DEGRADATION OF SOME POLYMER BLENDS

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D E C L A R A T I O N

I hereby declare that this thesis has been written by me and that it is a record of my own research work. It has not been presented in any previous application for a higher degree. All quotations are indicated and the sources of information are specifically acknowledged by means of references.

A. G. I. Avoaja

March, 1983

Dedicated

to

Diane

for everything and more

A C K N O W L E D G E M E N T S

I acknowledge, with gratitude, the guidance, advice and diligence of my Supervisor, Dr. E. G. Kolawole throughout this programme.

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A B S T R A C T

Blends of PVA with PVC, PMMA and PS and PS/PMMA, that cover the entire compositional range have been subjected to outdoor weathering, thermal oxidation and ultraviolet irradiation. With the application of infra-red technique it was possible to detect any structural changes taking place. With the aid of Instron testing instrument it was possible to find out the mechanical modifications that have taken place.

The present work investigates the effect of a second polymer on the weathorability of another. The author has observed that in all the cases investigated there was interaction between the dissimilar molecular chains, at least at the phase boundaries, for the two-phase systems. These interactions which may be intermolecular or intramolecular are observed in most cases to have deliterous effects on the structural stability and mechanical properties of the polymers. In a few cases, the interaction reduced the vulnerability of either or both homopolymers to weathering.

From the studies it has been observed that PMMA stabilises PVA against outdoor weathering and oven aging, while PVA stabilizes PMMA against ultraviolet degradation. For the PVA/PVC blends general deterioration of property was observed on blending with PVA destabilizing PVC and **vice** versa, with the effect of PVC on PVA being more pronounced.

For the PVA/PS blends, although rigidity was observed to increase with increase in PS in the blends, the presence of PVA was observed to cause general deterioration of mechanical properties, with a minimum in tensile strength, modulus and percentage elongation at 30% PVA in the blends. Vulnerability to thermal degradation was also observed to increase with increase in PVA in the blend. PMMA was observed to destabilize PS to outdoor weathering and on thermal aging all the blends had lower induction periods than the homopolymers.

From morphological studies, PVA/PMMA and PS/PMMA were found to be compatible while PVA/PVC and PVA/PS were incompatible.

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ABBREVIATIONS

PVA:	Polyvinyl acetate
PVC:	Polyvinyl chloride
PS:	Polystyrene
PMMA:	Polymethyl methacrylate
TVA:	Thermal volatilization Analysis
uv:	ultraviolet
ir:	infra-red.

CHAPTER 1

INTRODUCTION

1.1 DEFINITION

Polymer blends, polyblends or polymer alloys are physical mixtures of polymers, the mixing being done by dissolution in a common solvent or in the melt form. This excludes all cases of copolymerization in which the monomeric units are systematically introduced into the polymer main chain.

The concept of physically blending two or more existing polymers to obtain new products has been necessitated by the need to improve the properties of the existing polymers and enhance their ultimate end-use and service life without the attendant problems involved in copolymerisation like designing synthetic methods, suitable equipments for the production and, of course, the attendant huge investment costs.

The thermodynamics of polymer blends is of the most fundamental importance since it determines the morphology of the blend, the adhesion between the constituent polymers and consequently influences its properties and applications. "One of the first, but not the only, thermodynamic questions

concerns the equilibrium miscibility or solubility of the polymeric components in a blend" (1).

Polyblending of polymers often results in products with improved impact properties. Even where the blend exhibits two-phase behaviour, definite advantages can be derived, if mechanical compatibility can be achieved. With compatible polymer blends mechanical compatibility is assured and a property compromise between the constituents, is therefore achieved. Thus for compatible polymer blends a range of price/performance characteristics between the component polymers can lead to a large number of potentially useful and different products, not possible with either of the polymers comprising the blend (2). A number of polymer blends have achieved commercial importance and among these are a blend of poly(-2,6-dimethyl-1,4-phenylene oxide), PPO and polystyrene under the trade name Noryl (2) and PVC-nitrile rubber and various other PVC blends.

1.2 COMPATIBILITY AND MISCIBILITY OF POLYMERS

The terms compatibility and miscibility of polymer-polymer systems may vary in definition and applications depending on the investigator. To some compatibility may mean complete absence of phase separation and to others it may simply mean possession of desirable physical properties. But generally it is used to describe good adhesion between the constituent polymers and average mechanical properties. Solubility could also be used to describe molecular mixing in polymer-polymer blends and the term is accepted for

single phase, solvent-solvent and polymer-polymer mixtures. On the other hand, the term miscibility describes polymer blends with behaviour similar to that expected of a single phase system.

Incompatibility, similarly, in polyblending varies widely both in concept and application.

In-compatibility in polyblends is usually characterized by the presence of:

(i) two transition temperatures
(ii) two phases and
(iii) loss of transparency, except where the constituent polymers have close solubility parameters.

Compatible blends are characterized by one glass transition temperature, one phase, close-packing (less void) and a better spatial arrangement between the two polymers (4). The extent of miscibility depends on the size and distribution of phases, that is how finely dispersed the 'solute' polymer is in the solvent polymer and the segmental mobility of the polymer in one phase relative to another. This phenomenon termed interpenetrating network (IPN) determines polymer-polymer miscibility.

In bulk, compatible systems form transparent films and fibres that exhibit no heterogeneity under considerable

magnification in the phase contrast microscope. Incompatible blends form transparent films only if the refractive indices of constituent polymers are the same, but where these are different they form two-layered films, when the polymer solution is evaporated (6).

Polyblending offers some desirable properties in a polymer, particularly, where one of the constituents has superior mechanical properties.

1.3 THERMODYNAMICS OF POLYMER BLEND SOLUTIONS

A full discussion of polymer-polymer compatibility should involve a critical survey of the principles underlying the thermodynamic miscibility of polymers.

The ideal entropy expression which rests essentially on the assumed approximate interchangeability of solute and solvent molecules in solution cannot possibly hold for polymeric systems. The solubility of polymers has been studied extensively since 1942, when Flory and Huggins (8) and later Flory and Krigbaum (9) propounded theories governing the solubility of polymers. A consideration of the Flory theory and the Hildebrand solubility parameter provides essential tools for predicting polymer-polymer compatibility.

The solubility parameter is defined as the square root of the energy of vapourization per unit volume of the material and is given by the sympol δ (12).

$$\delta \equiv (\Delta E^{v}/V)^{\frac{1}{2}} \ (Cal/cm^{3})^{\frac{1}{2}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1.1)$$

Thus ò is proportional to the cohesion of the material or the strength of attraction between the molecules making up the material.

The concept is that materials with similar solubility parameter should show equal dispersion in the same solvent. The approach facilitates the characterization of a system using only one component properties and helps in the calculation of effects of pressure and temperature on the mixing free energy and probable changes of these with structure.

The Flory theory demonstrates that the mixture thermodynamic properties depend on the thermodynamic properties of the pure components. In this theory each component is characterized by three equations of state parameters: characteristic temperature, characteristic pressure and characteristic specific volume. Since these parameters can be determined from the pressure-volume-temperature (PVT) properties of the pure components, it is hoped that the thermodynamic properties of polymer solutions, including polyblends, can be determined from the equation of state parameters.

The older Flory-Huggins theory (10) which ignores the equation of state of the pure components, fails to describe the critical solution temperatures of polymeric systems.

The temperature effect arises from the observation that when temperature of polymer solution is raised or lowered, the solvent becomes thermodynamically poorer and demixing occurs at such extreme upper and lower temperatures, thereby

giving rise to the lower critical solution temperature (LCST) and upper critical solution temperature (UCST) respectively. Heat treatment may cause phase-separation in an otherwise miscible system.

The solvent type determines the LCST. The LCST affects the miscibility of a polymer-polymer system as in the case of PS and Poly(vinyl methyl ether) which gives transparent films with toluene but gives cloudy films with 2 tg's with trichloroethylene (7).

From the Flory theory, the magnitude and sign of the free ethalpy of mixing (ΔH^m) of a polymer-polymer system largely determines the compatibility of the system and to some extent, the entropy of mixing (ΔS^m) plays a significant role in extremely unfavourable cases.

The Flory and lattice fluid theories represent promising alternatives to the solubility parameter of Hildebrand for predicting the thermodynamic miscibility of polymer-polymer system. McMaster (11) carried out extensive analysis of the Flory theory for polymer blends. His findings are summarized below.

(i) Negative or very small positive value of the interaction χ_{12} favours compatibility.

(ii) Low molecular weight by one or both polymers favours compatibility.

(iii) Small thermal coefficients favour compatibility.

None of these theories can adequately account for the

polymer-polymer miscibility and until such a theory is developed it may be necessary to apply all three theoretical methods to a given polymer to facilitate the determination of compatibility.

1.4 SCOPE OF PRESENT WORK

The present work entailed studies on the binary polymer blends PVA:PVC, PVA:PMMA, PVA:PS and PS:PMMA. For an adequate understanding of the degradation of these blends, it was deemed necessary to carry out detailed studies on the factors which influence polymer degradation and the magnitude of these effects.

Studies on specific gravity and gross morphology of the blend films facilitated appreciation of the compatibility of the blends, since compatibility affects the ultimate properties and applications of a blend.

The degradation was in film form. The films were subjected to photolysis (UV irradiation), thermal oxidation and outdoor weathering. Studies in mechanical properties were carried out with a view to determining whether any of the blends had any properties superior or intermediate to either or both homopolymers comprising it and, as in the case of the PVA:PVC blends, whether the introduction of PVA into the blend, at any composition level, inhibited, retarded or accelerated the incidence of colouration on degradation.

In the course of these studies it has been possible to suggest possible mechanisms for the degradation of these

blends under the conditions of the study.

CHAPTER 2

STUDIES ON POLYMER DEGRADATION

Polymers are rarely available in their pure states due to the presence of hydroxides and ketones, formed due to the presence of oxygen during polymerization and the acquisition of end chain unsaturation due to chain transfer to monomer during termination reactions. These chromorphic groups, which are usually formed during polymer degradation serve as sites for initiation of degradation. The method of polymerization and the degree of polymerization influence the onset and the rates of degradation, since the rate of degradation is often inversely proportional to the polymer molecular weight.

Polymers degrade when subjeced to heating and high energy irradiation. Studies on polymer degradation have, therefore, often involved thermal oxidative degradation, photodegradation and environmental degradation.

2.1 METHODS OF STUDYING POLYMER DEGRADATION

The methods used in studying polymer degradation include:

(i) Thermal methods: these involve heating the polymer in an air oven and measuring changes in physical and chemical properties.

(ii) Thermal Volatilization Analysis (TVA).

(iii) Temperature programmed degradation.

(iv) Pre-irradiation with UV followed by thermal degradation.

(v) Ultra-violet irradiation and monitoring of changes in microstructure using infra-red and ultraviolet spectroscopy.

(vi) Differential Scanning Calorimetric (DSC) method.

2.2 DEGRADATION OF PVC AND ITS BLENDS

The degradation of PVC has been extensively studied (15-46), with much emphasis on thermal degradation (15-26).

Gupta and Pierre (15) studied the effect of oxygen on the thermal degradation of PVC. Swetly, Lukas and Kolinsky (16) observed that PVC degraded via dehydrochlorination, with dehydrochlorination being a consequence of constant concentration of active sites in the chain elimination of hydrochloric acid and suggested that the initiation of propagating polyene sequences occured via migration of activating groups between adjacent polymer chains. Elman (17, 18) was of the opinion that oxygen delayed thermal degradation of PVC while accelerating the rate of dehydrochlorination, thereby suggesting that in presence of oxygen the polyene sequence was interrupted by oxidation to the carbonyl group thereby inhibiting colour development. Talamini and Pezzin (19) thermally degraded PVC in both inert and oxygen atmosphere and were of the opinion that PVC degradation in oxygen was autocatalytic and that

dehydrochlorination proceeded along the chain in a mechanism of successive allylic activation. They attributed the increase in reaction rate with time to the autocatalytic effect of hydrochloric acid. They observed that thermal degradation in the absence of oxygen rapidly gave insoluble product but in the presence of oxygen, the molecular weight increased after an initial lowering. These opinions do to some extent summarize the impressions of other investigators (20-26).

Gupta and Pierre thermally degraded at 200°C pre-irradiated samples of PVC and observed that HCl evolution increased with pre-irradiation time and that pre-irradiated samples exhibited some free radicals at zero heating time. Recently, Scott and Tahan (28) observed that there was a linear relationship between colour formation and carbonyl growth for PVC and suggested that the conjugated carbonyl was responsible for colour formation, since during photo-oxidation broadening of the composite carbonyl peak below 1700cm^{-1} occured and was indicative of conjugated carbonyl group. This opinion has, however not been countered and is apparently an explanation to the observation of Elman (17, 18). Many other investigators have worked on the photodegradation of PVC (29-34). Their works reveal that crosslinking occured during irradiation but prolonged irradiation resulted in decrease in gel content (32) and that Young modulus of PVC increased with irradiation time, reached a maximum and then decreased (33).

Some work has been done on PVC blends and here, attention is directed to its blends with PVA. Grassie and McNeill (35, 36)

observed that acetic acid catalysed PVC break down in solution and suggested that it was possible the accelerating effect of HCl on deacetylation of PVA occured via HCl catalysis. They noted that there was considerable interaction between polymers in the blends with PVA destabilizing PVC and PVC destabilizing PVA. Jamieson and McNeill (40) observed that the polymers were incompatible and concluded that the destabilizing effect of each on the other could only take place at phase boundaries.

Working on the copolymers of vinyl acetate and vinyl chloride, Grassie and McLaren (44, 45) made similar observations as (35-39) and observed that the copolymers were considerably less stable than the homopolymers and that minimum stability occured at 30-40% vinyl acetate content in the copolymer.

Lots of work have been done on the stabilization of PVC. Kolawole and Mbamali (46) working in this laboratory observed that the plasticity of PVC increased with increase in ABS content in PVC/ABS blend.

2.3 DEGRADATION OF POLYVINYL ACETATE (PVA)

Seymour and Westwood (47) pyrolysed PVA and noted that PVA degradation occured by deacetylation followed by condensation of polyolefinic structures to polycyclic aromatic systems. Reiner (48) observed that on heating PVA decomposed via deacetylation and that subsequent deacetylation was facilitated by the double bond so formed. He was of the opinion that deacetylation was autocatalytic.

2.4 DEGRADATION OF POLY(METHYL METHACRYLATE), PMMA, AND ITS BLENDS

Gardner and McNeill (49) McNeill and Neil (50, 51) observed that PMMA was stable over 250°C when heated alone but broke down to give quantitative yield of monomer when heated with PVC. Degrading the blends of PMMA and PVC by TVA, they observed increase in monomer production at low temperatures and explained the chain scission as due to radical attack by hydrogen abstraction process leading to subsequent chain scission and depolymerization.

2.5 DEGRADATION OF POLYSTYRENE (PS) AND ITS BLENDS

During the oxidative degradation of PS, Beachell and Smiley (52) observed that there was preferential attack of oxygen on the α-hydrogen atoms leading to initial production of hydroperoxide. Grassie and Weir (53-56) irradiated PS and observed that the polystyryl radicals formed could crosslink and that insolubility and embrittlement of PS occured after relatively short periods of irradiation. Jellinek (58), Jellinek and Lipovac (59, 60) working on diffusion controlled degradation of isotactic PS at elevated temperatures observed that as soon as a link was ruptured, monomer units were broken off the newly formed chain until these active chains were deactivated.

Grassie, McNeill and Cooke (61) degraded blends of PS with PMMA. They carried out TVA and analysed the products by GLC determinations of molecular weight of solid polymer residues and observed interaction between the two

polymers and noted that on degrading both gave out large amounts of monomer by unzipping. They noted that degraded as a film no interaction occured bettween PS and PMMA.

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS

The polymers used for this research were polyvinyl acetate (PVA) supplied by BDH Ltd. with $\bar{M}n$ of 45.0×10^3 and density of $1.191 gcm^{-3}$ at 20^oC, polyvinyl chloride (PVC) supplied by BDH Ltd. with $\bar{M}n$ 54.2×10^3 and a density of $1.393 gcm^3$ at 20^oC, polymethyl methacrylate (PMMA) supplied by RAPRA with $\bar{M}n$ of 48.7×10^3 and with a density of $1.190 gcm^{-3}$ at 20^oC and polystyrene (PS) supplied by ALDRICH with undefined $\bar{M}n$ and a density of $1.111 gcm^{-3}$ at 20^oC.

3.2 SOLVENTS AND COMPOUNDING OF BLENDS

All the blends were studied as binary systems and the compounding was done in the following pairs: PVAc/PMMA, PVAc/PS, PS/PMMA and for these the solvent was chloroform supplied by M&B Ltd. and with a specific gravity of $1.474 gcm^{-3}$ and PVAc/PVC for which ANALAR tetrahydrofuran (THF) with specific gravity of $0.887 gcm^{-3}$ was used.

3.3 SOLUTION PREPARATION

All the blends were of 2% W/V concentration. For each

pair nine blends whose composition ranged from 90%:10% through 10%:90%. For example for the PVAC/PMMA pairs the blends were made as follows:

(a) 90% PVAc:10% PMMA, (b) 80% PVAc:20% PMMA,
(b) 70% PVAc:30% PMMA, (d) 60% PVAc:40% PMMA,
(c) 50% PVAc:50% PMMA, (f) 40% PVAc:60% PMMA,
(g) 30% PVAc:70% PMMA, (h) 20% PVAc:80% PMMA and
(i) 10% PAAc:90% PMMA.

These compositions will henceforth be written, for example, for the 50% PVAc:50% PMMA as 50:50 PVAc:PMMA. Similarly 2% W/V solutions of the unmixed polymers were prepared.

3.4 FILM CASTING

The films were made by solution casting on the surface of mercury contained in petri-dishes of the same diameter. The films for infra-red and ultraviolet spectroscopic studies were 0.02 ± .005mm thick while those for the determination of mechanical properties were of the dimensions 0.05 ± .005 x 8.0 x 30mm. The film preparation was done in fume-cupboard with the exhaust turned off. The films were covered with aluminium foil or stored in dark drawers until when needed.

3.5 METHODS OF FOLLOWING DEGRADATION

The blend films of thickness 0.02 ± 0.005mm were stapled onto cardboard papers with square holes. These were then placed against the round holes on a smooth plywood board. A similar plywood board with holes in alignment to those of the

first was then placed on the films. The films were then secured by clamping the two plywood boards together. This was then clamped onto retort stands on the rooftop of the Chemistry Departmental building for outdoor weathering. The angle of inclination of retort stands were constantly adjusted to make for maximum illumination.

The effects of outdoor weathering on the microstructure of the unmixed polymers and the blends were monitored by taking the infra-red spectroscopic measurements on PERKIN ELMER 1700 infra-red spectrophotomer. This enabled the determination of changes in microstructure by estimating the growth in absorbing peaks relative to a reference peak. The absorbing peaks used are the carbonyl ($\rangle C=O$) peaks at $1725cm^{-1}$ and the hydroxyl (-OH) peaks at $3400cm^{-1}$ while the methylene ($-CH_2-$) peak at $2910cm^{-1}$ was used as a reference. The transmittance recorded as peak height and peak base were converted to absorbance using a table of conversion of transmittance to absorbance provided by PERKIN ELMER LTD. These absorbances were then computed into carbonyl index for carbonyl absorptions and hydroxyl index for hydroxyl absorptions respectively for example, the carbonyl index is computed as follows:

$$\text{Carbonyl index, } C_I \equiv \frac{\text{Absorbance of } (\rangle c=o) \text{ (A)}}{\text{Absorbance of reference peak (B)}}$$

$$A \equiv \frac{\text{Peak height of } \rangle CO \text{ absorption}}{\text{Peak base of } \rangle CO \text{ absorption}}$$

$$B \equiv \frac{\text{Peak height of reference peak}}{\text{Peak base of refence peak.}}$$

The indices were plotted against outdoor exposure time to

follow the pattern of degradation and calculate the induction time for the degradation. The infra-red spectroscopy for each homopolymer and blend was taken at zero time and at regular intervals thereafter. The degradation was also followed by taking ultraviolet spectra of the films using UNICAM SP1800 ultraviolet spectrophotometer.

Most of the films were left exposed on the roof top from the month of September 1982 to January 1983.

3.51 Method of thermal oxidative degradation

Wallace air oven with regulated air inflow of about 92cc/min was used for the thermal oxidative degradation. The oven was maintained at 100°C. The films, stapled on cardboard papers, were hung on the hangers in the oven. The infra-red of each film was taken at zero time and at regular intervals thereafter using PERKIN ELMER 1700 infra-red spectrophotometer. The absorptions of interest are as discussed in 3.5. The carbonyl and hydroxyl indices were similarly computed and plotted against heating time and the induction time for the thermal degradation of each blend calculated. The measurements were continued until each film embrittled.

3.52 Method of ultravilet degradation

The films of 0.02 ± 0.005mm thickness mounted on cardboard papers with square holes were mounted on a board, with the aid of pins, in the darkroom in the department. The rays from Gallenkamp Ultraviolet equipment with a 365nm bulb and kept at distance of 15cm from the films were muscled on the films. The

infra-red and ultraviolet spectra of the films were taken before irradiation and at regular intervals thereafter until the films embrittled.

For the infra-red spectra, the bands of interest are as discussed in Section 3.5 and the results obtained were treated similarly.

3.53 Embrittlement test

The films were tested for embrittlement by bending to an angle of 180° on both sides. The embrittlement indicates the time of breakdown in the microstructure of the system understudy.

3.6 METHOD OF MEASURING MECHANICAL PROPERTIES

The instrument used is the Instron Universal testing instrument, model 1026. The films used were of dimension 0.005 x .8 x 3cm. The magnification factor was five and the maximum load used was 2kg, except for PVC homopolymer for which maximum load of 5kg was used. The runs were made at zero hour and every 48 hours thereafter until there was a drop in the tensile strength of the sample. An average of three film strips was used for each blend for each run. From the traces on the chart paper, the strain and stress were computed. The plots of these and the modulus refer to original and graphs in Chapters 4 to 7. Tensile strengths and percentage elongation were also calculated from the above paper.

3.7 CRITERIA FOR DETERMINATION OF COMPATIBILITY

3.71 Specific density measurements

Using a $50cm^3$ specific gravity bottle, the specific gravity of each solution was measured. Making use of the densities of the homopolymers and specific gravities of the solvents, and assuming the additivity of volumes of the solutes and solvents, the thoretical specific gravity of each solution was calculated. For each set of blends, the practical and theoretical specific gravities were plotted against composition of the blend.

3.72 Determination of morphology

The light micrographs of the 80:20, 50:50 and 20:80 composition blends of each set of blends were taken using the light microscope model LEIT 2 ortholux 2 Pol B4 in the Geology Department. The micrographs were taken at a magnification of 30. This was to determine whether layers occured on the films and if crystallization occured following solvent evaporation.

3.8 VISCOSITY MEASUREMENTS

The viscosities of the degrading polymer films exposed for outdoor weathering were measured at regular time intervals. The plots of the intrinsic viscosities obtained against exposure time are as contained in the report.

CHAPTER 4

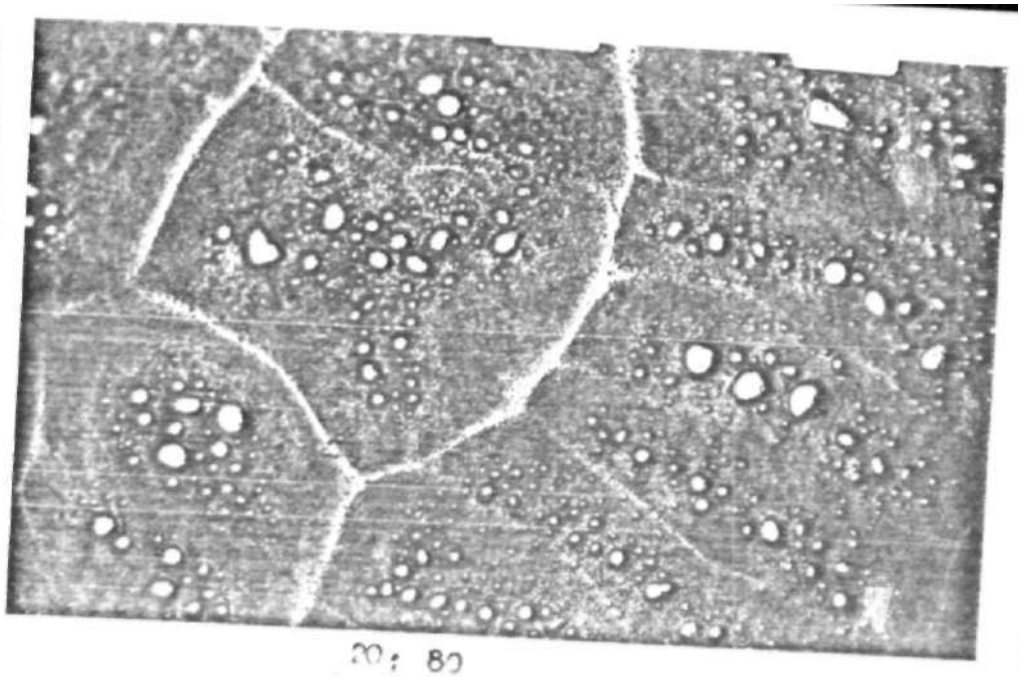
STUDIES ON PVA/PVC BLENDS

In this work studies were carried out on the influence of composition on density, morphology and mechanical properties. Changes in chemical properties were followed using the IR Spectra of the unmixed polymers and their blends on exposure to outdoor weathering, thermal oxidation and ultraviolet irradiation.

