS at 100°C (particularly as far as its degradative products are concerned.) Also from thermal analysis data[113] it was noted that the threshold degradation temperature is lowered by the introduction of acrylonitrile units into PB. This is most probably associated with the introduction into the polymer (PB) molecule of tertiary hydrogen atoms, the tertiary hydrogen being further weakened by the presence of

nitrile unsaturation in the & position. Thus the initiation of the overall radical degradation sequence is facilitated. It must however be remembered that the ratio of the styrene, butadiene and acrylonitrile in ABS is a very important factor in determining its degradative behaviour. Generally the higher the polybutadiene content in ABS the greater the photooxidation of its thin films[79]

Conclusion:-

PS has a stabilising effect on ABS both under photooxidativ and thermal oxidative conditions. The ABS on the other hand has no stabilising effect on PS as far as weatherability is concerned. However ABS when blended with PS in the ratio of 1:1 and 3:1 shows some stabilising effect when these compositio of the blend are heated in an air oven. For fresh sample the presence of ABS in PS does not improve most of its mechanical properties except ductity. Graph 2.12 sums up the total effect of ABS on the mechanical properties of PS. ABS is an important engineering product. From fig 2.11 it is seen that the presence of 25% PS in ABS imparts some induction period. Thus for engineering articles requiring ABS in thermal operations PS could be added to cheapen the cost and improve performance. This is also true for outdoor uses.

Table I

	POLYMER/BLEND	OUTDOOR EXPOSURE		THERMAL EXPOSURE	
		INDUCTION PERIOD	Embrittlement time	Induction Period	Embrittlement time
(1)	100% ABS	-	96.00hours	-	61.00hours
(2)	75% ABS/25%PS	-	151.00hours	550hours	1256.25 "
(3)	50% ABS/50%PS	-	151.00hours	-	1256.25 "
(4)	25% ABS/75%PS	-	151.00hours	430hours	1256.25 "
(5)	10% ABS/90%PS	-	120.00hours	230hours	546.00 "
(6)	100% PS	170hours	more than 864		548.00 "

PS/ABS Blend 10 OUTSIDE

REMARKS

PS - 25% ABS 75%

ORIGIN

PURITY

PHASE

CONCENTRATION

THICKNESS

DATE

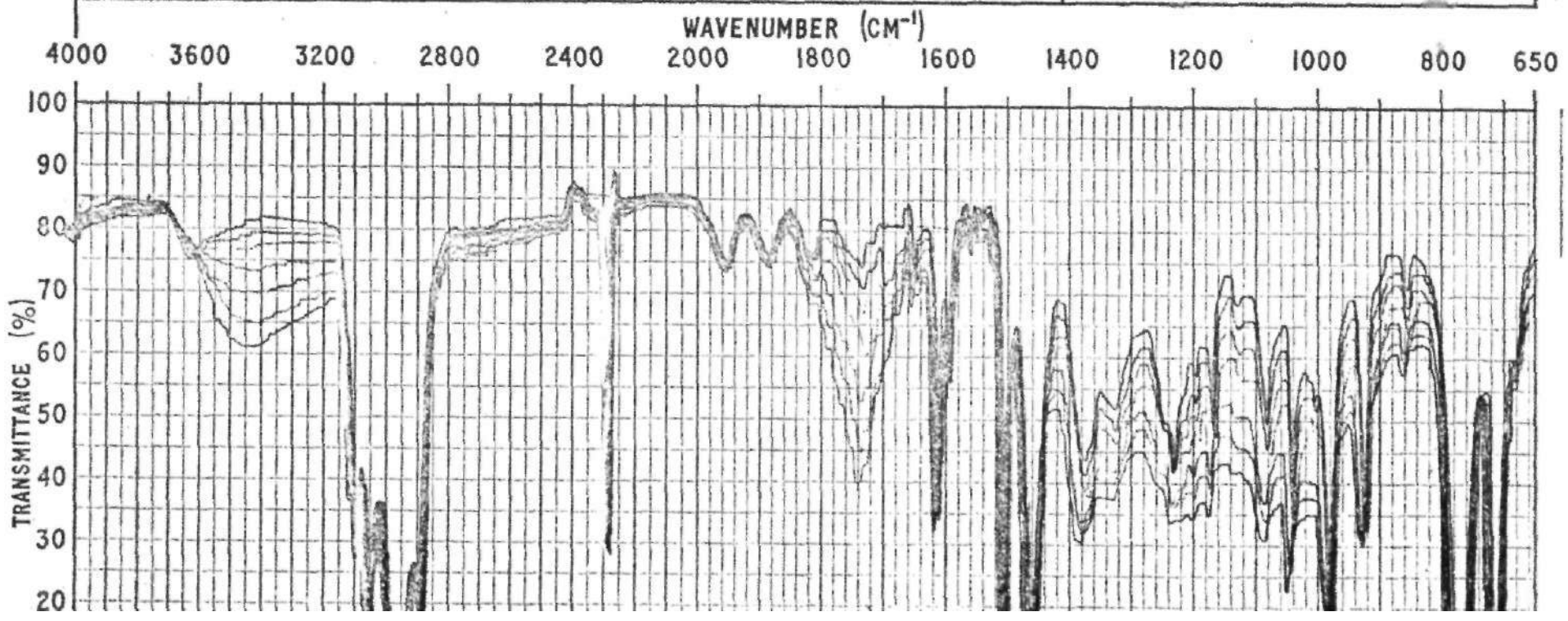
OPERATOR

PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1

SAMPLE 2



SAMPLE

SPECTRUM NO.