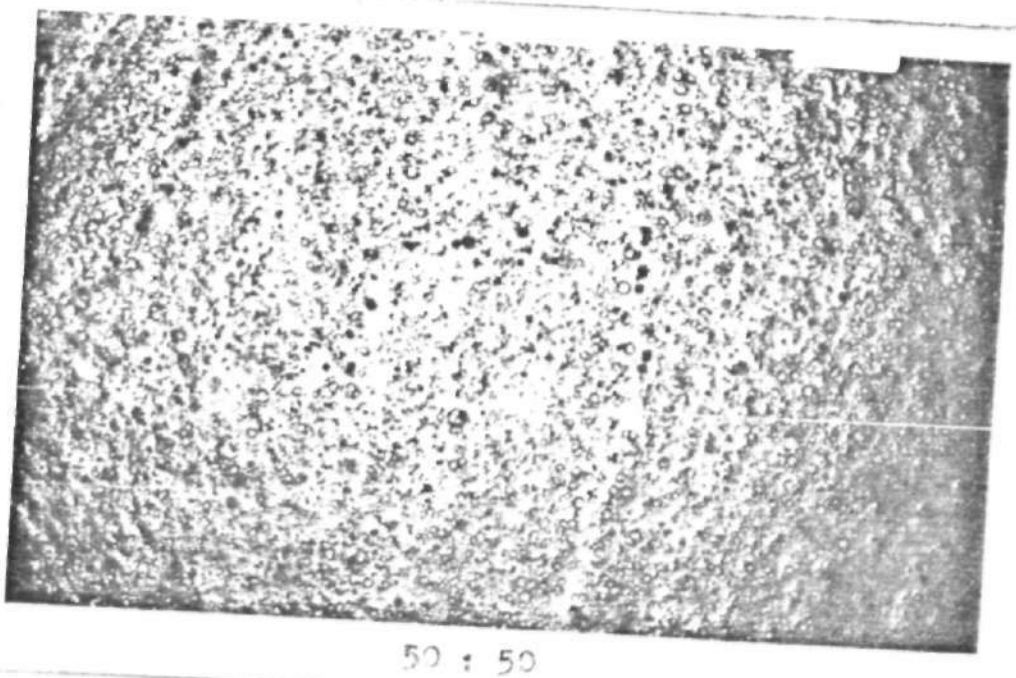
4.1 RESULTS AND DISCUSSION

4.11 Density measurements

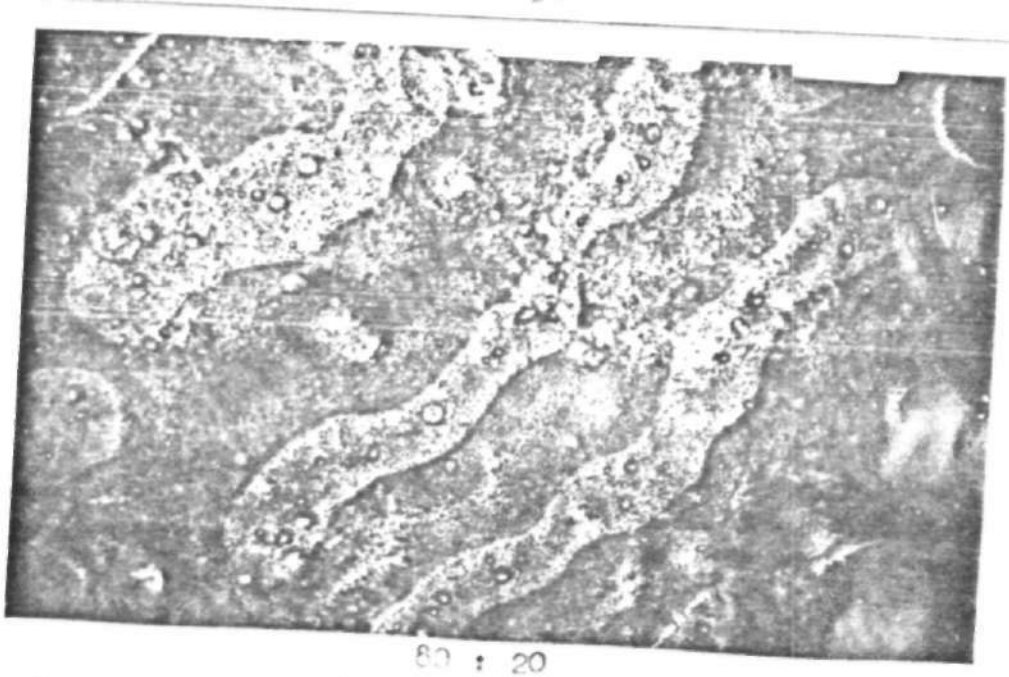
Figure 4.1 shows a plot of theoretical and measured densities of the homopolymers and their blends. The lower value of the measured density relative to the calculated one, assuming the additivity of volumes, suggests incompatibility of the polymers. This is so because increase in volume and hence a decrease in density occurs only when there is repulsion and little or no interaction between the dissimilar polymers. Increase in density occurs only where there is extensive interaction of the homopolymers, although this does not necessarily indicate the presence of a single phase (4, 5, 14).



20 : 80



50 : 50



80 : 20

Plate 1: Light micrographs of PVA:PVC blends; magnification x 50

4.12 Morphology

The light micrographs of the 20:80, 50:50 and 80:20 PVAc:PVC blends show phase separation between the homopolymers. Plate 1 shows the micrographs of the 20:80, 50:50 and 80:20 PVAc:PVC blends. Grassie, McLaren and McNeill (15) made similar observations and noted that the polymers were incompatible, with the result that even in film form the system is heterogenous. Interaction between the dissimilar molecules can therefore only be envisaged, if it were to occur at all, as happening at phase boundaries. In the micrographs the continuous phase is formed by the PVC component while the rubbery, crystalline PVAc is embedded in its matrix.

4.2 OUTDOOR WEATHERING

Figure 4.2 shows the stress-strain curves of freshly prepared PVA, PVC and PVA/PVC blends. The unmixed PVA is typically soft and tough. The blends have properties which are closer to those of the homopolymer forming the major component. Thus, it is observed that while 80:20 PVA:PVC blend is typically soft, it is tougher than the unmixed PVA. The 20:80 PVA:PVC blend, though hard, is softer than the unmixed PVC. On extension, the films showed some necking and the extent of necking decreased with increase in PVC in the blend.

Figure 4.3 shows the percentage elongation, tensile strength and tensile modulus of the unmixed polymers and their blends. The continuous lines show these properties for the freshly prepared films while the dotted lines show the

properties after 18 days outdoor weathering. At zero time, it is observed that tensile modulus and tensile strength decreased with increase in PVA concentration while percentage elongation increased remarkably in that direction. The trend is in conformity with the observed incompatibility of the polymers. After 18 days of outdoor weathering percentage elongation showed the same trend as observed for this property at zero time. Both tensile strength and modulus showed a minimum at 80:20 PVA:PVC. Generally, both modulus and tensile strength increased on exposure while elongation decreased. It is observed that percentage elongation shows a minimum at both 20:80 and 30:70 PVA:PVC compositions. These decreases in property may be ascribed to loss of phenomenon rather than to loss of property since the films showed necking and cold-drawing on extension.

Figure 4.4 shows the variation of tensile strength with exposure time for PVC, PVA and PVA:PVC blends. For each of the blends there was progressive increase in tensile strength until a maximum was reached followed by a decrease. Although from the plates, separation seemed to have occured, it would appear that improved tensile strength could be achieved if a little degradation sets in. In all cases maximum tensile strength was obtained after 10-12th day, thereafter the fall in property means uselessness of the blends. That a maximum was obtained with the blends would suggest that some degree of interaction might have taken place. It is observed that as the concentration of PVA in the blend decreased tensile strength increased and none of the blends had, at anytime during the study period, a tensile strength close to that of

PVC. It is noteworthy that the tensile strength of 50:50 PVA:PVC is much nearer that of PVA than intermediate between those of the homopolymers. For the 80:20 PVA:PVC blend, the tensile strength, although initially higher than that of 100% PVA, fell very much below the value for PVA immediately after reaching a maximum. Generally, the higher the PVA concentration in the blend the shorter the time to attain a maximum tensile strength and the lower the value at this point. Thus, there is a preferential composition when the property is maximum.

Figure 4.5 shows the dependence of tensile modulus of PVA, PVC and PVA:PVC blends on exposure time. It is observed that except for PVA, PVC and the 20:80 PVA:PVC blend for each of which there was a continuous rise in modulus until a maximum was attained, each of the rest of the blends first showed a drop in modulus, then a rise up to a maximum and finally a fall in modulus.

The initial fall in modulus suggests spontaneous loss of property immediately on exposure. The rise in modulus after an initial fall suggests an increase in rigidity which can result only if there is interaction which may be intermolecular or intramolecular. Although the 20:80 PVA:PVC blend showed a very sudden rise in modulus over and above that of even the unmixed PVC, it suddenly dropped, below those of unmixed PVC, 30:70, 50:50 PVA:PVC blends respectively. It is observed that the lower the PVA concentration in the blend the shorter the time it took the blend to attain its maximum modulus. This suggests that increase in rigidity

could have arisen through increase in carbon-carbon double bonds.

Talamini and Pezzin (19) observed a similar trend for the PVC on outdoor weathering. The same has been observed for PVA in this work.

It may be suggested that the initial increase in modulus was due to the formation of conjugated diene chains with, probably some degree of crosslinking. The sudden fall after reaching a maximum might be due to incidence of increased chain scission and a drop in the rate of polyene formation and crosslinking.

Figure 4.6 shows the dependence of percentage alongation of PVA, PVC and PVA/PVC blends on outdoor weathering time. The higher the percentage of PVA in the blend, the higher the percentage elongation. It is observed that only the 20:80, 80:20 PVA:PVC blends and the homopolymers, PVA and PVC, showed increases in percentage alongation, passed through a maximum and then showed a drop in percent elongation. For the 30:70, 50:50 and 70:30 PVA:PVC blends there was progressive decrease in property as soon as the films were exposed. The 30:70 PVA:PVC blend initially had a percent elongation greater than those of the 20:80 PVA:PVC blend and the unmixed PVC, but immediately on exposure the percentage elongation dropped, falling below those of 20:80 PVA:PVC blend and PVC. This shows that the higher the concentration of PVA in the blend the greater the loss of phenomenon on exposure.

It is observed that while for the 20:80 PVA:PVC blend a minimum was observed in both tensile strength and modulus

on exposure, the same blend showed an increase in percentage elongation on exposure.

In these films there was rapid discolouration on exposure. The presence of even 20% PVC in a blend with PVA produced marked lowering of mechanical properties of PVA. This effect was even more pronounced at higher concentrations, since in each case the 30:70, 50:50 and 70:30 PVA:PVC blends showed worse properties than the 20:80 and 80:20 PVA:PVC blends and the unmixed PVA and PVC. Hence PVA also causes loss in property of PVC even at very low concentrations. The presence of PVA neither inhibits nor retards the discolouration of the blends. There is, therefore, a general deterioration of tensile strength, modulus and percentage elongation of the two homopolymers on blending.

Table 1 and Figure 4.7 show the induction and embrittlement times and growth in indices of carbonyl absorption peaks respectively of PVA:PVC blends and the unmixed polymers on outdoor weathering. Only the unmixed PVA showed an induction period. The unmixed PVC and the blends started degrading soon on exposure. PVA and the 80:20 PVA:PVC showed continuous increase in carbonyl growth. For the 70:30 and 30:70 blends, there was retardation followed by a levelling out of the initial growth rate. This suggests that at these compositions stability to oxidation is attained on exposure. For the 80:20 and 20:80 PVA:PVC there was rapid growth, a gradual levelling out, a fast increase in growth rate and finally a levelling off. Looking at the shapes of these blend curves, it is possible to suggest a two stage degradation, one preceeding

the other, for the blends. With the degradation of PVC, probably starting before that of PVA.

Jamieson and McNeill (40) noted that degraded as a blend considerable interaction occurs between the degrading polymers (15, 17, 18, 29, 30), the distabilization of PVA being particularly evident.

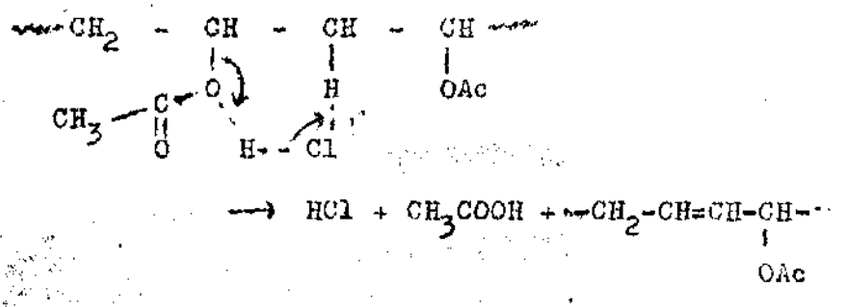
Table 1

Induction and embrittlement times of PVA, PVC and PVA:PVC blends exposed to outdoor weathering

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PVC	-	777
20:80 PVA:PVC	-	777
30:70 PVA:PVC	-	777
50:50 PVA:PVC	-	777
70:30 PVA:PVC	-	965
80:20 PVA:PVC	-	875
100% PVA	180	1440

The flattening out of the carbonyl indices particularly of 30:70 and 70:30 PVA:PVC blends may be due to the acceleration of deacetylation of the PVA component by the hydrogen chloride liberated during the dehydrochlorination of the PVC component of the blends. If this is so, the accelerating effect of hydrogen chloride on the deacetylation of PVA occurs via a mechanism similar to that proposed by Grassie and McNeill (35) for the catalytic effect of HCl on

the dehydrochlorination of PVC



Subsequent deacetylation should then be facilitated by allylic activation of acetate units by adjacent double bonds.

This continuous loss of CH_3COOH and formation of more carbonyl groups by oxidation may well account for the seemingly no-net growth in the indices of carbonyl peaks in these blends. The 50:50 PVA:PVC blend showed a trend which is not suggestive of rapid carbonyl growth and for this blend, the explanation above may equally hold.

Figure 4.8 shows the growth indices of hydroxyl peaks for PVA, PVC and the PVA:PVC blends exposed for outdoor weathering. The unmixed PVA did not show any changes in hydroxyl absorptions. It is observed that the growth rate of hydroxyl indices decreased with increase in PVA content of the blend. For the unmixed PVC there was a steady decrease until a minimum is reached followed by a rise. The initial drop may be accounted for by the rapid oxidation of the hydroxyl to carbonyl groups. In each case, either there was an initial increase up to a maximum as for 80:20 PVA:PVC or small increase and a levelling off as for 30:70, 20:80 and 50:50 PVA:PVC or a continuous decrease, as for 70:30 PVA:PVC.

Figure 4.9 shows the dependence of intrinsic viscosities of the unmixed PVA and PVC on outdoor exposure time. The PVC showed an initial drop in molecular weight followed by a period of constant molecular weight. The initial loss may be attributed to the loss of hydrogen chloride due to the dehydrochlorination of PVC. For PVA a rapid decrease in molecular weight occured early on exposure, and no increase was recorded. This therefore suggests that when both polymers are degraded separately by outdoor weathering crosslinking reactions do not take place. The polymers undergo dehydrochlorination and deacetylation respectively.

$$\sim CHCl\text{-}CH_2\text{-}CH\ Cl\text{-}CH_2\sim \longrightarrow \sim CHCl\text{-}\dot{C}H\text{-}CHCl\text{-}CH_2\sim \ I + H\cdot$$

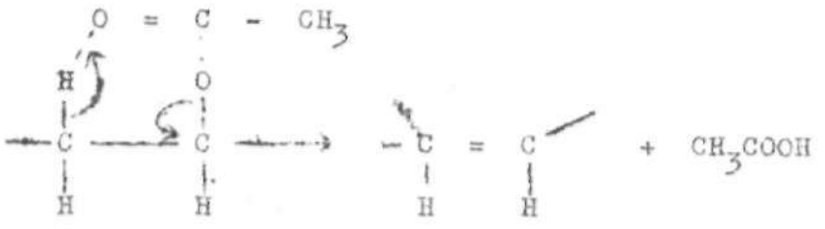
$$\sim CHCl\text{-}\dot{C}H\text{-}CHCl\text{-}CH_2\sim \longrightarrow \sim CHCl\text{-}CH{=}CH\text{-}CH_2\sim + \cdot Cl$$

$$\sim CHCl\text{-}CH{=}CH\text{-}CH_2\sim \longrightarrow \sim CHCl\text{-}CH{=}CH\text{-}\dot{C}H\sim + HCl$$

The propagation stage consists of the rearrangement of the PVC macroradical (I) to give a carbon-carbon double bond and a free chlorine atom which abstracts the nearest hydrogen atom, normally adjacent to the methylene group. The macroradical (I) could also capture an oxygen molecule to form a peroxy radical. The reaction could be autocatalysed, but the extent to which autocatalysis is envisaged in the films must be low, since the hydrogen chloride generated cannot be in intimate association with the polymer.

For PVA, a similar mechanism is tenable, with deacetylayion being facilitated by a six-membered ring interaction existing between the carbonyl groups and β-hydrogen atom of the alcohol residue (48).

Reiner (48) explained the tendency for adjacent units in PVA to react to produce conjugation in terms



of the electron attracting properties of carbon-carbon double bond activating the methylene groups.

Grassie and McNeill (35, 36), Braun and Bender (39) and Jamieson and McNeill (40) worked on the blends of PVA:PVC and observed that, degraded as blends, considerable interaction occured between the degrading polymers, the destabilization of PVA being particularly evident. They noted that PVA also destablized PVC, this being less effective than the effect of PVC on PVA.

Grassie, McLaren and McNeill (35, 36) observed, during their studies on the copolymers of PVA and PVC, that minimum stability occured at about 30 to 40% vinyl acetate monomer concentration in the copolymers and observed that PVA destablized PVC and vice versa, the copolymers being considerably less stable than PVC, which in turn is less stable than PVA.

These results of the investigations on the blends and copolymers of PVA and PVC are consistent with the results of the present studies on the PVA:PVC blends.

4.3 THERMAL OXIDATIVE DEGRADATION

For PVC, PVA and all the blends there was progressive development of colour from yellow to very dark brown, the intensity of colour development being most marked for the unmixed PVC.

Figure 4.10 shows the dependence of modulus, tensile strength and percentage elongation of PVC, 20:80, 50:50 and 80:20 PVA:PVC blends on heating time. In the modulus and tensile strength all the blends showed similar trend; an initial increase up to a maximum at the 24th hour followed by a gradual decrease while in percentage elongation all showed rapid decrease immediately on heating. In modulus and tensile strength, PVC showed an initial increase, a fall and rose to a maximum on the third day while in modulus it showed the reverse trend. For the blends the fall in percentage elongation was most marked for the 80:20 PVA:PVC and decreased with decrease in PVA concentration in the blend.

The pattern of change in the modulus of PVC is in agreement with the observations of Kwei and Kwei (32, 33). The marked increase in tensile strength with increased heating time suggests that although the polymer degrades via chain scission and crosslinking, the rate of crosslinking outstrips the rate of chain scission on heating, with the rate of crosslinking increasing with heating time up to a point when maximum gelation must have taken place and then decreased, as observed by Reiner (48).

For the blends, the observed rapid fall in percentage

elongation, although suggesting increase in rigidity indicates the destabilizing effect of PVA on PVC.

Figure 4.11 shows the indices of carbonyl absorption peaks for the unmixed PVA, PVC and PVA:PVC blends. Table 2 shows the induction and embrittlement times of PVA, PVC and their blends heated in the air oven.

Table 2

Induction and embrittlement times for carbonyl absorption of PVA, PVC and PVA:PVC blends heated in the air oven

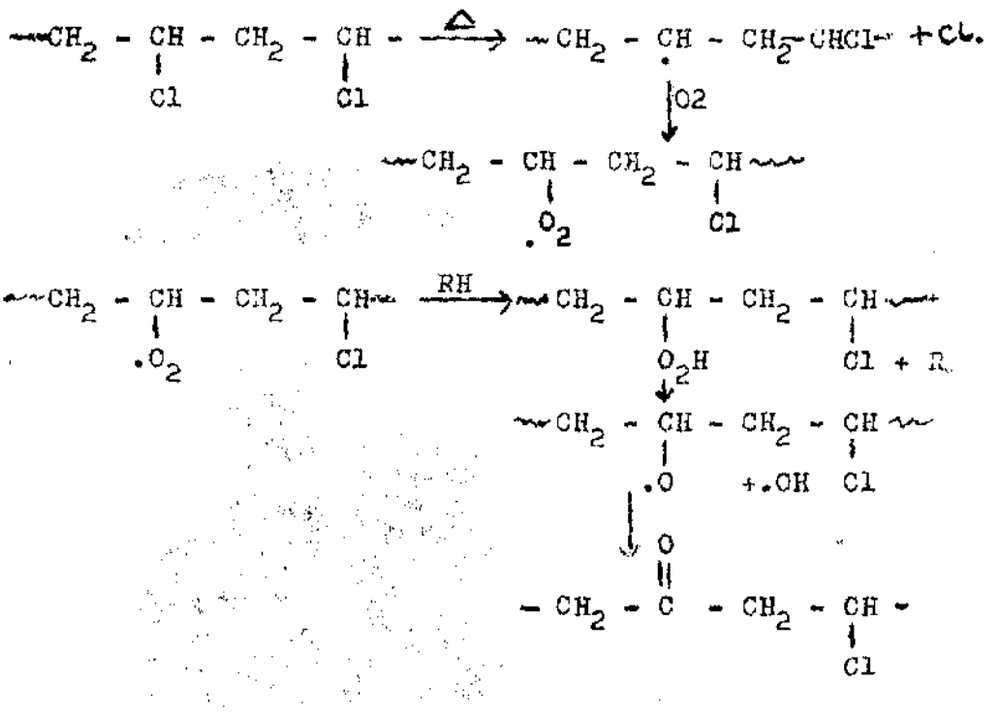
Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PVC	-	456
20:80 PVA:PVC	-	456
30:70 PVA:PVC	-	456
50:50 PVA:PVC	-	348
70:30 PVA:PVC	-	348
80:20 PVA:PVC	-	348
100% PVA	12	29

None of the blends and PVC showed an induction period. For the unmixed PVA, there was a rapid decrease in indices of carbonyl growth after the induction period. The rapid rate of degradation of PVA on heating occurs by decomposition via deacetylation (48). Once the initial deacetylation has taken place, successive units decompose at fast rate, with the rate increasing with reaction time. This suggests that

the deacetylation of PVA is autocatalysed. It is observed that for the 80:20, 70:30 and 50:50 PVA:PVC blends, there was an initial decrease in carbonyl index followed by a gradual increase. The initial decrease may be explained in terms of the decomposition of the PVA component of the blend. It is observed that the embrittlement time for the blends increased with increase in the PVC component.

Figure 4.12 shows the indices of hydroxyl absorption peaks for PVA, PVC and PVA/PVC blends on oven heating. None of them showed an induction period and embrittlement time in each case is as for the carbonyl absorption. The blends 30:70 and 50:50 showed almost the same indices of hydroxyl absorption. The curves of 20:80 and 30:70 PVA:PVC blends are observed to level off in each case after 330 hours. This levelling off suggests the stabilization of PVA by PVC, since at about this time most of the blends containing higher concentrations of PVA had already embrittled. For PVC, it is observed that the carbonyl indices of growth is steeper than for the hydroxyl. This could be accounted for by the oxidation of the hydroxyl groups into carbonyl units. Winkler (20) suggested that thermal oxidative degradation resulted in the formation of alkyl peroxy radicals and, possibly crosslinks and chain scission. The slow rate of hydroxyl indices growth could be accounted for in terms of oxidation to the carbonyl group.

The following mechanism is therefore proposed for the thermal oxidative degradation of PVC



The formation of the alkyl peroxide and ketone accounts for the increase observed for the carbonyl and hydroxyl groups.

4.4 ULTRAVIOLET DEGRADATION

Figure 4.13 shows the dependence of indices of carbonyl absorption peaks of PVA, PVC and PVA/PVC blends on ultraviolet irradiation time and Table 3 shows the induction and embrittlement times for the carbonyl absorptions of PVA, PVC and PVA/PVC blends.

Table 3

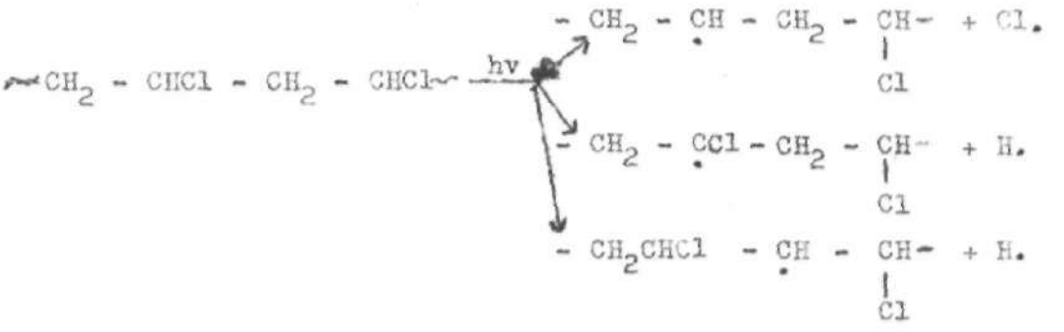
Induction and embrittlement times for carbonyl absorptions of PVA, PVC and PVA/PVC blends on ultraviolet irradiation

Polymer/blend	Induction times (hrs)	Embrittlement times (hrs)
100% PVC	250	2000
20:80 PVA:PVC	200	1500
30:70 PVA:PVC	600	2000
50:50 PVA:PVC	350	1500
70:30 PVA:PVC	400	1500
80:20 PVA:PVC	450	1500
100% PVA	1000	2826

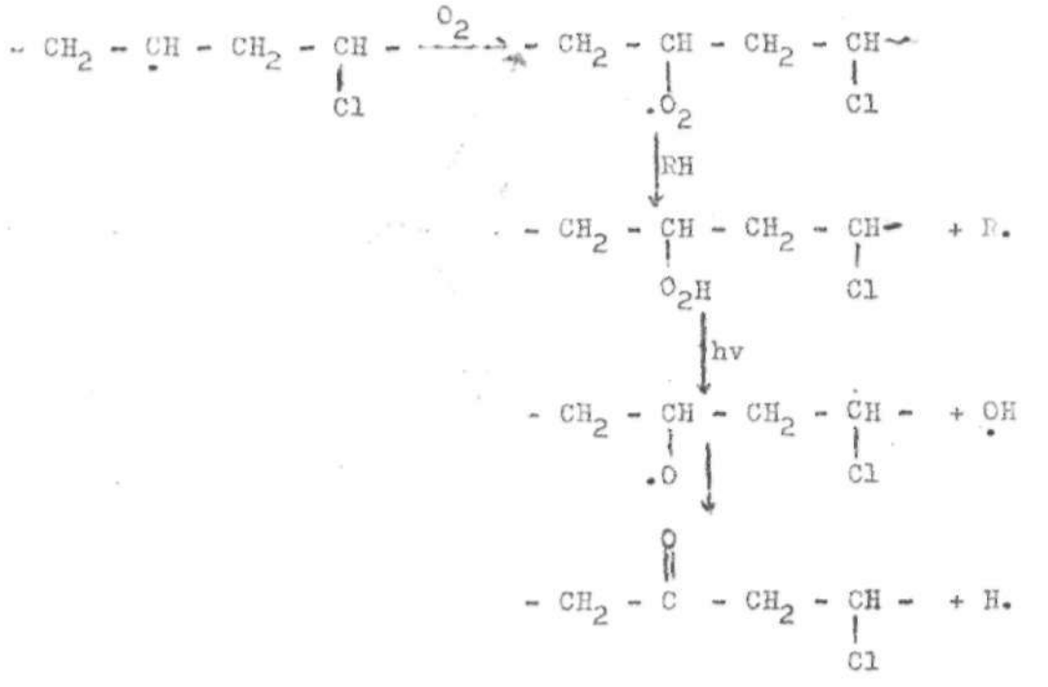
Both the Table and the Figure show PVA to be very stable towards ultraviolet degradation while PVC is very vulnerable to ultraviolet degradation. This may be due to the more labile nature of the chlorine atom relative to the bulky ($CH_3COO.$) group, despite the non-selective nature of ultraviolet degradation. The unmixed PVC is observed to have shown the fastest growth in indices of carbonyl absorption peaks. It is observed generally that the higher the PVC in the blend the steeper the curve of carbonyl indices, except in the case of the 80:20 PVA:PVC blend. The later case may be because of the ability of the chloride radical formed from the photo-degradation of PVC to abstract a hydrogen atom from the PVA chain, thereby creating sites for oxygen attack and hence formation of carbonyl groups. In this case the PVA is being destablized by even low concentration of

PVC in the blend. This suggests interaction between the homopolymers in the blends.

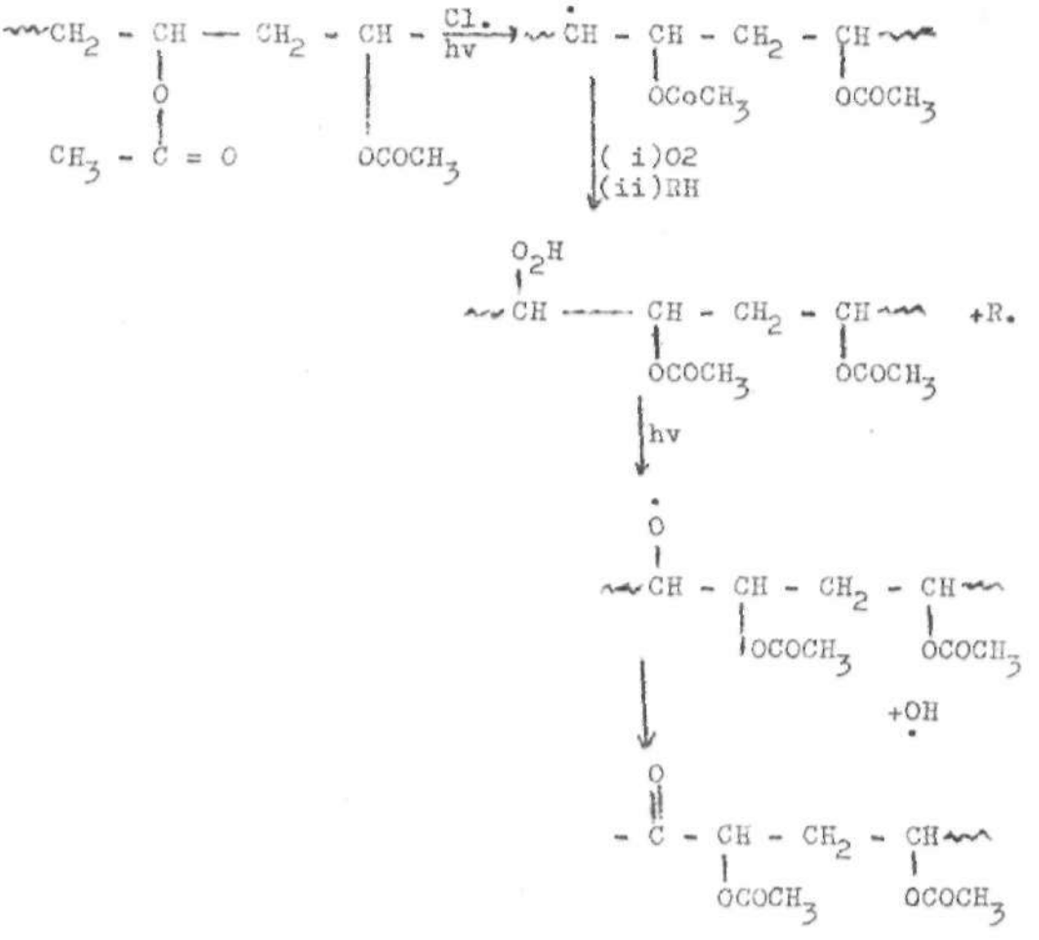
The following mechanisms are proposed for the photodegradation of PVA, PVC and for the interaction between PVA and PVC during photodegradation.



These macroradicals so formed, could give rise to crosslinks (31), the amount of gel decreasing with irradiation due to the formation of more soluble materials on prolonged irradiation. The radicals could react with oxygen.



The chloride radical from the photodegradation of PVC could abstract a hydrogen atom from PVA. The abstraction of the acetate radical may not lead to decrease in carbonyl index, since the temperature of irradiation is low for acetic acid volatilization



4.5 CONCLUSION

PVC destabilizes PVA and PVA destabilizes PVC, the former being more pronounced even at very low concentrations of PVC in the blends. None of the blends exhibits properties superior to those of the homopolymers. It was observed that the presence of PVA neither inhibited nor reduced discolouration of the blend films. The observed improved mechanical

properties on the degradation of the blends may be due to improved interaction between the polymers. Studies on PVA/PVC blends should, as a result of the observed general deterioration of properties, be viewed as purely an academic exercise and as of no relevance to industrial applications.

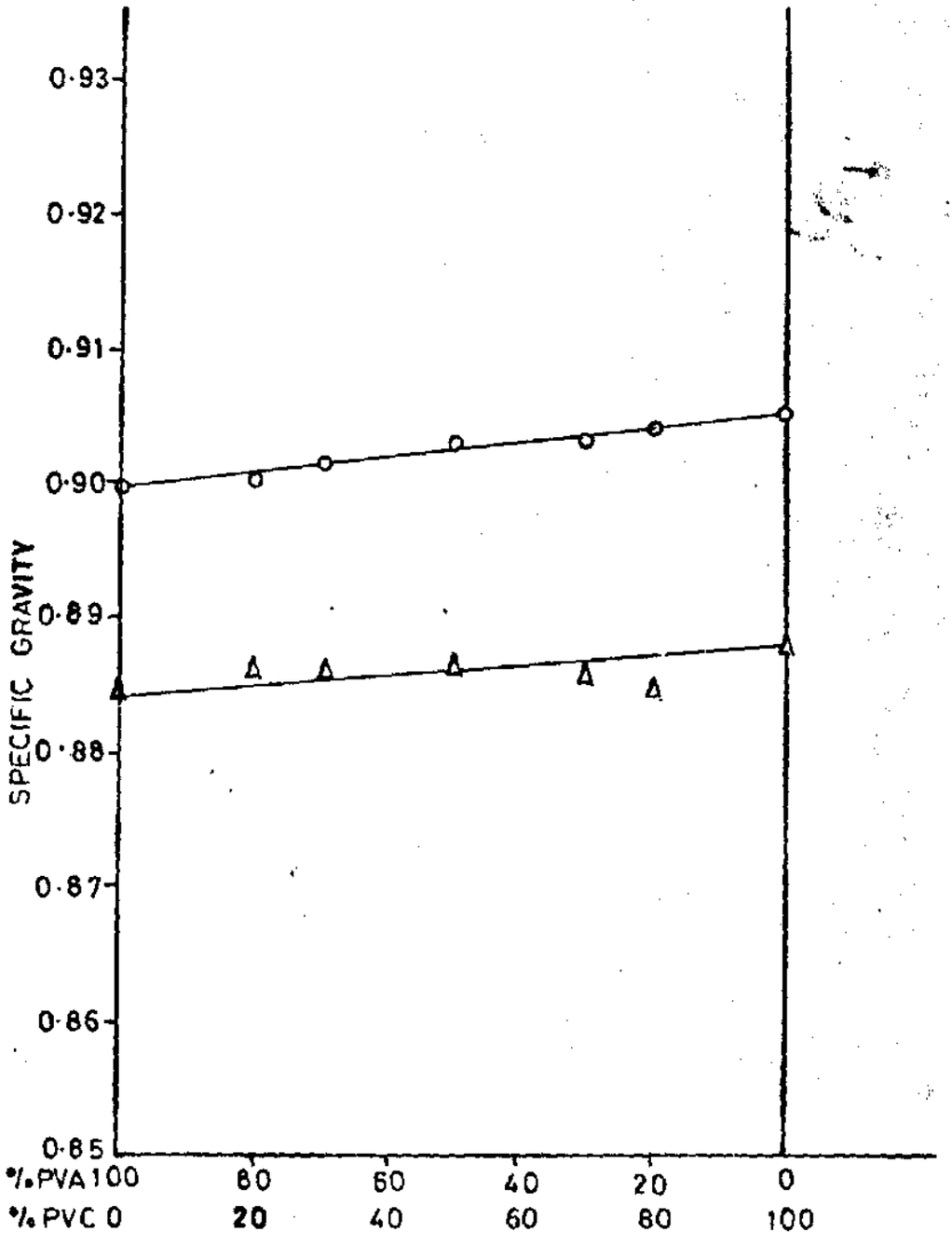


FIG. 4·1 VARIATION OF SPECIFIC GRAVITY WITH % COMPOSITION OF PVA/PVC BLENDS

o Theoreticol Values

Δ Practicol Values

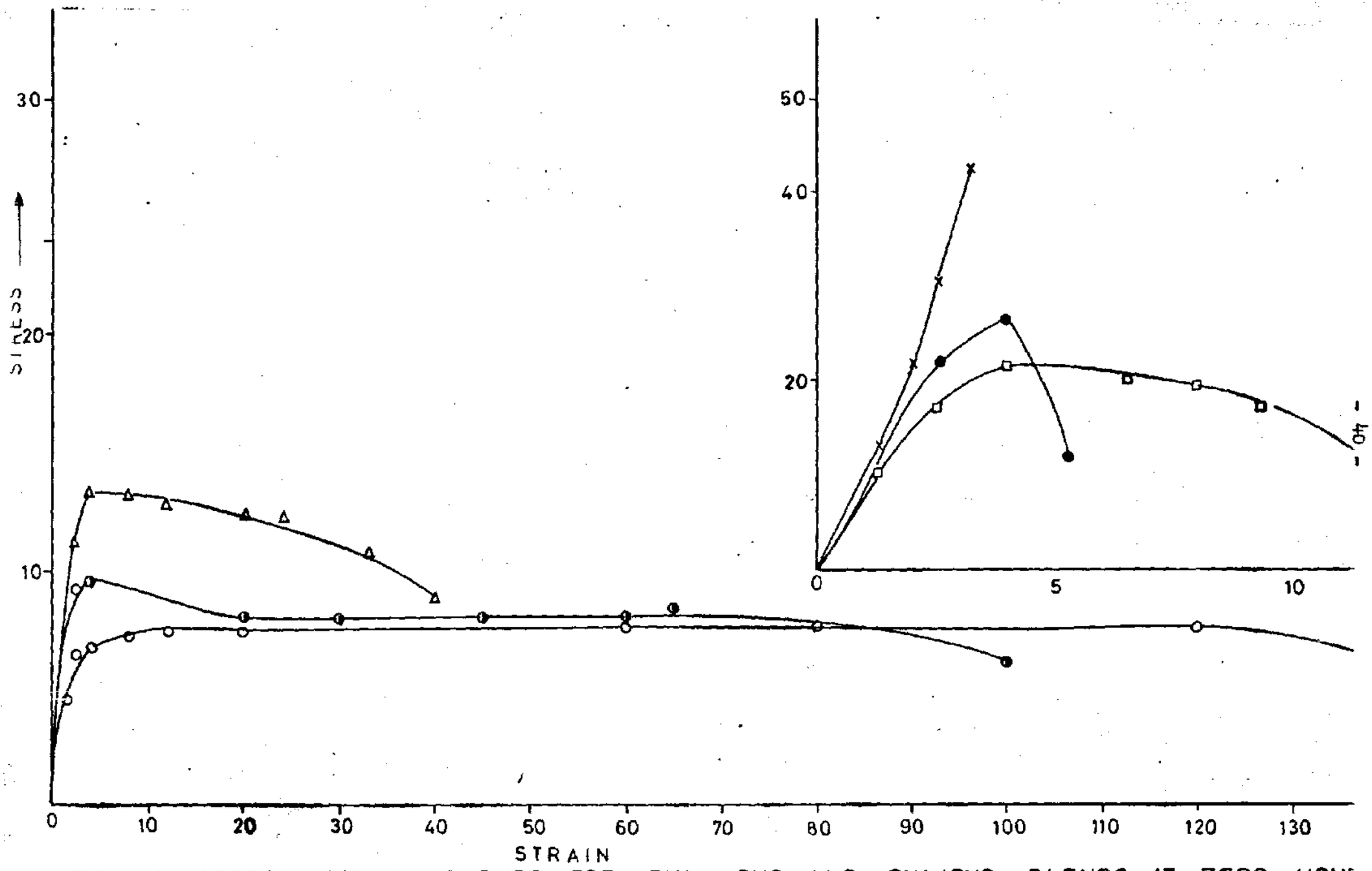


FIG. 4·2 STRESS STRAIN CURVES FOR PVA PVC AND PVA/PVC BLENDS AT ZERO HOUI

○ 80:20PVA:PVC ◑ 70:30PVA:PVC △ 50:50PVA:PVC □ 30:70PVA:PVC ● 20:PVA:PVC × 100% PVC

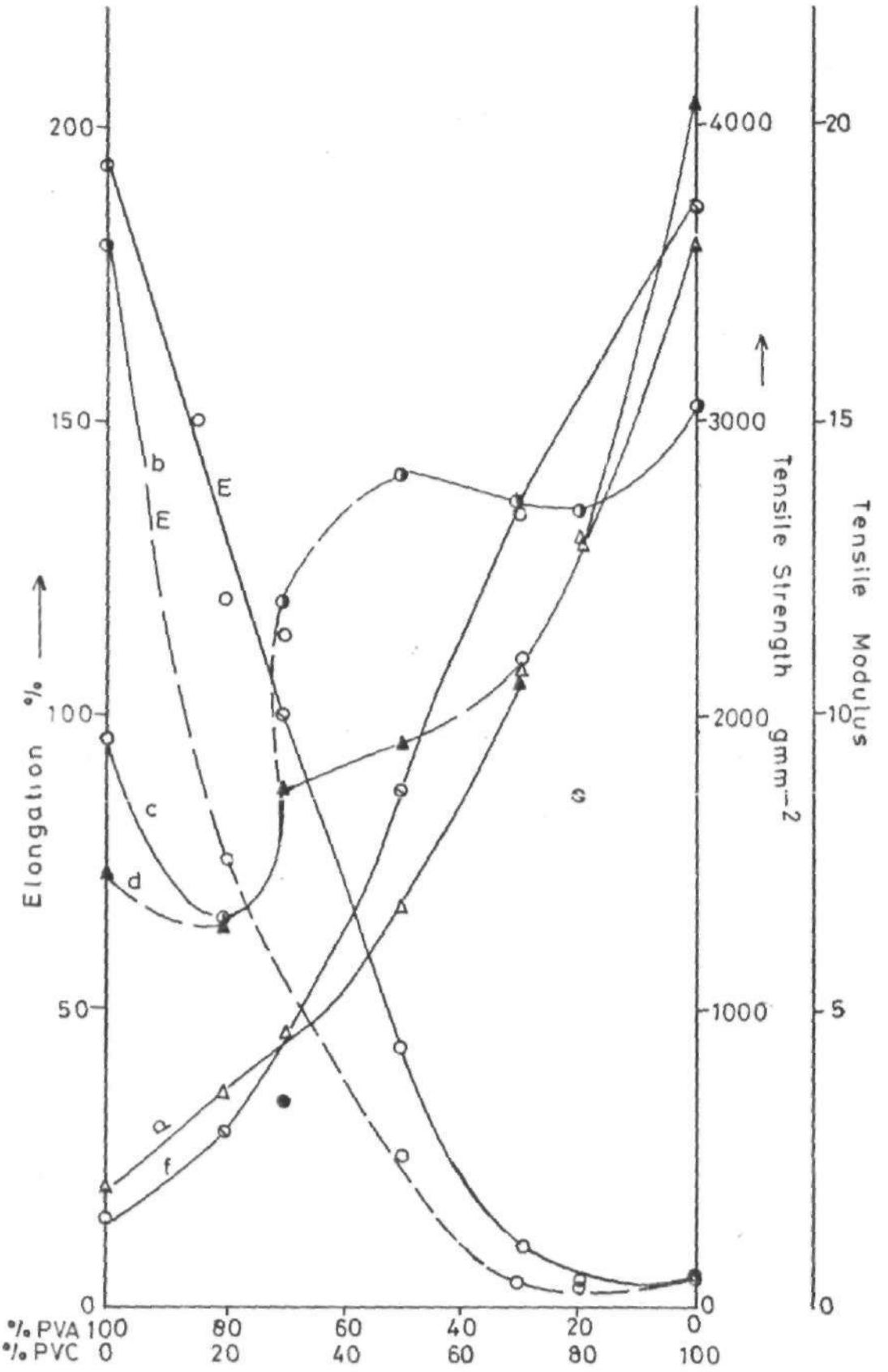


FIG. 4·3 DEPENDENCE OF MECHANICAL PROPERTIES ON COMPOSITION OF PVA/PVC BLENDS AT ZERO AND AFTER 18 DAYS OUTDOOR WEATHERING

○ % ELONGATION AT ZERO HOUR ● % ELONGATION AT 18 DAYS
△ TENSILE STRENGTH AT ZERO HR. ▲ TENSILE STRENGTH AT 18 DAYS
⊘ TENSILE MODULUS AT ZERO HOUR ◑ TENSILE MODULUS AT 18 DAYS

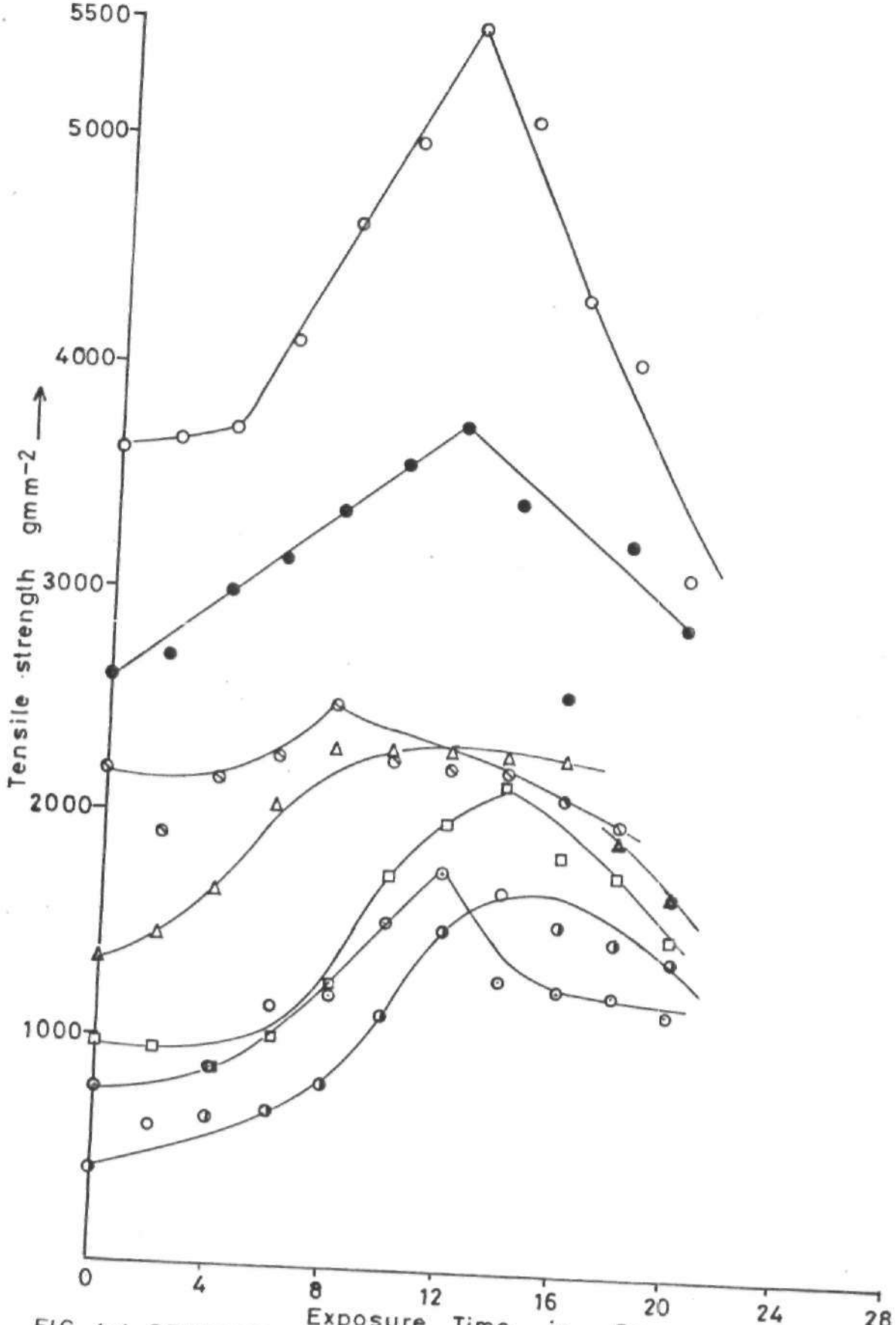


FIG. 4·4 DEPENDENCE OF ULTIMATE TENSILE STRENGTH ON EXPOSURE TIME

○ 100% PVC ◑ 100% PVA ⊙ 80:20 PVA:PVC □ 70:30 PVA:PVC
△ 50:50 PVA:PVC ⊘ 30:70 PVA:PVC ● 20:80 PVA:PVC

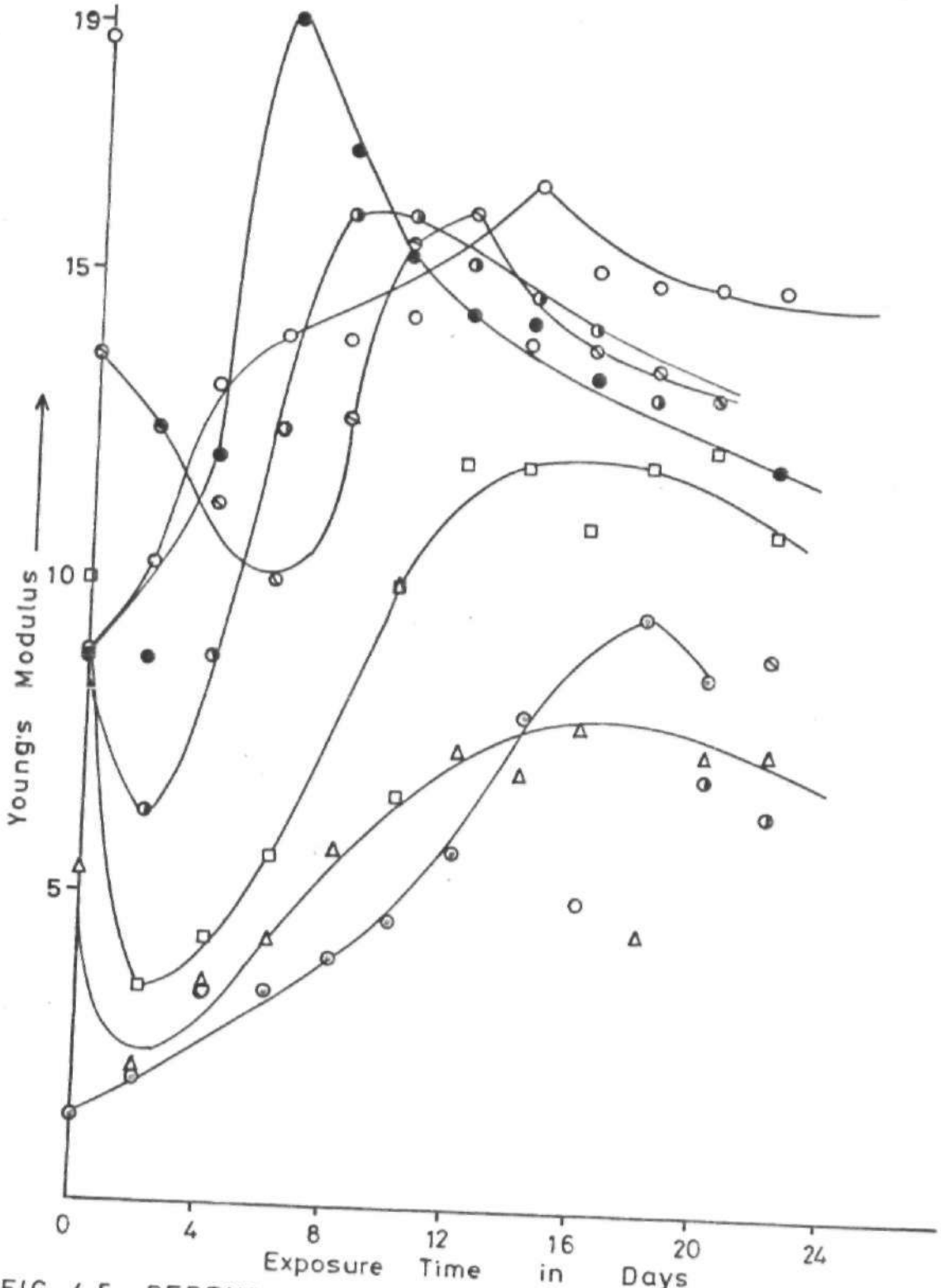


FIG. 4·5 DEPENDENCE OF YOUNG'S MODULUS ON EPOSURE TIME. ● 100% PVC ◑ 50:50PVA:PVC △ 80:20PVA:PVC ◔ 30:70PVA:PVC □ 70:30PVA:PVC ⊙ 100%PVA ○ 20:80PVA:PVC