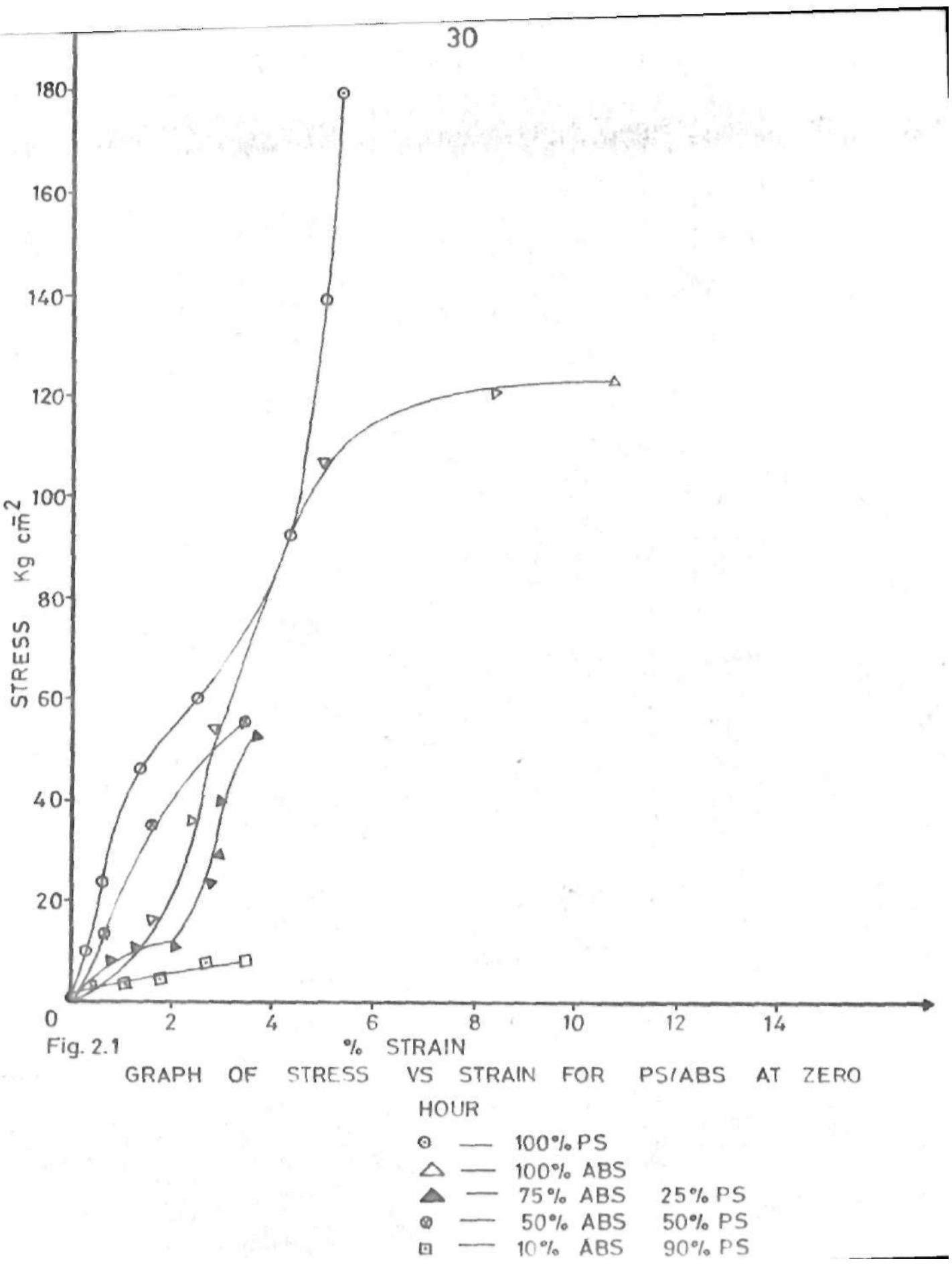


Fig. 2.1 GRAPH OF STRESS VS STRAIN FOR PS/ABS AT ZERO HOUR

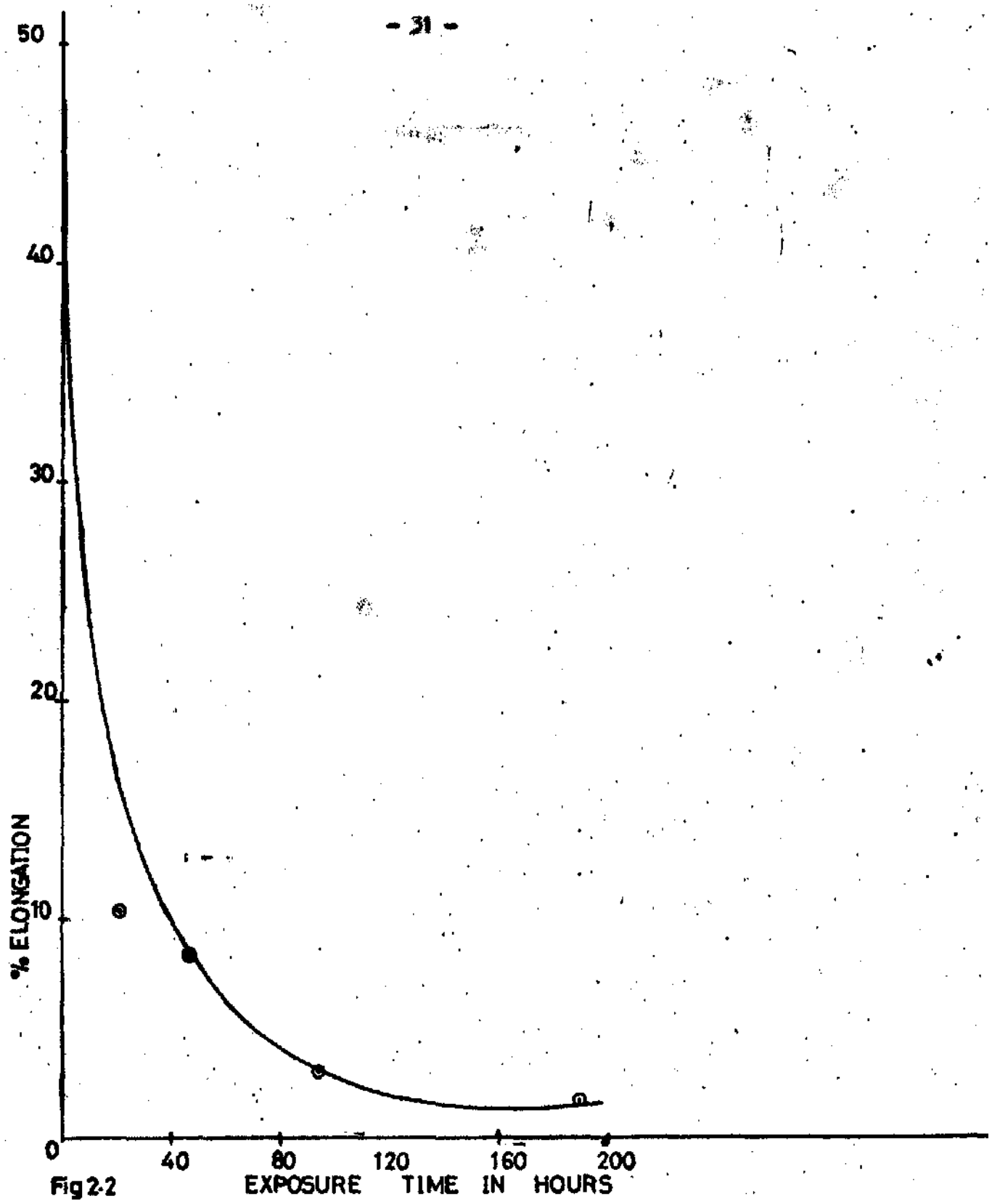


Fig 2.2 DEPENDENCE OF % ELONGATION OF 100% ABS ON EXPOSURE TIME

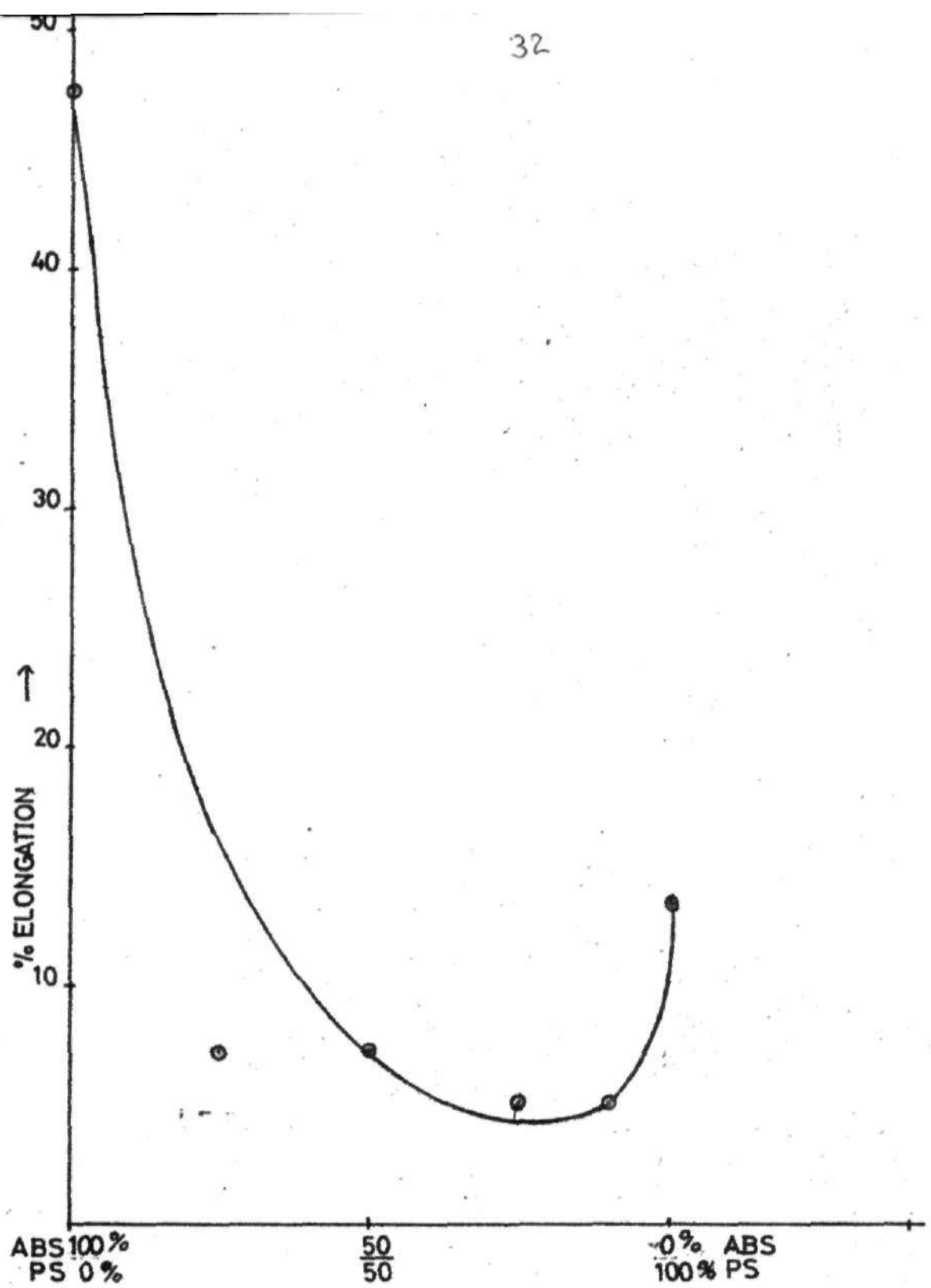


Fig 23 DEPENDENCE OF % ELONGATION ON COMPOSITION OF PS/ABS BLEND

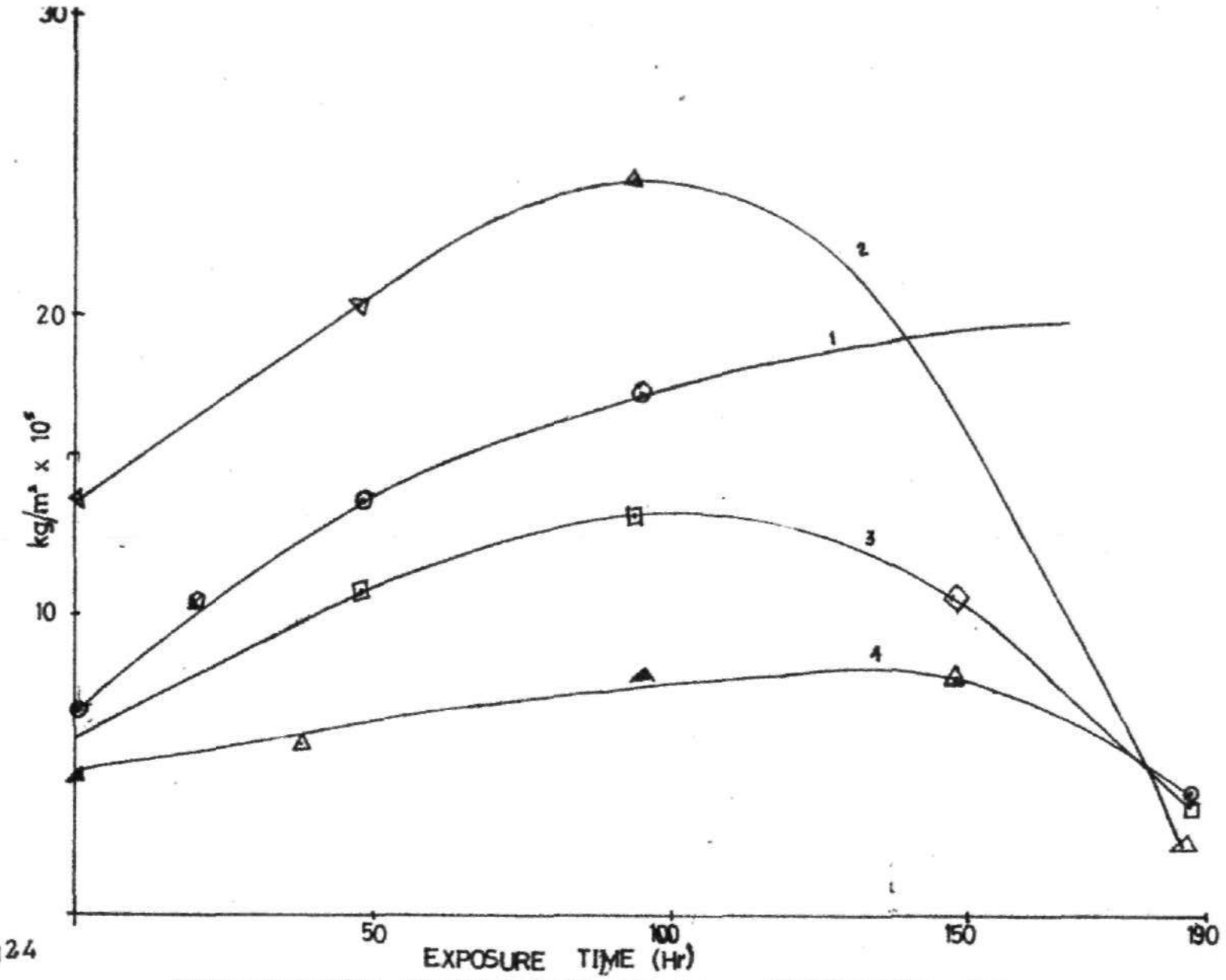


Fig 24

DEPENDENCE OF ULTIMATE TENSILE STRENGTH ON EXPOSURE TIME

● 100% PS
▲ 100 % ABS
▲ 75% ABS 25% ABS
▣ 10 % ABS 90% PS

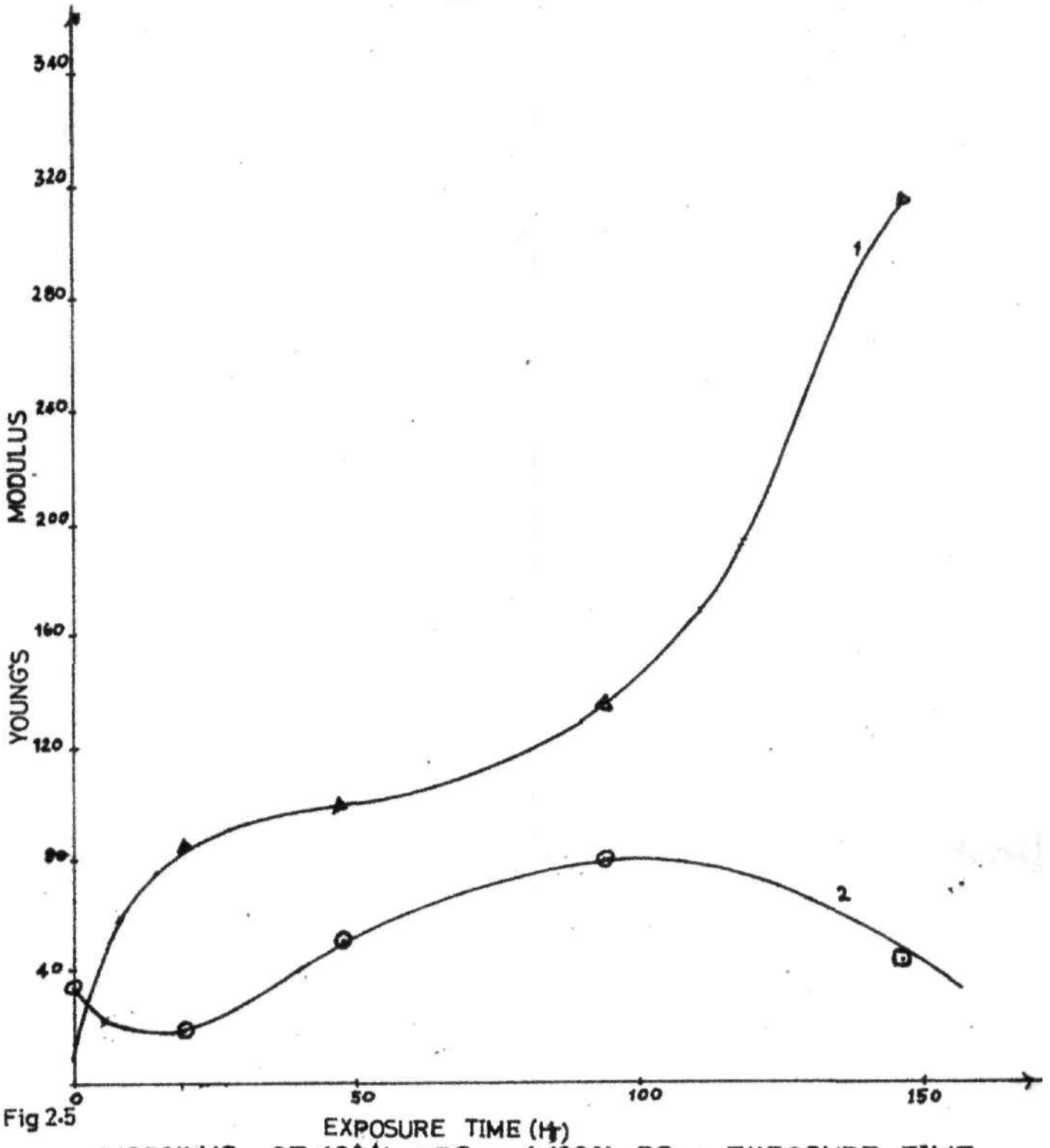


Fig 2.5

MODULUS OF 100% ABS and 100% PS vs EXPOSURE TIME

△ 100% ABS – 1

⊙ 100% PS – 2

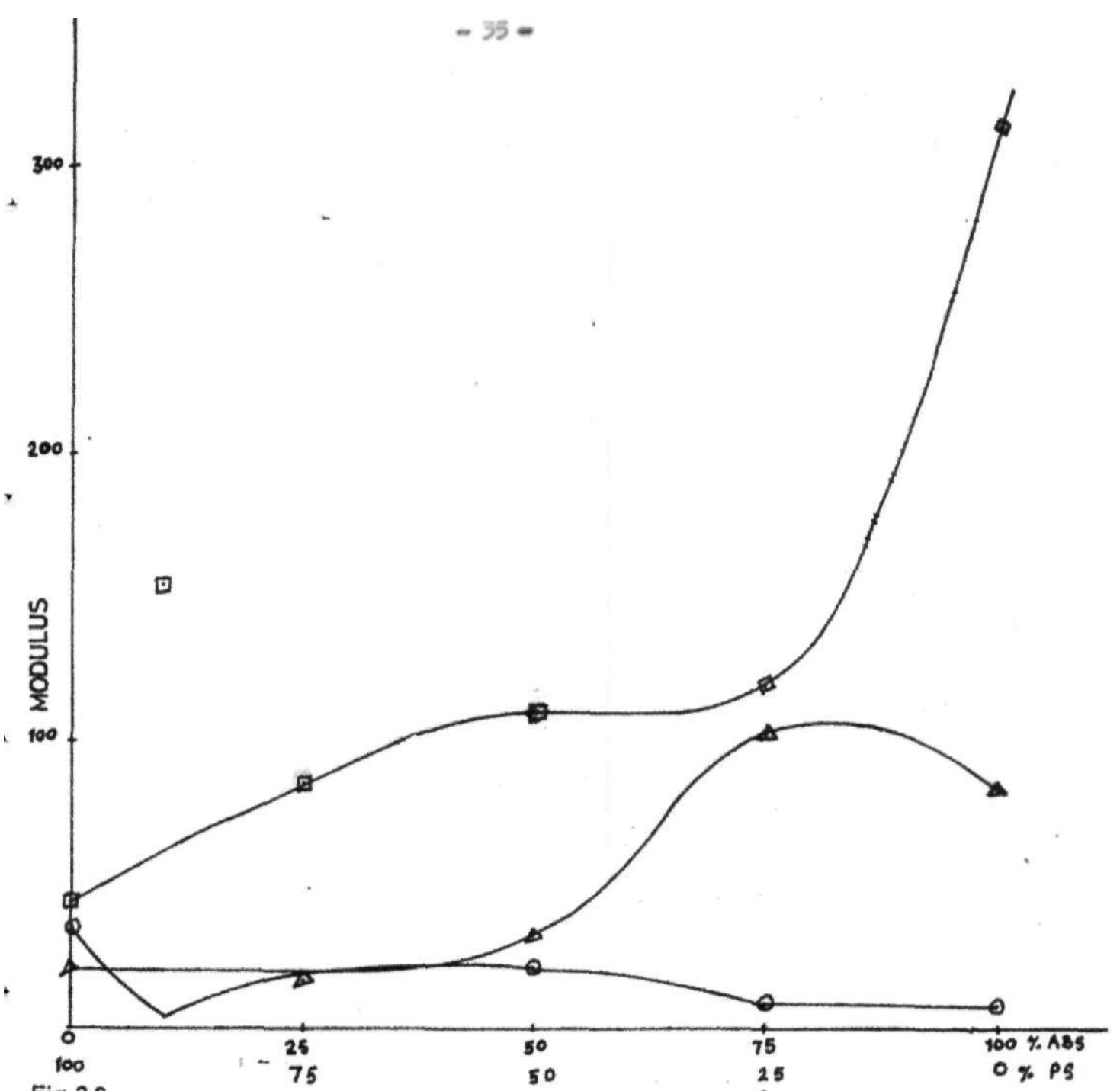


Fig 2-6

MODULUS vs COMPOSITION FOR DIFFERENT HOURS OF EXPOSURE

● - BEFORE EXPOSURE

▲ AFTER 20 HOURS

□ AFTER 146½ HOURS

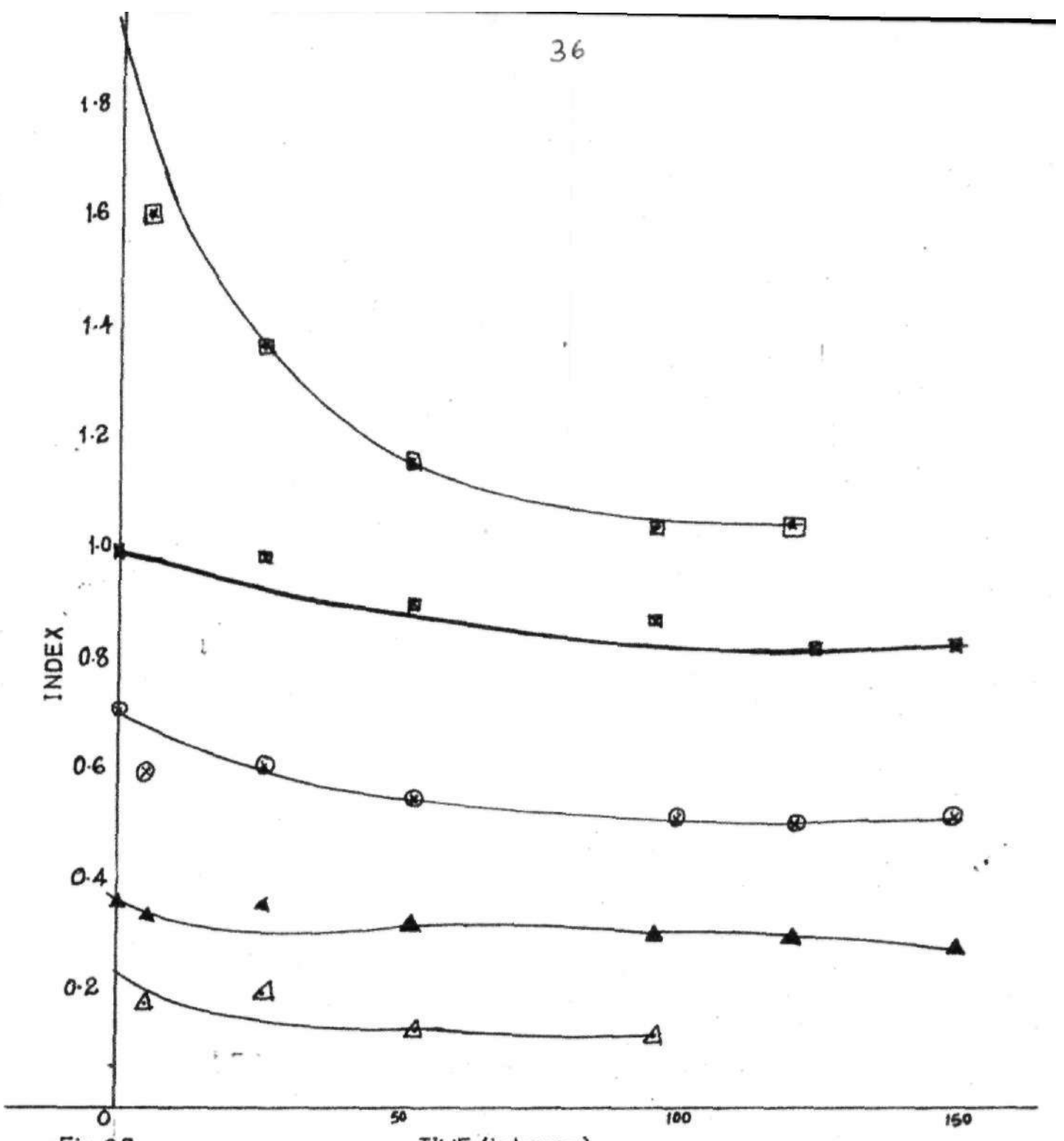


Fig 2·7

DEPENDENCE OF -c=c- AT 912 cm^{-1} ON EXPOSURE

▲ 100% ABS
▲ 75 % ABS 25 % PS
● 50 % ABS 50 % PS
⊠ 25% ABS 75% PS
⊡ 10% ABS 90% PS

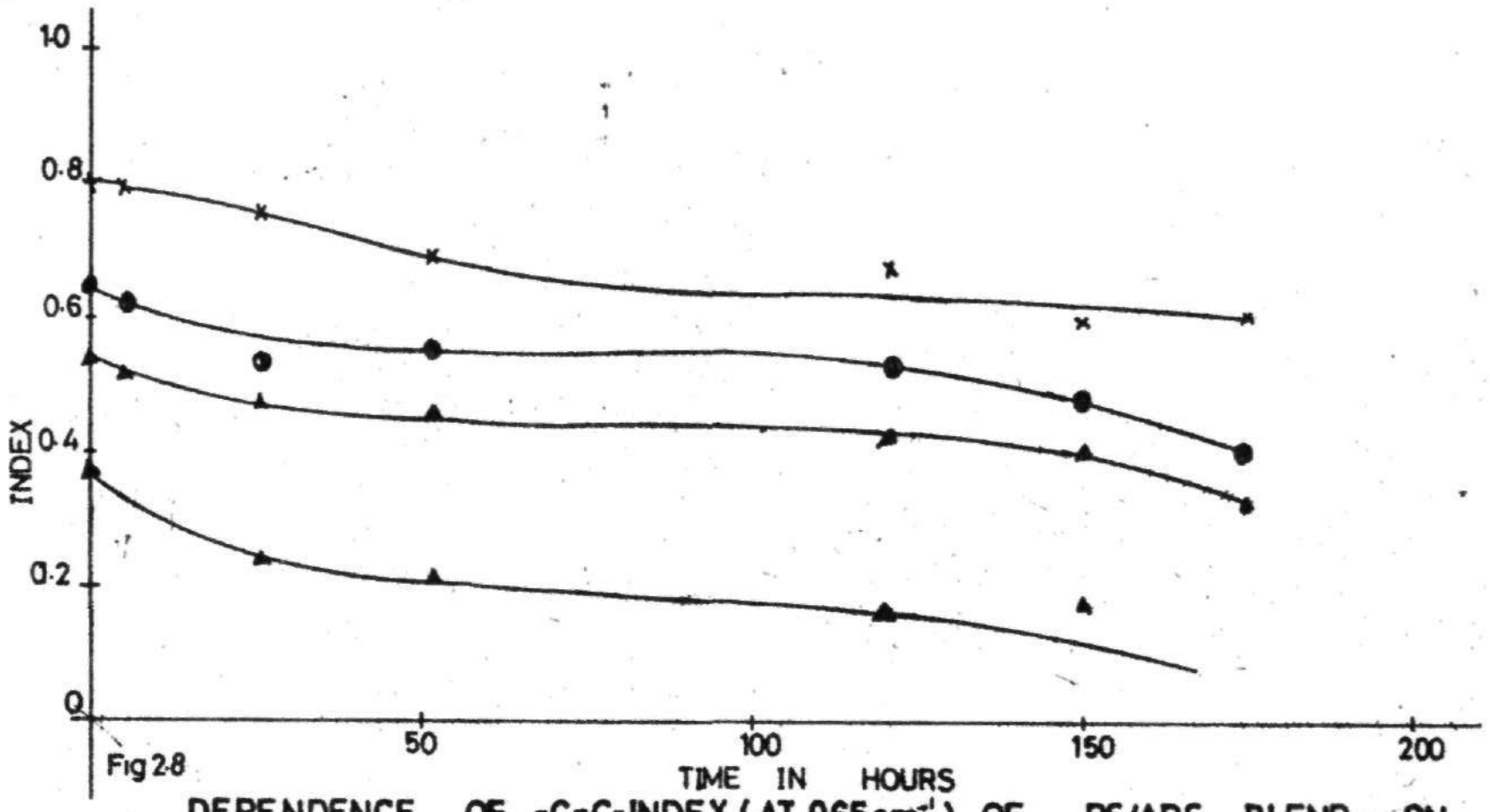


Fig 2.8

DEPENDENCE OF -C=C-INDEX (AT 965cm^{-1}) OF PS/ABS BLEND ON TIME OF OUTDOOR EXPOSURE

△ – 100 % ABS
▲ – 75 % ABS
⊗ – 50 % ABS
× – 25 % ABS

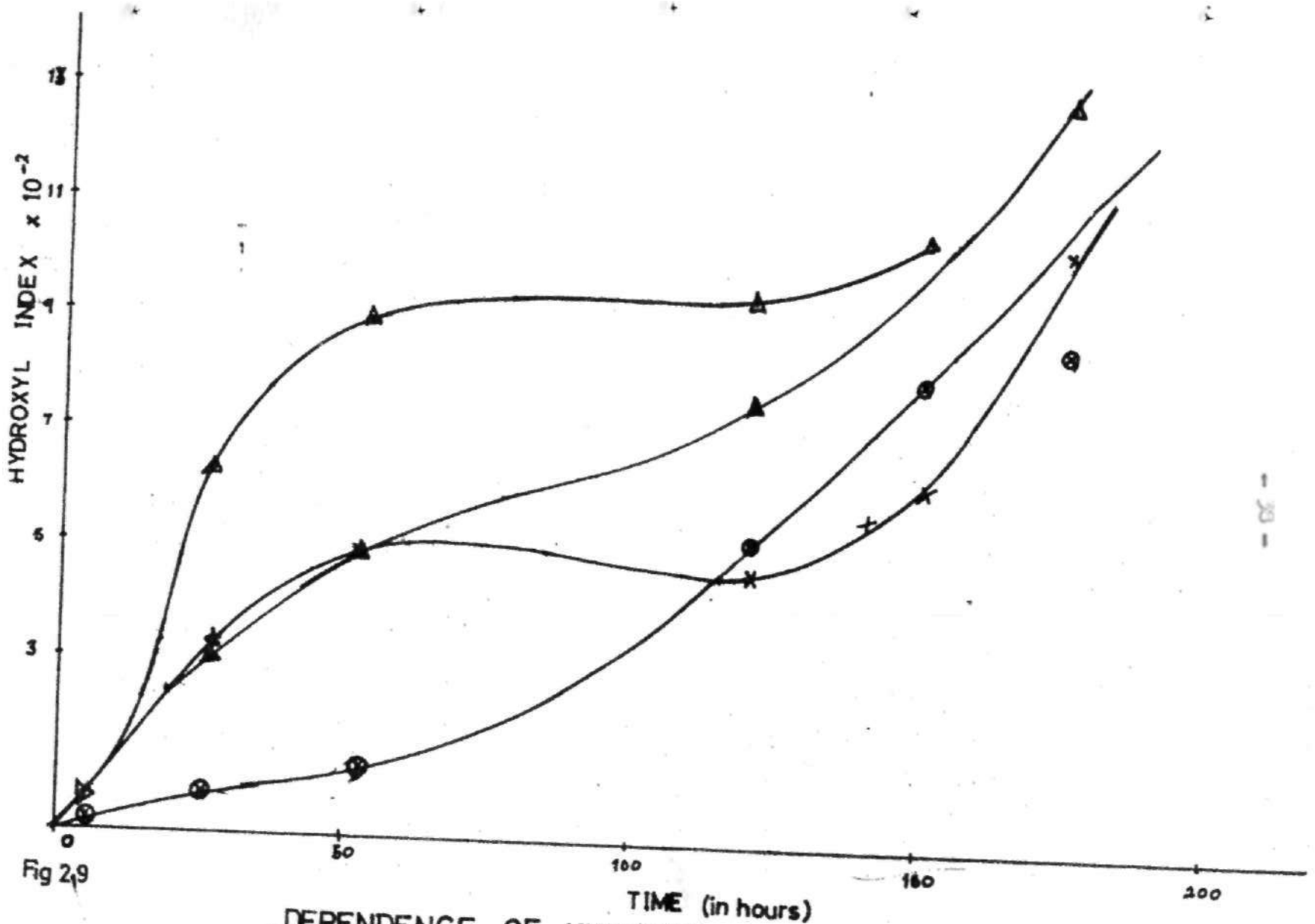


Fig 2.9

DEPENDENCE OF HYDROXYL INDEX (at 3450 cm^{-1}) ON OUTDOOR EXPOSURE TIME

△ - 100% ABS
▲ - 75% ABS
⊗ - 50% ABS
× - 25% ABS

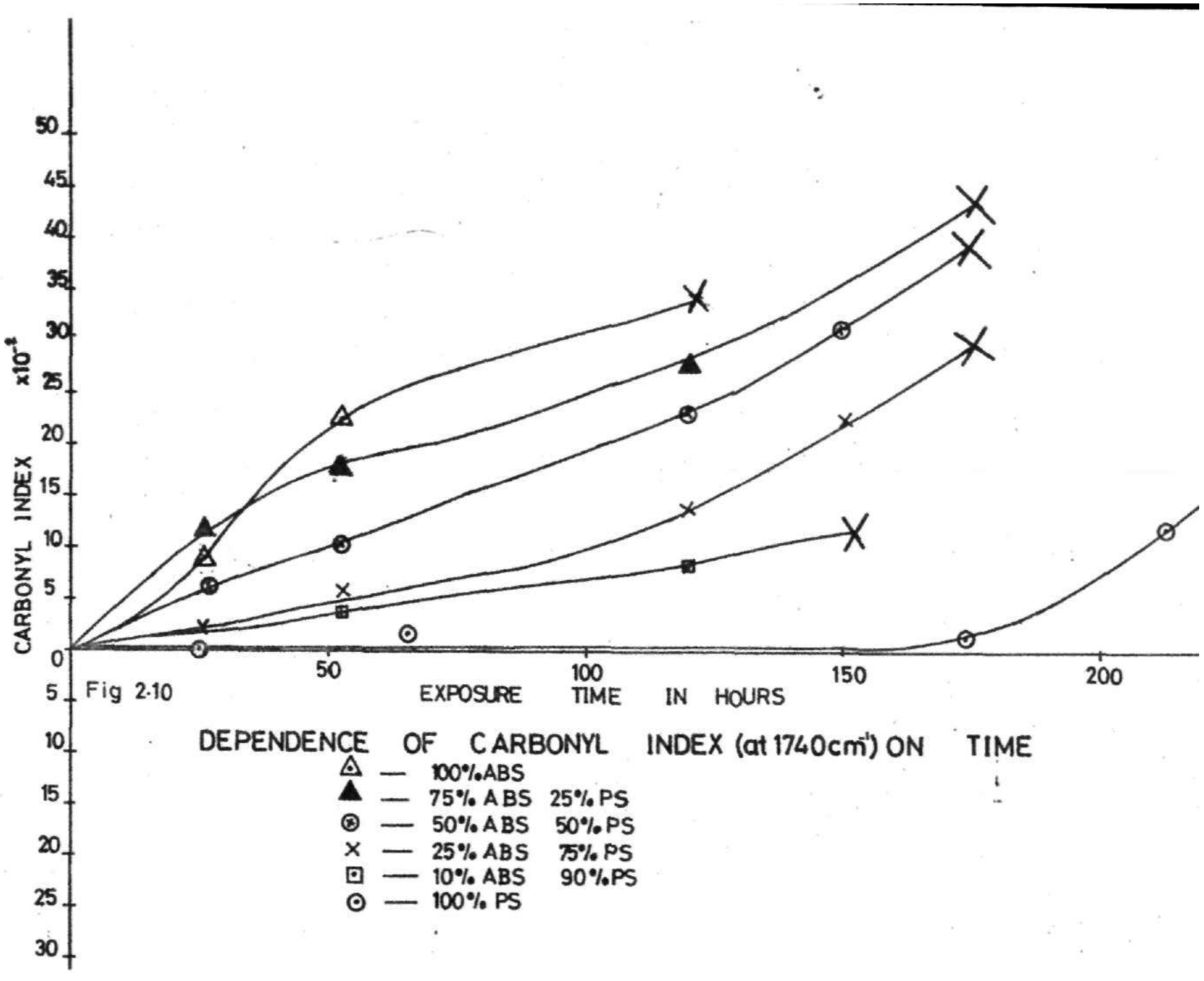


Fig 2·10

DEPENDENCE OF CARBONYL INDEX (at 1740cm⁻¹) ON TIME

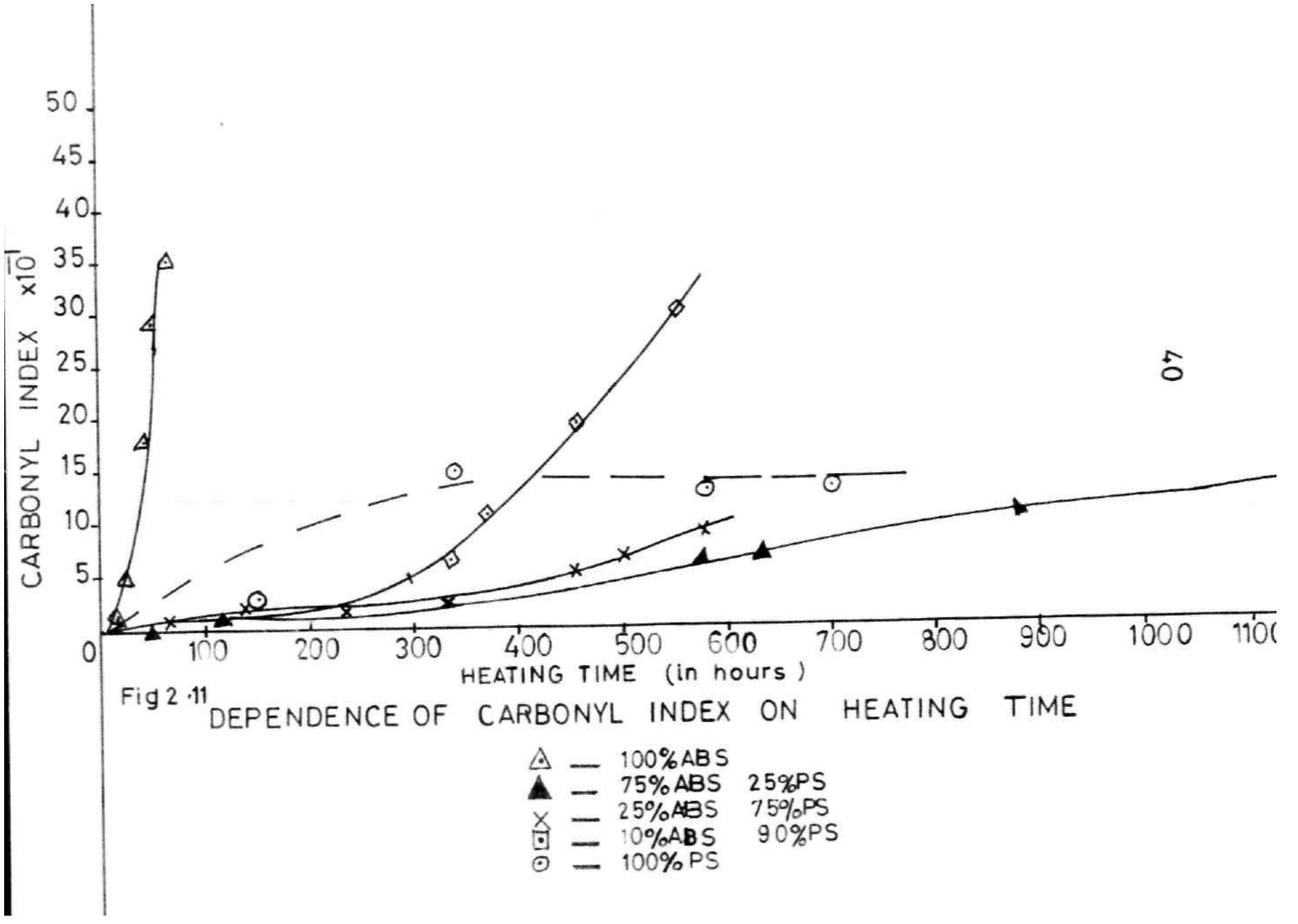


Fig 2·11 DEPENDENCE OF CARBONYL INDEX ON HEATING TIME

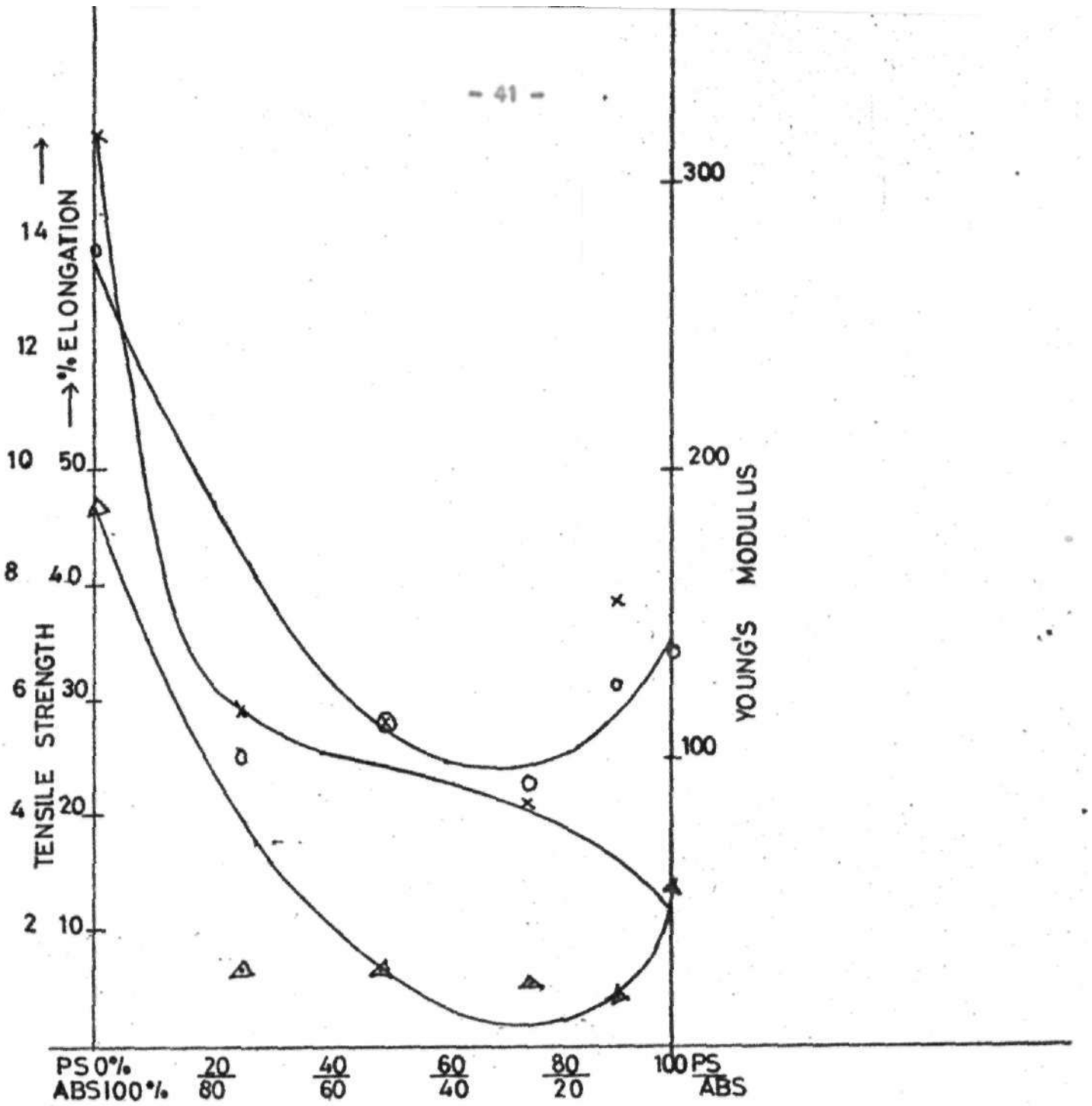


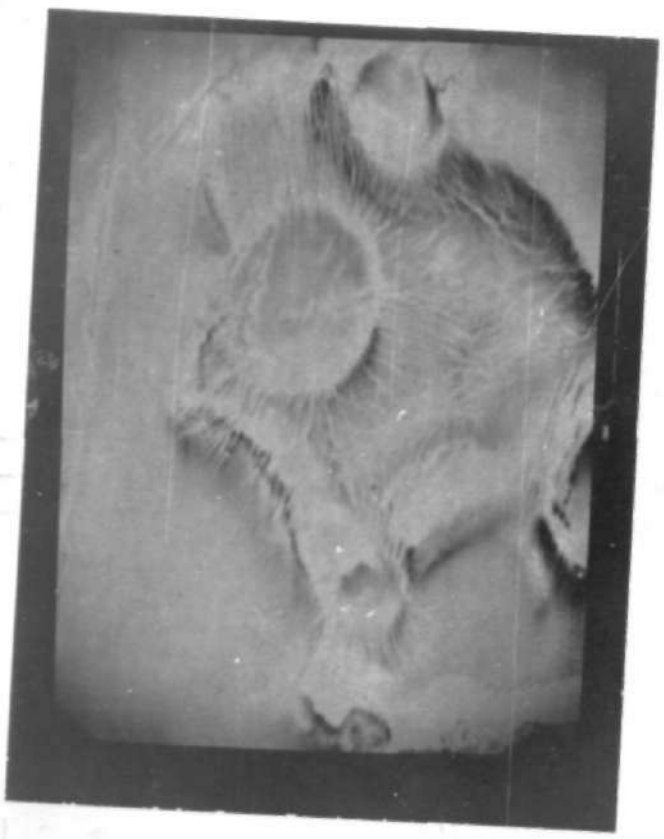
Fig 2.12

DEPENDENCE OF VARIOUS FACTORS ON % COMPOSITION OF PS/ABS BLEND

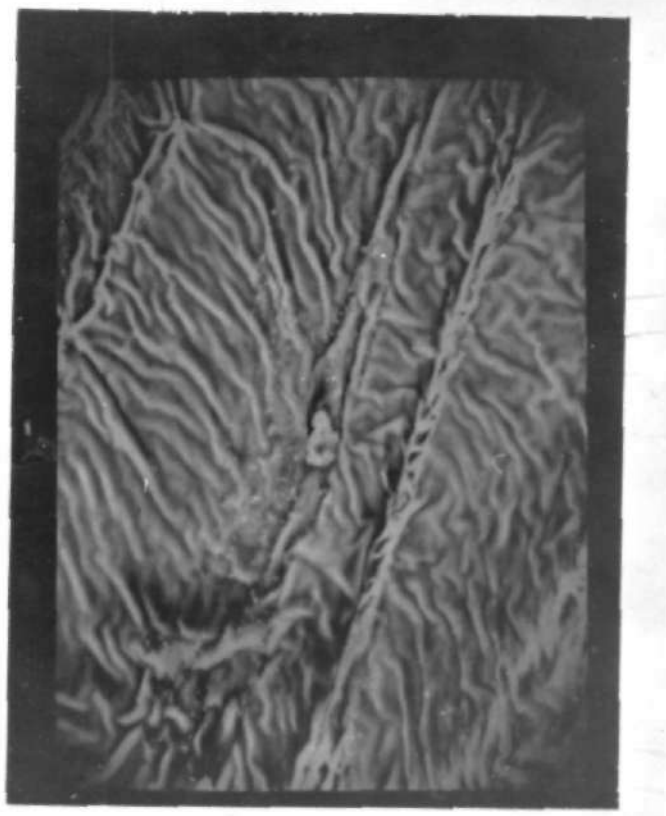
△ — % ELONGATION VS COMPOSITION

X — MODULUS AFTER 14^1 HOURS OF EXPOSURE

O TENSILE STRENGTH



ELECTION MICROGRAPH OF SOLUTION CAST PS/ABS FILM.