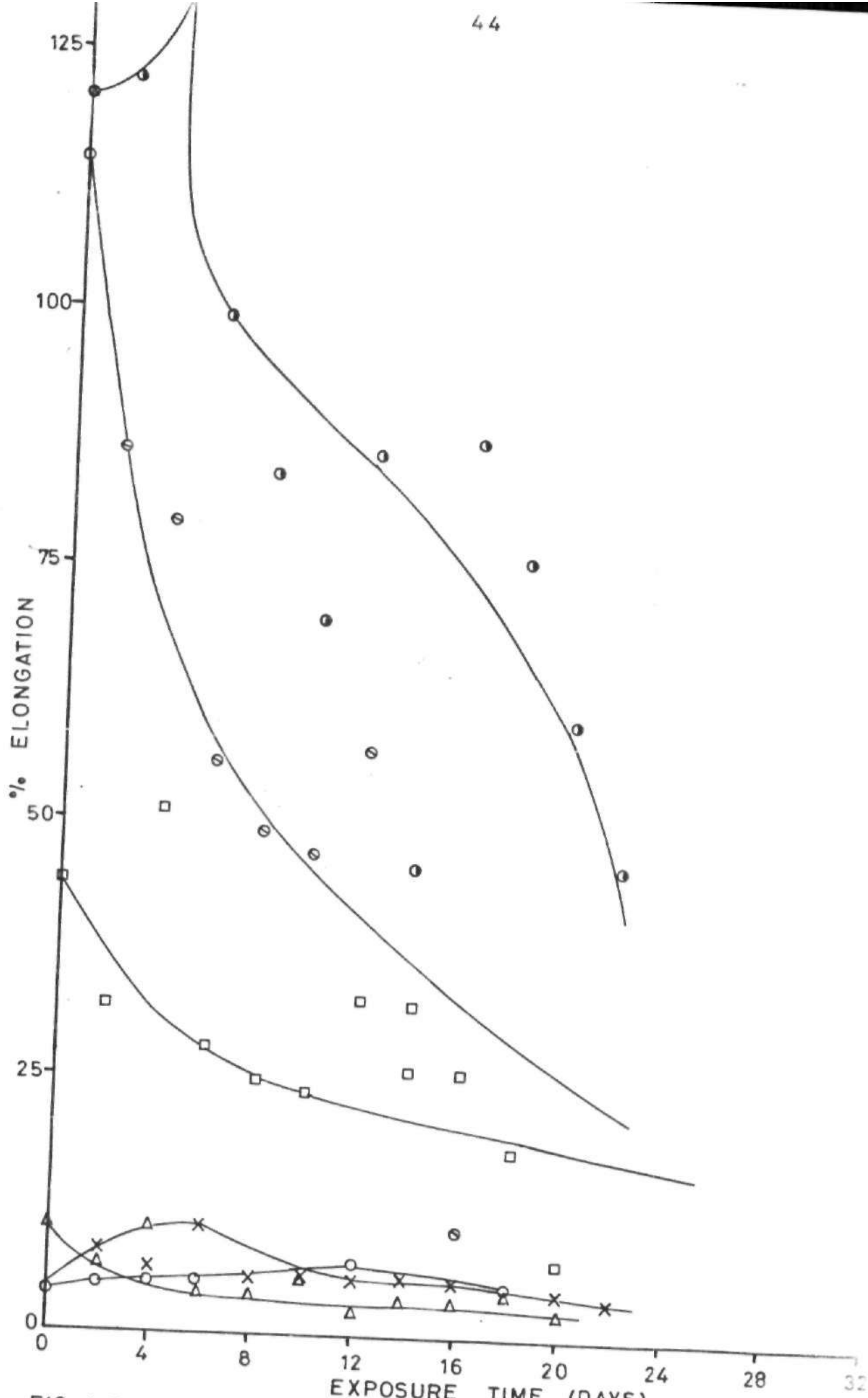


FIG. 4·6 DEPENDENCE OF % ELONGATION OF PVA/PVC BLENDS ON EXPOSURE TIME ○ 100% PVC ◑ 80:20 PVA:PVC ⊘ 70:30 PVA:PVC □ 50:50 PVA:PVC △ 30:70 PVA:PVC × 20:80 PVA:PVC

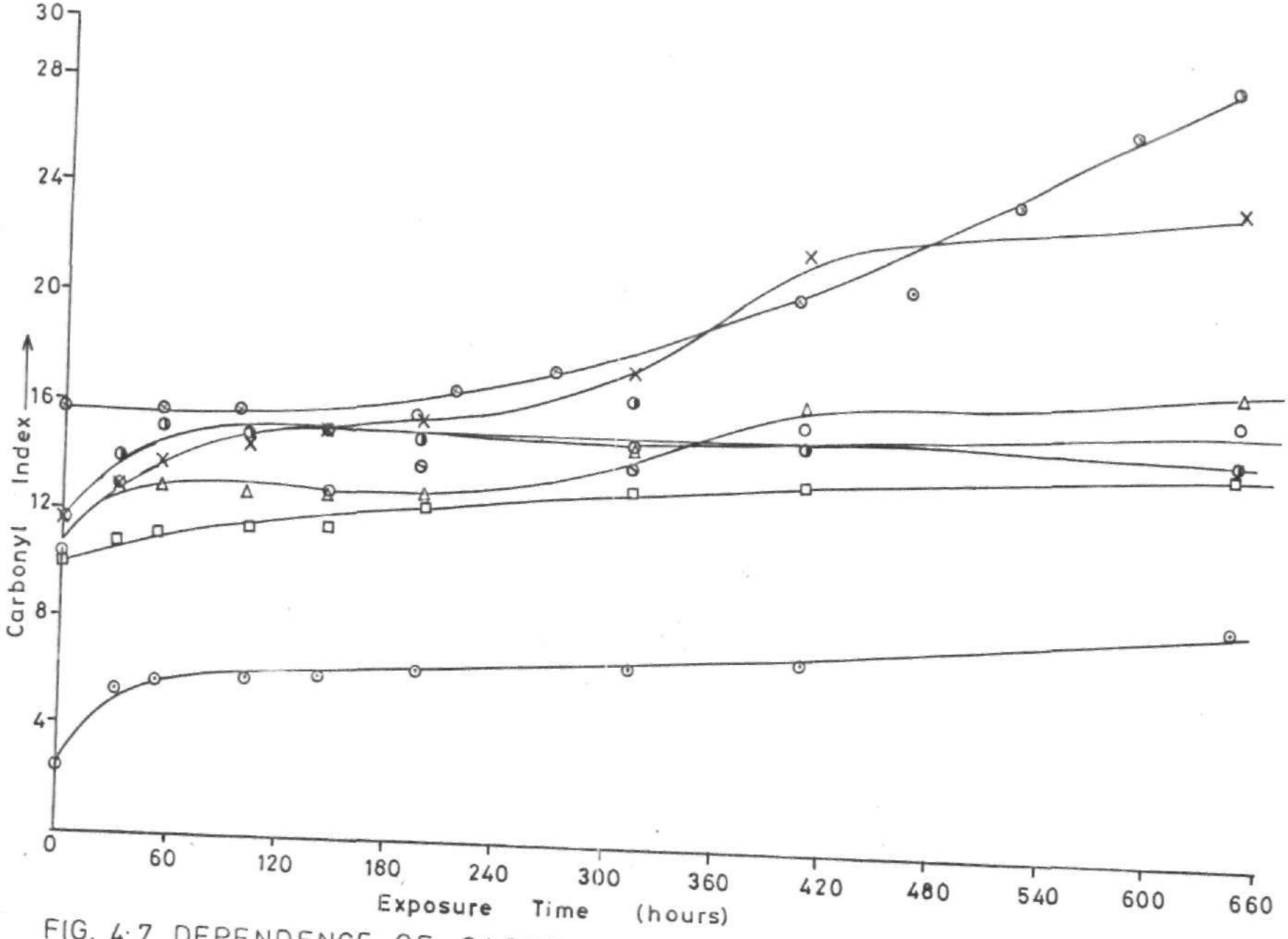


FIG. 4·7 DEPENDENCE OF CARBONYL INDEX ON EXPOSURE TIME (OUTDOOR) FOR PVA/PVC BLENDS

⊙ 100% PVC ⊗ 100% PVA △ 20:80 PVA:PVC ◑ 30:70 PVA:PVC □ 50:50 PVA:PVC
⊘ 70:30 PVA:PVC × 80:20 PVA:PVC

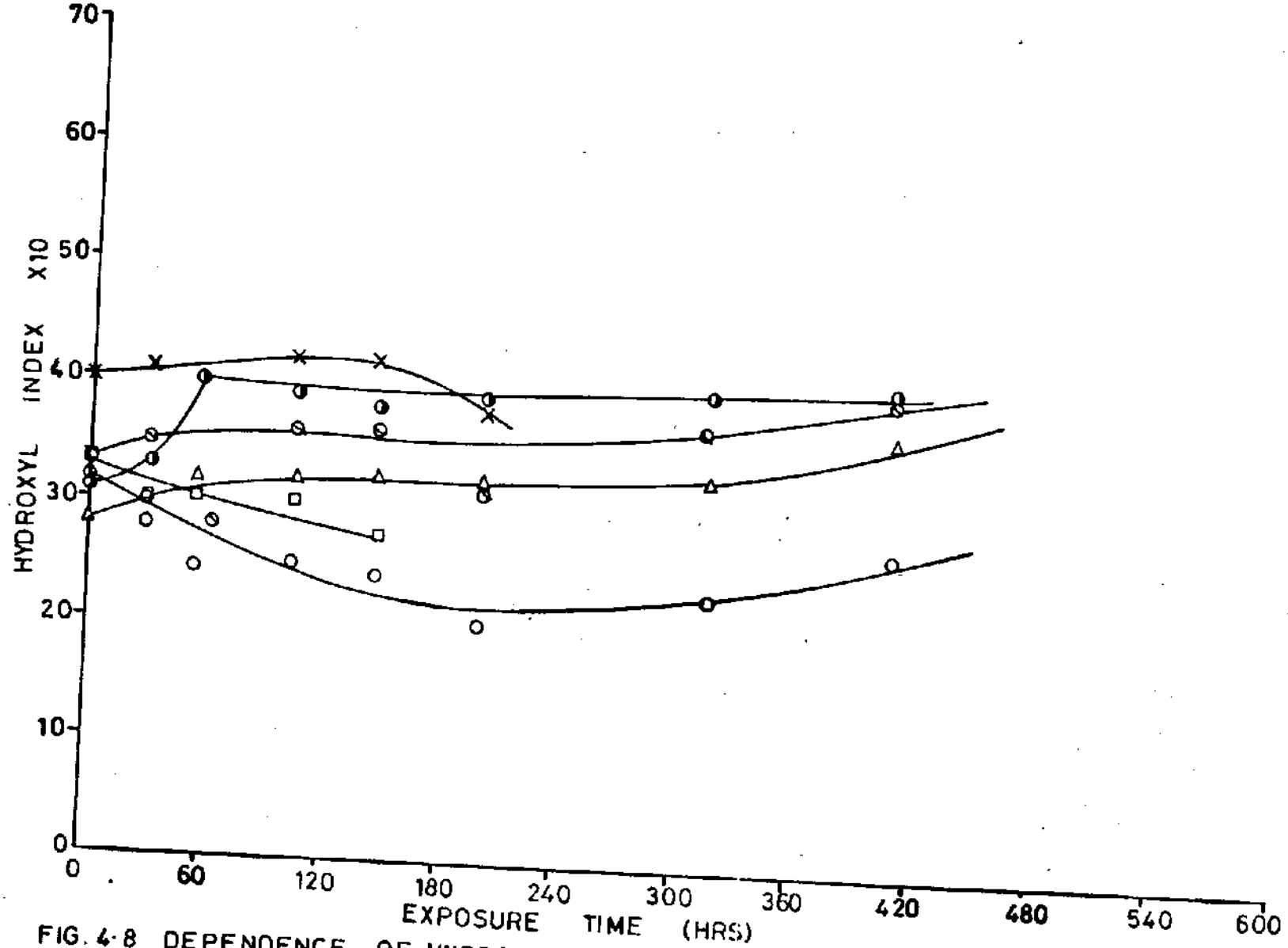


FIG. 4·8 DEPENDENCE OF HYDROXYL INDEX ON OUTDOOR EXPOSURE TIME FOR PVA/PVC BLENDS

○ 100 % PVC ⊗ 20:80 PVA:PVC ◑ 30:70 PVA:PVC △ 50:50 PVA:PVC

□ 70:30 PVA:PVC × 80:20 PVA:PVC

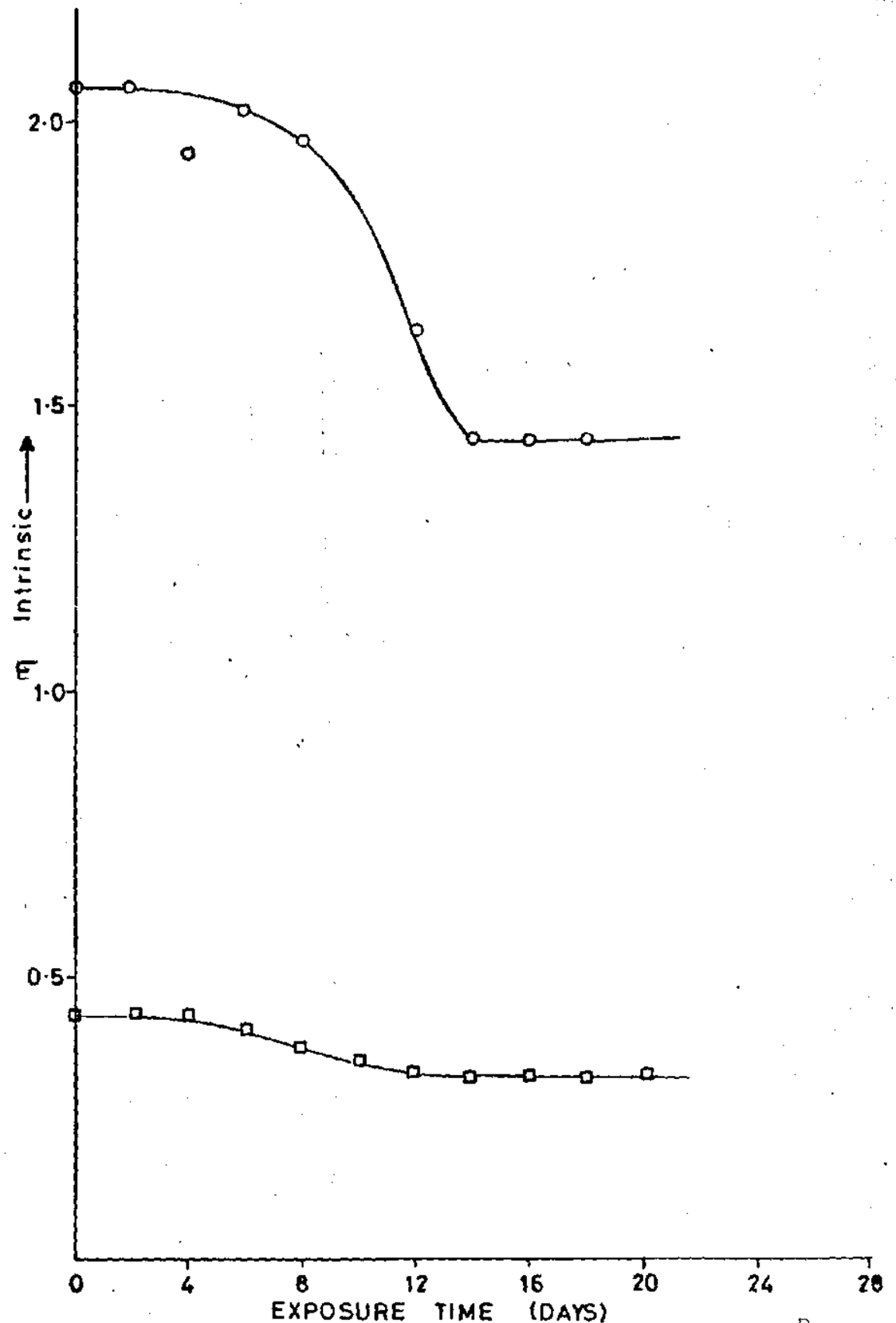


FIG. 4·9 DEPENDENCE OF INTRINSIC VISCOSITY ON EXPOSURE TIME FOR UNMIXED PVA & UNMIXED PVC ○ PVA, □ PVC

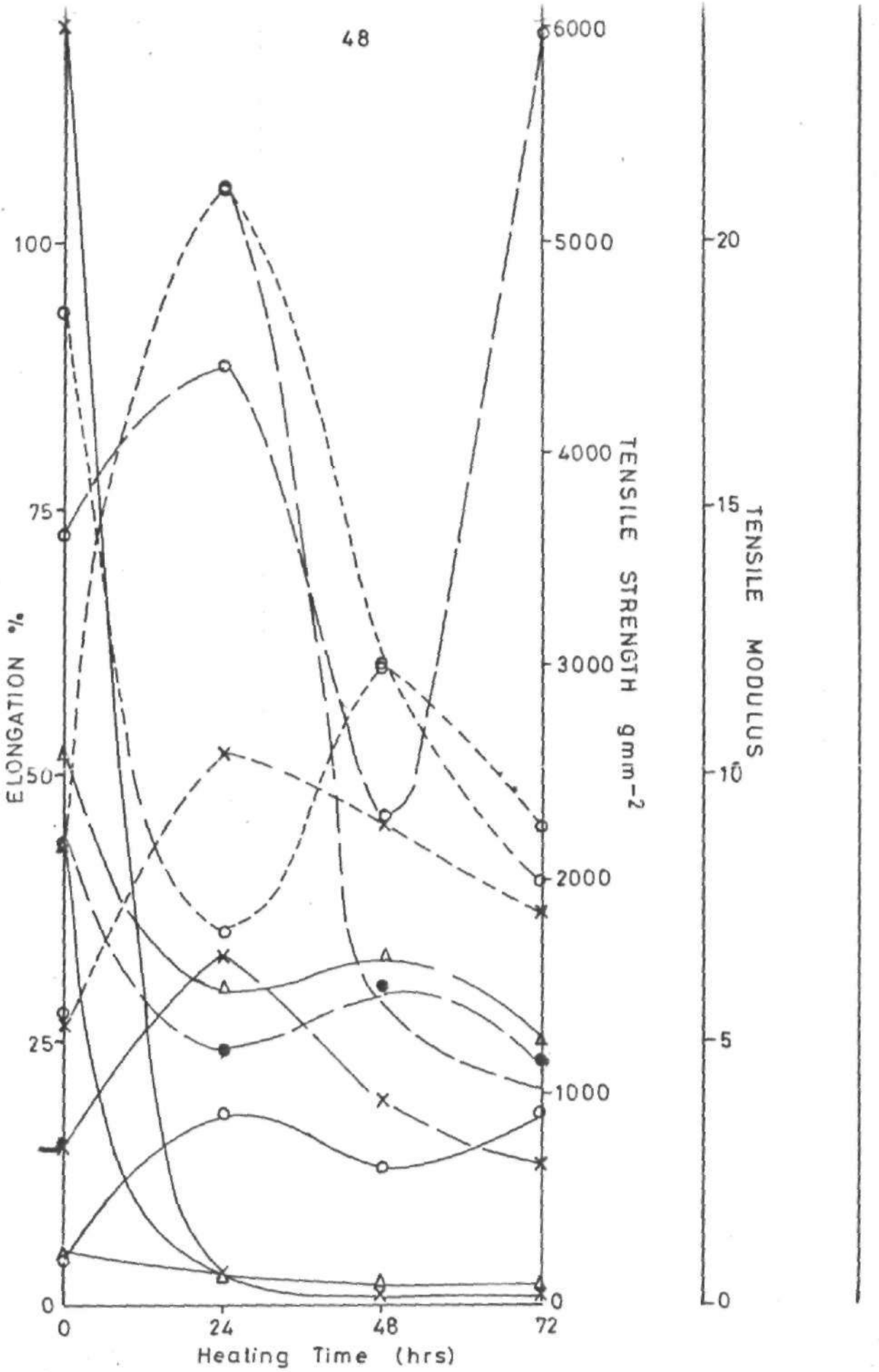


FIG. 4:10 DEPENDENCE OF MECHANICAL PROPERTIES ON % COMPOSITION AND HEATING TIME FOR PVC: PVA= PVA BLENDS

○ 100% PVC
△ 20:80 PVA:PVC
● 50:50 PVA PVC
× 80:20 PVA:PVC

% ELONGATION ————————
TENSILE STRENGTH — — — —
MODULUS - - - - - -

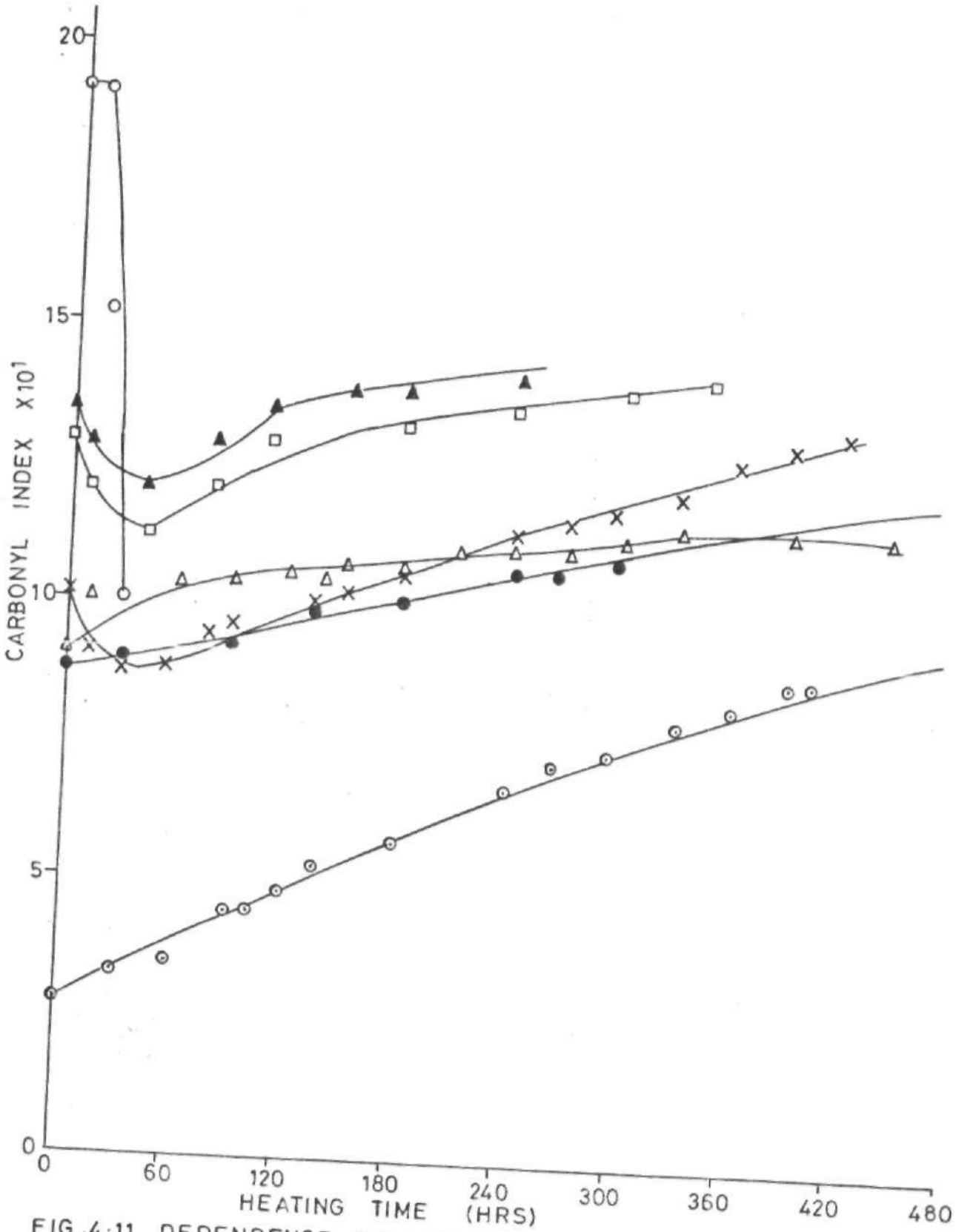


FIG. 4·11 DEPENDENCE OF CARBONYL INDEX ON OVEN HEATING FOR PVA PVC AND PVA/PVC BLENDS

○ 100% PVA ⊙ 100% PVC ● 20:80 PVA:PVC △ 30:70 PVA:PVC
× 50:50 PVA:PV □ 70:30 PVA:PVC ▲ 80:20 PVA:PVC

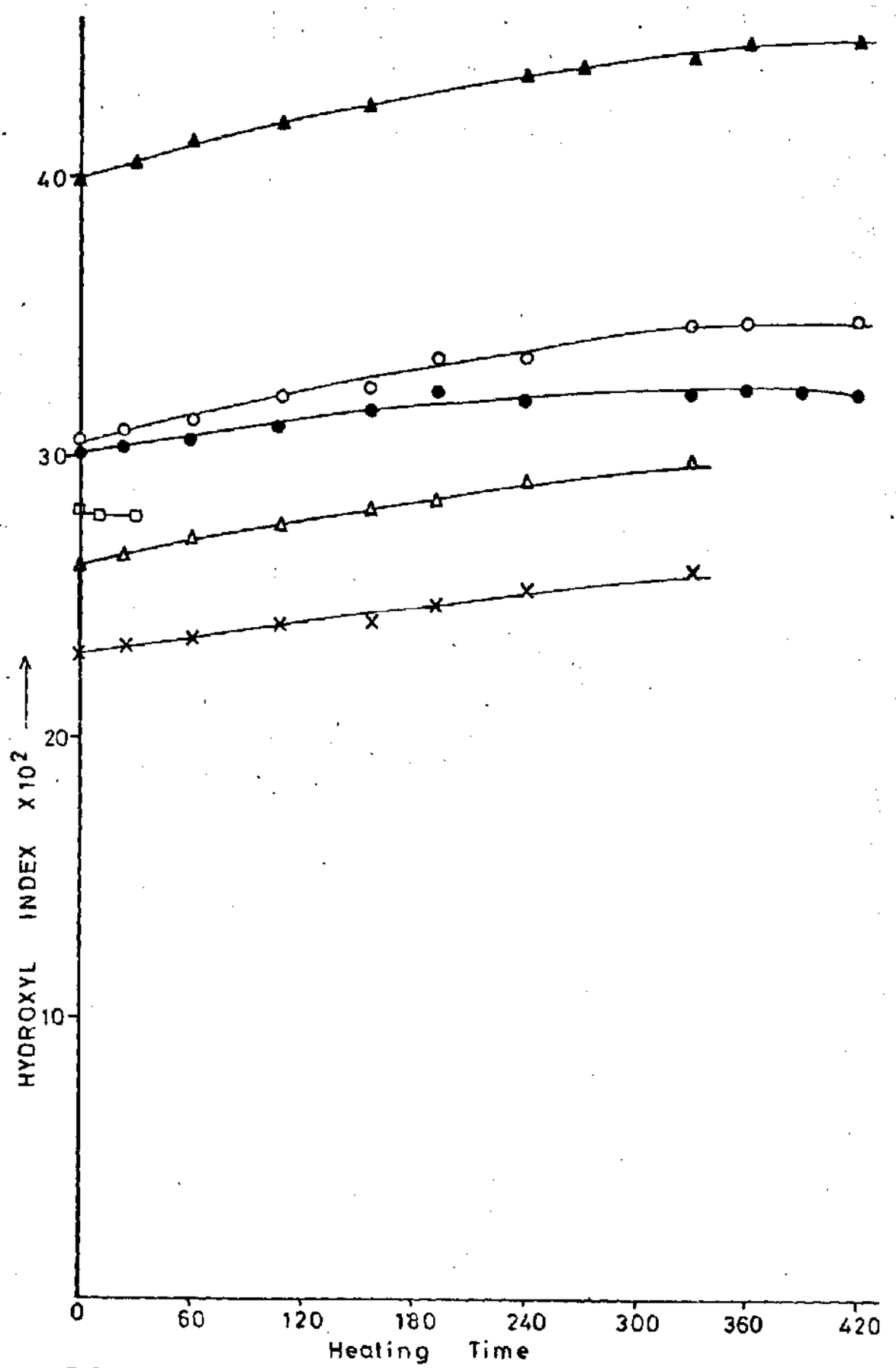


FIG. 4·12 DEPENDENCE OF HYDROXYL INDEX ON OVEN HEATING TIME FOR PVA, PVC AND PVA:PVC BLENDS
○ 20:80 PVA:PVC ● 30:70 PVA:PVC ○ 50:50 PVA:PVC
△ 70:30 PVA:PVC X 80:20 PVA:PVC □ 100% PVA ▲ 100% PVC

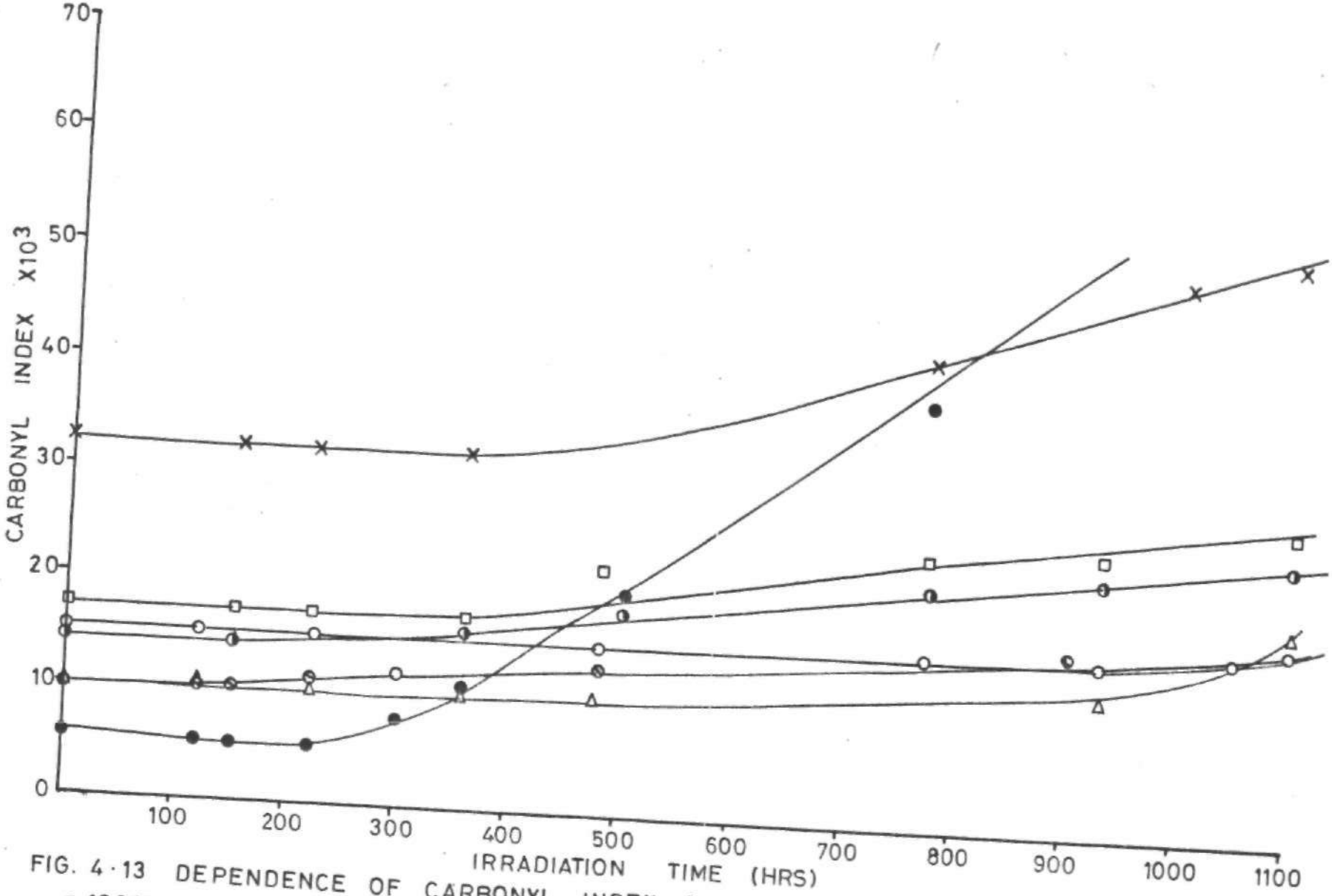


FIG. 4·13 DEPENDENCE OF CARBONYL INDEX ON UV IRRADIATION TIME FOR PVA/PVC BLENDS

○ 100% PVA ⊘ 20:80PVA:PVC △ 30:70PVA:PVC ◑ 50:50PVA:PVC □ 70:30PVA:PVC

× 80:20PVA:PVC ● 100% PVC

CHAPTER 5

STUDIES ON PVA/PMMA BLENDS

In this work studies were carried out on density, morphology and mechanical properties of the unmixed polymers and their blends. Changes in microstructure were monitored using the infra-red spectra of the unmixed polymers and their blends on exposure to outdoor weathering, thermal oxidative degradation and ultraviolet irradiation.

5.1 RESULTS AND DISCUSSION

5.11 Morphology

Figure 5.1 shows the plots of calculated and measured densities of the homopolymers and their blends. The measured and calculated densities agree very well. The agreement between the calculated and measured densities, assuming the additivity of volumes, suggests the miscibility of the polymers, resulting in closer-packing probably due to interaction between PVA and PMMA molecules in the blends (4, 5, 13). The light micrographs of the 20:80, 50:50 and 80:20 PVA:PMMA blends were very clear, indicating the blends to be completely amorphous and showing no phase separation. From these two evidences it may be concluded that the polymers are compatible.

5.12 Outdoor weathering

Figures 5.2(a) and (b) show the stress-strain curves of the unmixed polymers and their blends at zero hour. Figure 5.3 shows the same properties after 21 days outdoor weathering. In each graph, the last point on each curve indicates the elongation at break. PVA and the blends showed necking and cold-drawing, with the tendency to stress-necking decreasing with decrease in PVA in the blends. Figure 5.4 shows the dependence of tensile strength, modulus and percentage elongation of the unmixed polymers and their blends on composition at zero hour and after 17 days outdoor weathering.

From Figure 5.2, it is observed that PMMA is a hard and brittle polymer, while PVA is a soft, and ductile polymer. The blends show properties that seem much influenced by the properties of the major component in the blend. Figure 5.3 shows that on exposure both the homopolymers and their blends become more rigid. It is observed that by the 21st day of outdoor weathering, the 80:20 PVA:PMMA showed lower modulus, a lower yield stress than the 90:10 PVA:PMMA.

It is observed from Figure 5.4 that at zero hour tensile strength showed a minimum at the composition 90:10. Modulus and tensile strength showed the same trend; increased with PMMA component in the blend, while percentage elongation decreased in that direction. The same trend is observed after 17 days outdoor weathering. At this point tensile strength and modulus showed a minimum at the blend compositions 90:10 and 80:20 respectively.

Figures 5.5, 5.6 and 5.7 show the dependence of percentage elongation, tensile strength and modulus respectively on outdoor weathering time. In modulus and tensile strength similar trends are observed for both homopholymers and the blends; an increase in property up to a maximum followed by a decrease. Only PMMA homopolymer showed an initial decrease in modulus, followed by an increase. The increase in modulus indicates increase in rigidity with exposure time.

It is observed from Figure 5.5 that except for the unmixed PMMA which showed an initial increase in percentage elongation, reached a maximum and then decreased, all the blends and PVA showed the same trend. Each showed an initial decrease in property, followed by a gradual increase and finally a decrease. The initial increase shown by PMMA is accounted for by loss of rigidity initially shown by the polymer.

The trends shown in tensile strength, modulus and percentage elongation by these blends tend to suggest that the blends degraded in two stages in which chain scission and crosslinking occured. But while at the onset there was little or no main-chain scission while side group chain scission led to crosslinking, main-chain scission and decreased rate of crosslinking became dominant on prolonged outdoor weathering.

Figure 5.8 shows the dependence of intrinsic viscosities of PVA and PMMA respectively on outdoor weathering time. Both homopolymers are observed to show continuous decrease in intrinsic viscosity for some time after which each levelled off. This indicates that for the homopolymers chain scission is mode of degradation.

In addition to these studies on mechanical properties of the unmixed polymers and their blends studies on microstructure were carried out. The ultraviolet spectra showed no obvious changes in absorptions and will not be mentioned further in this text. The infra-red spectra of the films were computed into carbonyl and hydroxyl indices. But there were no observable changes in the hydroxyl absorption at 3400cm^{-1} absorption band.

Table 1 and Figure 5.9 show the induction and embrittlement times and the dependence of indices of carbonyl absorption peaks on outdoor exposure time respectively for PVA, PMMA and PVA:PMMA blends.

Table 1

Induction and embrittlement times for PVA, PMMA and PVA:PMMA blends on outdoor weathering

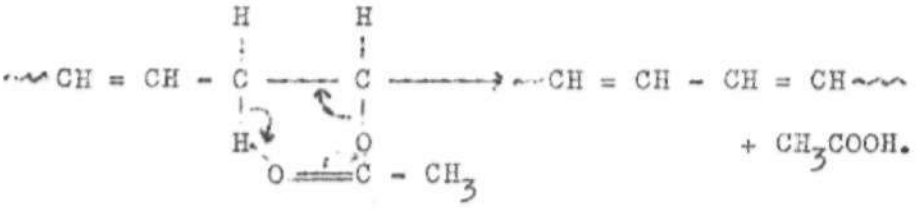
Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PVA	240	1440
90:10 PVA:PMMA	80	1293
80:20 PVA:PMMA	150	1293
70:30 PVA:PMMA	120	1293
60:40 PVA:PMMA	120	1439
50:50 PVA:PMMA	400	1293
40:60 PVA:PMMA	250	1439
30:70 PVA:PMMA	70	1293
20:80 PVA:PMMA	70	1253
10:90 PVA:PMMA	60	1293
100% PMMA	150	946

The high embrittlement period of the 40:60 and 60:40 PVA:PMMA blends suggest that at these blend compositions PVA stabilizes PMMA against outdoor weathering while the presence of PMMA has no effect on the rupture time of PVA.

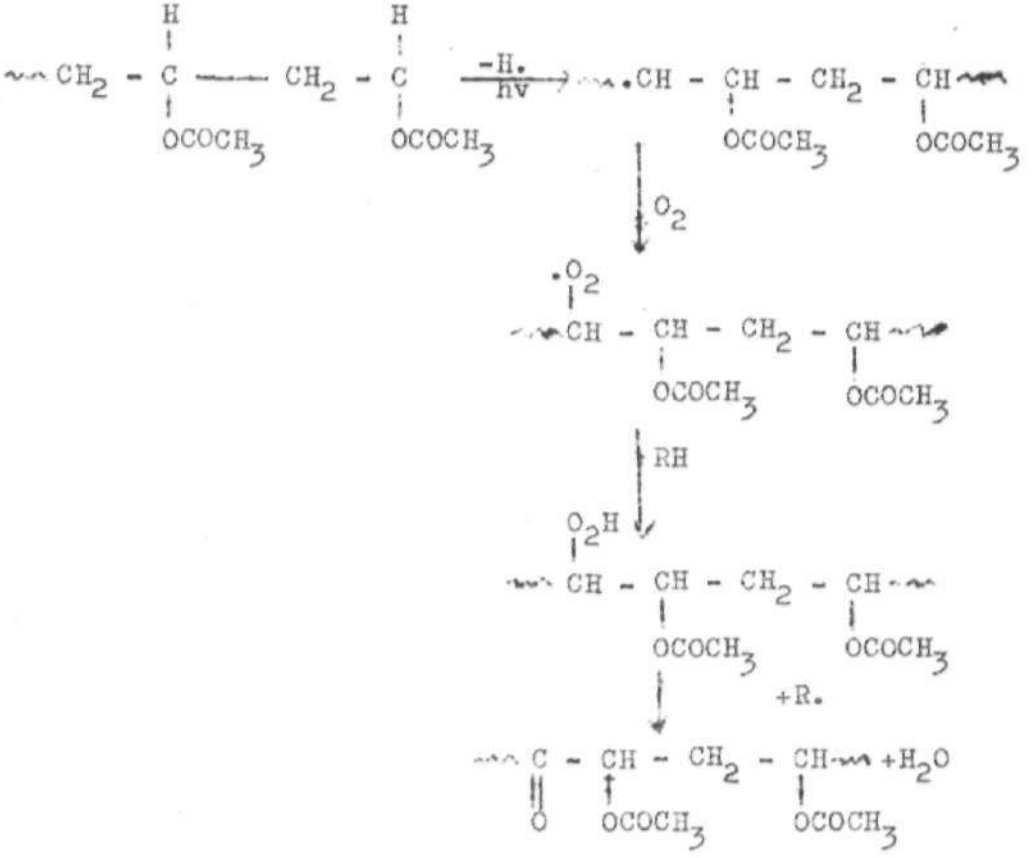
From Figure 5.9 it is observed that although 50:50 PVA:PMMA blend had a long induction period the growth in carbonyl index was fast. PVA showed a very rapid growth in peak height. This would be surprising since the polymer is supposed to degrade via deacetylation. May be, temperature of outdoor weathering is too low to induce rapid deacetylation, in which case oxygen attacks the macroradical formed following the loss of hydrogen.

Stomberg, Stratus and Achhammer (38) suggested that in the degradation of PVA, the acetic acid molecule splits away leaving a double bond and that this chain reaction proceeds via a chain mechanism. Grassie and McNeill (35) Braun and Bender (39) suggested that further deacetylation was facilitated by allylic activation of acetate units adjacent to a double bond. Reiner (48) suggested that the deacetylation of PVA was facilitated by a six-membered ring interaction existing between the carbonyl groups and the B-hydrogen atom of the alcohol residue. He further stated that the tendency for adjacent units in PVA to react to produce conjugation could be explained in terms of electron attracting properties of the carbon-carbon double bond activating the adjacent methylene groups.

The deacetylation of PVA may be represented thus:



The macroradical formed and the polyene could pick oxygen to form hydroperoxy and hydroxyl groups which are subsequently oxidised to carbonyl groups.



This and the reduction in the number of methylene reference group could well account for the increase in carbonyl indices shown by PVA and the blends.

Figure 5.9 shows 100% PMMA as showing a fairly rapid growth in carbonyl indices. The blend with PVA seems to have a stabilizing effect and at the same time a destabilizing effect on PMMA, as is evident from the carbonyl indices curves

and Table 1.

5.13 Oven aging

Figure 5.10 shows the dependence of tensile strength, modulus and percentage elongation of PMMA, the 20:80, 50:50 and 80:20 PVA:PMMA blends on oven aging time. PVA is omitted since it embrittled soon on oven aging. All the blends showed the same trend in tensile strength as is evident from the graph. In the plot of percentage elongation the blends showed rapid decrease in property on the first two days, an increase on the third day and finally reached a minimum on the fourth day.

Generally, the higher the PVA component in the blend the greater the decrease in percentage elongation the greater the increase in modulus and tensile strength. The latter is indicated by the maximum shown by each blend on the third day. Thus, although PMMA had the highest tensile strength at zero time, it showed the lowest values in tensile strength throughout the heating time and although PVA embrittled by the first day, the blends showed increases in this property. The improvements in mechanical properties illustrate the compatibility of the homopolymers and the stabilization of PVA by PMMA and vice versa.

Changes in the microstructure of the unmixed polymers and their blends on oven aging were monitored using their infra-red spectra. Table 2 shows the induction and embrittlement times and Figure 5.11 shows the indices of carbonyl absorption peaks of PVA, PMMA and their blends on oven aging.

Table 2

Induction and embrittlement times for carbonyl absorptions of PVA, PMMA and PVA:PMMA blends on oven aging

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PMMA	no changes in absorption	1337
10:90 PVA:PMMA	80	1337
30:70 PVA:PMMA	40	1020
40:60 PVA:PMMA	170	208
50:50 PVA:PMMA	-	70
60:40 PVA:PMMA	160	960
70:30 PVA:PMMA	100	137
80:20 PVA:PMMA	-	943
90:10 PVA:PMMA	-	189
100% PVA	12	29

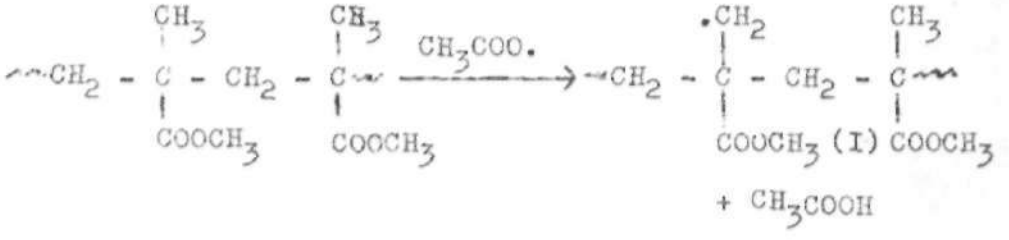
Figure 5.11 and Table 2 show PMMA as showing no changes in absorption until it embrittled while PVA had 12 hours induction period after which it underwent rapid decomposition and embrittled within 29 hours.