LECTION MICROGRAPH OF SOLUTION CAST PS/ABS FILM, IRRADIATED FOR 140 HOURS

CHAPTER THREE

3. STUDIES ON PS/PVC BLENDS

3.1 In this work, changes in the chemical as well as physical properties as a result of degradation of PS, PVC and PS modified by PVC have been studied using mechanical test on cast films. The ir spectra were also run in order to follow changes in the micro-structure on exposing the above polymers and their blends to outdoor weathering and thermal oxidative ageing. Film preparation (tetrahydrofuran, was used as solvent) and methods of study are the same as in the previous section 2.3. The methylene peak at 2910cm^{-1} was used as the reference peak in this study.

3.2 RESULTS AND DISCUSSIONS

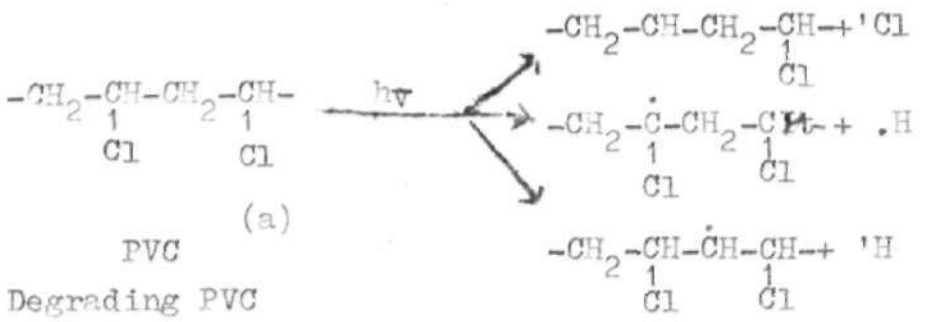
The ir spectra obtained for PS has already been discussed in section 2.4. For the PVC the ir spectra showed the hydroxyl peak converging at around 3400cm^{-1} while that due to the carbonyl was at 1725cm^{-1}. These peaks were found to increase with time of exposure. The peak for -C=C- also showed at 965 cm^{-1}. This peak decreases with time of exposure and eventually levels off.

The spectra of the 1:1 and 1:3 PS:PVC in the PS/PVC blend were also studied. For the blends, the hydroxyl converged at 3450cm^{-1} while the carbonyl converged at around 1725cm^{-1}. The comparative behaviour of the PS, PVC and blends as related to the hydroxyl and carbonyl index are shown in figs 3.1 and 3.2.

respectively. From fig 3 1 it is apparent that the hydroxyl index from PVC has an induction period of about 175 hours. From this graph it may be deducted that both polymers have a stabilising effect on each other. the 1:1 ratio showing greater stability than the 3.1 PVC:PS. Similarly from fig 3.2 each of the different compositions of the blend shows an induction period of about 220 and 275 for the 1:1 and 3:1 PVC/P while there is a gradual increase in the production of the carbonyl by the 100% PVC. Here, it appears that the presence of PS in PVC tends to stabilise PVC. Whereas the presence of PVC has got an opposite effect on the stability of PS. The stability of the blend on exposure to sunlight cannot however be fully explained by their average composition. This has also been found to be true for the high stability of styrene-methyl-methacrylate copolymers.[114] The thermal degradation of the graf copolymers of PVC and PS has been studied in details.[115] By use of TVA and TG McNeill et. al[116] found that when PS/PVC graft copolymers were degraded the PVC dehydrochlorination was delaye and that small chain fragments of low volatility were produced from the PS in the temperature range of 150 - 250°C. The observed stabilising effect of the PS on the PVC might be explained as follows:-

(1)

(1)

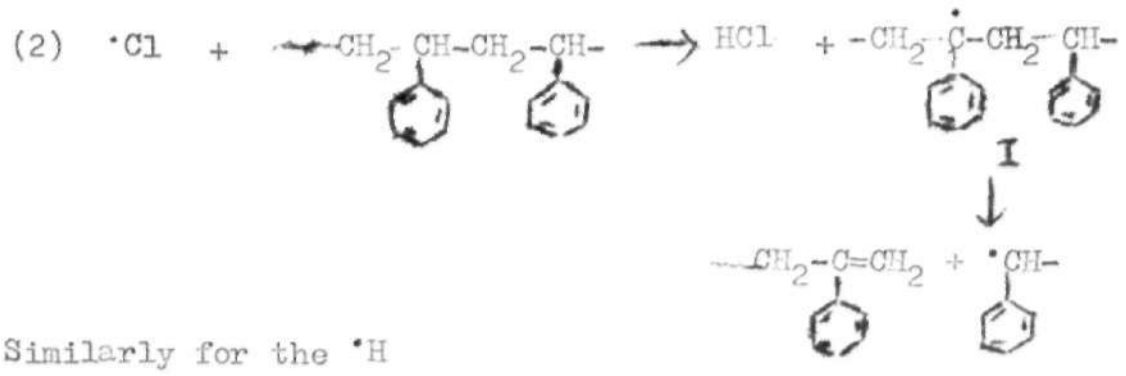


(a)

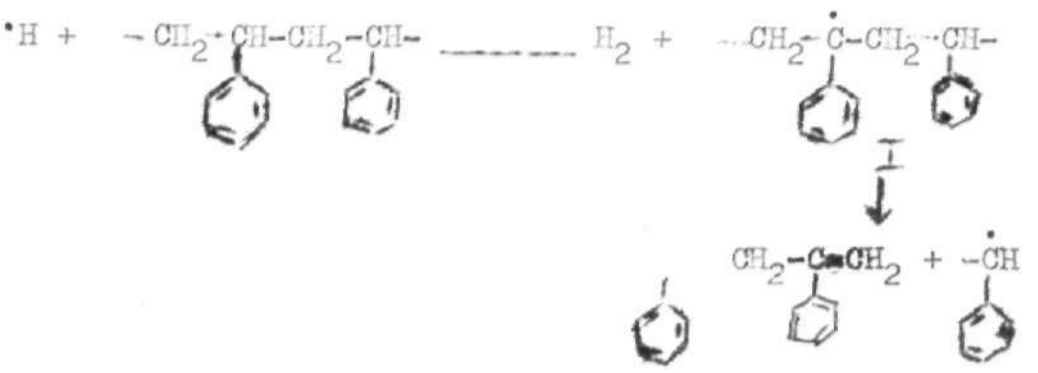
PVC

Degrading PVC

The chlorine radicals from the degrading PVC can abstract hydrogen atoms from PS producing polystyryl radicals which then undergo scission and transfer reaction. Similarly the hydrogen radical from the degrading PVC. (a) can abstract hydrogen from PS. (b) thus producing polystyryl radicals. (I) and hydrogen gas.

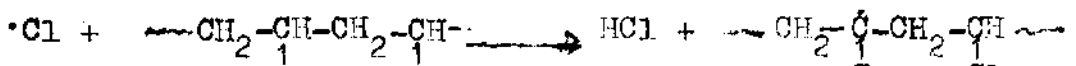
(2) 

Similarly for the ·H



The tertiary hydrogen atom on the PS is more readily abstracted than that on the PVC by chlorine radical because of the presence of the benzene ring which is electron releasing while the chlorine attached to the tertiary carbon in PVC is electron with drawing.

A more important reason for the preferential abstration of the tertiary hydrogen on the PS by the chlorine or hydroge radical is the fact that the radical so produced is more stable than that produced by similar attack on the PVC. The stability of the polystyryl radical is due mainly to the resonance stability caused by the presence of the benzene ring. I is mor stable than II.



II

Thus while the presence of PS might have a stabilising effect on PVC the presence of PVC might have only a slight stabilising effect on PS only in as far as the polystyryl radicals produced in equation (2) are reluctant to depolymerise at low temperature This has been found[115] to be the case at temperature of about 200°C They[115] noted that no styrene was produced.

Figs 3.3 and 3.4 show the variation in stress-strain relationship of PVC and PS as the composition of their blend varied for fresh samples and for samples at 340 hours of exposu In general, the PVC used shows the characteristic shape of stron and tough materials. The PS is hard and brittle.

The presence of PVC does not appear to improve the toughness of PS. A comparative study of figs 3.3 and 3.4 shows that there is increase in the toughness of all the films even after a long outdoor exposure. Fig 3.5 shows the dependence of % elongation at break on the composition of the PS/PVC blend. PVC has a greater extensibility than PS. The elongation for all of them decreased with exposure. This shows that there must be increase in the rigidity of the films.

The above statement is confirmed by fig 3.6. Here Young's modulus is observed to increase with exposure time. The values of Young's modulus for the different compositions of the blends however fall within those for the pure polymers. Fig 3.7 shows the variation of the ultimate tensile strength of PS, PVC and the different compositions of the blends. PVC has a greater ultimate tensile strength than PS, the blend containing 10% PS to 90% PVC also has a higher value than PS again for the different compositions there is increase in ultimate tensile strength as the time of exposure increases (Fig 3.8). This again shows an increase in rigidity and hence more energy is required to break the sample. Increase in rigidity results from cross-linking reactions occuring as the macroradicals produced during degradation get linked up.

Very slight yellow colouration was found in the exposed PVC film. Scott[117] has found that the intensity of the colour formed in PVC increased with an increase in carbonyl groups.

Similar results have been found by Martin and Tilley[118] who related the discolouration of PVC to oxidation and formation of carbonyl groups. It has been found that the development of yellow colouration in PVC films requires a minimum of seven conjugated double bonds in a sequence [119, 120, 121]

CONCLUSION

Fig 3.9 summarises the variation of some mechanical properties with % composition of the blend. The 1:1 ratio appears to give a good compromise of these mechanical properties.

The presence of PS in a PS/PVC blend has a stabilising effect on the degradative behaviour of PVC. PVC also has some stabilising effect on PS in a PS/PVC blend. The degree of stability cannot however be fully explained by their compositions.

TABLE I

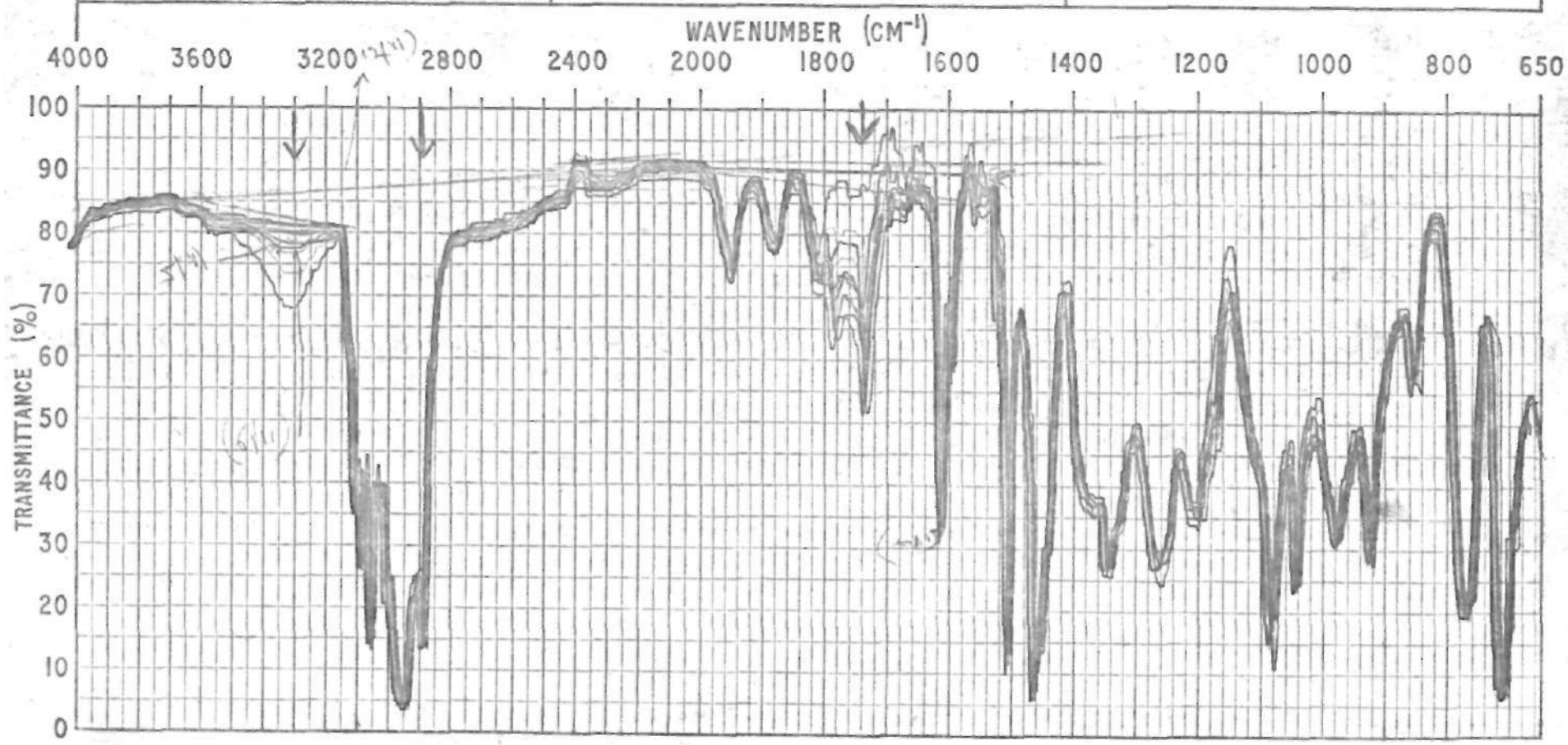
POLYMER/BLEND	OUTDOOR EXPOSURE	
	INDUCTION PERIOD (in Hours	EMRITTLEMENT TIME (in hours
100% PS	170	364
50% PS:50%PVC	-	1659
25%PS:75:PVC	-	1717
100% PVC	-	2064

REMARKS PVC/PS (50%)
blue - 8.35 am (3/11/75
red - 4.50 pm (3/11/75)
(5/11/75)
red - 3pm (6/11/75)
red 10.30 am (12/11/75)
blue 10.25 am (13/11)
red (blank) 15/11/75 12.45 noon.

ORIGIN
PURITY
PHASE
CONCENTRATION
THICKNESS
DATE 8.35 am 3/11/75
OPERATOR

PERKIN-ELMER

SPECTRUM NO.
SAMPLE 1
SAMPLE 2



SAMPLE
SPECTRUM NO.