That 10:90 PVA:PMMA showed an induction period of 80 hours while 50:50 PVA:PMMA decomposed without showing any induction period shows that as little as 10% PVA in a blend with PMMA destabilizes PMMA, with the blending of PVA and PMMA showing the least thermal oxidative stability at 50% PVA concentration in the blends. This also shows that 40% PMMA offers

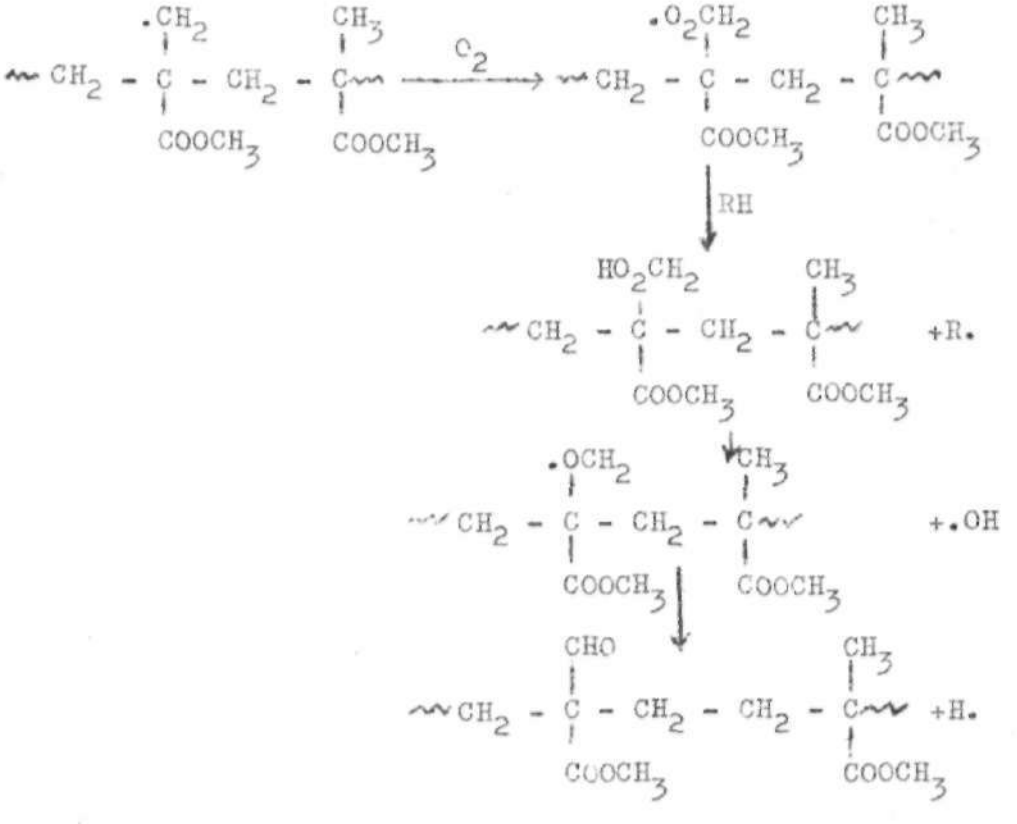
PVA:PMMA the greatest thermal stability. PMMA is observed to be of greater thermal stability. This is in agreement with the observations of McNeill and Neil (50). They noted that PMMA was stable to heating in an oven at 250°C when heated alone. Reiner (48) noted that below 160°C the depolymerization of PMMA is inhibited by lack of diffusion. McNeill and Neil (50) and Grassie, McNeill and Cooke (61) observed that on thermal degradation PMMA degrades by depolymerization. McNeill and Neil (50) observed that PVC destabilized PMMA on blending. They concluded that this could be explained in terms of initial chlorine attach on PMMA. PVA could have a similar effect but depolymerization of PMMA could be inhibited by lack of diffusion and therefore result in a build up of monomer, dimer et cetera in the film. The temperature at which the heating is done is too low to induce depolymerization, since the intermediate products of depolymerization are free radicals which should be susceptible to oxidative attack and subsequently formation and increase in carbonyl absorption. Hence PMMA showed no changes in absorption until it embrittled.

Stromberg, Stratus and Achhammer (38), Gressie and McNeill (36), Braun and Bender (39) observed that PVA degrades by the splitting away of acetic acid molecules and suggested that further deacetylation of PVA was facilitated by allylic activation of acetate units adjacent to a double bond. The activation of the methylene group by the carbon-carbon double bond increases with reaction time. This results in auto-catalysed decomposition of PVA. This is evident from the complete decomposition of PVA between the 12th and 29th hour of heating.

The increase observed in carbonyl index on thermally degrading the PVA:PMMA blends and the reduced thermal stability of PMMA on blending with PVA suggests the destabilization of PMMA by the abstraction of a methyl hydrogen by either the hydrogen or acetate radical from PVA.



The methylene hydrogen should be hindered and less vulnerable to abstraction. The macroradical (I) can undergo oxidative attack by oxygen.



The presence of PMMA units in the blends probably stabilizes PVA against decomposition. The above mechanism adequately accounts

for the observed increases in indices of carbonyl absorption peaks of the blend films.

The PVA components of the blends could show the reactions embodied in the mechanism in section 5.3 to cause an increase in the indices of carbonyl absorption.

5.4 Ultraviolet degradation

Films of the homopolymers and their blends were irradiated with ultraviolet rays and changes in microstructure monitored by running the infra-red and ultraviolet spectra of the films. Table 3 shows the induction and embrittlement times and Figure 5.12 shows the indices of carbonyl absorption peaks for PVA, PMMA and their blends. There were no traceable changes in hydroxyl absorptions recorded on the spectra.

Table 3

Induction and embrittlement times of PVA, PMMA and PVA:PMMA blends for carbonyl absorptions on ultraviolet irradiation

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PMMA	360	2000
10:90 PVA:PMMA	280	2000
30:70 PVA:PMMA	170	2000
50:50 PVA:PMMA	190	2000
70:30 PVA:PMMA	400	2000
80:20 PVA:PMMA	750	2826
90:10 PVA:PMMA	180	2221
100% PVA	1050	2826

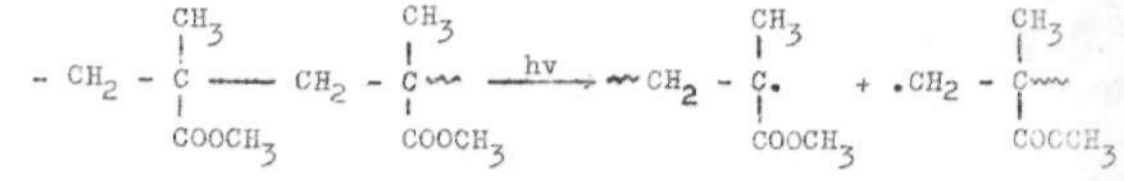
Figure 5.12 and Table 3 show PVA to be very stable to ultraviolet degradation; showing 1050 hours induction period and embrittlement time of 2826 hours. It is observed that among the blends, the 80:20 PVA:PMMA has the greatest stability towards ultraviolet degradation.

Table 3 shows PMMA to be more vulnerable to ultraviolet degradation than PVA. It is observed that the 70:30 and 80:20 PVA:PMMA blends show the best oxidative stability.

Reiner (48) observed that ultraviolet degradation of PMMA at low temperatures does not occur via depolymerization and noted that crosslinking could accompany the initial chain scission reactions and that there was rapid decrease in molecular weight early during the reactions.

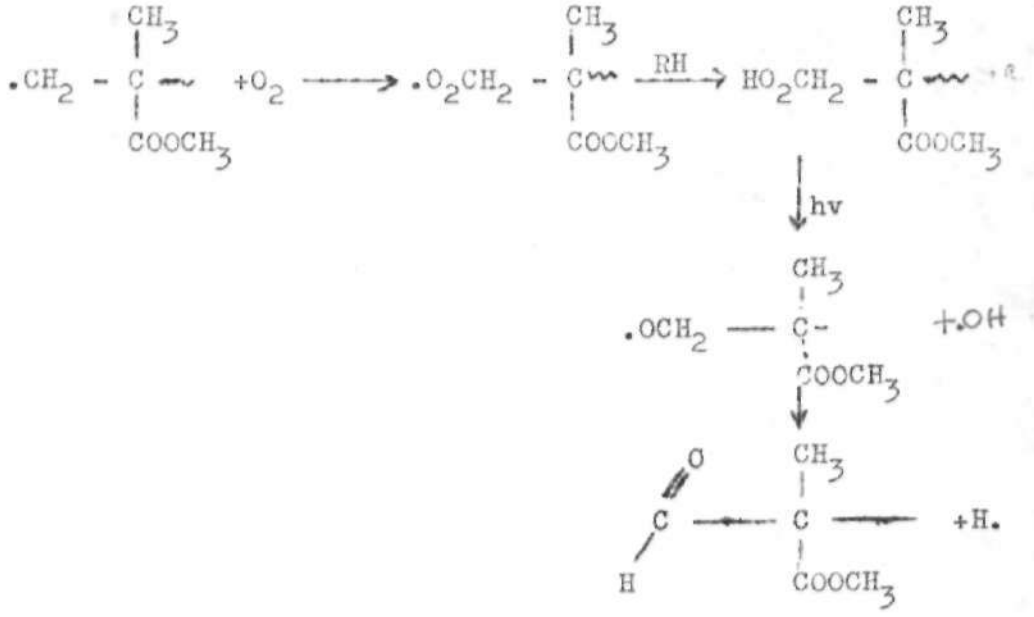
On ultraviolet irradiation, PMMA can show any of the following reactions (I) random homolytic scission of main chain carbon bonds, (II) scission of the side ester groups and (III) scission of methyl side groups.

Scission of main chain carbon-carbon bonds could take place as follows:



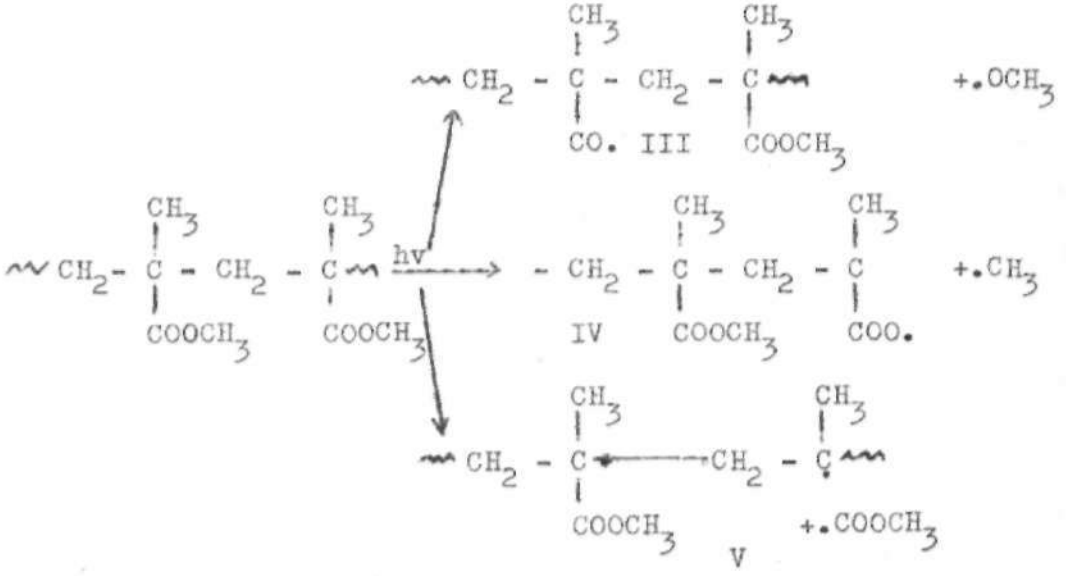
The macroradicals (I) and (II) can separately abstract a hydrogen atom from a PVA chain, crosslink with other radicals in the system or undergo oxidative attacks. The oxidative degradation of macroradical (II) could take the following

sequence



The stability of the hydroxyl and peroxy groups must be very low to account for the seemingly complete absence of changes in hydroxyl absorptions in the ir spectra of the homopolymers and their blends.

Scission of side chain ester groups may take place as follows:



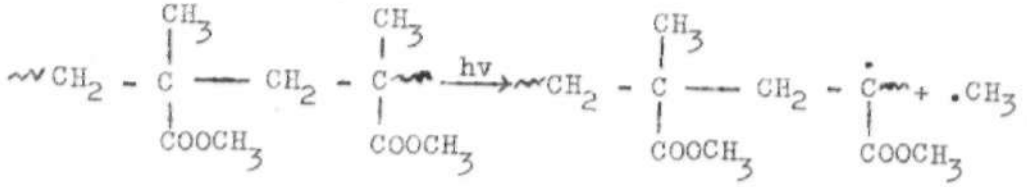
Any of these radicals can initiate degradation of PVA by hydrogen abstraction, for example

$$\cdot CH_3 + RH \longrightarrow CH_4 + R\cdot$$

Any of them could equally undergo oxidative attack. Macroradical (V) for example could easily be oxidised to a ketone.



On the other hand, scission of the methyl side groups should take place on uv irradiation.



These radicals can show any of the reactions already described. Degraded as a blend, the PVA component could degrade via an initial hydrogen abstraction by any of the

radicals generated during PMMA photolysis. These radicals formed can then undergo degradation or crosslink with any other free radical in the vicinity or abstract hydrogen from neigbouring chains. Deacetylation may not have taken place because of the temperature range within which the irradiation took place.

5.2 CONCLUSION

PVA stabilizes PMMA against ultraviolet degradation. PMMA stabilizes PVA against thermal oxidative degradation. On outdoor weathering degradation, cooperative stabilization is observed. The system is mechanically and chemically compatible with the greatest compatibility occurring at 40-60% PMMA in the blend.

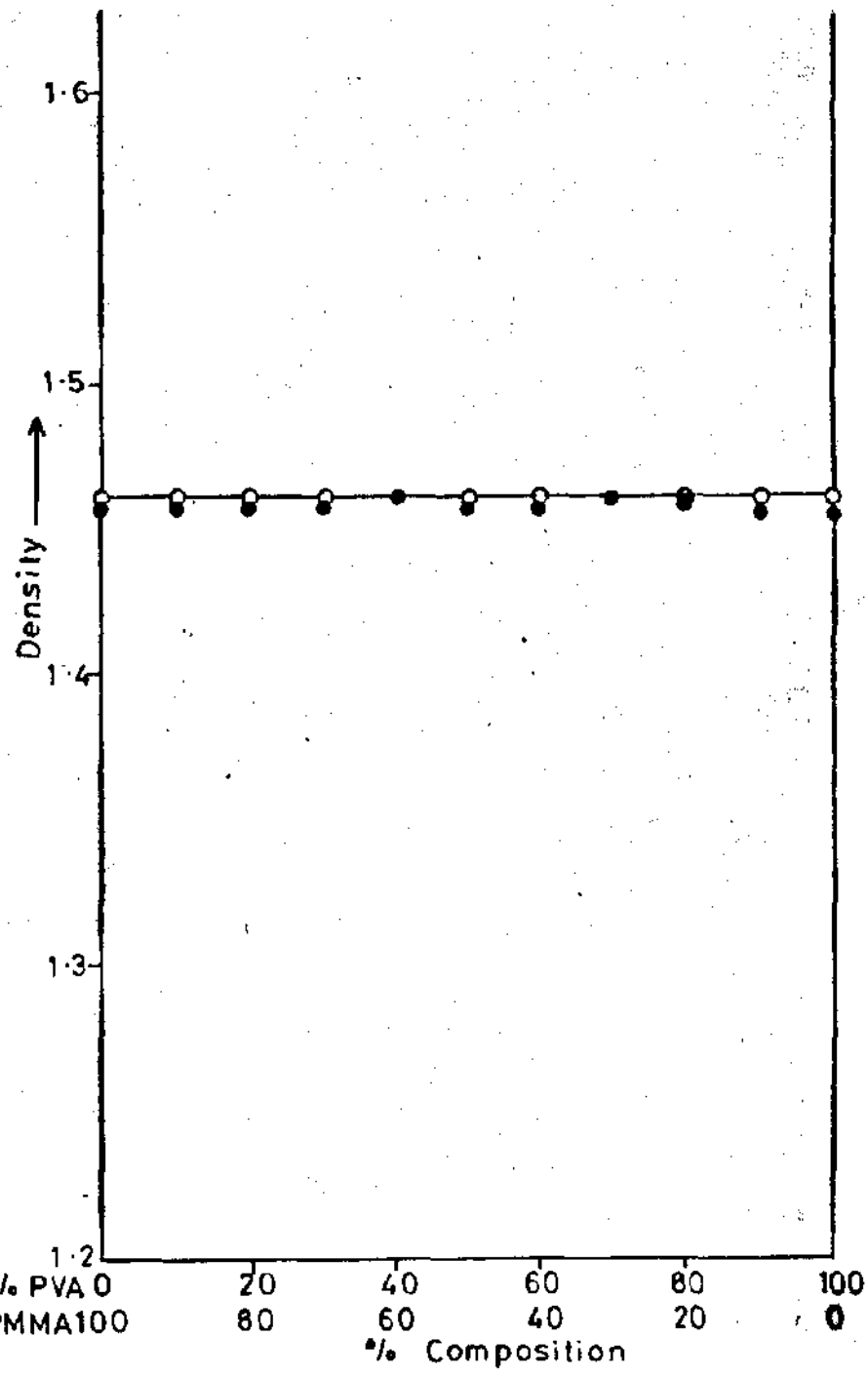


FIG. 5·1 VARIATION OF DENSITY WITH % COMPOSITION OF PVA/PMMA BLENDS

○ Theoretical Density. ● Practical Density

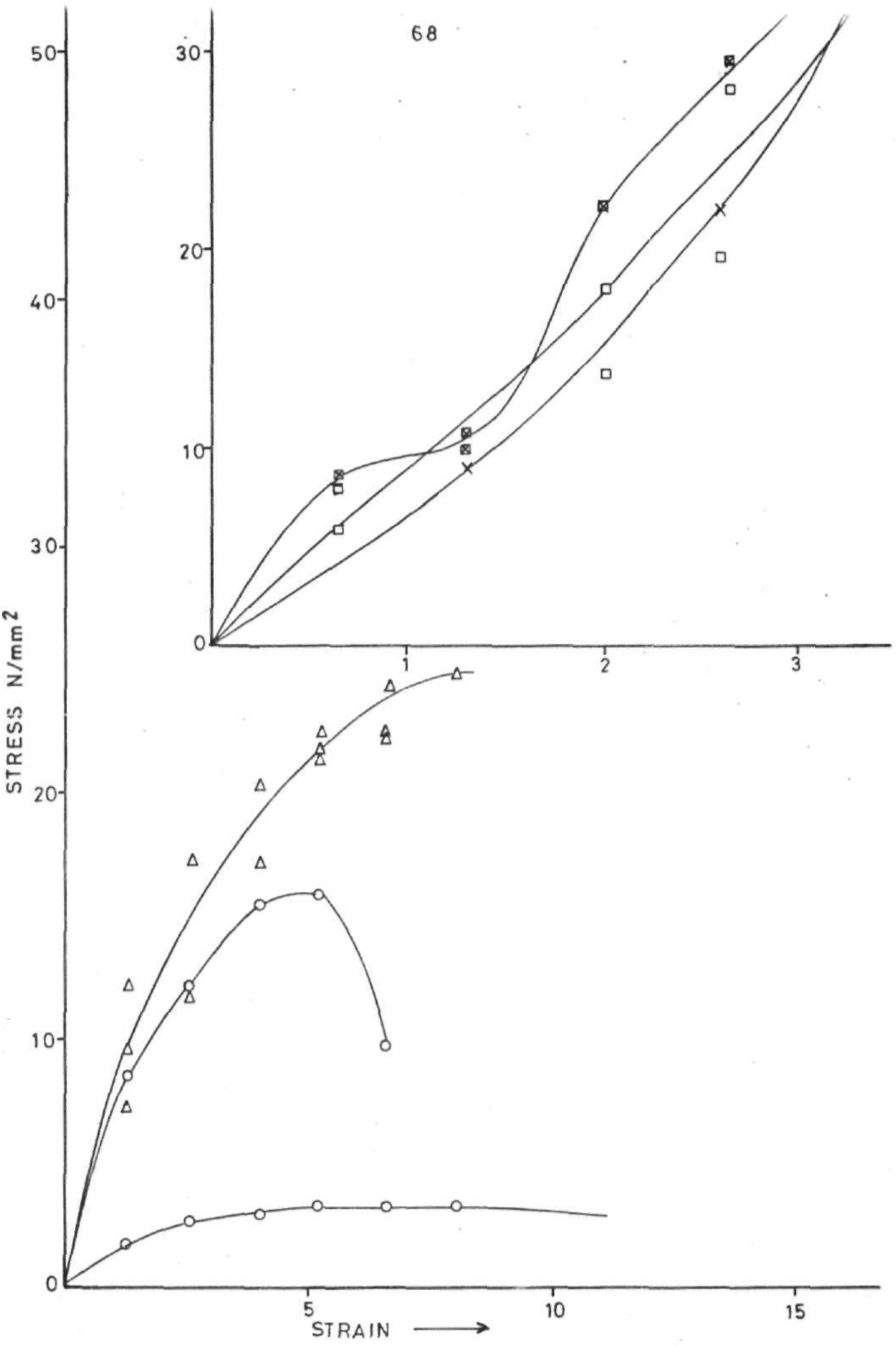


FIG. 5·2(a) STRESS STRAIN CURVES FOR PMMA AND PVA/PMMA BLENDS AT ZERO HOUR ○ 40:60 PVA: PMMA △ 30:70 PVA: PMMA ⊡ 20:80 PVA: PMMA ⊗ 100% PVA × 10:90 PVA: PMMA ⊠ 100% PMMA

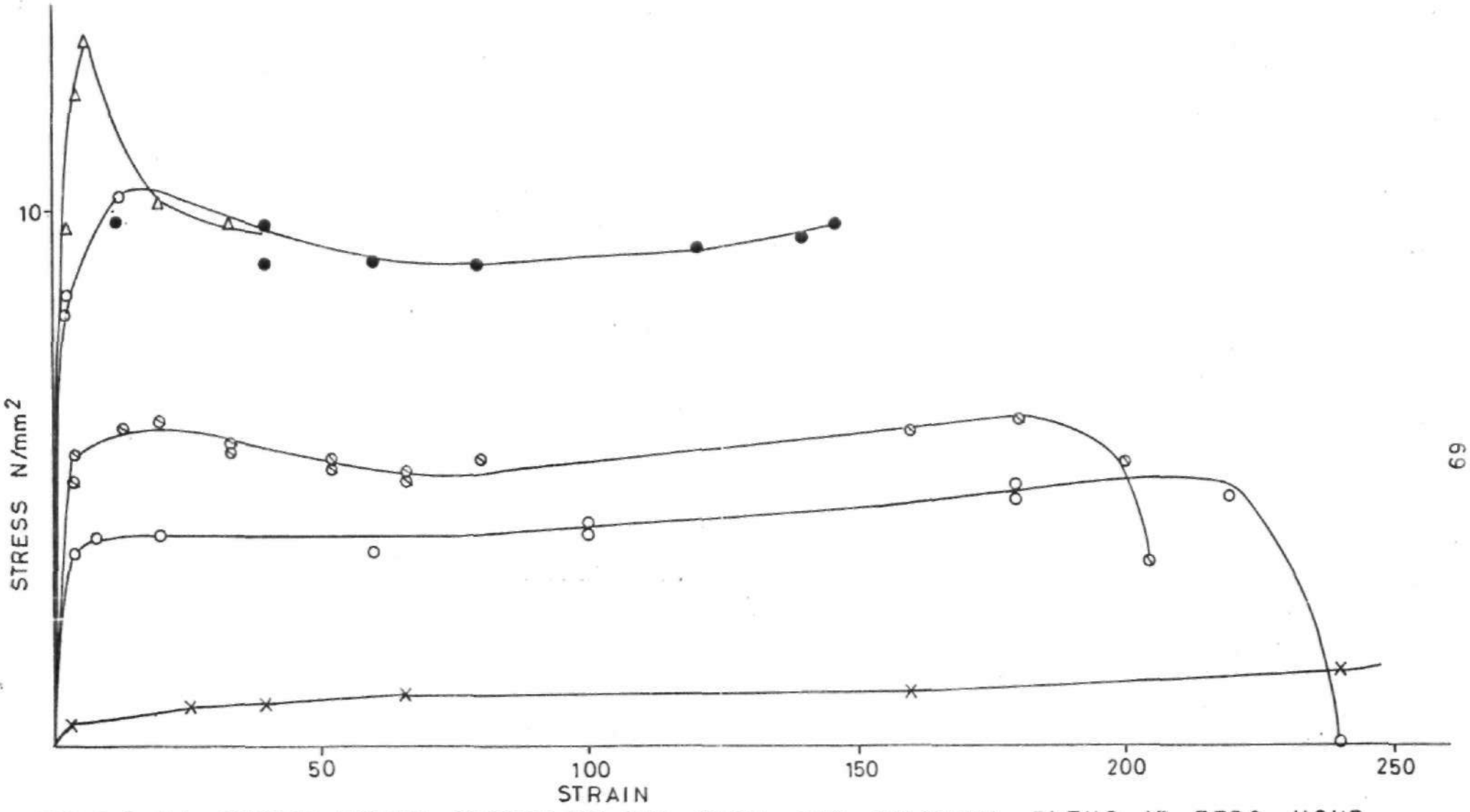


FIG: 5·2 (b) STRESS-STRAIN CURVES OF PVA, PMMA AND PVA/PMMA BLEND AT ZERO HOUR

× 90:10 PVA:PMMA ○ 80:20 PVA:PMMA ⊘ 70:30 PVA:PMMA ● 60:40 PVA:PMMA

△ 50:50 PVA:PMMA ○ 100% PVA

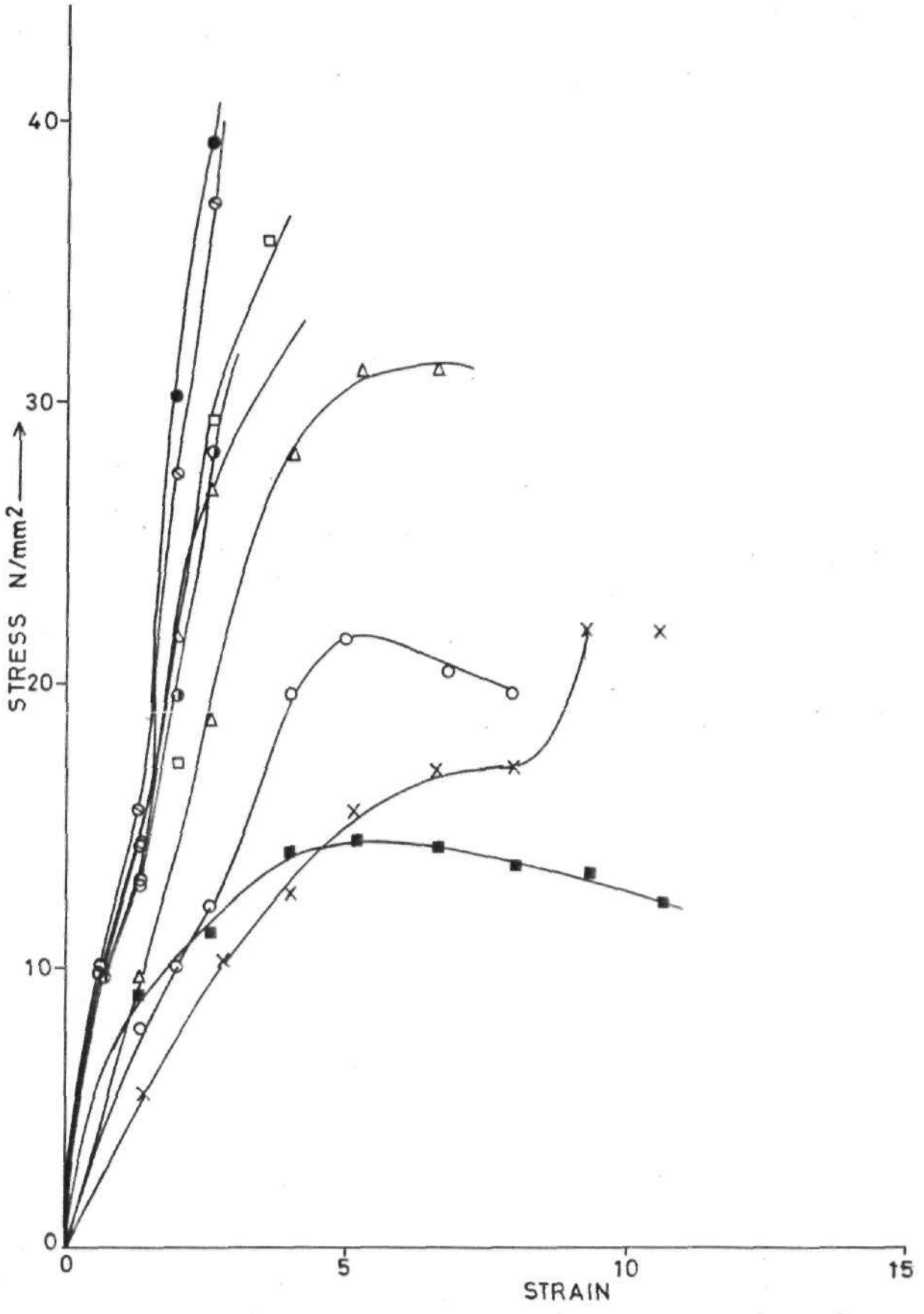


FIG. 5·3 STRESS-STRAIN CURVES FOR PVA, PMMA AND PVA/PMMA BLENDS AFTER 21 DAYS EXPOSURE (OUTDOOR)