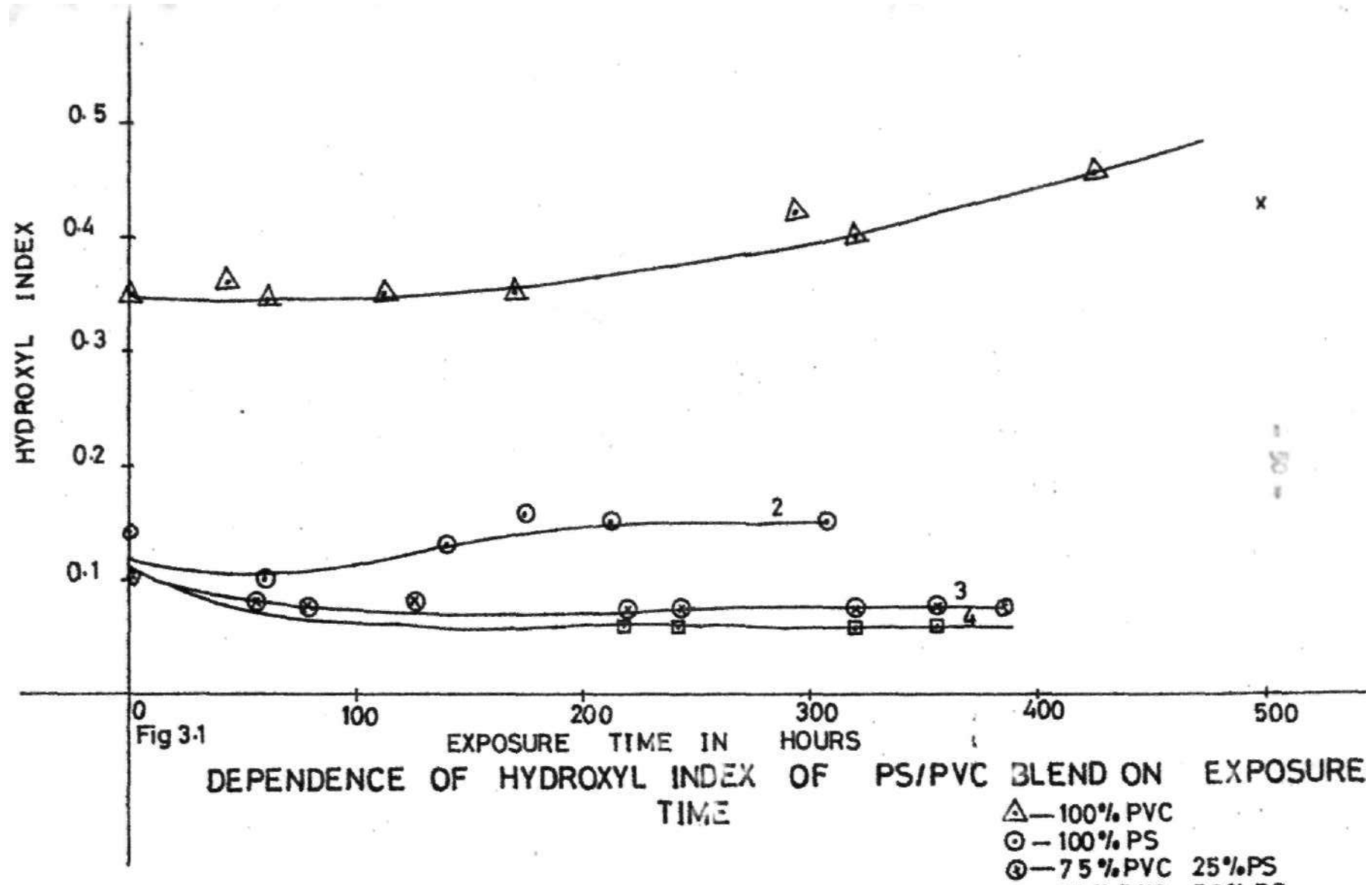


Fig 3·1 DEPENDENCE OF HYDROXYL INDEX OF PS/PVC BLEND ON EXPOSURE TIME

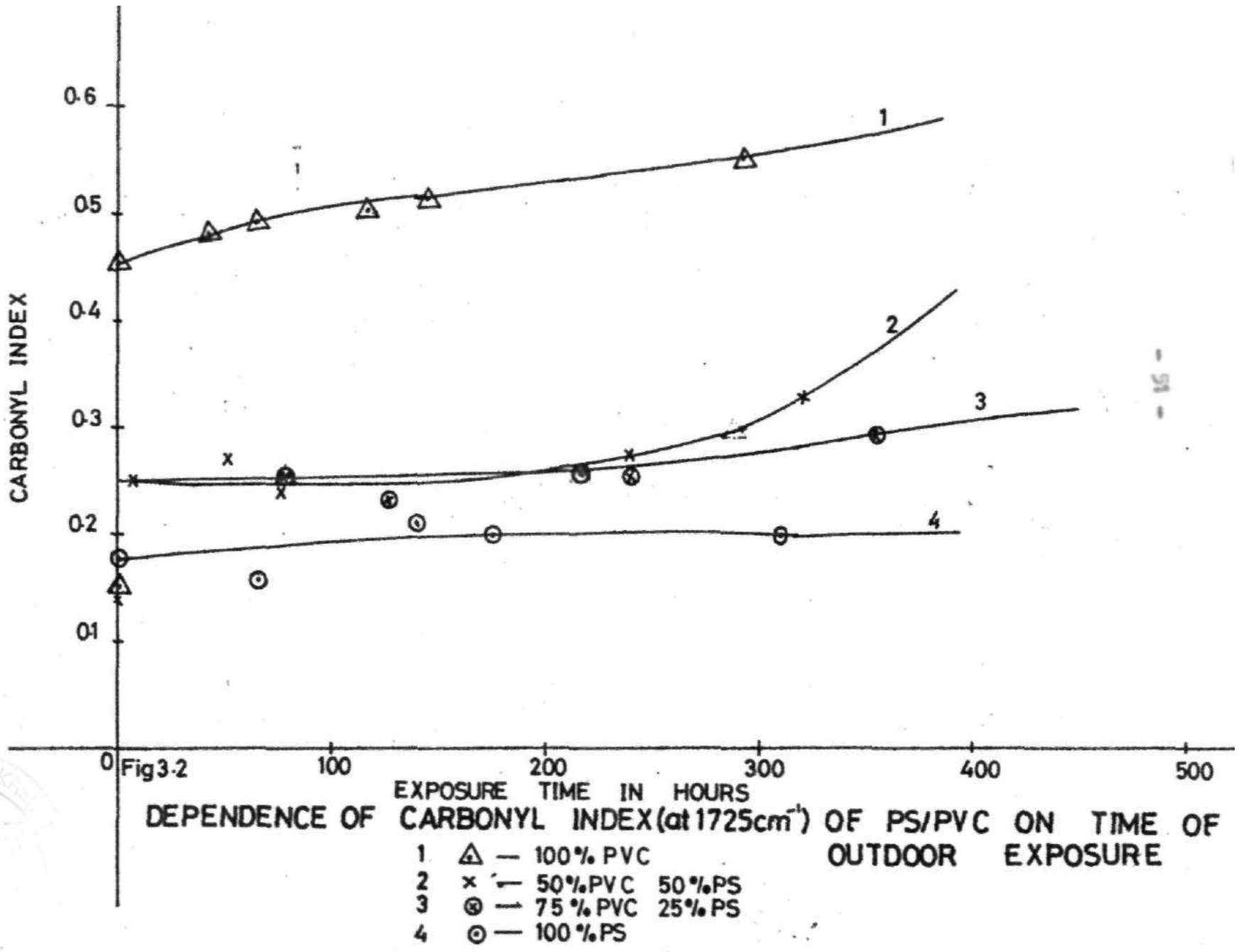


Fig 3.2

DEPENDENCE OF CARBONYL INDEX (at 1725cm^{-1}) OF PS/PVC ON TIME OF OUTDOOR EXPOSURE

1 △ — 100% PVC
2 × — 50% PVC 50% PS
3 ⊗ — 75% PVC 25% PS
4 ⊙ — 100% PS

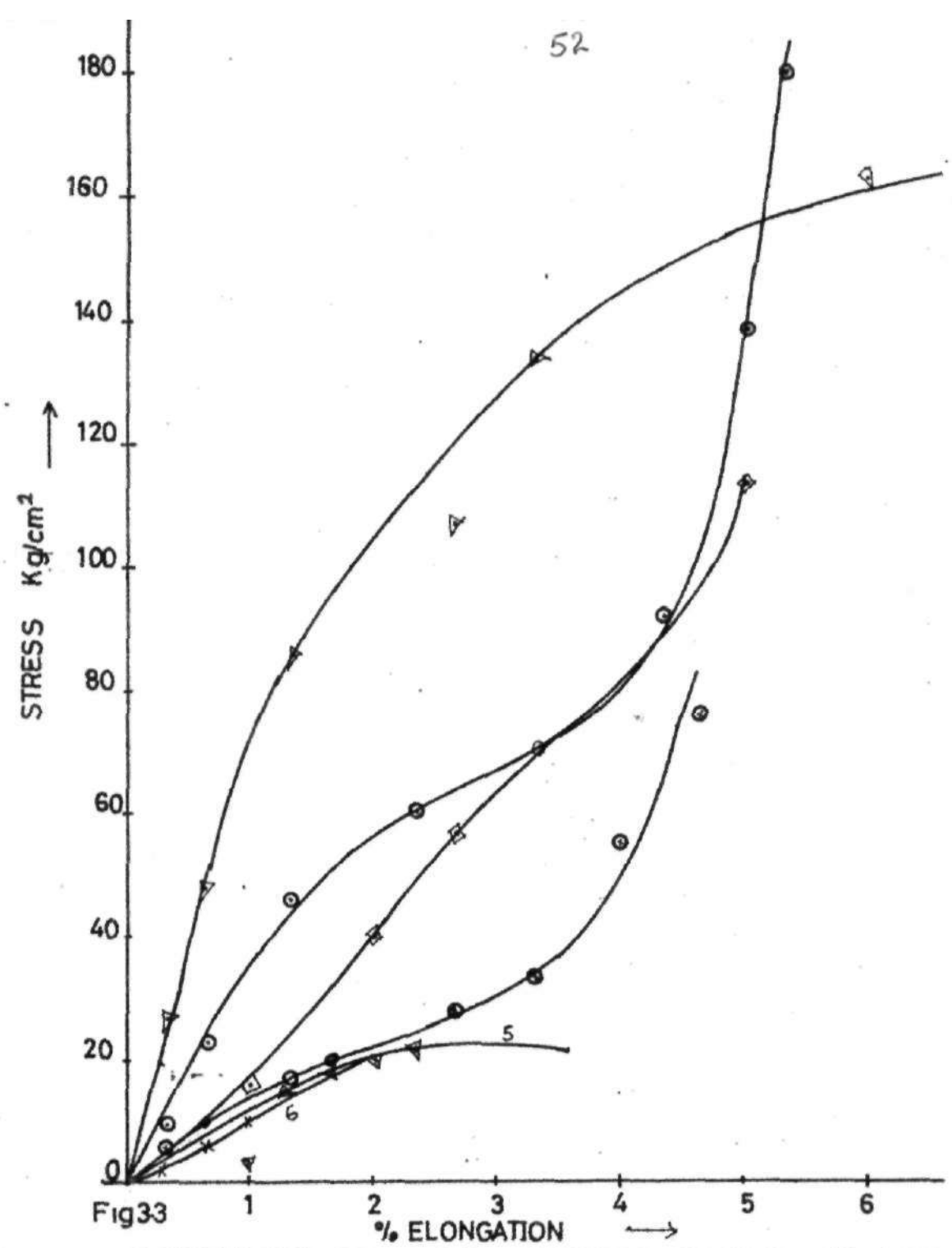


Fig33

STRESS/STRAIN FOR PS/PVC BLEND AT ZERO HOURS

△ — 100% PVC
⊙ — 100% PS
⊡ — 90% PVC 10% PS
⊗ — 75% PVC 25% PS — 4
△ — 60 % PVC 40% PS — 5
X — 50 % PVC 50% PS — 6

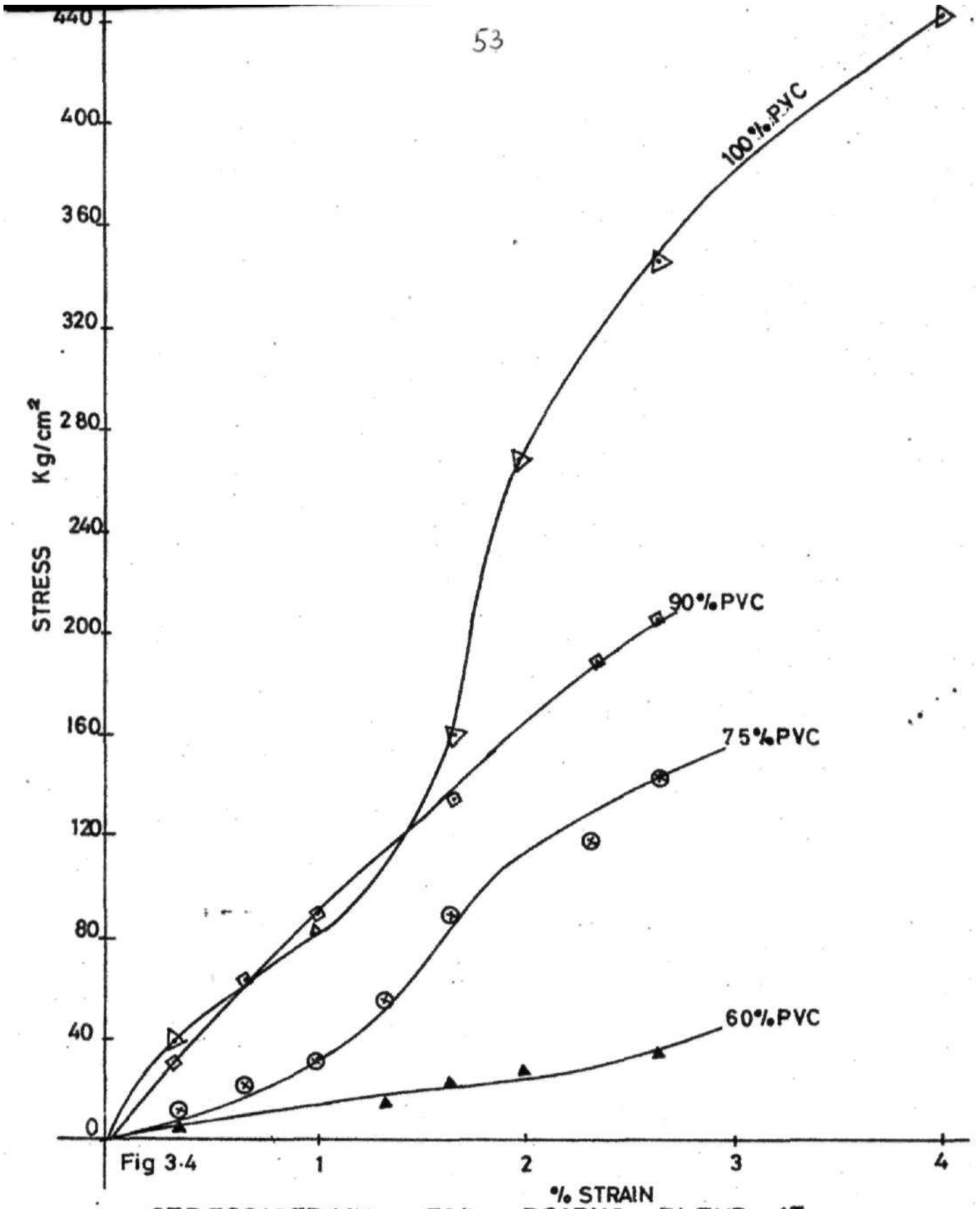


Fig 3.4

STRESS/STRAIN FOR PS/PVC BLEND AT 340 HOURS

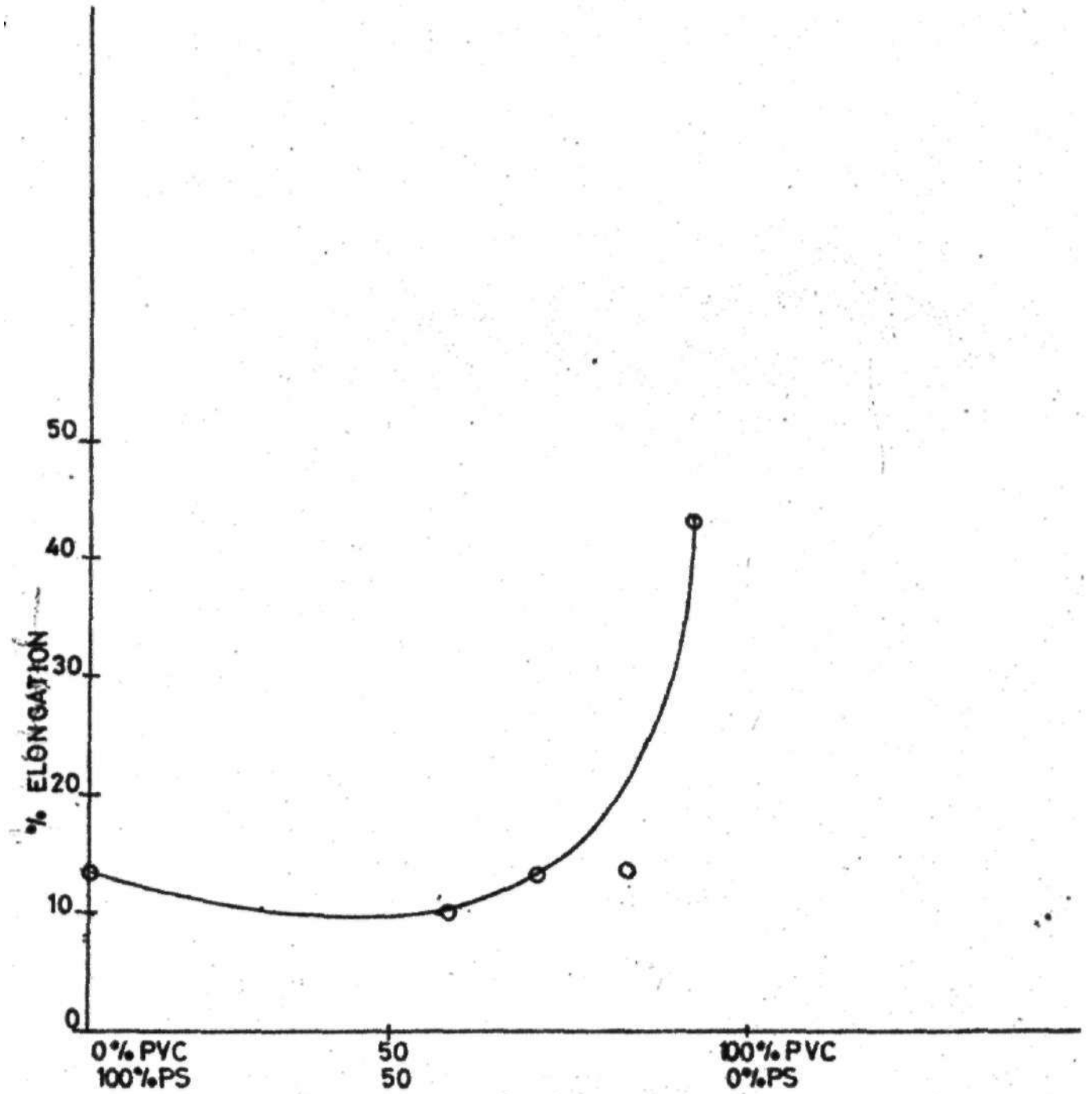


Fig 3.5 – DEPENDENCE OF % ELONGATION OF PS/PVC ON % COMPOSITION

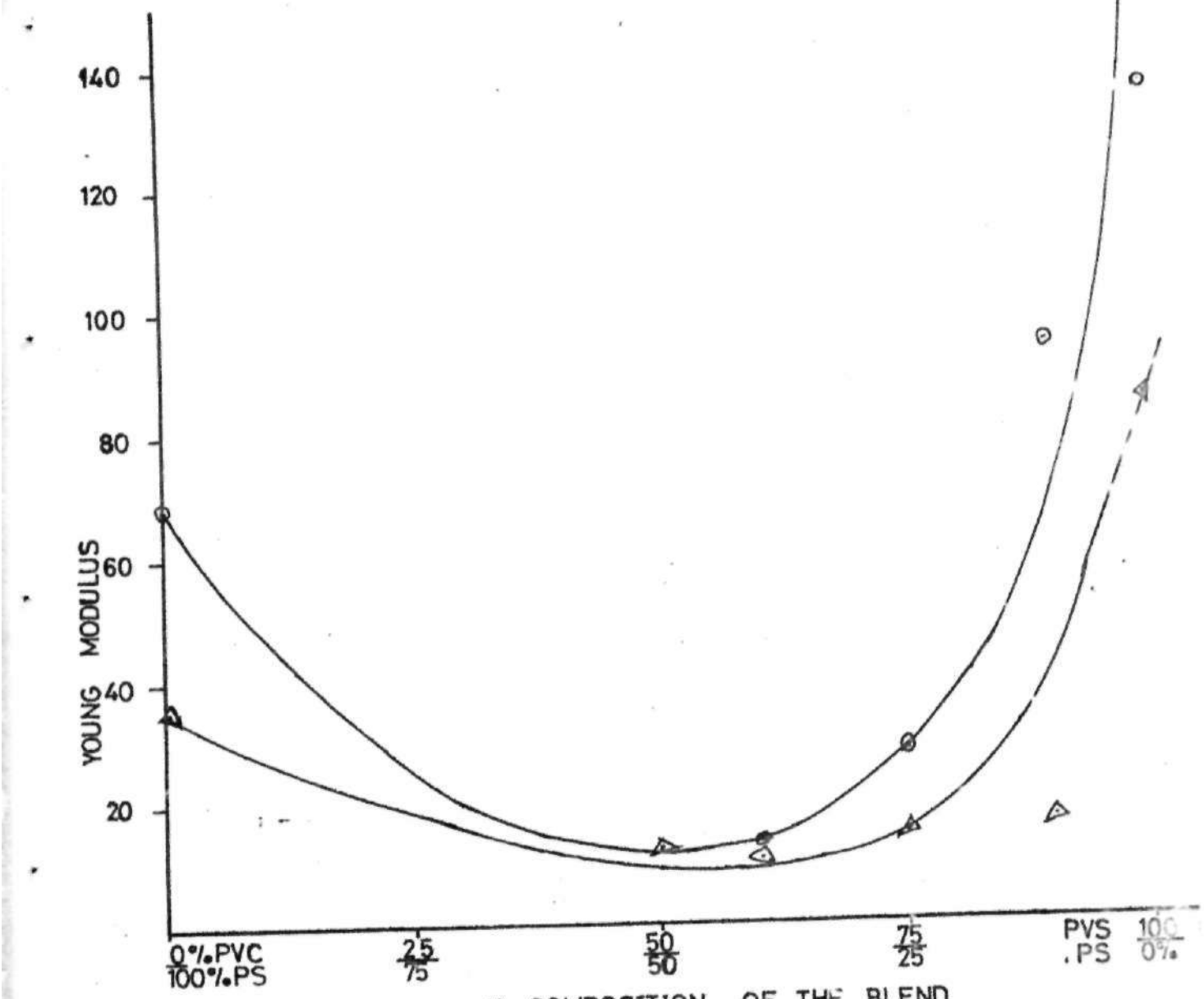


FIG 3.6

DEPENDENCE OF MODULUS ON % COMPOSITION OF PS/PVC BLEND.

△ — FOR FRESH SAMPLES

⊙ — FOR 340 HOURS

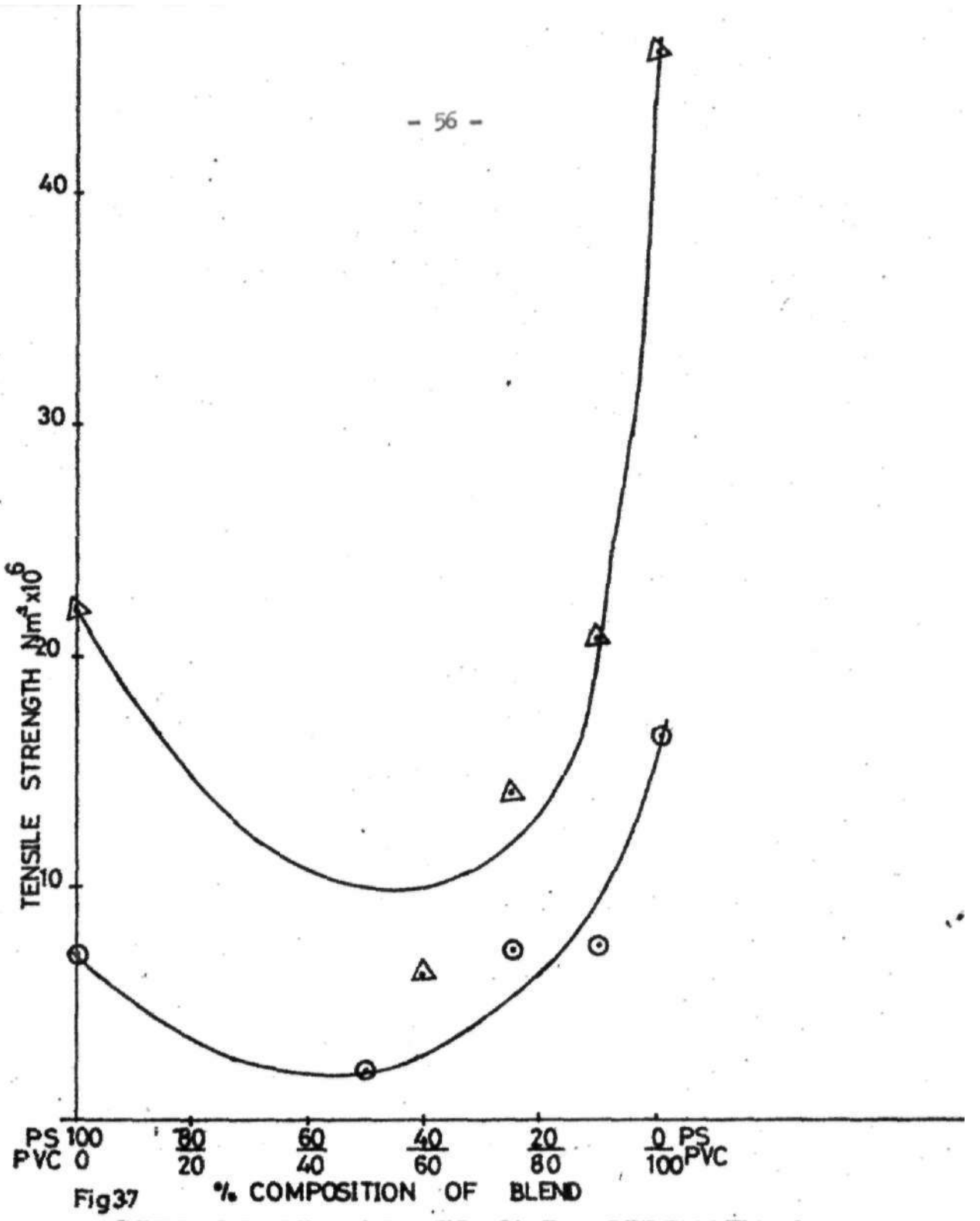


Fig37

DEPENDENCE OF TENSILE STRENGTH ON PERCENTAGE COMPOSITION OF PS/PVC BLEND

O — FRESH SAMPLE

△ — AT 340 HOURS

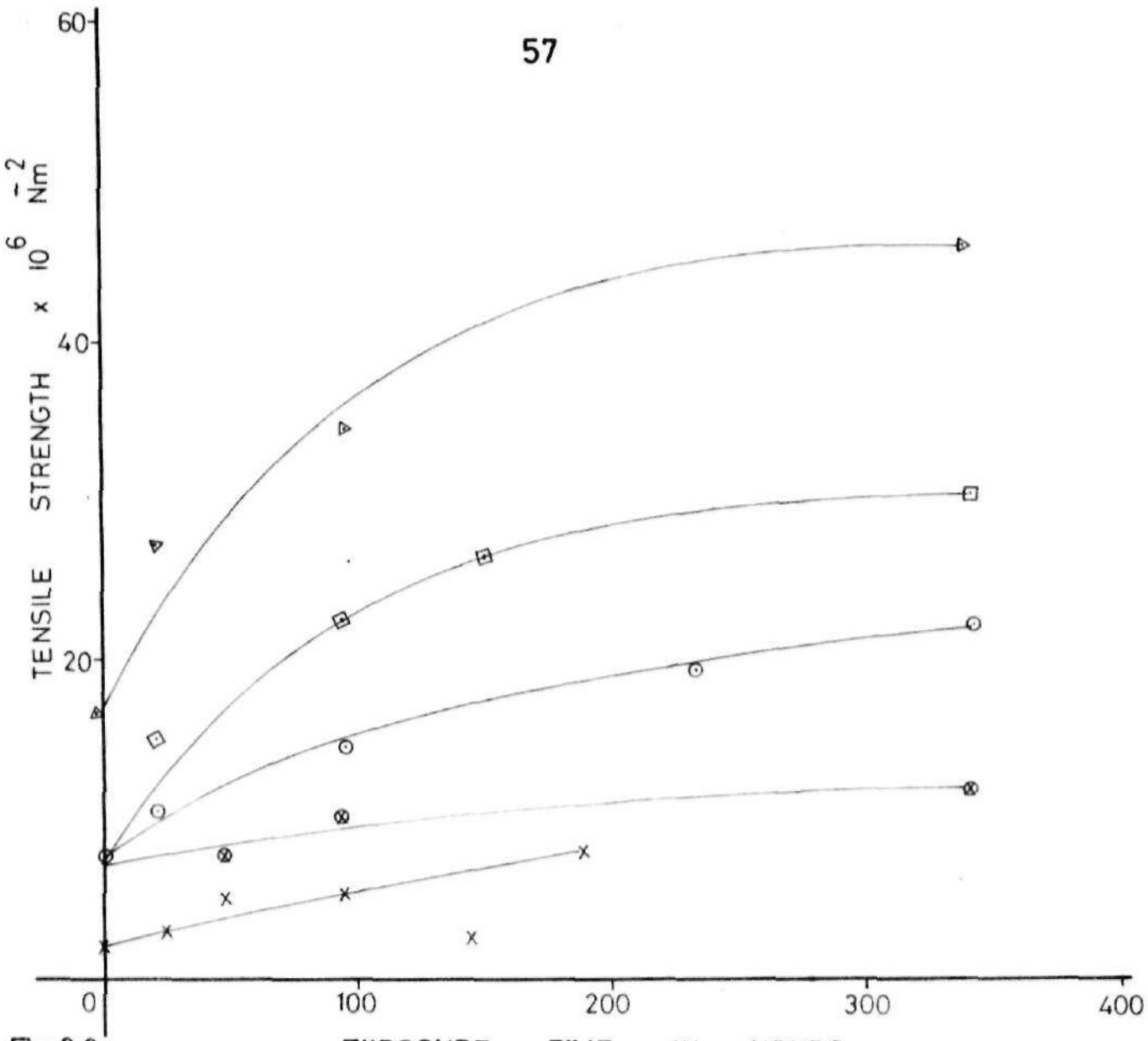


Fig. 3.8 DEPENDENCE OF TENSIL STRENGTH PS/PVC BLEND ON OUTDOOR EXPOSURE TIMER

△ — 100% PVC
⊡ — 90% PVC : 10% PS
⊗ — 75% PVC : 25% PS
x — 50% PVC : 50% PS
⊙ — 100% PS

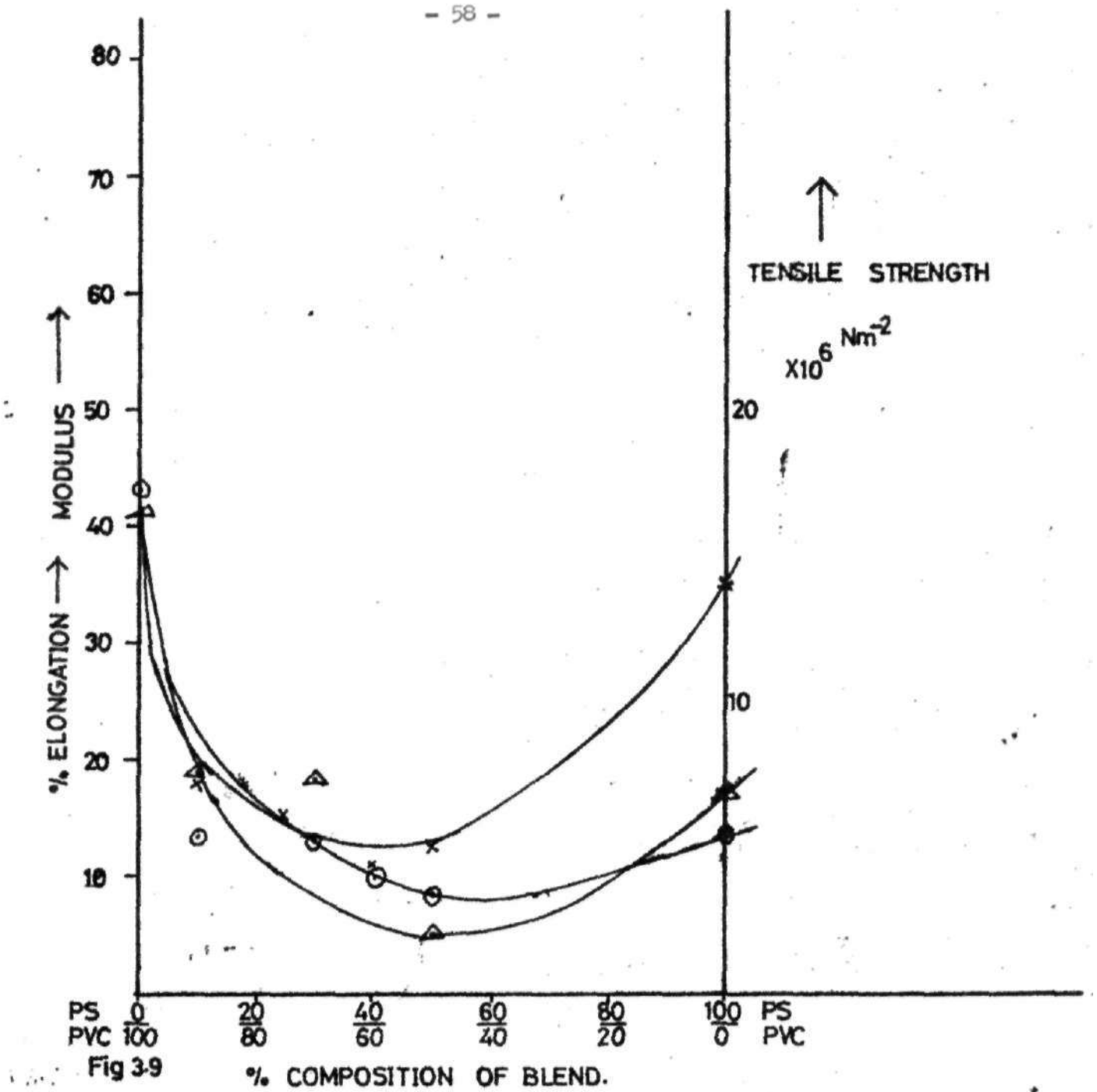


Fig 3-9

DEPENDENCE OF VARIOUS FACTORS ON % COMPOSITION OF PS/PVC BLEND.

× — MODULUS VS COMPOSITION
⊙ — ELONGATION %
△ — TENSILE STRENGTH

CHAPTER FOUR

4. STUDIES ON PS/PB BLEND

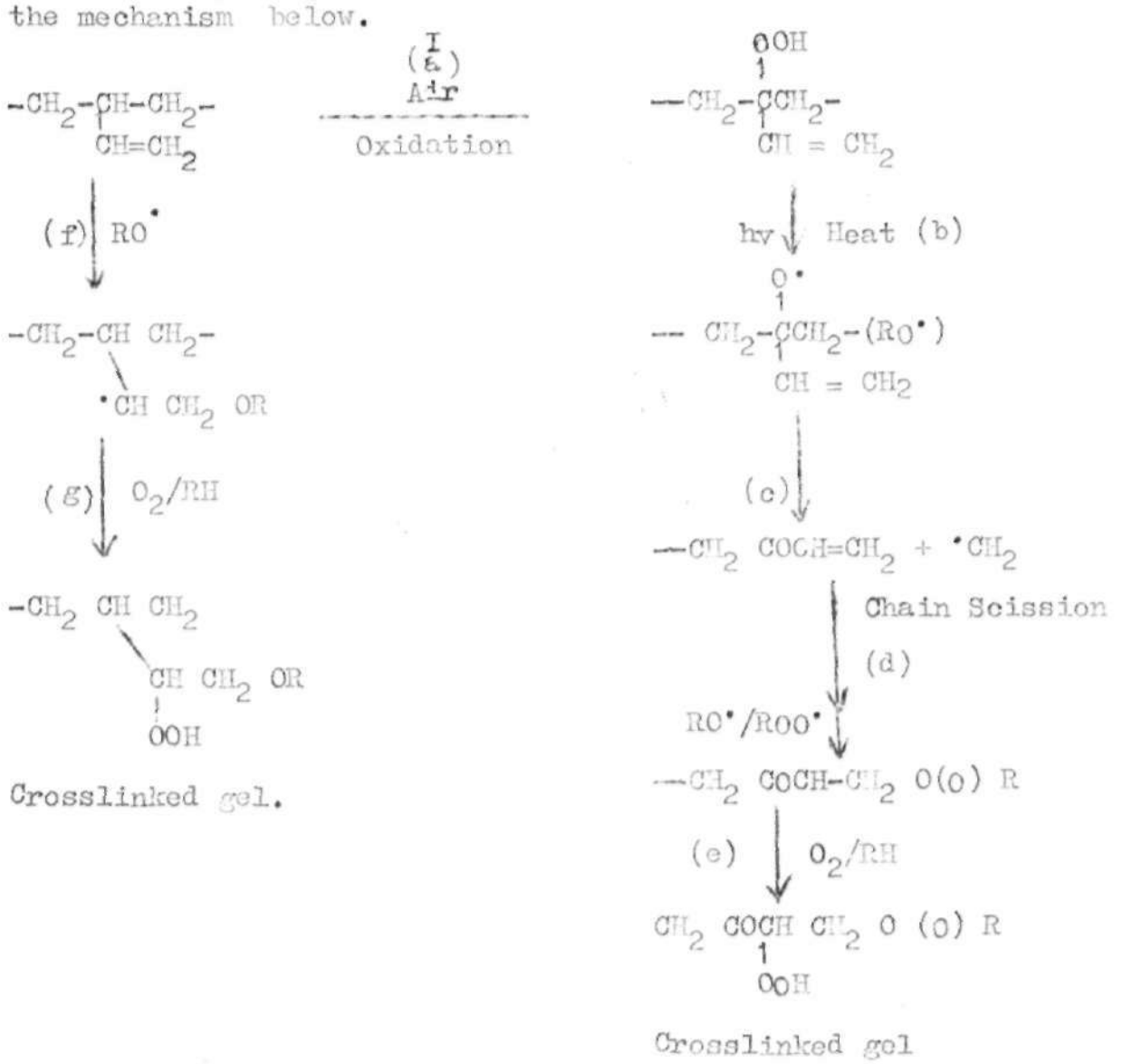
4.1 The presence of PB in PS is studied with a view to knowing how the presence of either of these polymers affects the degradability of the other as a result of exposure to outdoor weathering at $\simeq 30^{\circ}C$ and to heat at $100^{\circ}C$ in air. This was done by following the changes occuring in the mechanical properties of the blend on outdoor exposure. The ir spectra were also used to observe changes in the microstructure. Film preparation (using toluene as solvent) and methods of study were the same as in Section 2.3. Blend of three different compositions were made. X contained 75% PS 25% PB; G contained 50% PS : 50% PB while Y contained 25% PS 75% PB. The peak at $2910cm^{-1}$ corresponding to the methylene peak was used at reference for ir calculations. Measurement of mechanical properties was carried out as in previous studies section.

4.2 RESULTS AND DISCUSSIONS

Some of the results obtained from the mechanical testing are shown in Tables I and II and figs 4.1 - 4.5. Figs 4.1a and 4.1b show the stress-strain behaviour of 100% PS, 100% PB and the three other different compositions of their blend. The behaviour of 100% PB is very different from that of 100% PS, and also from those of the different compositions of the blend. 100% PB shows the "creep effect" (fig 4.1a) This is the region where there is an increase in elongation with constant stress.

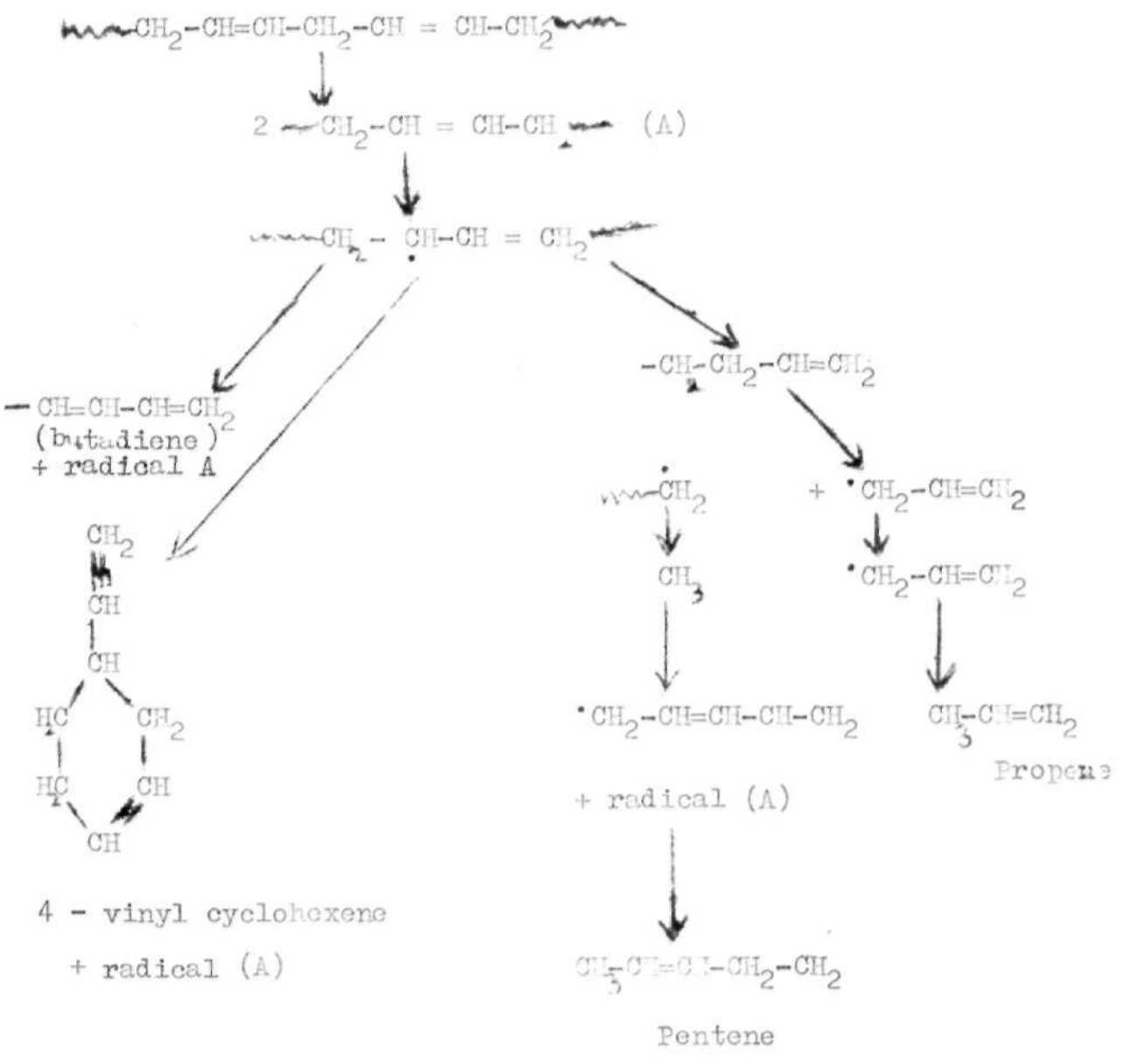
The graph of PB is typical of that for soft and tough polymers (typical of elastomers). The low value of its Young's modulus further confirms that it is a soft polymer. At any time of exposure it was found that the value of Young's modulus increases as the amount of PB decreases in the PS/PB blend. This shows that the presence of PB in PS weakens (i.e. makes soft) the structure of the PS. The area under the curve (which is also a measure of toughness) decreases with increase in the amount of PB. This reduction in toughness is further evident from the observation that increase in the amount of PB in the blend increases the % elongation at break. (Fig 4.2a). Table I shows the variation of % elongation at break with time of outdoor exposure. In general there is decrease in the % elongation at break with exposure. The rate of decrease initially is highest for 100% PB and lowest for PS. (Fig 4.2(b)) Thus it appears that crosslinking reactions takes place in degrading polybutadiene. Similar suggestions have been made about the behaviour of degrading PB.[1] Another observation made in this study is that there is an increase in the thickness of the film (particularly the PB 100%) with increase in exposure time. This is probably caused by the suggested crosslinking reaction which may be going on on heating. Table II shows how young's modulus of the different samples varied with time of outdoor exposure. In general there is an increase of modulus with exposure. From Table II it is evident that at any time during outdoor weathering, the Young's modulus increases as the amount of PS in the blend increases.

The Graph shown in Fig 4.9 shows a typical example. With PB a peak is reached and then there is a fall. While the others show a continued increase. It is not unlikely that there might be crosslinkages and then later, possibly followed by chain scission. That both processes could occur is seen in the mechanism[86] below.



Another mechanism [122] proposed by McNeill et all on the degradation of PB at 350°C is shown below.

II



Even though this mechanism II has been proposed for the behavior of PB at 350°C it is not impossible for PB to behave similarly on outdoor exposure since the energy given by sunlight could correspond to that at high temperatures. That these products are produced is not confirmed in this study since the degradative products were not identified. The continued increase noted in the Young's modulus of the 100% PS and those of all the blend compositions might be due to the presence of polystyrene in these samples.



III

There has been enough evidence that polybutadiene[123] forms hydroperoxide very readily. This could readily abstract hydrogen from PS to form polystyryl radicals as shown in the above equation (III). The presence of polystyryl radicals will thus increase the number of radicals in the system and thereby increase the possibility of crosslinkages occuring (We should however keep in mind that the polystyryl radical can also undergo chain scission). Thus there will be increase in rigidity hence increase in the value of Young's modulus. The 1:1 ratio of PB/PS shows the greatest increase.

Both 100% PS and the 1:1 blend show a continued increase in the ultimate tensile strength up to 600 hours (Fig 4.3) whereas for both 100% PB and the 75% PB 25% PS blend the ultimate tensile strength reaches a maximum and then falls. Increase in tensile strength corresponds to increase in rigidity and as such greater energy is needed for the breaking of the bonds present in the blend. Fig 4.9 shows plots of the ultimate tensile strength (UTS), Young's modulus and elongation at break against composition of the blends. As can be seen there is an initial drop in UTS on addition of PB while there is a marked increase in % elongation at break thus suggesting that the PB makes the structure less rigid. The 1:1 ratio of PS:PB appears to give a good compromise of all these properties.

Oven Ageing. The ir spectra observed for PS has been discussed in section 2.4. From the ir spectra of polybutadiene the following observations were made. The hydroxyl peak was broad extending from 3600 - 3200cm^{-1}. Initially there was no growth until after 20 hours for the outdoor exposed film and after 200 hours for the film of PB heated at 100°C in an air oven. The hydroxyl growth was very fast after the induction. The carbonyl peak showed at 1685 and 1725cm^{-1}. The faster growth was found at 1725cm^{-1}. The -C=C- showed at 912 and 965cm^{-1}. Fig 4.4 shows the comparison of the growth of the hydroxyl for both outdoor weathering and oven ageing. The rate of growth was very fast after an initial induction period, the rate being faster for the film heated at 100°C.

In each of the cases there is a fall and levelling up immdiately after. In both cases, the hydroxyl index rises to a peak and then decreases to level up later.

A comparative study of the changes in the hydroxyl and carbonyl indices of the different compositions of the blend for the thermal exposure can be very well made from Figs 4.5 and 4.6 respectively. The rate of production of the hydroxyl increases as the amount of PB in the blend increases. In all the cases a maximum is reached after which there is a fall. The time of reaching this maximum increases as the amount of the PB in the blend increases and the value of the maximum increases in the same order. The 100% PS shows an induction period of 150 hours. The amount of hydroxyl formed decreases as the amount of PB in the blend decreases. This is related to the hydroperoxide formation.

From Fig 4.6, it is evident that the rate of formation of the carbonyl decreases as the amount of PB in the blend decreases 100% PB has the highest rate while 100% PS has the lowest rate. The carbonyl index also shows a peak for 100% PB, 75% PB 25% PS and 25% PB 75%PS. This peak occurs at about 150 hours in all cases mentioned above. In the case of the 50% PB 50% PS and 100% PS no peak is observed and the rate of carbonyl production appears to be very gradual. From these observations it could be concluded that the presence of PS in PB improves its stability t heating at 100^{o}C.

(It also appears from Fig 4.6 in particular that the 50% PB 50% PS is the most stable among the blends to thermal oxidation).

Outdoor Weathering. From Fig 4.7, there is not much difference between the rate of hydroxyl production of the 75% PB 25% PS and 50% PB 50% PS. The rate for the 25% PB 75% PS is however very small compared with the other two. The 25% PB 75% PS shows an induction period of 75 hours whereas the other compositions of the blend do not. (Fig 4.8) The rate of carbonyl production here also appears dependent on the amount of PB in the blend. The lower the amount of PB the lower the rate of production and amount of the carbonyl. One could also conclude that for the outdoor exposure PS has some stabilising effect on PB.

This behaviour of PS/PB blend is not surprising because from previous studies of uv irradiated high impact polystyrene it has been observed that the rubber segment is the initial point of attack of oxygen giving rise to allylic hydroperoxide. Whereas from this study, it is observed that PS stabilises PB but a corresponding effect of PB on PS is not apparent. Thus it appears as if the rubber component acts as a photoactivator for the photo oxidation. This becomes much more evident when the pattern of degradation of 75% PS 25% PB in outdoor exposure is compared to that attaindon heating at 100°C. The rate of degradation is higher in the outdoor exposed sample. That photolysis of hydroperoxide, leads to crosslinking of the rubber component by addition of alkoxy radicals to 1, 2 polybutadiene

and conjugated carbonyl formed by alkoxy breakdown is again confirmed by the increase observed in both the Young's modulus and UTS and the rapid decrease of % elongation at break of these samples. Also, the absence of growth of conjugated carbonyl and the dominant development of saturated carbonyl has also been associated with the crosslink reaction.

CONCLUSION

The presence of PS in PB improves the stability of PB to both outdoor weathering and heating at 100°C in air. The presence of PS in PB also improves its mechanical properties. In term of good UTS, Young's modulus and % elongation at break and also good stability to both heat and outdoor weathering the 50% PB 50% PS gives the best compromise.

Table I

Variation of % Elongation at break with Time of Exposure

Elongation At Break (%)					
Time in hours	100% PB	75% PB 25% PS	50% PB 50% PS	25%PB 75%PS	100%PS
0	810	453.3	66.66	40.00	10.33
100	300	227	50.00	10.00	6.00
169	112	42	20.00	6.66	5.33
262	47.5	6.6		6.66	5.33
412	36.6	6.6	13.00	6.66	
607	40	6.6			
1587	26.66	6.6	13.0		

Table II

Variation of Modulus of PS/PB Blend with Time of Exposure

	YOUNG'S MODULUS				
	YOUNG'S MODULUS				
Time in hours.	100% PB	75% PB 25% PS	50% PB 50% PS	25% PB 75% PS	100% PS
0	0.0600	0.400	1.615	5.151	15.152
100	0.0625	0.500	3.788	30.09	16.65
262	5.654	6.426	106.25	35.114	104.01
412	2.429	6.364	-	58.66	104.01
607	.173	15.00	106		104
1,587	1.552				

TABLE III

Variation of Tensile Strength of PS/PB with exposure time

TIME in hrs.	TENSILE STRENGTH $Nm^{-2} \times 10^6$			
	100% PB	75% PB 25% PS	50% PB 50% PS	100% PS
0	.07266	.1649	0.704	9.677
100	0.425	.551	3.777	10.525
169	0.533	1.1409	5.373	11.898
262	3.569	4.807	11.098	12.602
412	0.9733	1.310		15.560
585	0.621	0.700	11.410	16.220

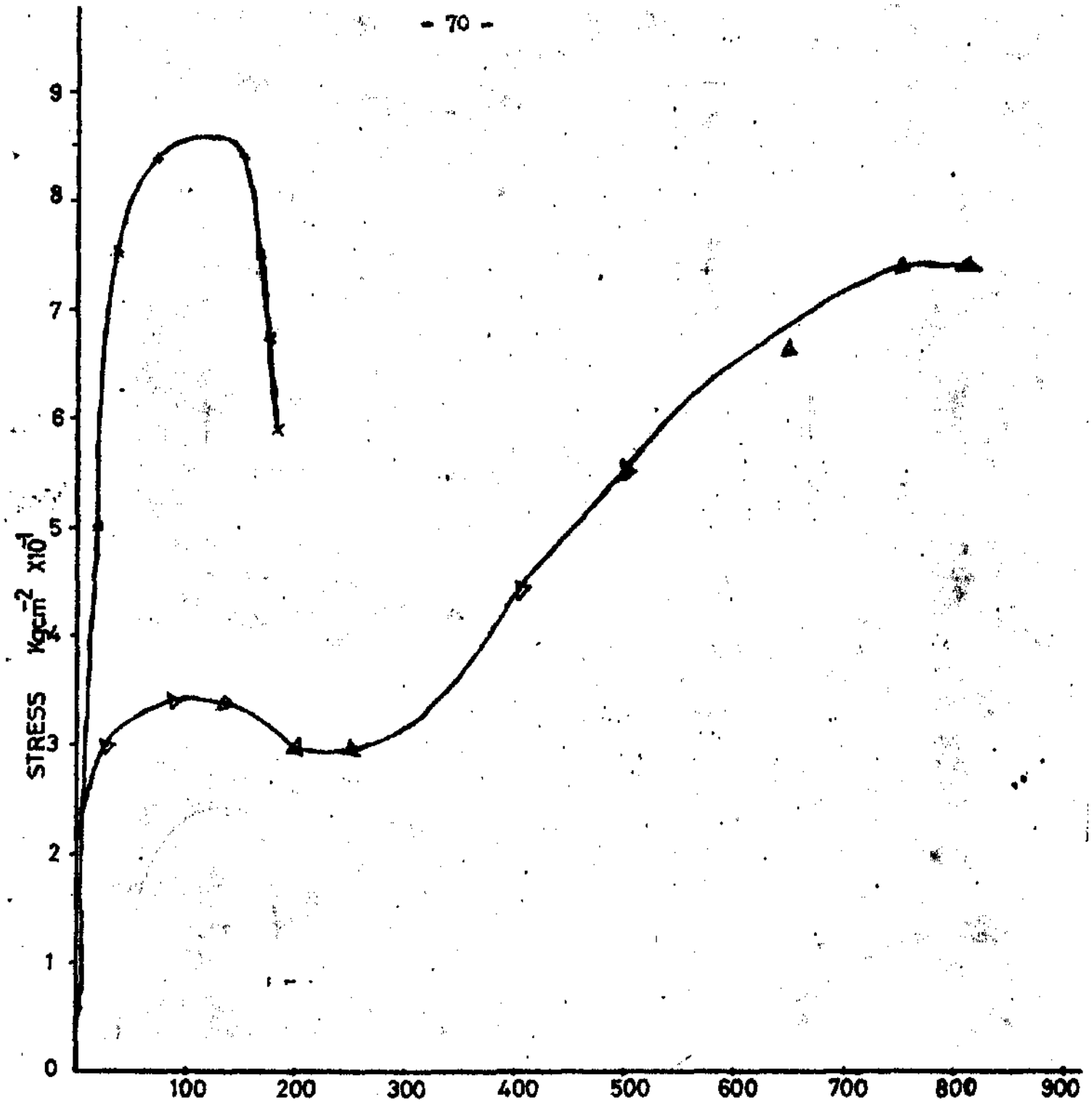


FIG 4.1a

STRESS/STRAIN FOR PS/PB BLEND (FRESH SAMPLE).

▲—100% PB

X—75% PB 25% PS

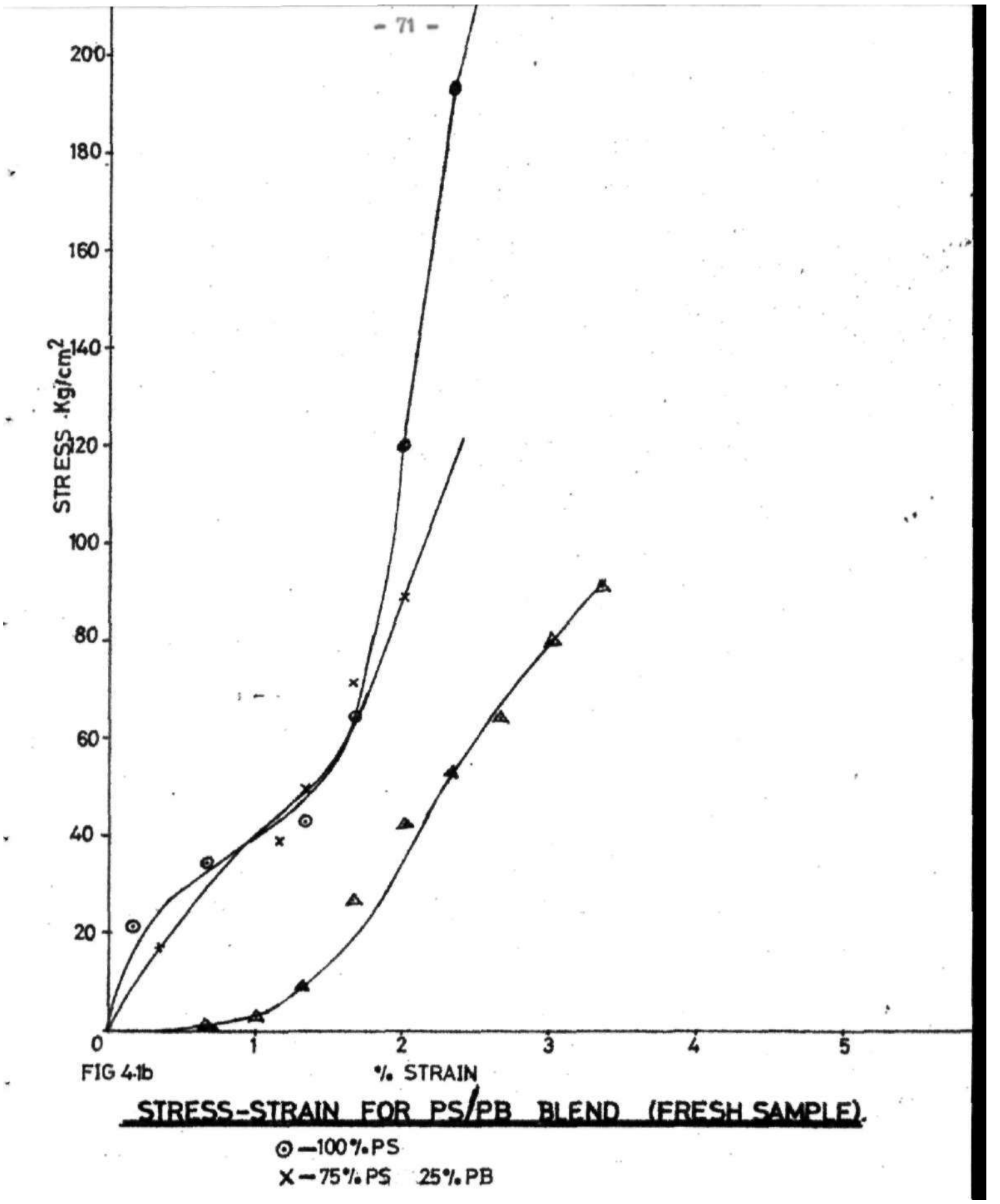


FIG 4-1b

STRESS-STRAIN FOR PS/PB BLEND (FRESH SAMPLE).