○ 90:10 PVA:PMMA × 80:20 PVA:PMMA △ 60:40 PVA:PMMA
□ 50:50 PVA:PMMA ◍ 40:60 PVA:PMMA ▲ 30:70 PVA:PMMA
⊘ 20:80 PVA:PMMA ● 100% PMMA ■ 100% PVC

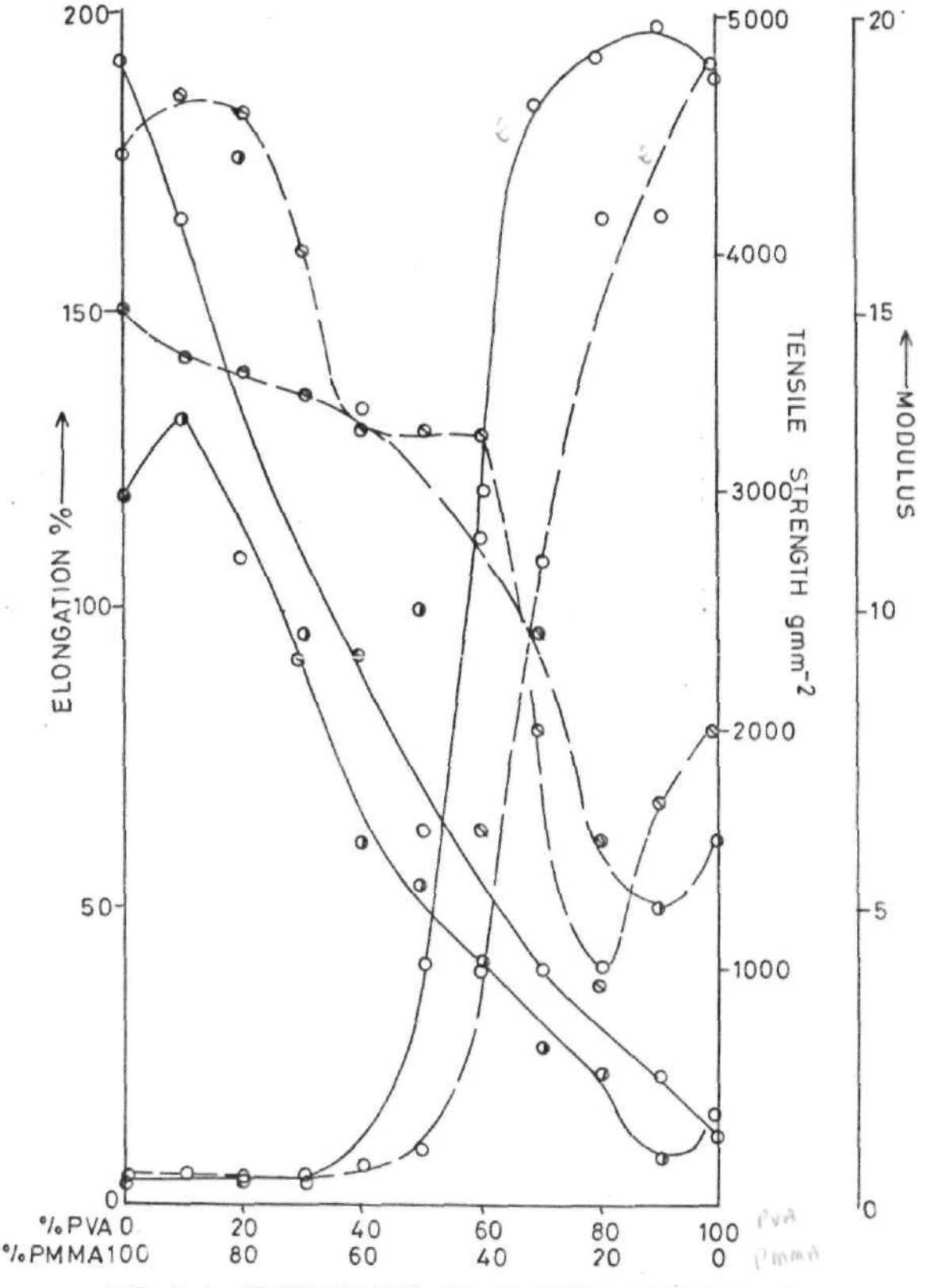


FIG. 5·4 DEPENDENCE OF VARIOUS FACTORS ON COMPOSITION OF PVA/PMMA BLENDS

○ % ELONGATION ——— ZERO TIME

◑ TENSILE STRENGTH — — 17 DAYS EXPOSURE

⊘ MODULUS

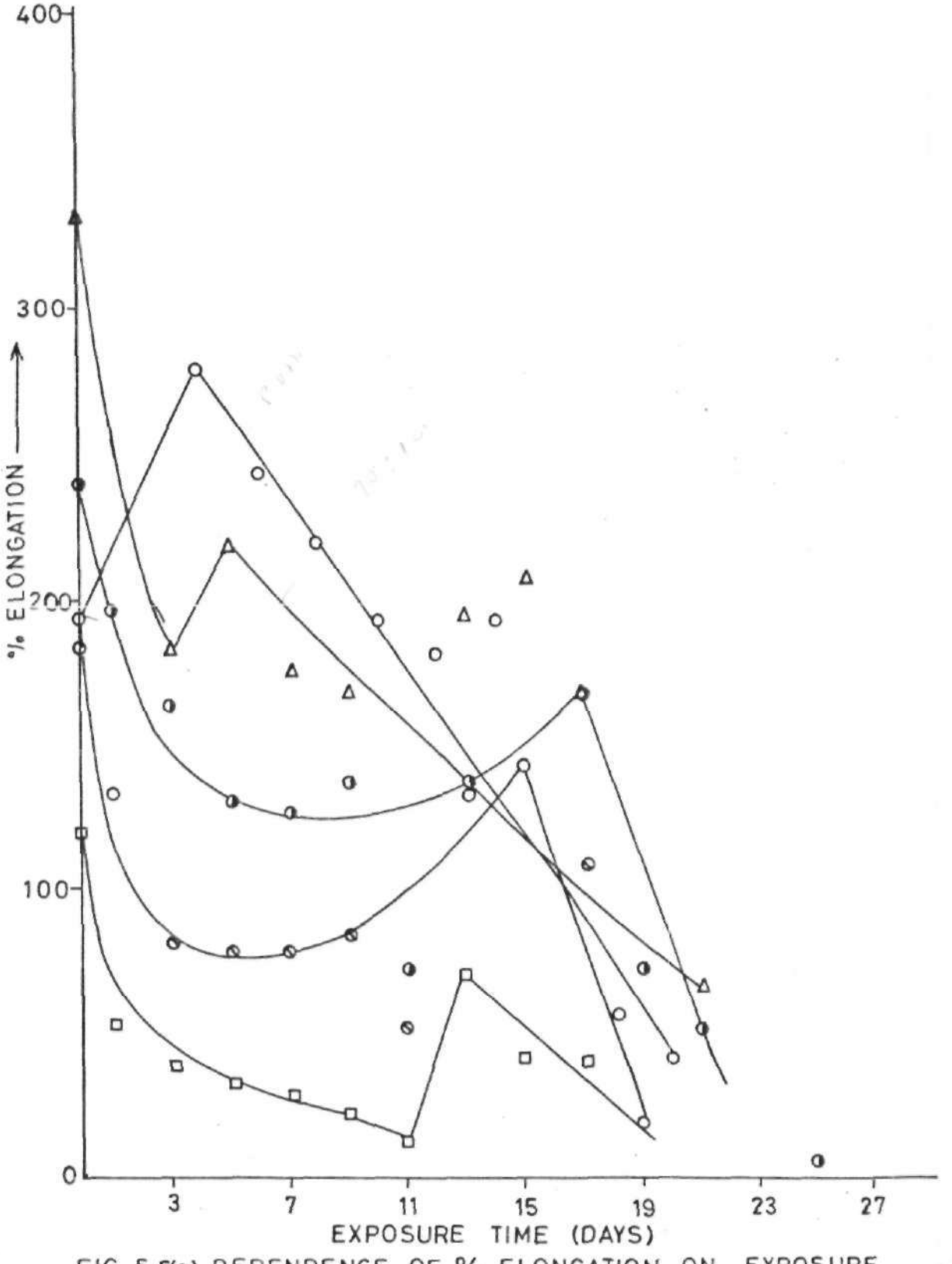


FIG. 5·5(a) DEPENDENCE OF % ELONGATION ON EXPOSURE FOR PVA/PMMA BLENDS

○ 100% PVA ◔ 70:30 PVA:PMMA ◑ 80:20 PVA:PMMA

△ 90:10 PVA:PMMA □ 60:40 PVA:PMMA

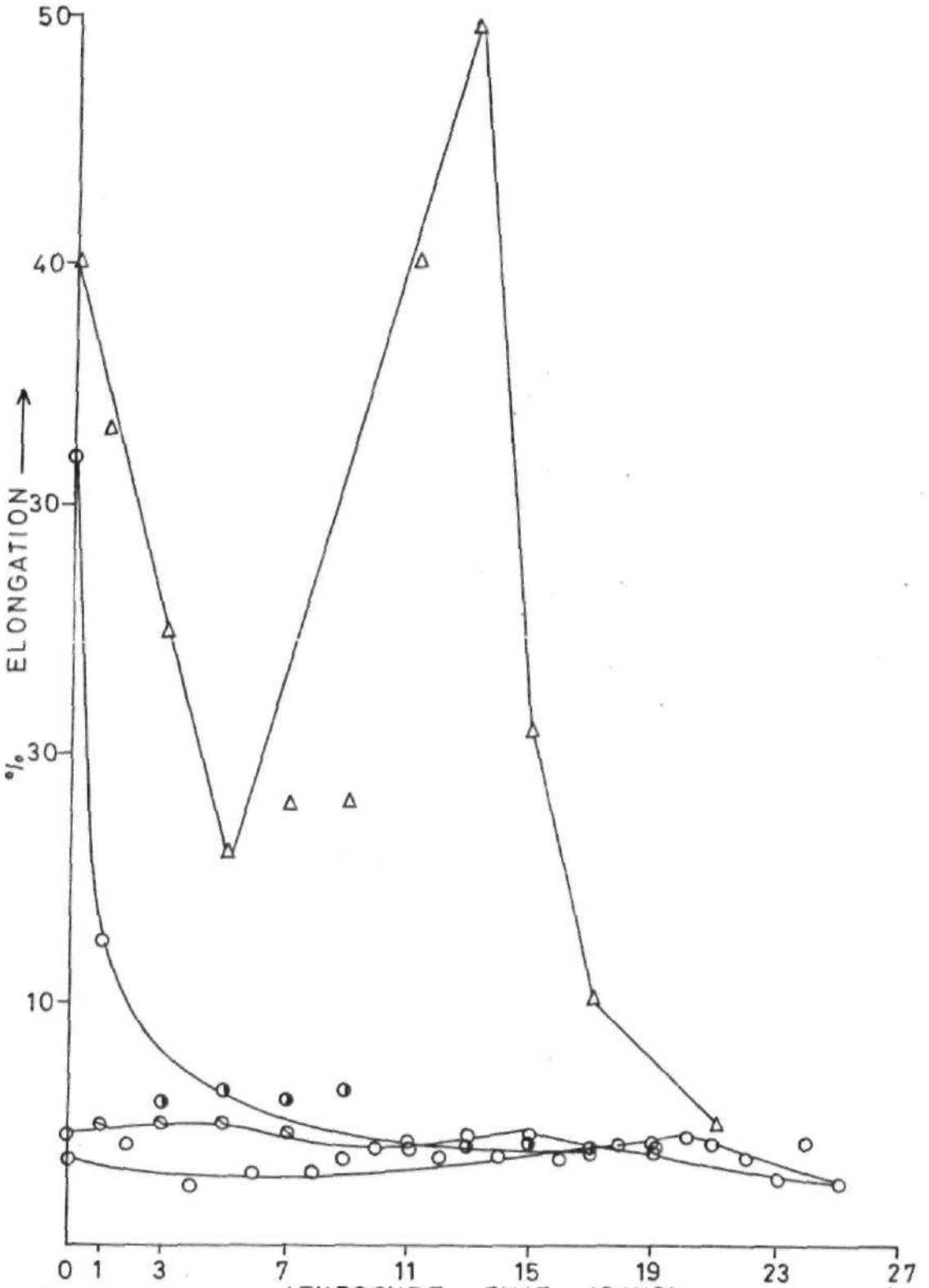


FIG. 5·5(b) DEPENDENCE OF ELONGATION ON EXPOSURE TIME FOR PVA/PMMA BLENDS

○ 100% PMMA ◔ 10:90 PVA:PMMA ◑ 30:70 PVA:PMMA

△ 50:50 PVA:PMMA

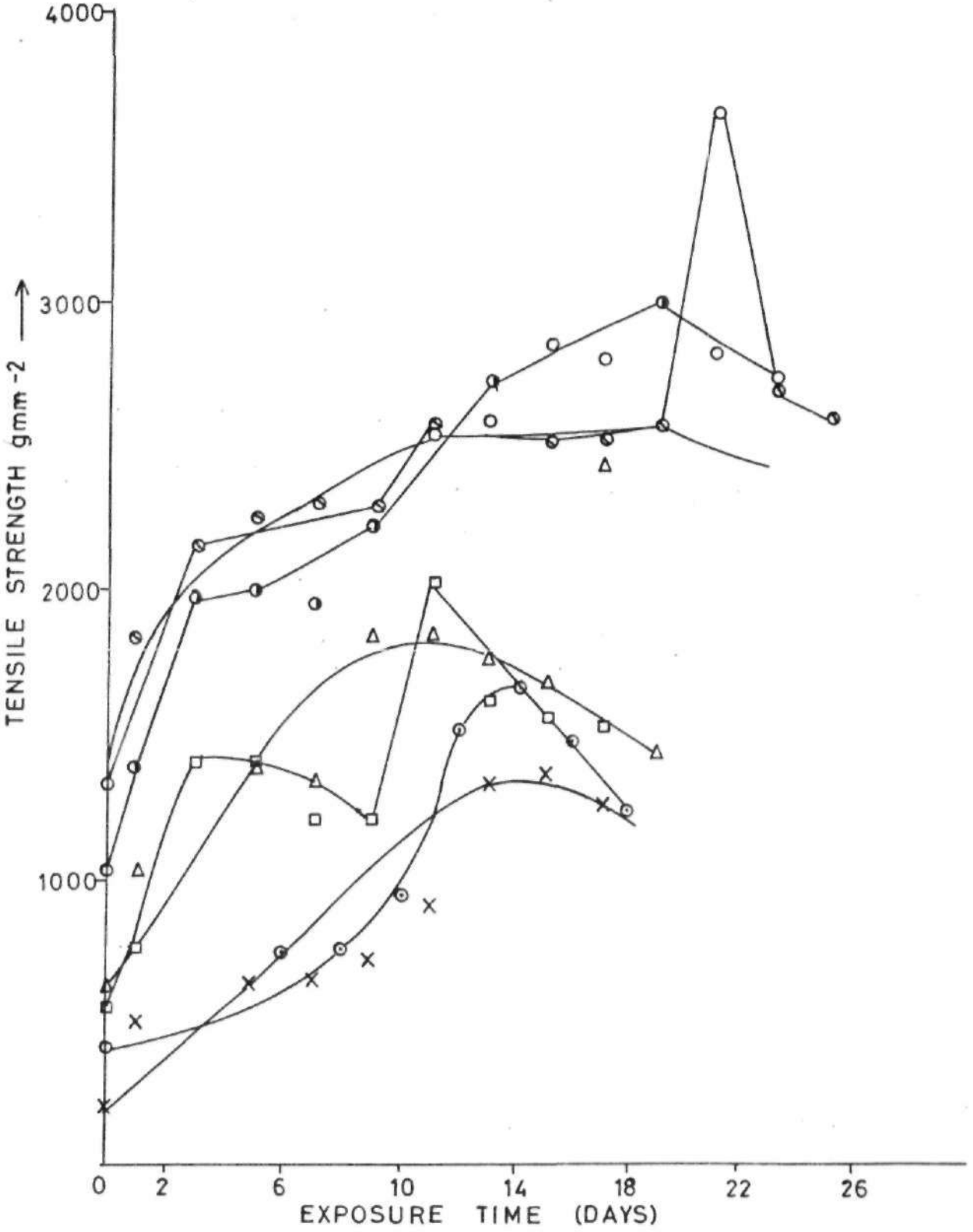


FIG. 5·6 (a) DEPENDENCE OF TENSILE STRENGTH ON EXPOSURE TIME FOR PVA/PMMA BLENDS
⊙100 % PVA ⊘ 50:50 PVA:PMMA ◑ 60:40 PVA:PMMA
△ 70:30 PVA:PMMA □ 80:20 PVA:PVA:PMMA ×90:10 PVA:PMMA