⊙ — 100% PS

X — 75% PS 25% PB

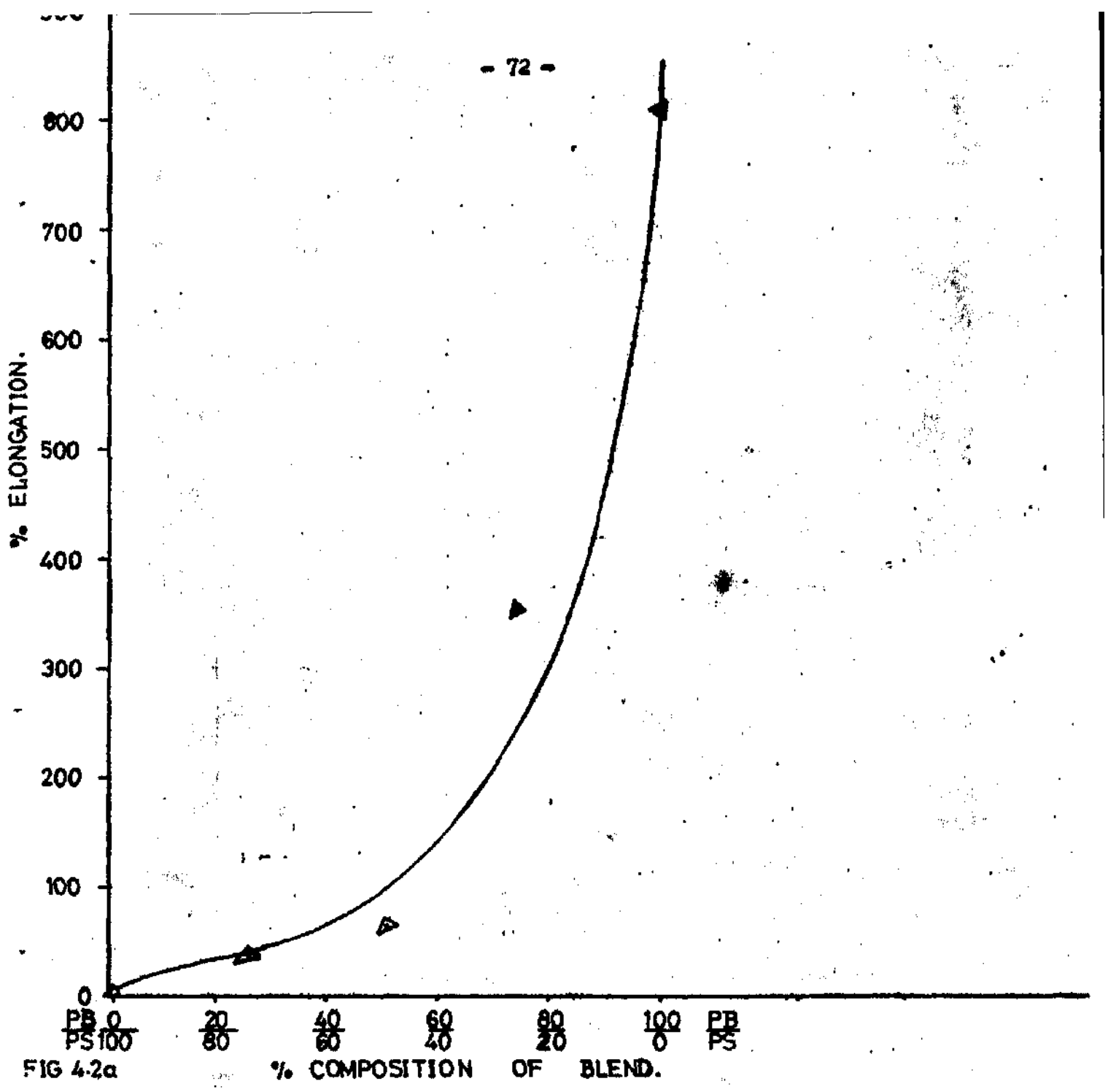


FIG 4-2a

DEPENDENCE OF % ELONGATION AT BREAK ON COMPOSITION OF PS/PB.

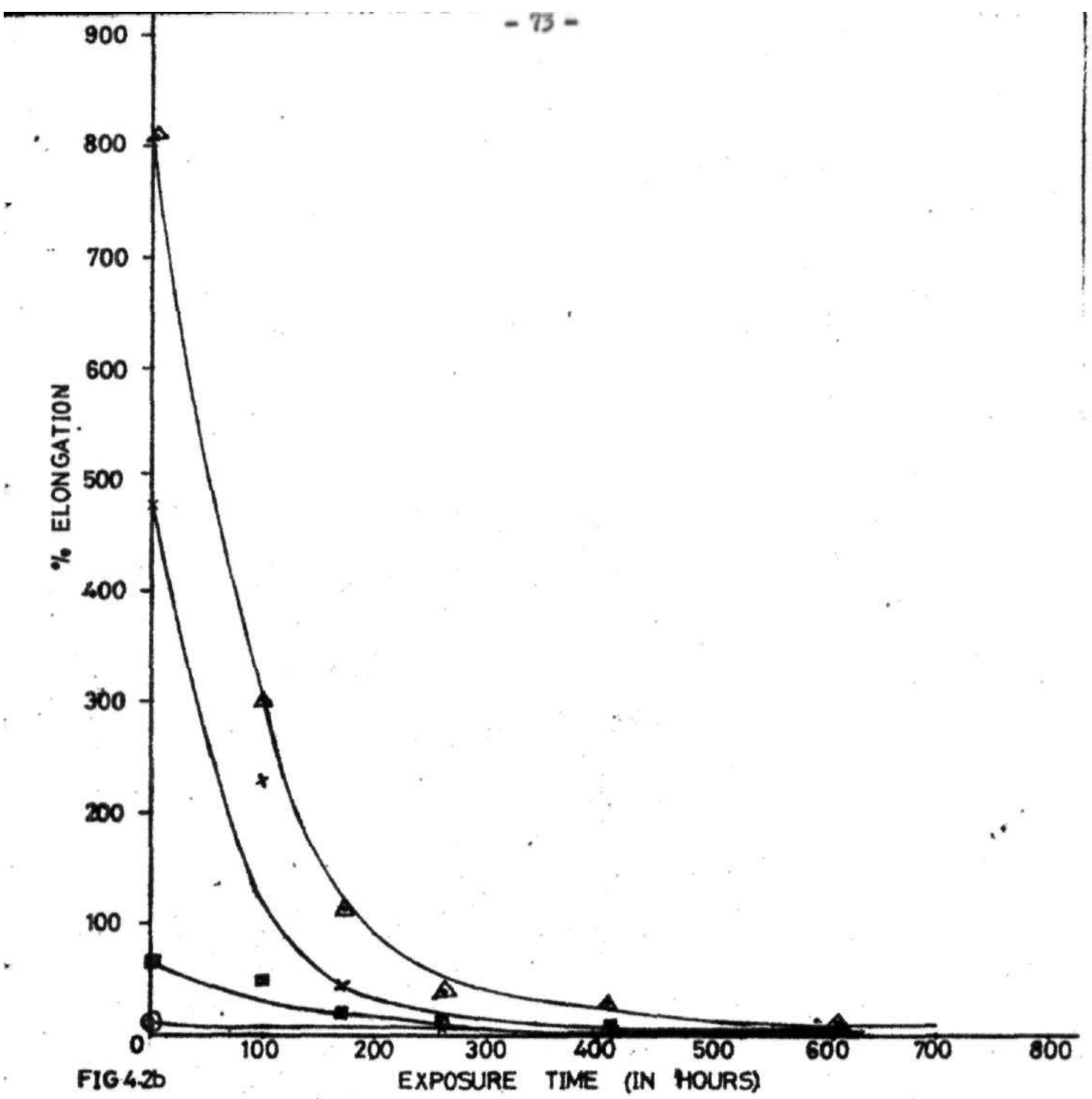


FIG 4.2b

DEPENDENCE OF % ELONGATION AT BREAK OF DIFFERENT COMPOSITION OF PS/PB BLEND.

▲—100% PB
X—75% PB 25% PS
⊡—50% PB 50% PS
⊙—100% PS

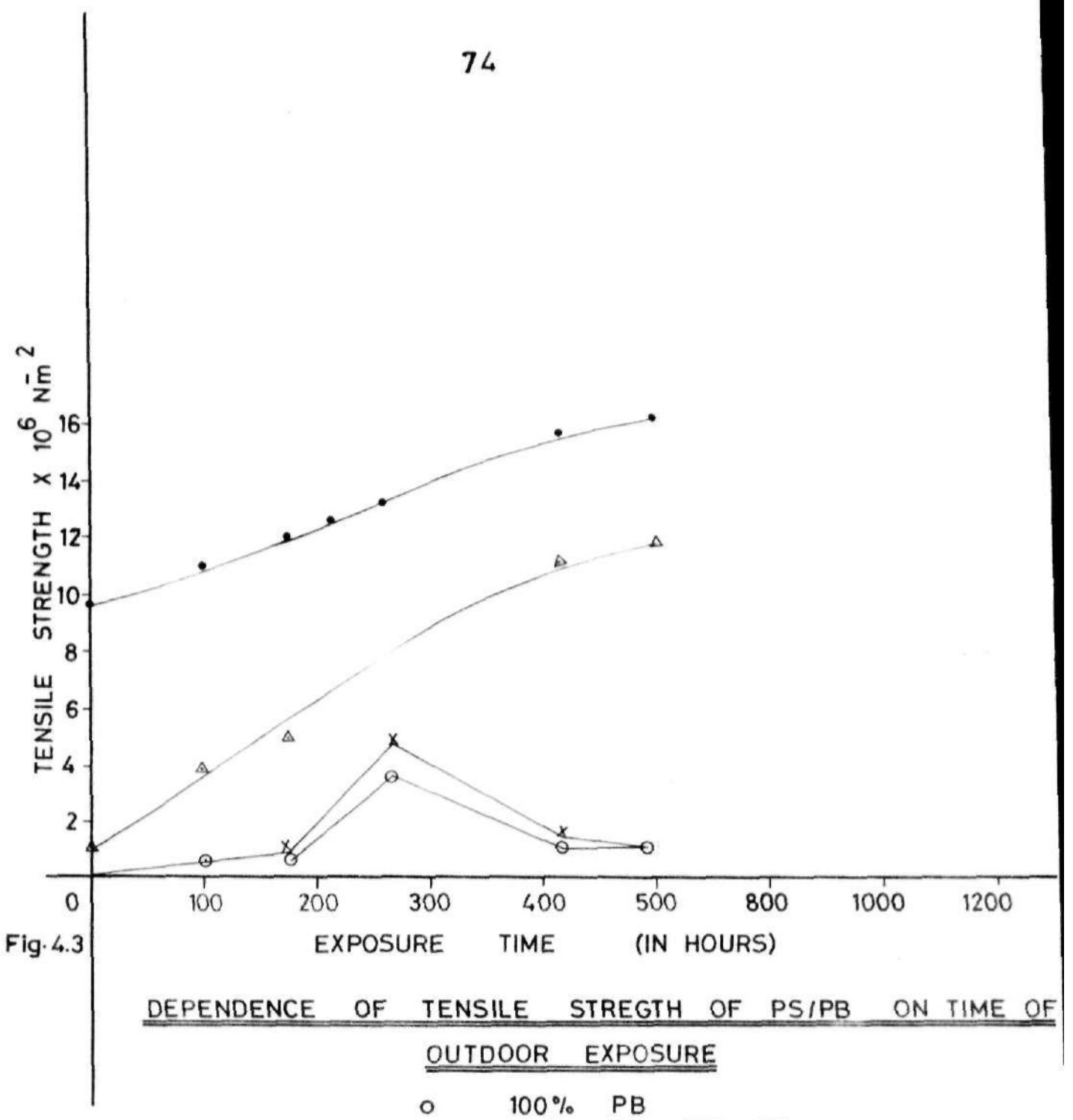


Fig. 4.3 DEPENDENCE OF TENSILE STREGTH OF PS/PB ON TIME OF OUTDOOR EXPOSURE

o	100%	PB
×	75%	PB : 25% PS
△	50%	PB : 50% PS
•	100%	PS

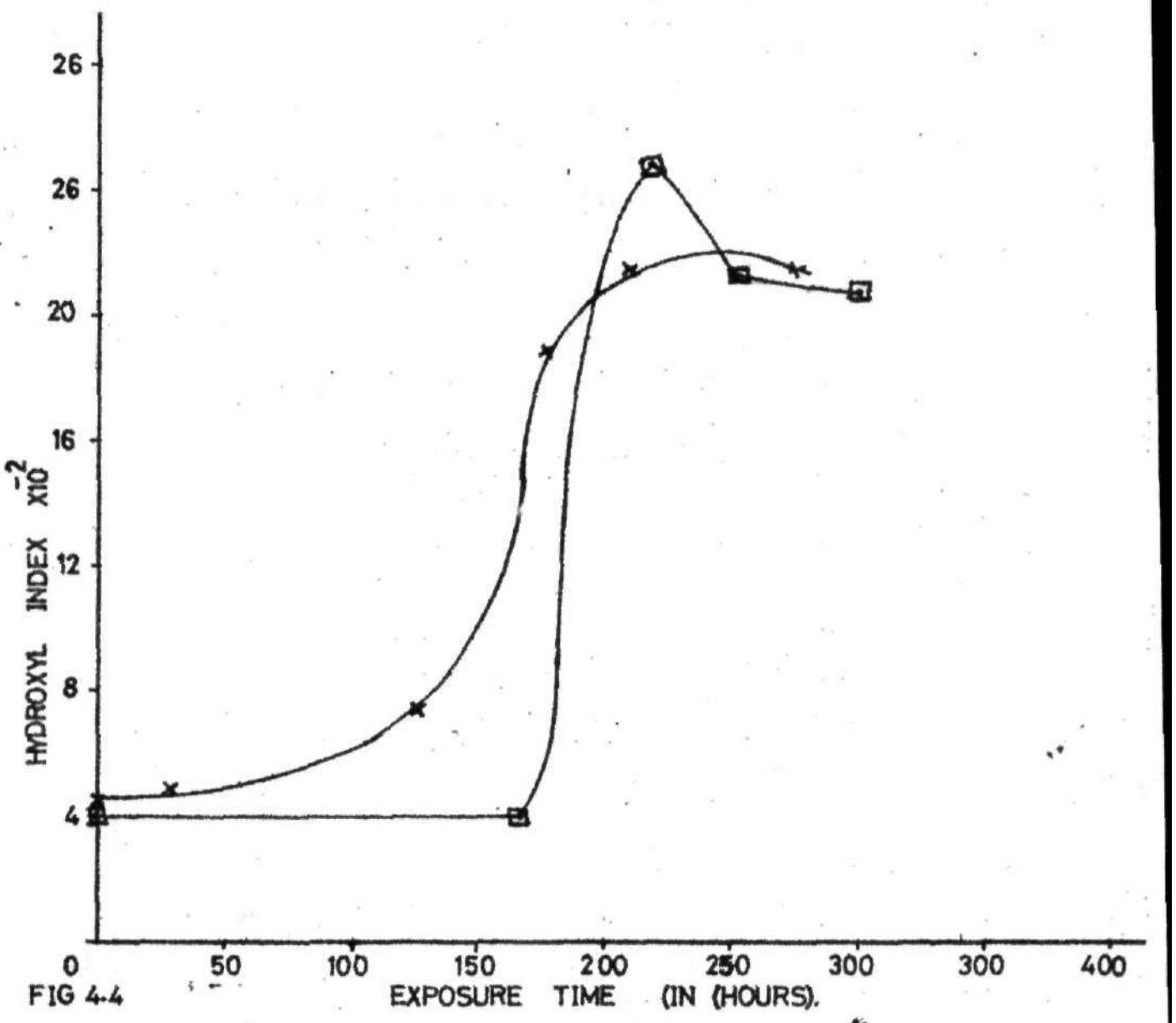


FIG 4.4 DEPENDENCE OF HYDROXYL INDEX (AT 3450cm^{-1}) OF 100% PB ON EXPOSURE TIME.

⊡ — THERMAL EXPOSURE

X — OUTDOOR EXPOSURE.

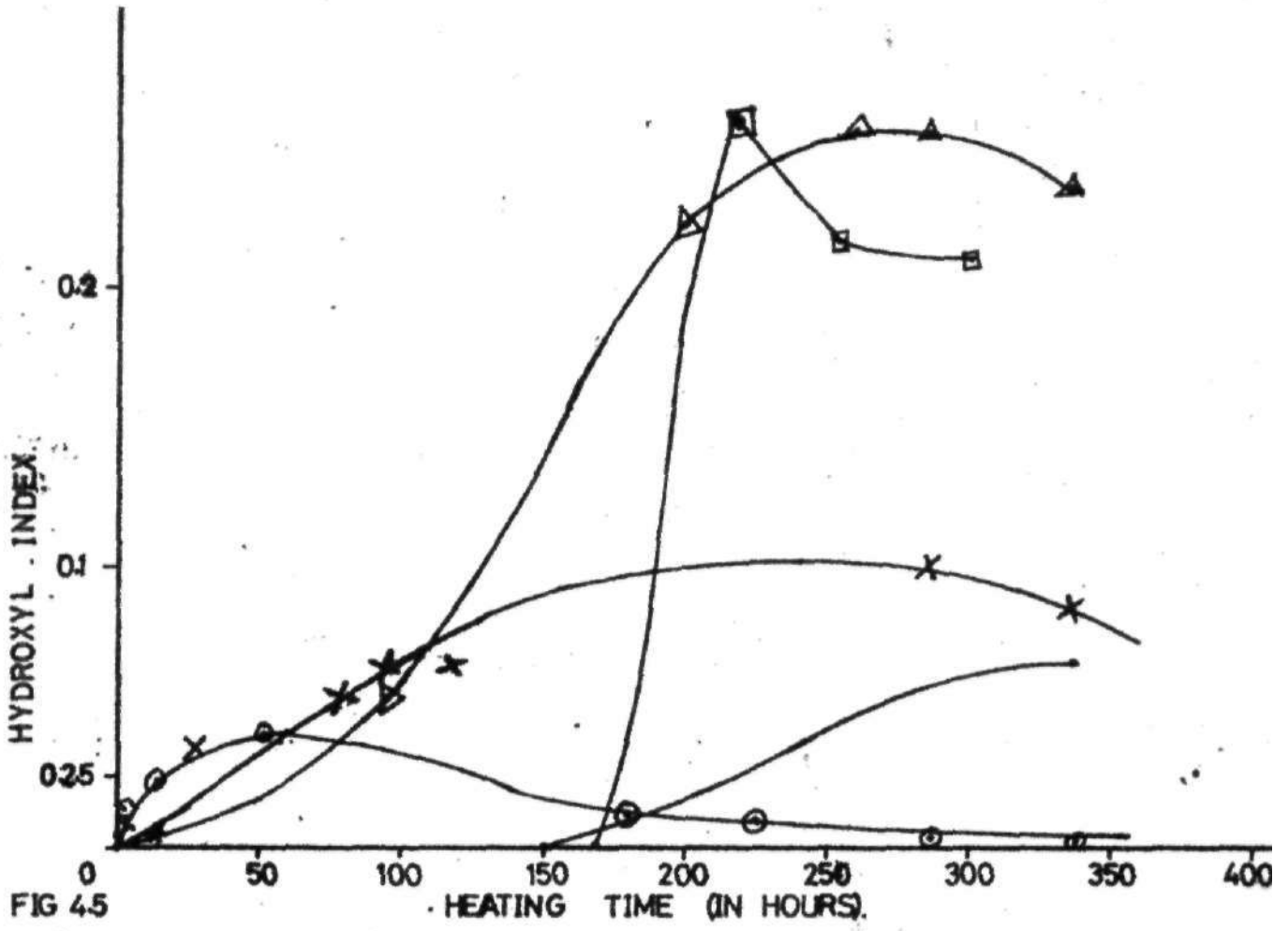


FIG 4.5

DEPENDENCE OF HYDROXYL INDEX OF PS/PB BLEND ON THERMAL EXPOSURE.

- □ — 100%.PB
- △ — 75%.PB 25%.PS
- × — 50%.PB 50%.PS
- ⊙ — 25%.PB 75%.PS
- • — 100%.PS

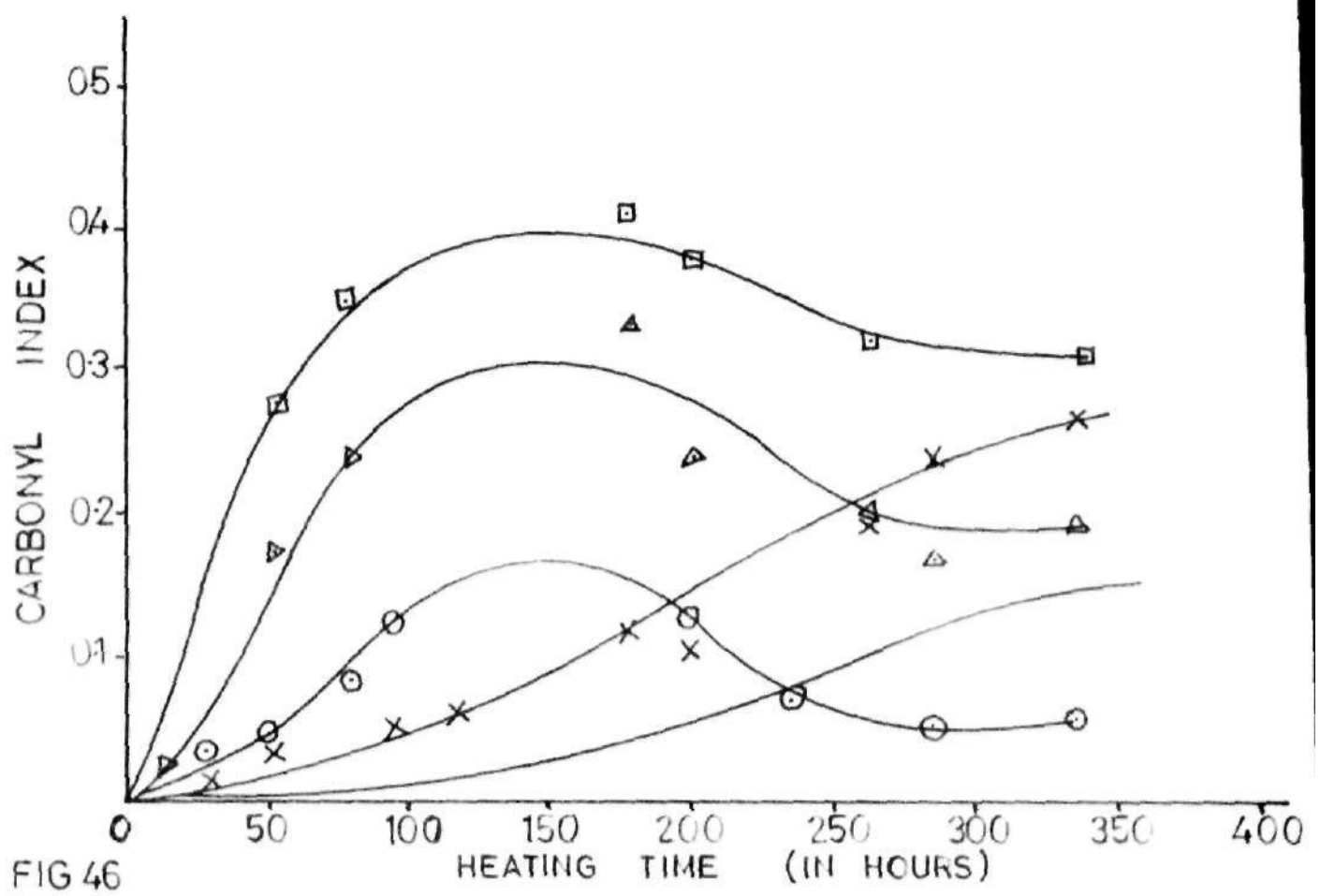


FIG 46

DEPENDENCE OF CARBONYL INDEX AT (1725cm^{-1}) OF PS/PB ON THERMAL EXPOSURE

⊡ — 100% PB × — 50% PB 50% PS ● — 100% PS
△ — 75% PB 25% PS ⊙ — 25% PB 75% PS

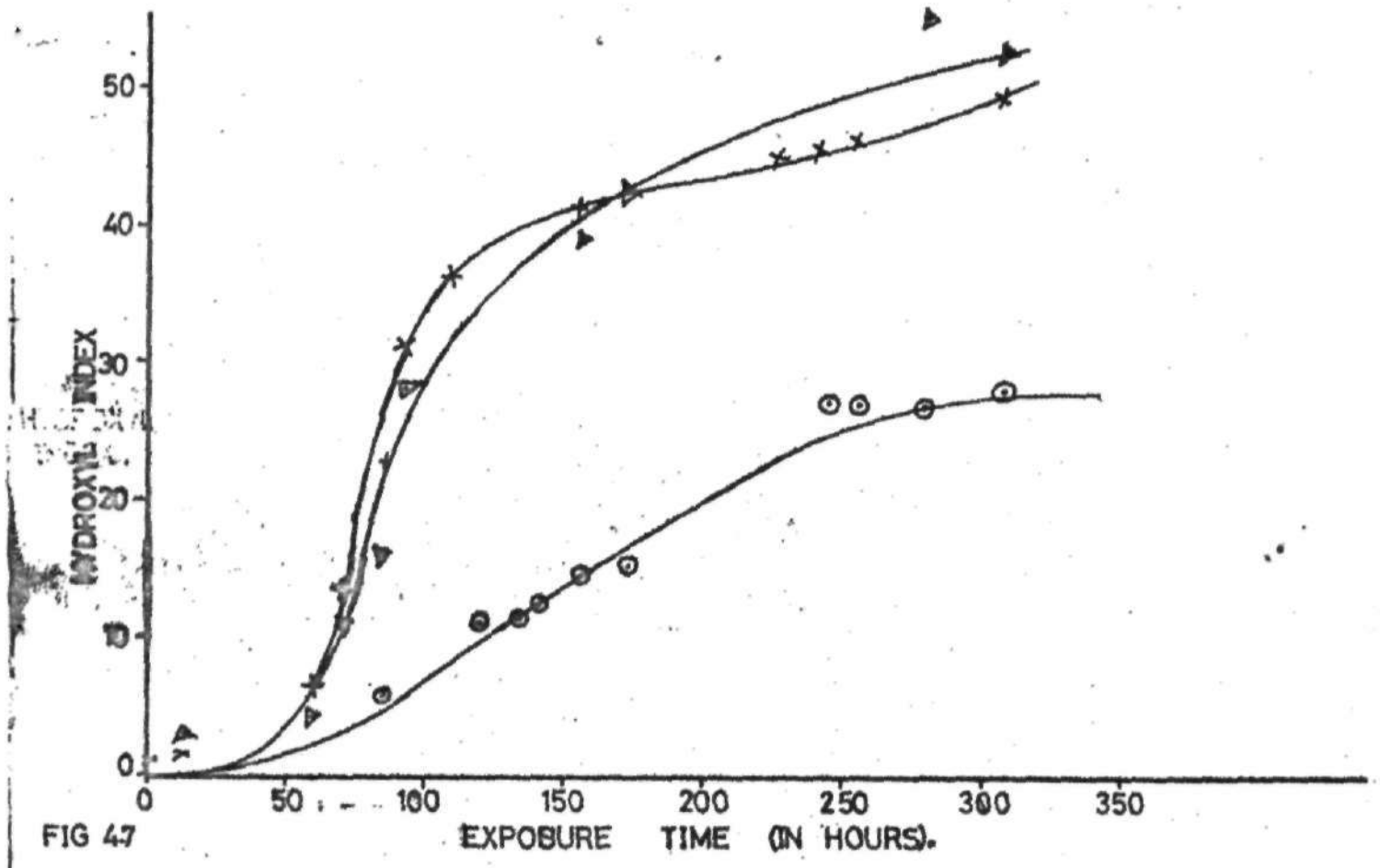


FIG 4.7 DEPENDENCE OF HYDROXYL INDEX ON OUTDOOR EXPOSURE.

△ — 75%.PB

× — 50%.PB

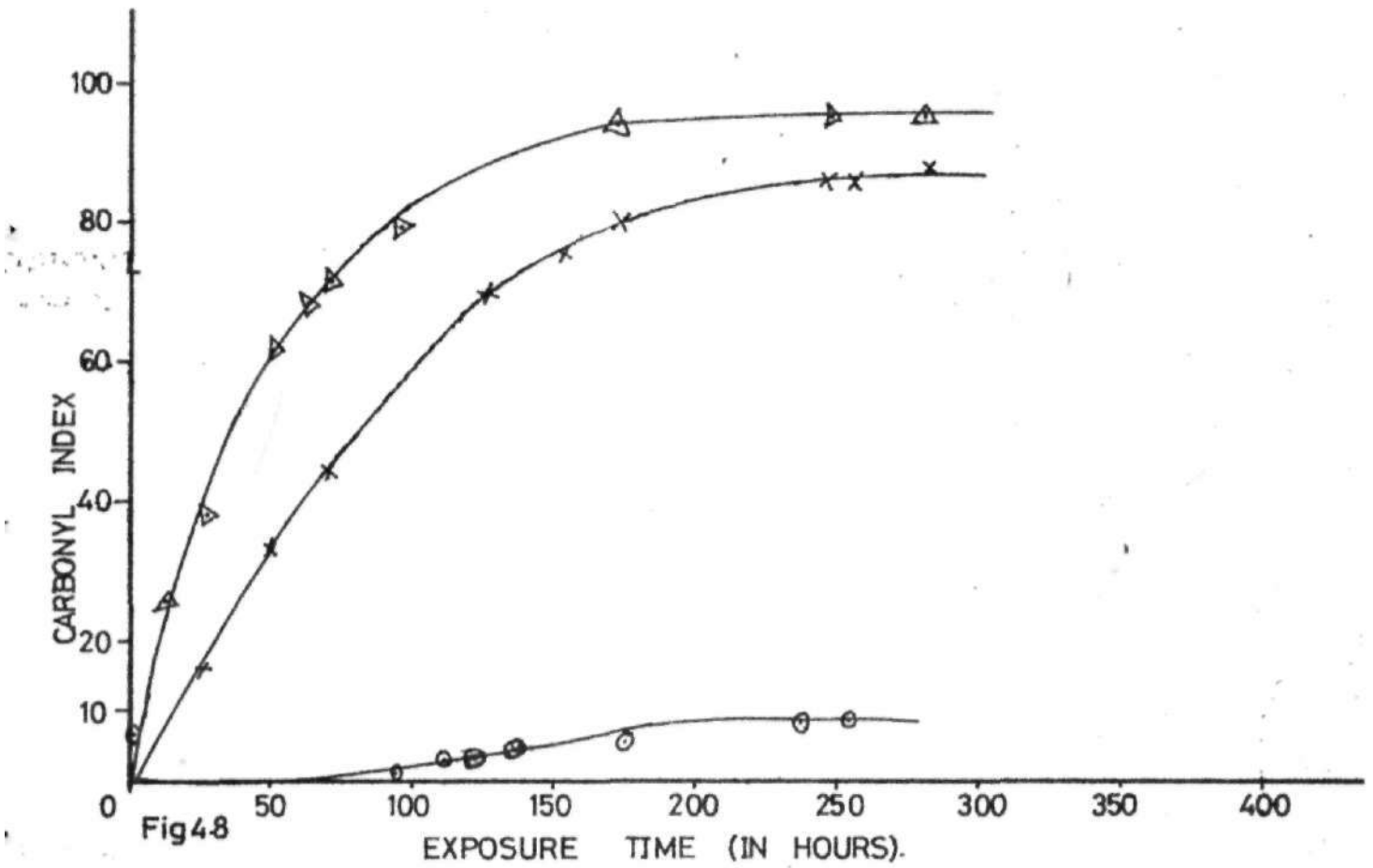


Fig 4.8

DEPENDENCE OF CARBONYL INDEX (AT 1725cm^{-1}) OF PS/PB ON OUTDOOR EXPOSURE.

△ — 75% PB
× — 50% PB
⊙ — 25% PB

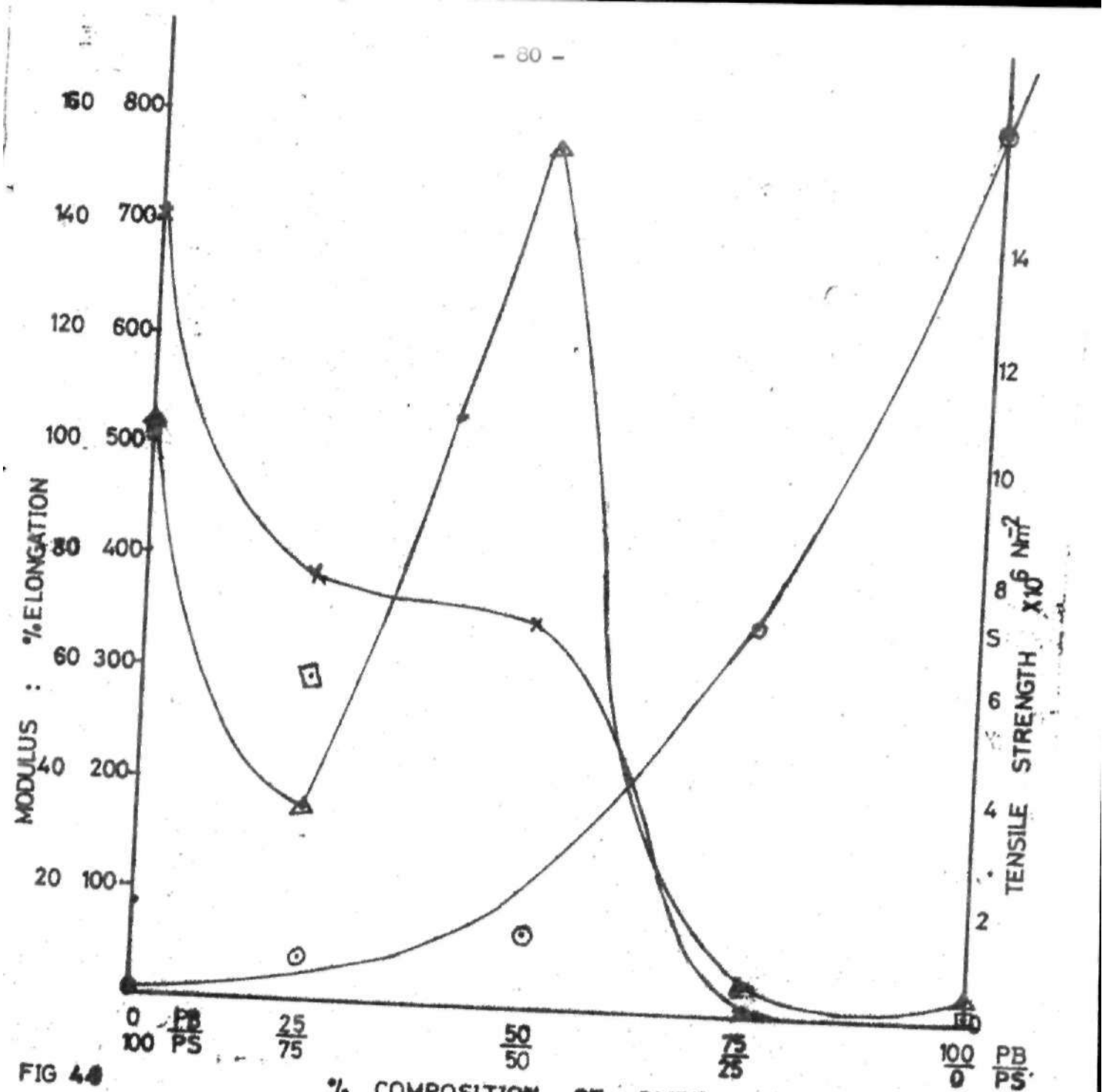


FIG 44

VARIATION OF SOME FACTORS WITH % COMPOSITION OF BLEND.

△— MODULUS AT 262 HOURS

X— TENSILE STRENGH OF FRESH SAMPLES

⊙— % ELONGATION.

CHAPTER FIVE

5. STUDIES ON PVC/PB BLEND

5.1 PVC is a polymer of high commercial importance. It is known to degrade on exposure to light. It is however found to be a fairly stable polymer. Some work[124] has been done on PVC/AB blend. The present study is made in order to know how the presence of PVC affects PB stability to light and to heat and vice versa. The effect of PVC on the mechanical properties of PB is also of great interest. The above objectives are attained by studying the ir spectra of PVC/PB blend of different composition on exposure to outdoor weathering and also to heat at 100°C Film preparations (using tetrahydrofuran as solvent) and methods of study are the same as in Section 2.3.

5.2 Results and Discussions

Results obtained from the mechanical studies are shown in tables I, II, III, IV and Fig 5.1. The % elongation at break decreases from 100% PB and then increases after the 25% PB 75% PVC i.e. as the amount of PB decreases in the blend elongation decreases. Elongation also decreases with time of exposure. The rate of decrease being fastest for 100% PB (table I). This is reflected in the values obtained for the modulus (fig 5.1; table II) In general modulus increases with time of exposure for all the different compositions of the blend. The rate of increase is fastest for the 100°C PB.

It appears that the degradation of PB involves a lot of formation of crosslinks and may be very little bond cleavage at the early hours of exposure (see 4.2)

From Fig 5.1 it can be seen that (i) the elongation falls as the amount of PB in the blend decreases (ii) as the amount of PVC in the blend increases, both the UTS and modulus increase. It was also observed that the film thickens on exposure. This means that the presence of PVC in the blend makes the blend more rigid.

The ir spectra of PVC has been discussed in Section 3.2 while that of PB has been discussed in Section 4.2. In the spectra of the three different compositions of the blend produced the following were noted. The carbonyl peak at the 1725cm^{-1} grew fastest than those at 1620, 1665 and 1685. The carbonyl peak at 1725cm^{-1} was the one observed in this study. The methylene peak at 2910cm^{-1} was used as the reference peak. The hydroxyl showed a very broad peak between 3600 - 3200cm^{-1} finally converging at 3450cm^{-1} as exposure hours increased Fig 5.2 shows the dependence of the hydroxyl index on the time of outdoor exposure while that on thermal exposure is on Fig 5.3. It could be seen that the OH index rises to a peak and levels off No particular order was observed, but of the blends, the 50/50 blend seems to have better performance than the rest. Similar observation could be made for the outdoor weathering.

Also the presence of 25% PB in PVC has a stabilising effect on the PVC (Fig 5.2) It can be observed for the outdoor exposure that after the initiation, the rate of production of the hydroperoxide decreases in the order of 100% PB> 75% PB 25% PVC> 50% PB 50% PVC> 100%PVC> 25% PB 75% PVC. For the thermal exposure, the rate of hydroxyl production for the blend decreases in the order 75% PB 25% PVC> 25% PB 75% PVC> 50% PB 50% PVC.

Figs 5.4 and 5.5 show the dependence of the carbonyl Index of the different blend compositions on exposure outdoors and on heating respectively. In both cases the rate of formation of the carbonyl is less for 100% PVC and 100% PB than for any of the compositions of the blend. The rate for the blend however decreases from 75% PB 25% PVC 25% PB 75% PVC 50% PB 50% PVC. Among the blend compositions the 1:1 ratio has the greatest stability (Figs 5.2 - 5.5). Table IV shows the embrittlement periods of these samples. From this table stability to thermal exposure decreases from 25% PB 75% PVC> 100%PVC> 50% PB 50% PVC> 75% PB 25% PVC> 100% PB.

CONCLUSION:

The carbonyl index has been used as a measure of chemical degradation taking place. From Fig 5.4 it can be seen that of the blends the 50/50 blend proves to be more stable to outdoor weathering than the other blends.

Table I

Variation of % Elongation of PVC/PB Blend with Time of Exposure

	ELONGATION AT BREAR				
TIME (HRS)	100% PB	50% PB 50% PVC	25% PB 75% PVC	100% PVC	Time hr
0	727.50	10.56	12.27		0
58		8.56	10.24	79.17	20
229	168.09		6.56	19.78	47½
1224	8.34	7.46	6.09	9.17	187.75

Table II

Variation of Young's Modulus with Exposure Time

	YOUNG'S MODULUS				
TIME (HRS)	100% PB	50% PB 50% PVC	25% PB 75% PVC	100% PVC	Time (HRS)
0	0.181	5.51	6.887	75	0
58	7.813		20.3		20
229	0.192	48.48	60.61		187.75
1224	84.82	121.2	205.4	133	340

Table III

Variation of Ultimate Tensile Strength of PVC/PB Blend With Exposure Time

	TENSILE STRENGTH in $Nm^{-2} \times 10^6$				
TIME (HRS)	100% PB	50% PVC 50% PB	25% PB 75% PVC	100% PVC	TIME (HRS)
0 0	0.160	1.55	1.862	16.500	0
58	0.384	10.339	1.900	27.177	20
229	1.369	13.183	10.296	34.658	93.5
1224	1.425	14.113	16.6814	45.965	340

$X10^6$

Table IV

Polymer/Blend	Type of Exposure	Induction Period in hours	Embrittlement Period in hours
100% PB	OUTDOOR	20 hours	1896
100% PB	Thermal	170	
75% PB 25% PVC	OUTDOOR	-	1992
75% PB 25% PVC	Thermal	-	
50% PB 50% PVC	OUTDOOR	-	2040
50% PB 50% PVC	Thermal	-	
25% PB 75% PVC	OUTDOOR	-	2112
25% PB 75% PVC	Thermal	-	
100% PVC	OUTDOOR	-	2064
100% PVC	Thermal	-	2064

NO. 5-100-0309

4a

PVC / PB Blend

REMARKS PVC/PB (PVC-75%)
PVC - 75% ; PB - 25%

ORIGIN

PURITY

PHASE

CONCENTRATION

THICKNESS

DATE 3/11/75

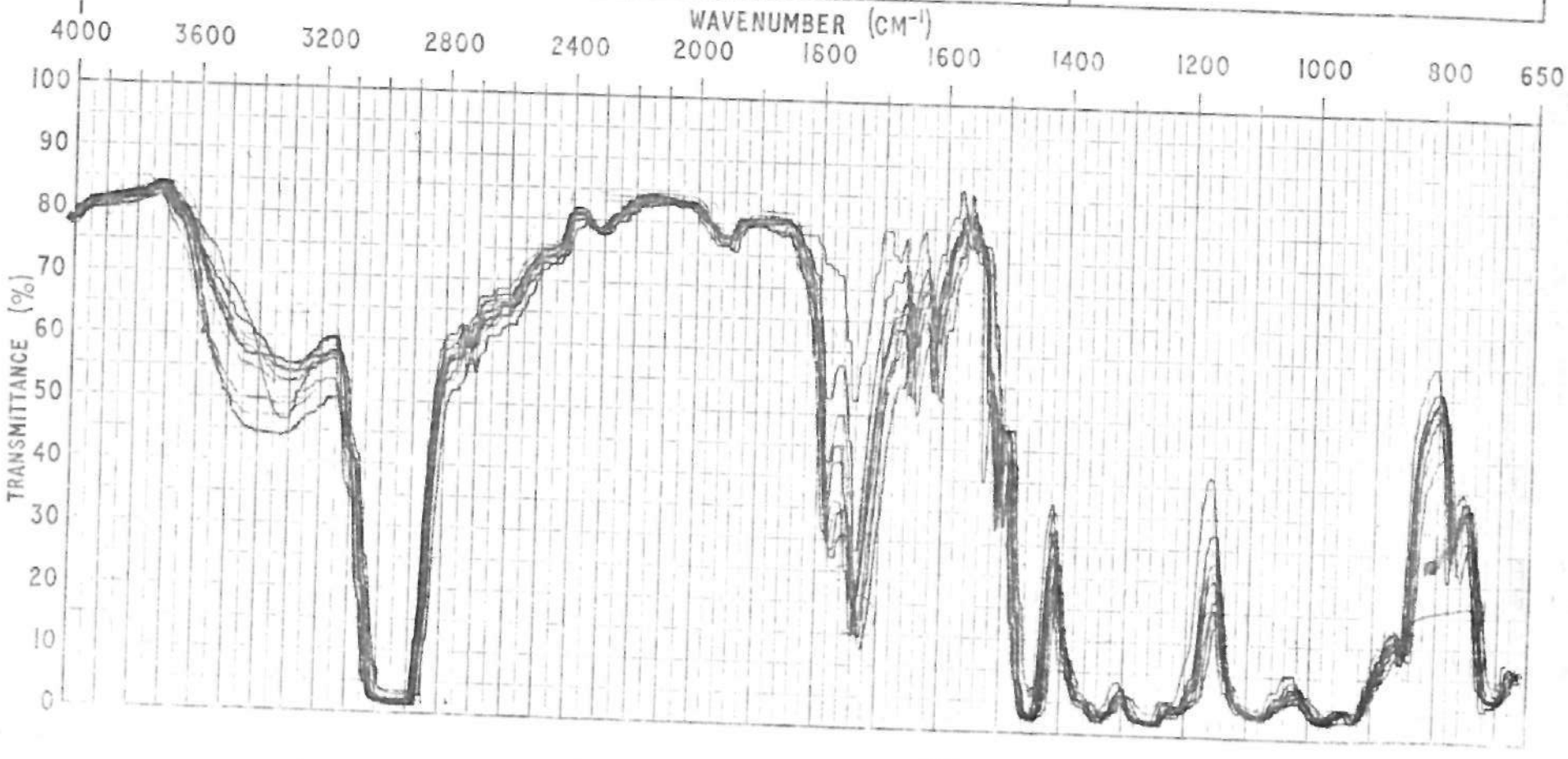
OPERATOR

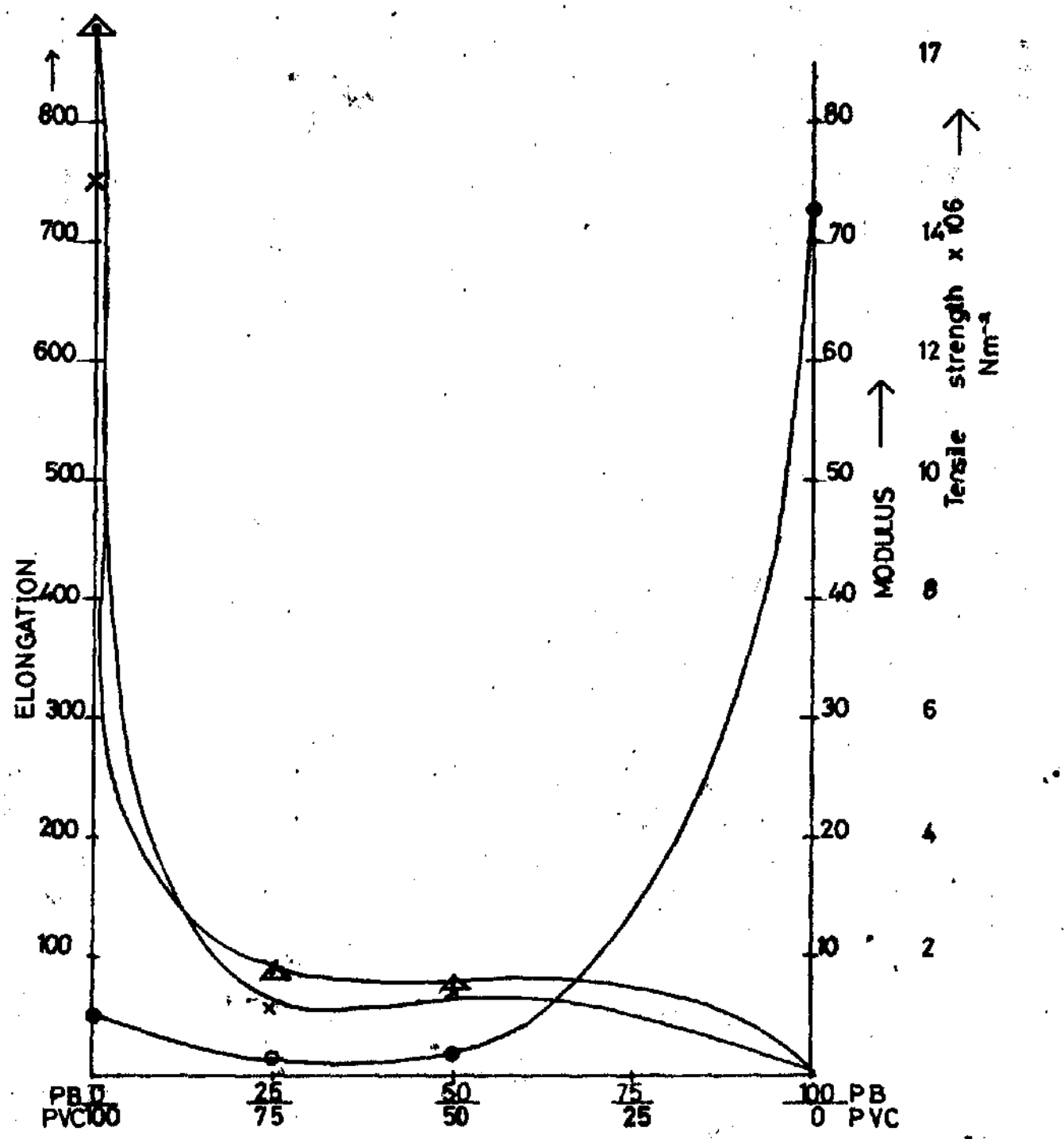
PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1

SAMPLE 2





DEPENDENCE OF SOME FACTORS ON THE COMPOSITION OF PVC/PB BLEND

COMPOSITION OF BLEND

△ — ULTIMATE TENSILE SRENGTH

Θ — % ELONGATION

X — MODULUS

Fig 51

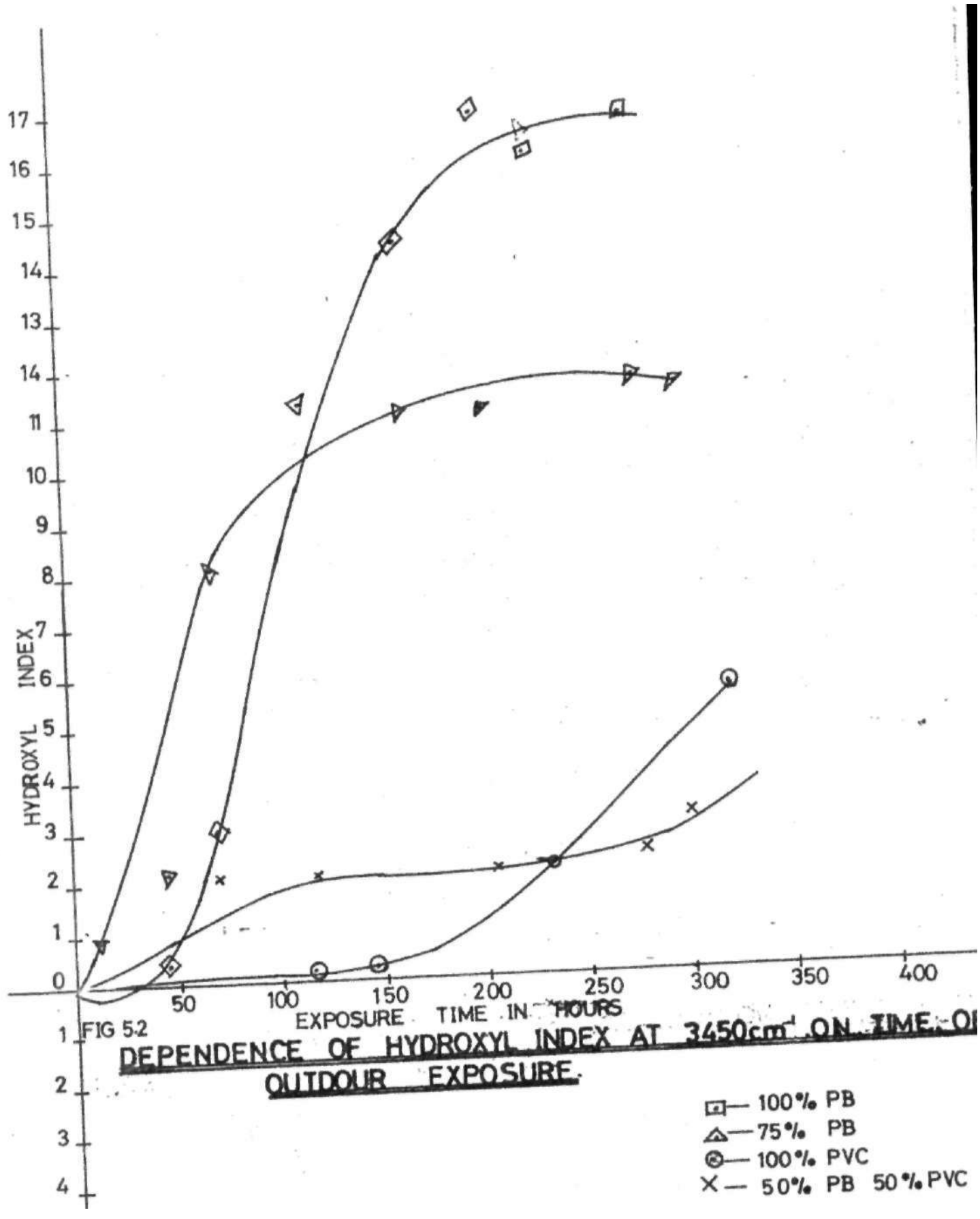


FIG 5.2 DEPENDENCE OF HYDROXYL INDEX AT 3450cm^{-1} ON TIME OF OUTDOUR EXPOSURE.

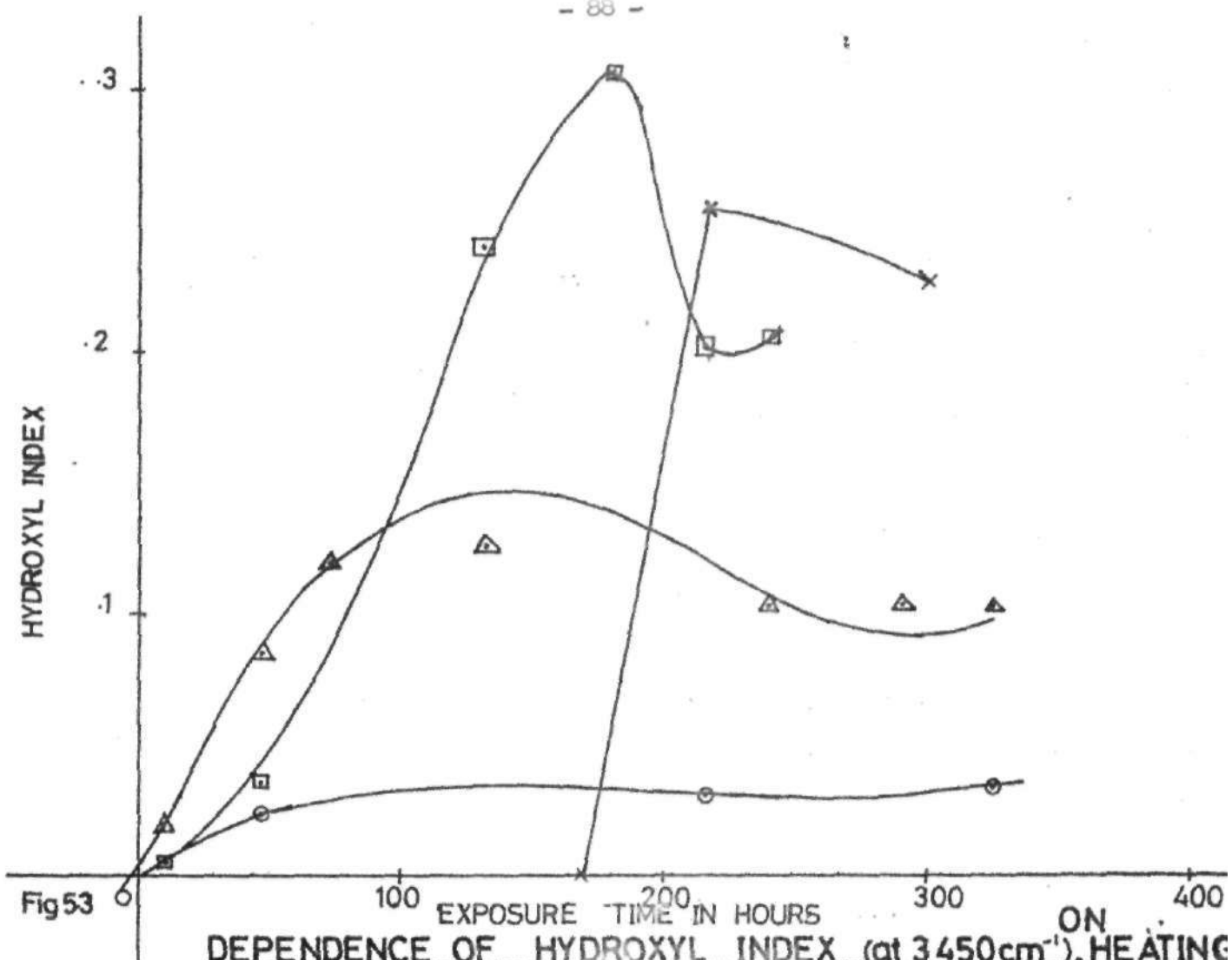


Fig 53 DEPENDENCE OF HYDROXYL INDEX (at 3450cm^{-1}) ON HEATING

⊡ — 75% PB 25% PVC
△ — 25% PB 75% PVC
⊙ — 50% PB 50% PVC
× — 100% PB

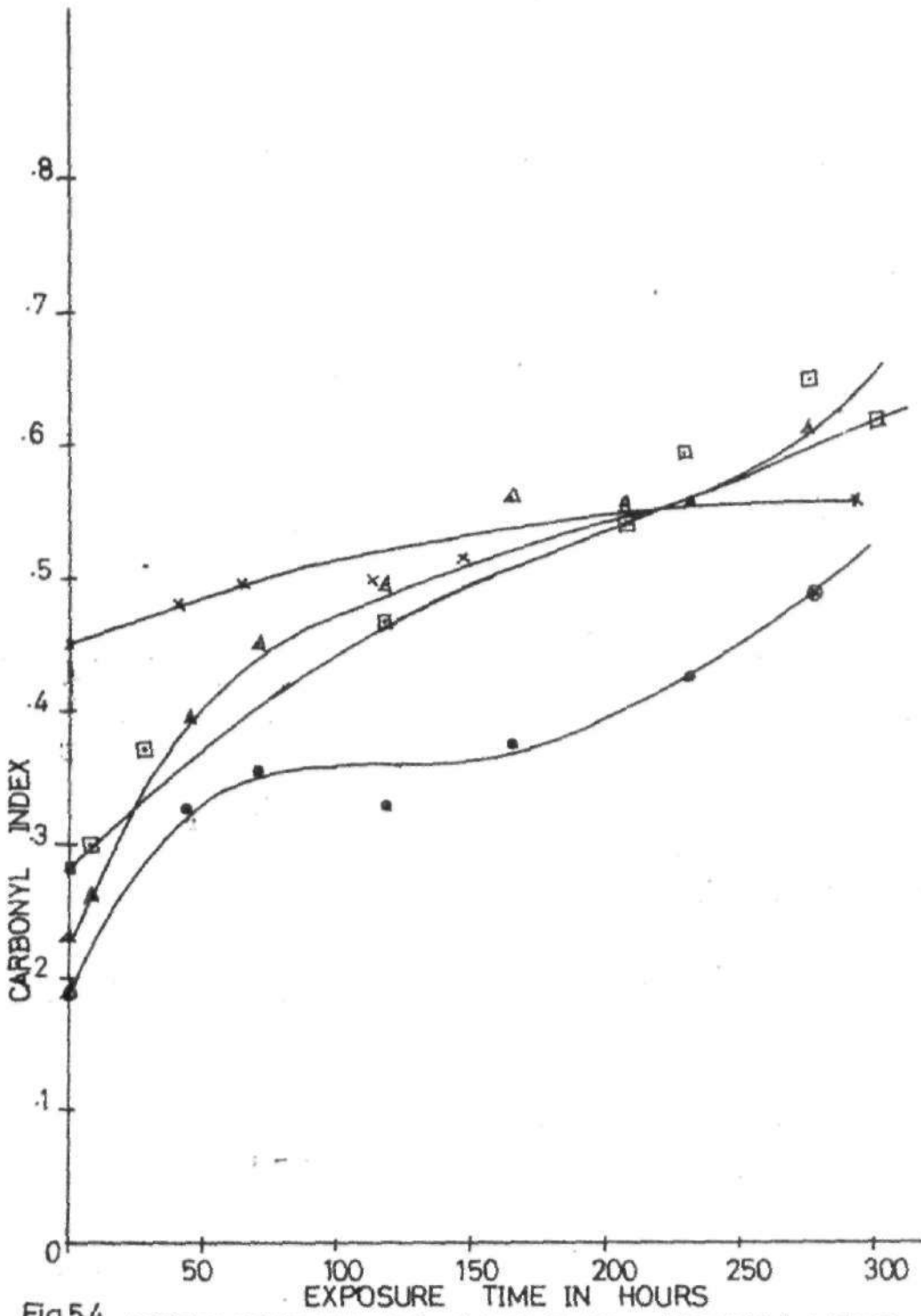


Fig 5.4 DEPENDENCE OF CARBONYL INDEX (at 1725 cm^{-1}) OF PVC/PB ON TIME OF OUTDOOR EXPOSURE.

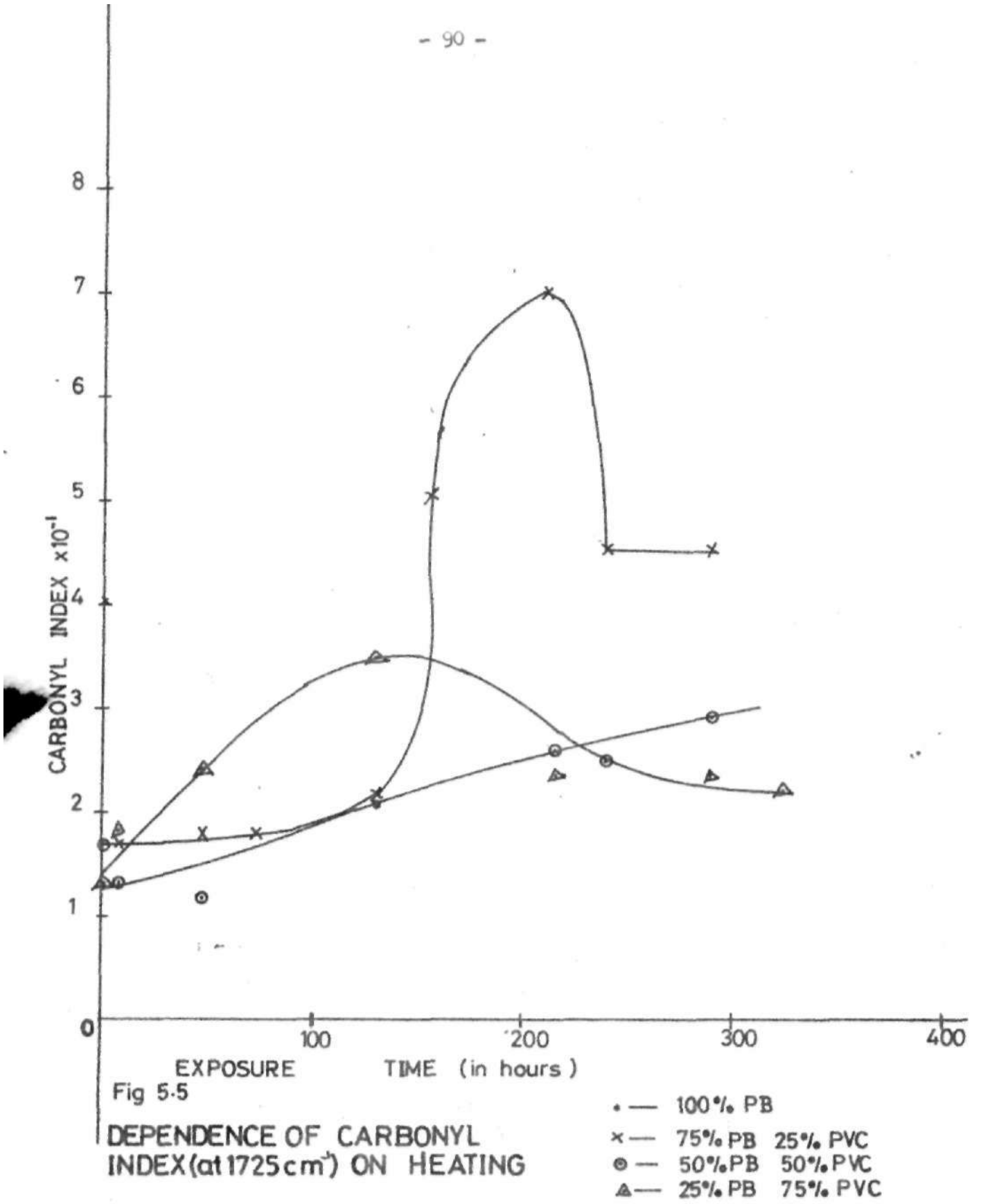


Fig 5.5

DEPENDENCE OF CARBONYL INDEX (at 1725 cm⁻¹) ON HEATING

CHAPTER 6

COMPARISON OF DATA

In Chapters 2, 3 and 4 interest was centred on how the presence of ABS, PVC and PB affect the degradability of PS on exposure to both outdoor weathering and heating at 100°C in air oven and vice versa. In Chapter 5 was discussed how the presence of PVC affected the stability of PB to outdoor exposure and also to oxidative oven ageing at 100°C. In the present Chapter interest is centred on finding out which of the polymers PVC, ABS and PB gives the best blend with PS as far as improving the chemical stability and mechanical properties of PS is concerned. It is also worthwhile to find out in which of the above polymers PS is most effective in improving stability and mechanical properties. Finally it's of interest to know which of PVC and PS gives a more useful blend with PB.

Carbonyl index has been used as a measure of chemical degradation taking place in a polymer. From a comparison of Figs 2;11 and 4.6 (figures showing the dependence of carbonyl indices of PS/ABS and PS/PB respectively on thermal exposure) the following observations can be made:- the carbonyl indices of the PS/ABS blends increased with time while each of those of PS/PB blends reached a maximum followed by a fall. Induction periods are observed in the PS/ABS blends whereas no induction period is observed for the PS/ABS. It thus appears that degradation sets in at an earlier time in the PS/PB blends than in the PS/ABS blends.

The pattern of degradation observed for the 50% PS: 50% PB blend appears similar to that observed for the PS/ABS blends in general (fig 2.11 and 4.6) - the carbonyl index increased gradually with time of exposure. It may be concluded that ABS imparts greater stability to PS than PB imparts to PS when PS/ABS and PS/PB blends are exposed to heat at 100°C in air. The rate of degradation of pure ABS is however faster than that in the pure PB.

For the outdoor exposure the carbonyl indices for the PS/ABS blends increased with time (Fig 2.10) in the PS/PB blends the carbonyl index of each of the different compositions also increased with time (Fig 4.8) (although more rapidly than in the PS/ABS) to reach a maximum and remained constant. No fall is observed. No induction period is observed in both types of blends i.e. for PS/ABS and PS/PB. As in the case of thermal exposure above the PS/ABS blends appeared to be less susceptible to photooxidation than the PS/PB.

ABS also imparts better mechanical properties to PS than PB. (Figs. 2.4 & 4.3 also fig 2.12 & 4.9) This may not be too surprising ABS itself is a terpolymer consisting of three polymeric materials - acrylonitrile, butadiene and styrene and each of these components of ABS serves a specific function in the polymer with which ABS is blended. Polybutadiene secures elasticity and absorbs the energy of the external stresses; polyacrylonitrile gives good chemical resistance and rigidity

while polystyrene is supposed to improve thermoplasticity and processability. Polybutadiene is very susceptible to oxidation. Photooxidation leads to cross linking of the rubber accompained by chain sussion. In ABS the scission of the graft between rubber and matrix follows the cross linking occuring in the rubber phase as a result of photooxidation.
Consequently there is a rapid loss of impact strength[125] Degradation is faster in the PS/PB blends than in the PS/ABS blends. This has been found true above in the present work. Thus it is evident that ABS gives better chemical stability and mechanical properties to PS than PB.

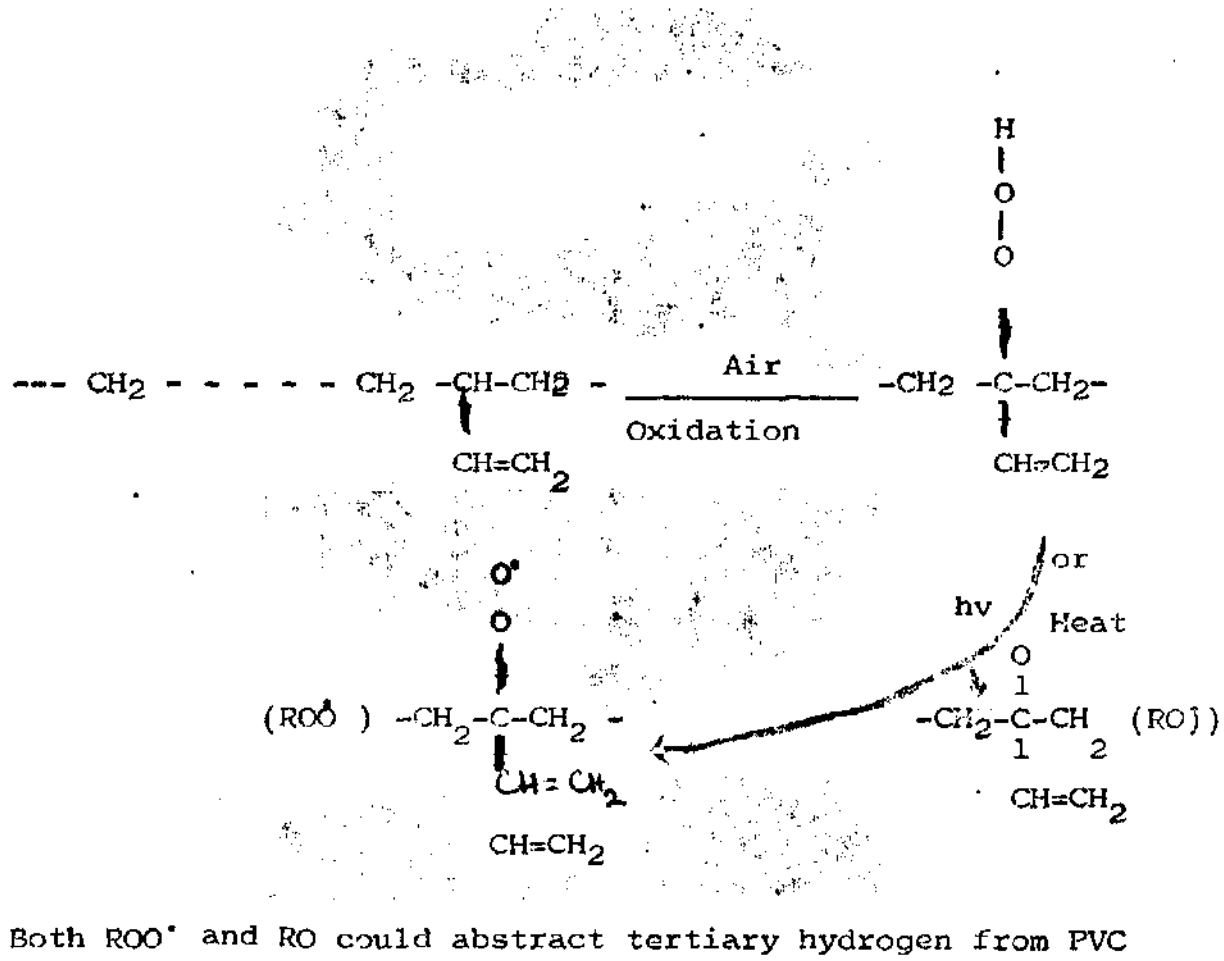
PS/ABS and PS/PVC can be compared presently. In terms of chemical stability the PS/PVC is more stable than PS/ABS. This is evident from results obtained from the embrittlement tests (Chapter 2 table I; Chapter 3 table I) and also from the rate of increase of carbonyl indices in the PS/ABS and PS/PVC blends (Figs 2.10 and 3.2) The dependence of ultimate tensile strength of PS/ABS and PS/PVC blends on exposure time are shown in figs 2.2 and 3.8 respectively. PS/PVC blends had higher values of ultimate tensile strength than PS/ABS. This may not be too surprising since 100% PVC had ultimate tensile stregth of higher value than 100% ABS. The extensibility of PS decreased on addition of either PVC or ABS. The values of the extensibility of the blends fell within those of the pure polymers. ABS itself had a slightly higher extensibility than PVC at 28^{o}C.

This is expected because the rubber content of ABS makes it more elastic than PVC. The elastic properties of ABS has been found[126] to be highly temperature dependent. At high temperatures, PVC has a higher extensibility. This is because as temperature increases ABS loses its extensibility because of cross links occuring as a result of the chemical instability of the rubber component. PVC however being thermoplastic has better extensibility at high temperatures.

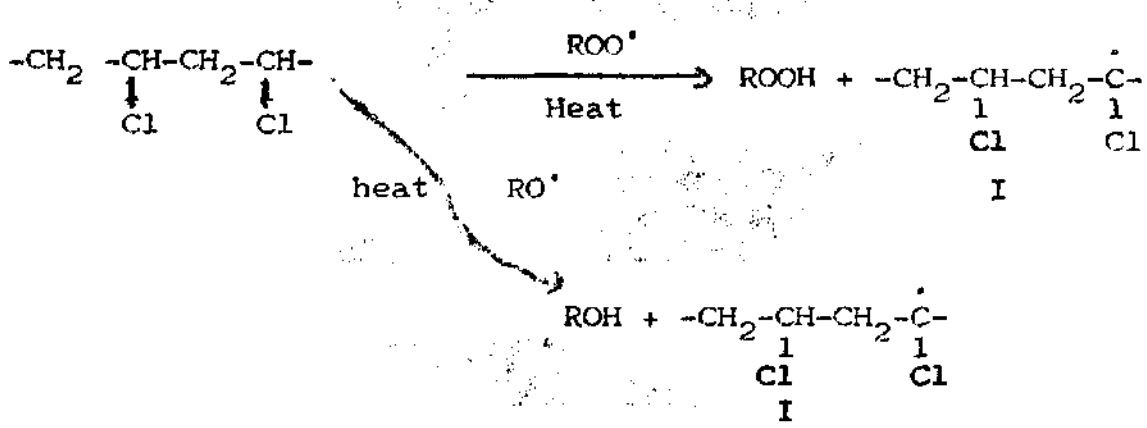
The extensibility of each of the PS/PVC blend is higher than those of the PS/ABS blends (Fig 6.1). This may be related to the fact that ABS is incompatible with PS (**Pages 42,** 43)

Figs 4.6 and 5.5 show the dependence of the carbonyl indices of PS/PB and PVC/PB respectively on heating time. The 75% PB 25% PVC shows an induction period of 110 hours. No induction period is observed for the 75% PB 25%PS The rate of formation of the carbonyl increased more rapidly for the 75% PB 25% PS. In the case of the 50% PB 50% PS the rate of increase was gradual. No maximum was observed. This is true for the 50% PB 50% PVC also. The rate of carbonyl formation was however higher in the 50% PB 50% PVC than in the 50% PB 50% PS. There was also an increase of the carbonyl index of the 25% PB 75% PVC with heating time. A maximum was reached and this was followed by a fall. The same is true for the 25% PB 75% PS However the rate of increase is higher in the 25% PB 75% PVC than in the

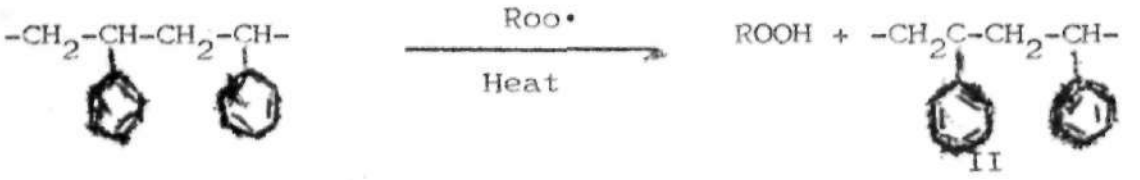
25% PB 75% PS. Thus it appears that PB/PS blend is more stable than the PB/PVC blend. Below is a proposed mechanism for the oxidation and photooxidation.



Both ROO· and RO could abstract tertiary hydrogen from PVC and PS as follows



Similar with PS ad follows



The radicals resulting from the hydrogen abstraction of PVC and PS are shown as I and II above respectively. From these structures it becomes obvious that PS/PB will be more stable than PVC/PB on heating at 100°C and on exposure to outdoor weathering. This is because structure II is more stable than structure I. The stability of II i.e. the Polystyryl radical is due mainly to the resonance stability caused by the presence of the benzen ring.

CONCLUSION

From the discussions above it is clear that the PS/PVC blends are more chemically stable than any of PS/ABS, PS/PB and PVC/TB blends. In general the 50% PS 50% PVC appears to be the most stable composition of all the blends studied.

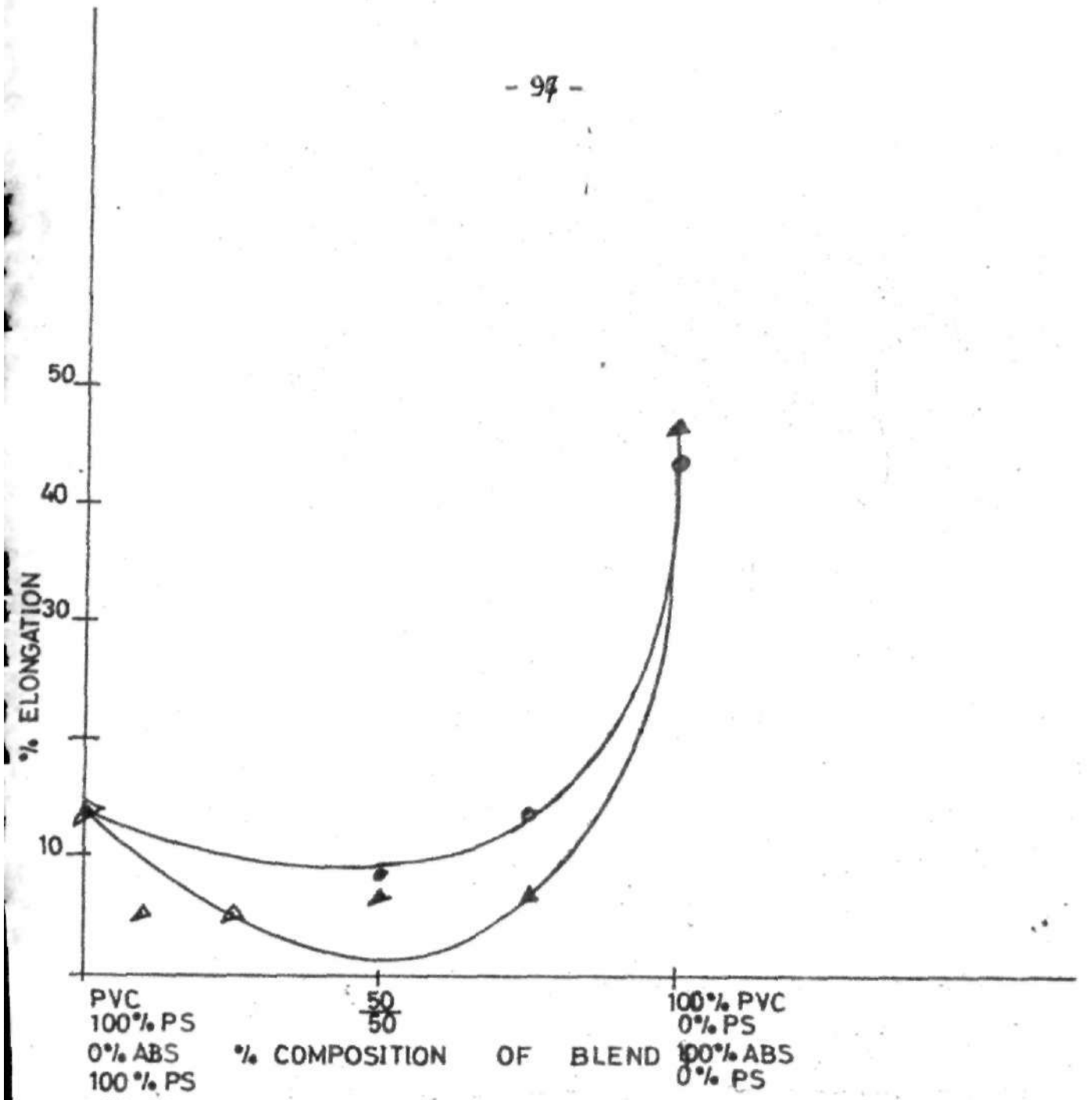


Fig 61

DEPENDENCE OF ELONGATION AT BREAK ON % COMPOSITION OF PS/PVC AND PS/ABS BLENDS

● —PS/PVC
△ —PS/ABS

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