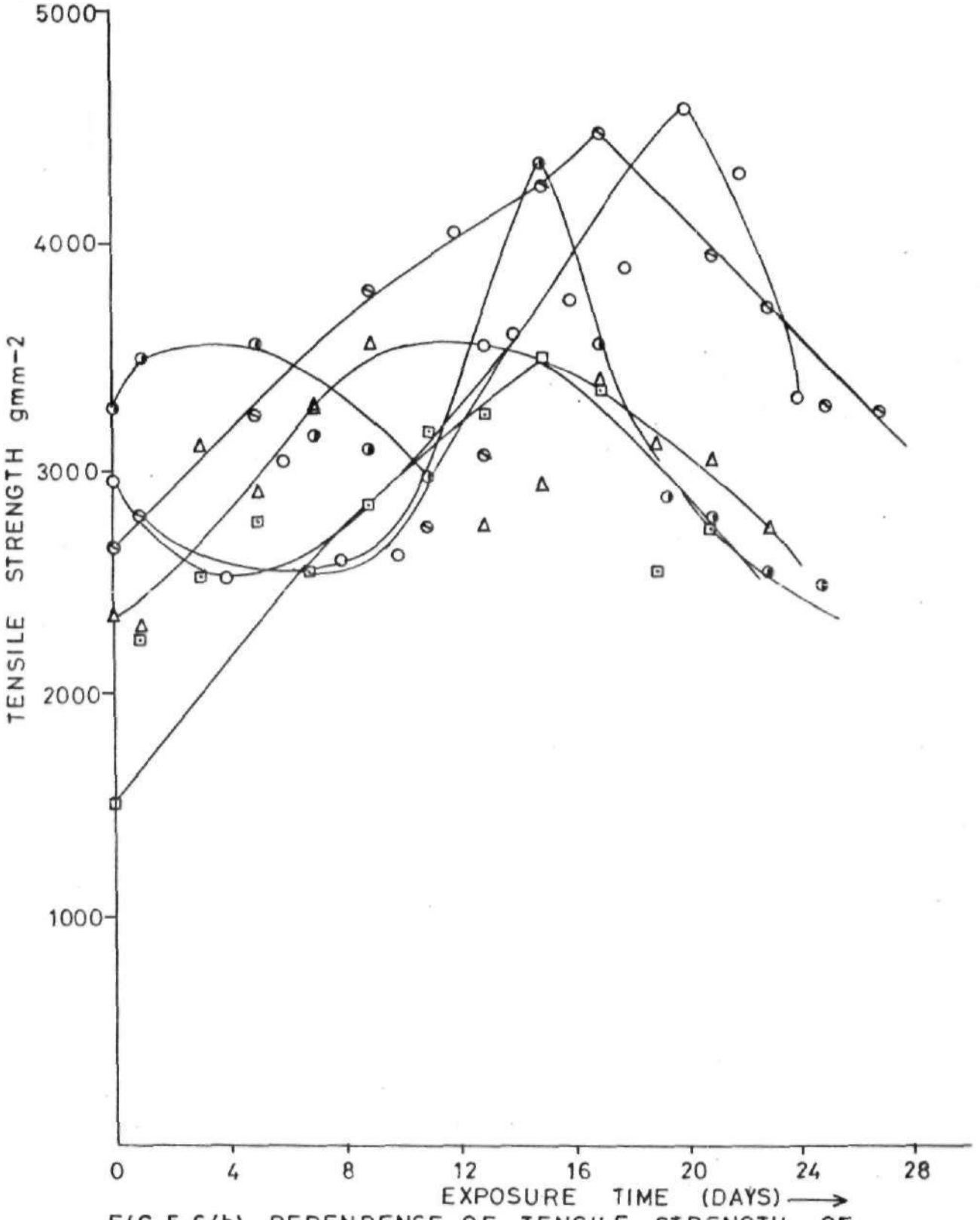


FIG.5·6(b) DEPENDENCE OF TENSILE STRENGTH OF EXPOSURE TIME FOR PVA/PMMA BLENDS

○ 100% PMMA ◑ 10:90 PVA:PMMA ⊖ 20:80 PVA:PMMA

△ 30:70 PVA:PMMA ⊡ 40:60 PVA:PMMA

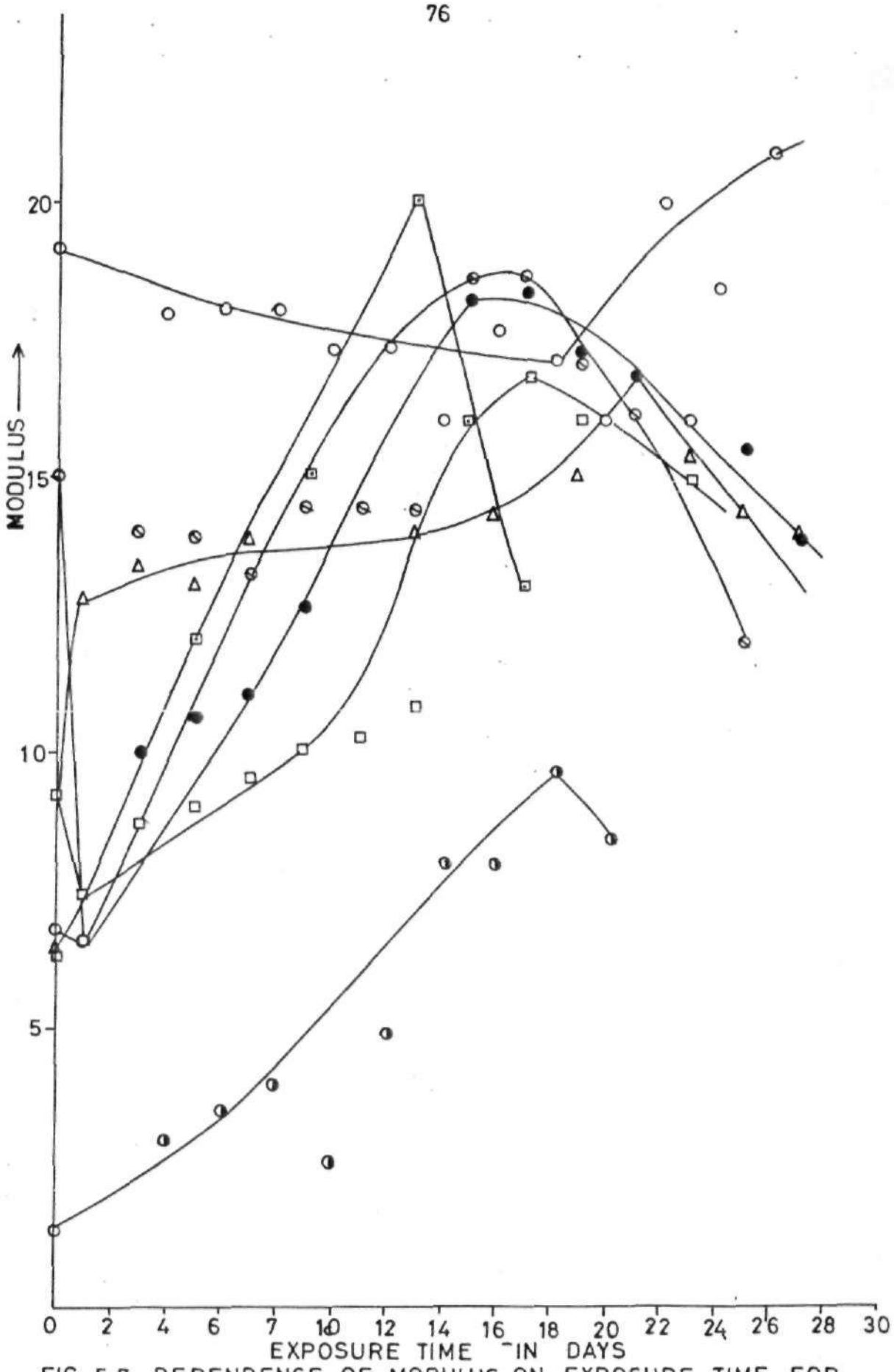


FIG. 5·7 DEPENDENCE OF MODULUS ON EXPOSURE TIME FOR PVA/PMMA BLENDS

○ 100% PMMA ◐ 100% PVA ◎ 10:90 PVA:PMMA ● 20:80 PVA:PMMA

□ 30:70 PVA:PMMA △ 40:60 PVA:PMMA ⊡ 50:50 PVA:PMMA

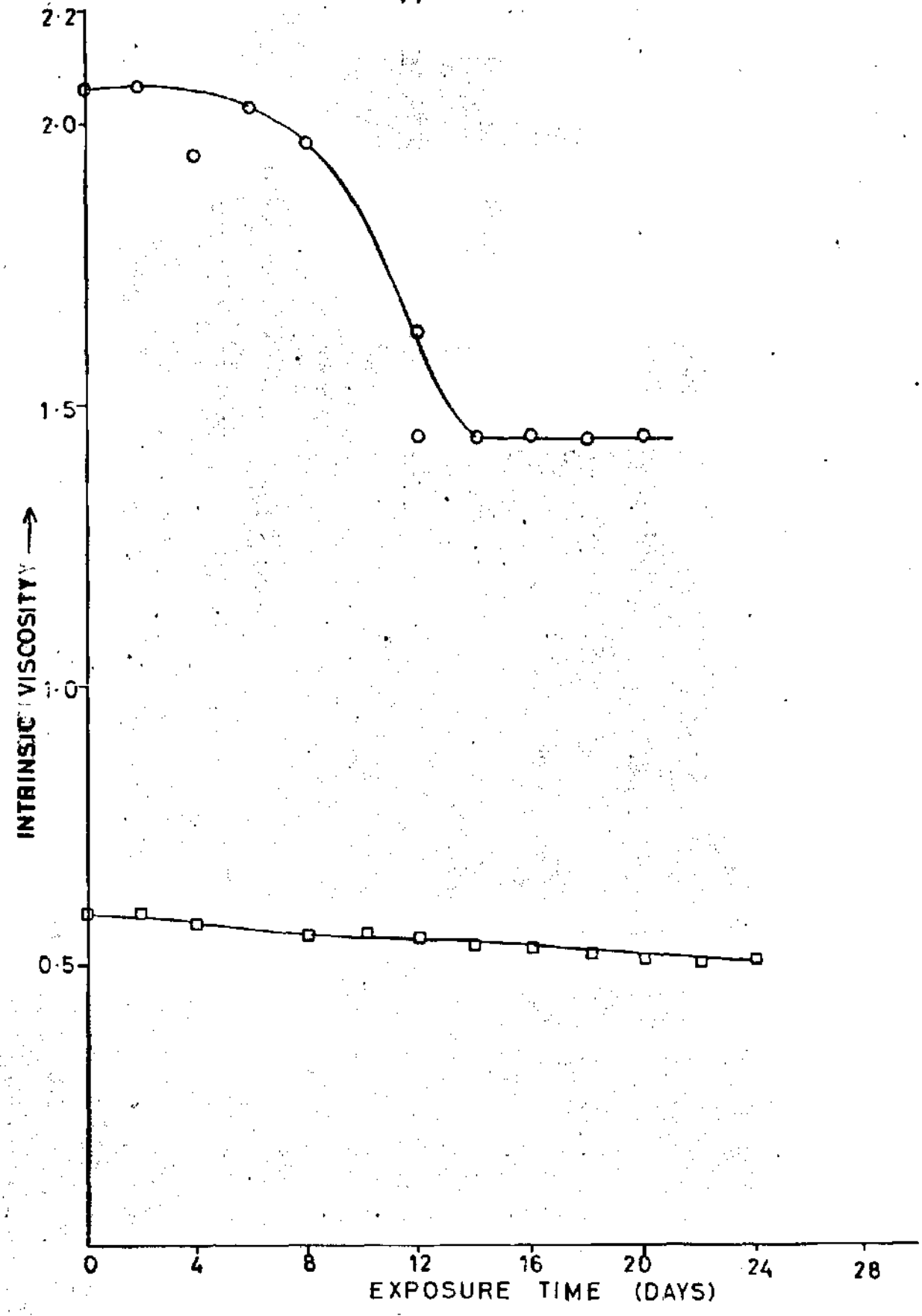


FIG. 5·8 DEPENDENCE OF INTRINSIC VISCOSITIES OF PVA AND PMMA ON OUTDOOR WEATHERING TIME

○ PVA □ PMMA

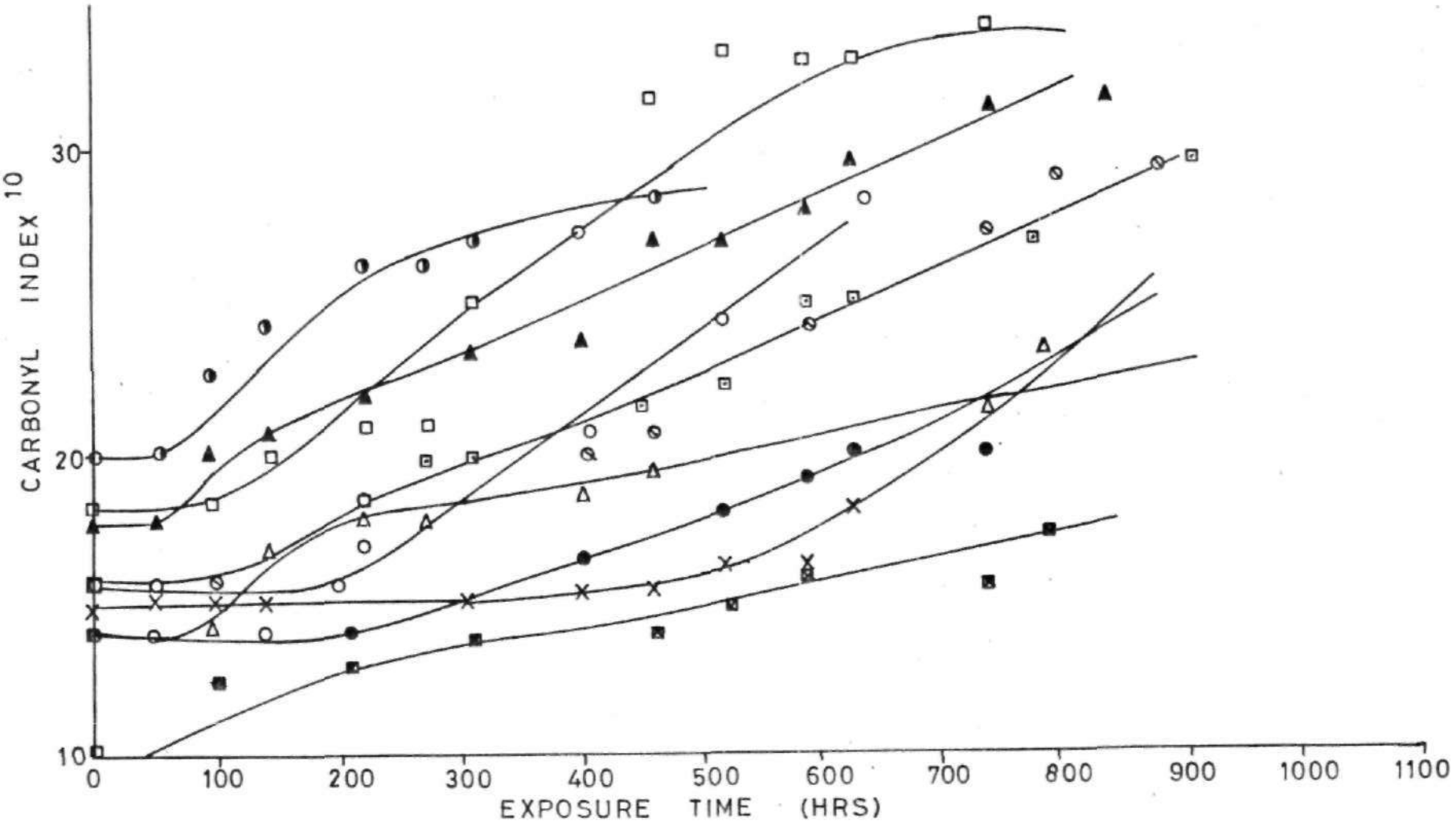


FIG. 5·9 DEPENDENCE OF CARBONYL INDEX ON OUTDOOR EXPOSURE TIME FOR PVA/PMMA BLENDS

○ 100% PVA ⊘ 100% PMMA ◑ 90:10PVA:PMMA ⊡ 80:20PVA:PMMA □ 70:30PVA:PMMA
△ 60:40PVA:PMMA X 50:50PVA:PMMA ● 40:60PVA:PMMA ▲ 30:70PVA:PMMA ■ 10:90PVA:PMMA

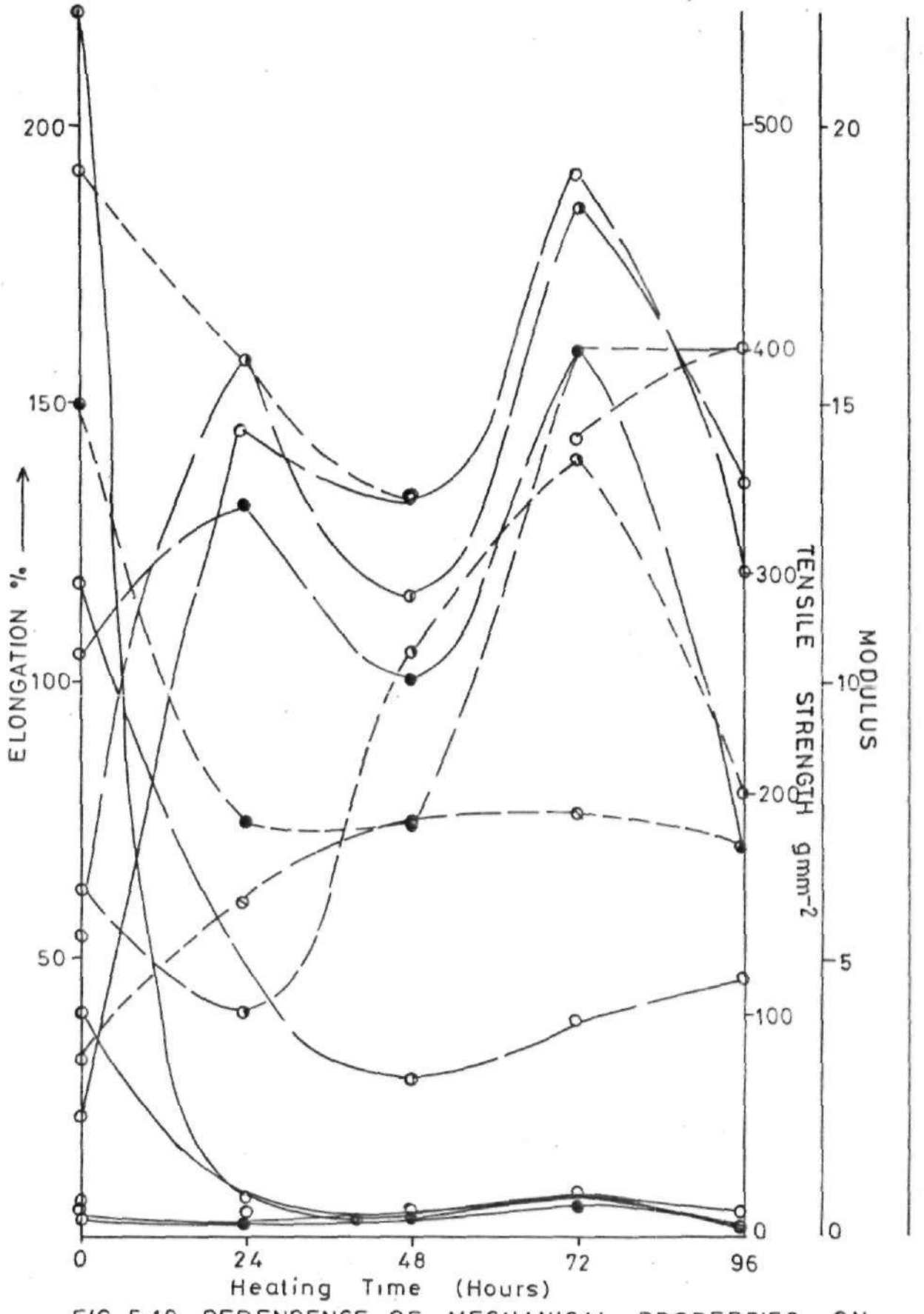


FIG. 5·10 DEPENDENCE OF MECHANICAL PROPERTIES ON HEATING TIME FOR PVA, PMMA AND PVA: PMMA BLENDS ON HEATING TIME

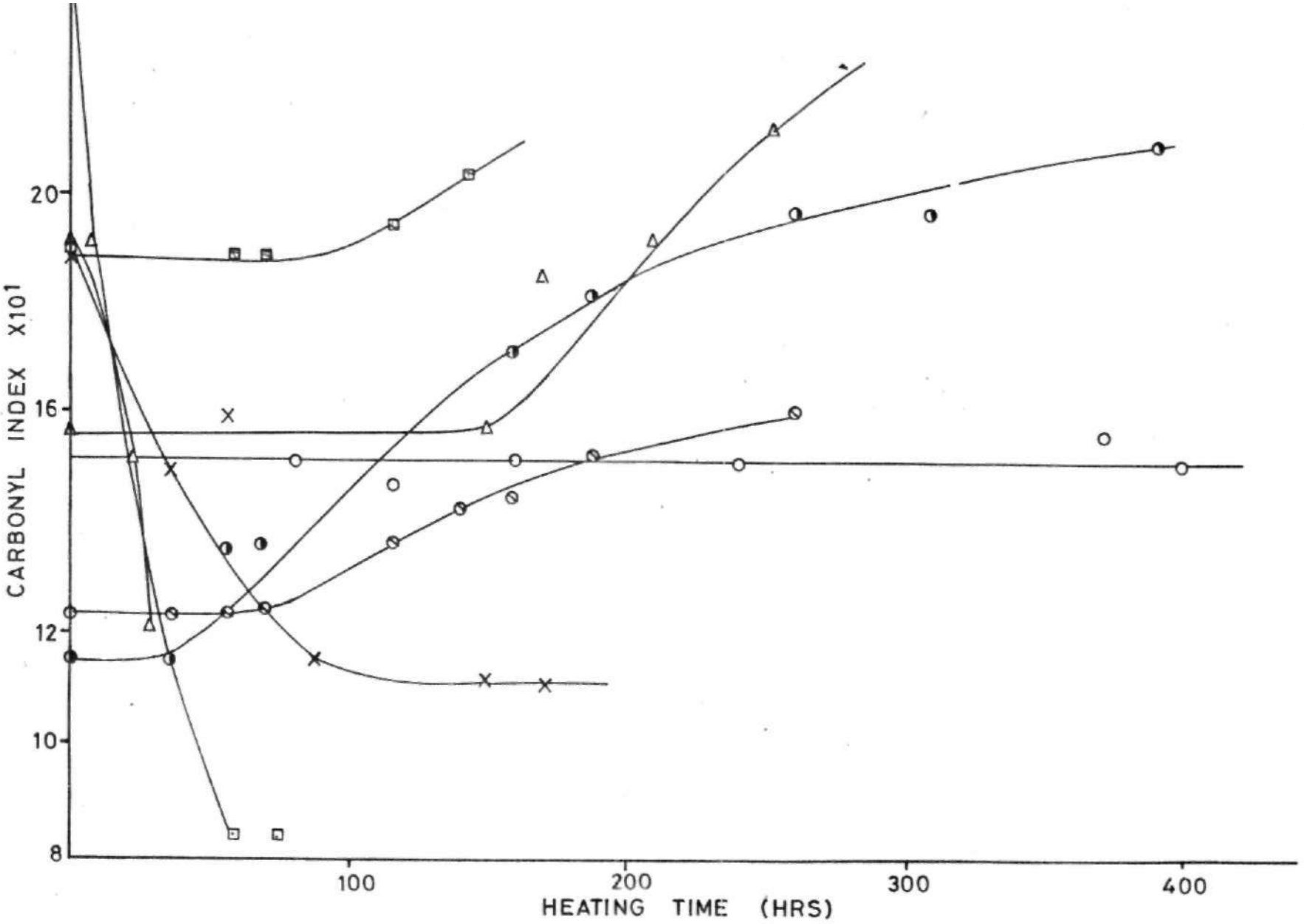


FIG. 5·11 DEPENDENCE OF CARBONYL INDEX ON HEATING TIME FOR PVA/PMMA BLENDS
○ 100% PMMA ◎ 10:90 PVA:PMMA. ◑ 30:70 PVA:PMMA × 40:60 PVA:PMMA □ 50:50 PVA:PMMA
△ 60:40 PVA:PMMA ▣ 70:30 PVA:PMMA ⊙ 80:20 PVA:PMMA ▲ 100 % PVA

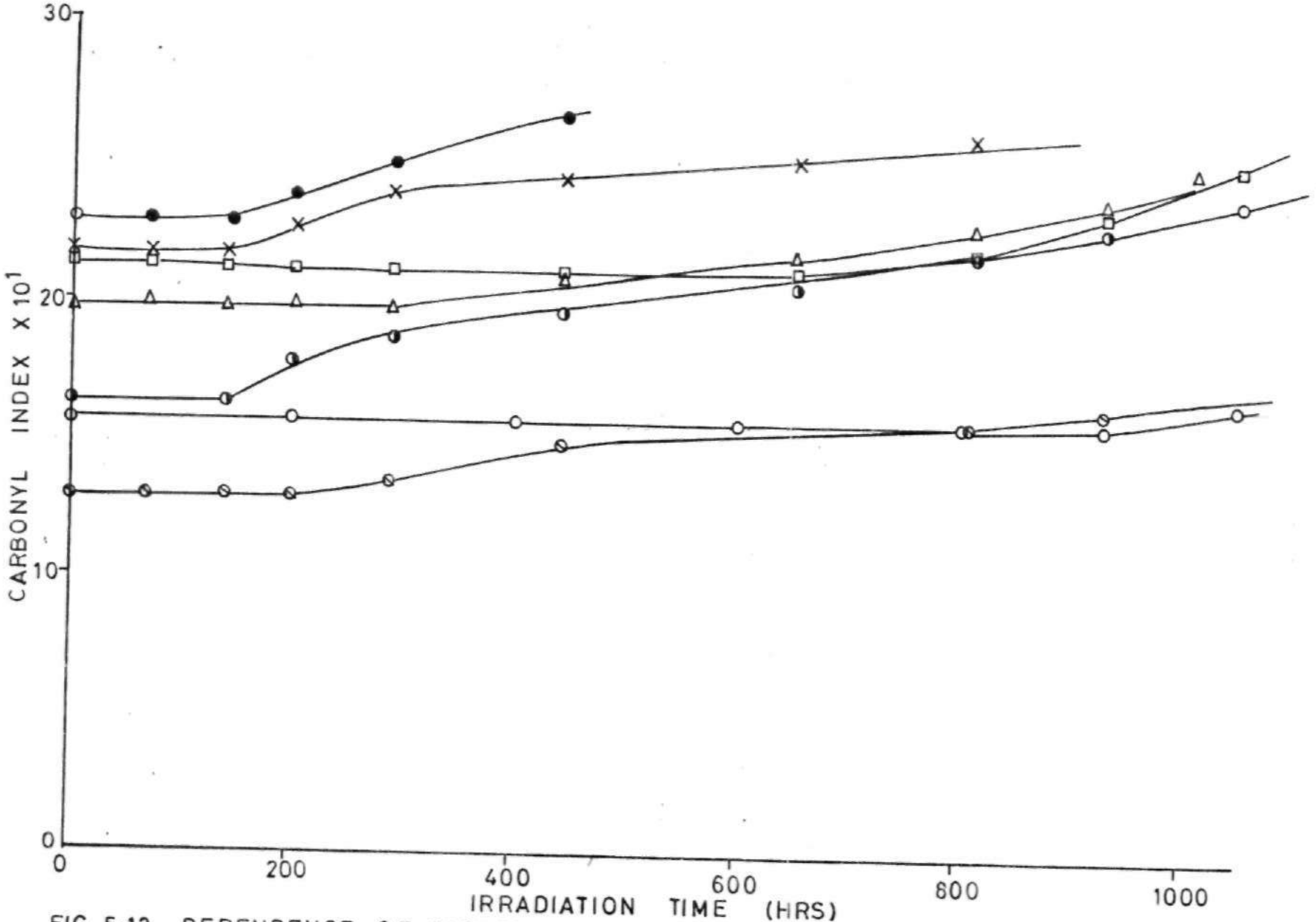


FIG. 5·12 DEPENDENCE OF CARBONYL INDEX ON UV IRRADIATION TIME FOR RVA/PMMA BLENDS

○ 100% PVA ◎ 10:90PVA:PMMA △ 70:30PVA:PMMA ◑ 30:70PVA:PMMA

□ 80:20PVA:PMMA × 50:50PVA:PMMA ● 90:10PVA:PMMA

CHAPTER 6

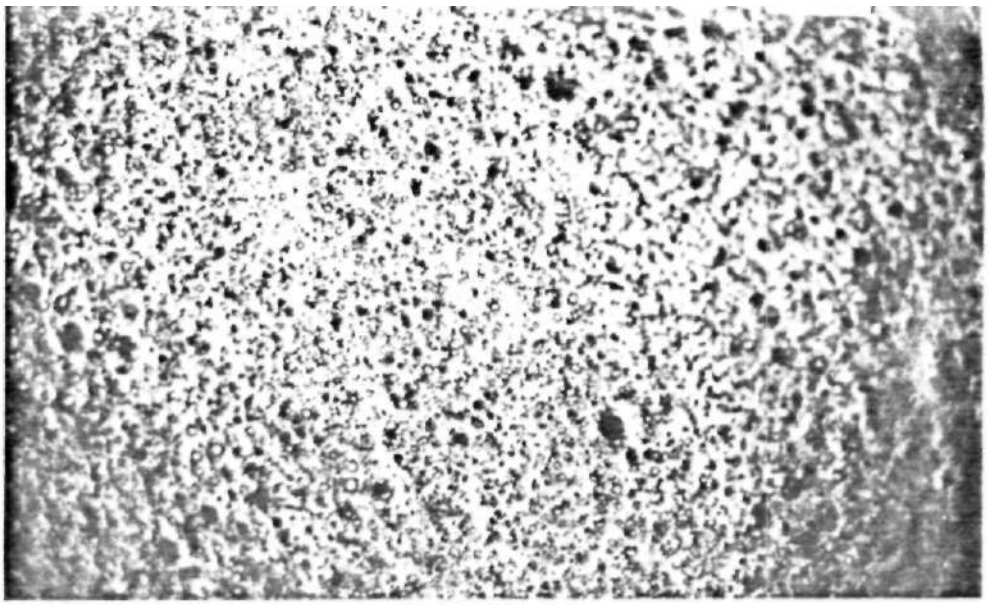
STUDIES ON PVA/PS BLENDS

In this work studies were carried out on density, morphology, mechanical properties and microstructure of the unmixed polymers and their blends. Changes in microstructure were monitored using the infra-red spectra of the films. The homopolymers and their blend films were subjected to outdoor weathering, thermal oxidative degradation and irradiation with ultraviolet rays. The techniques adopted in these studies are as contained in Chapter 3.

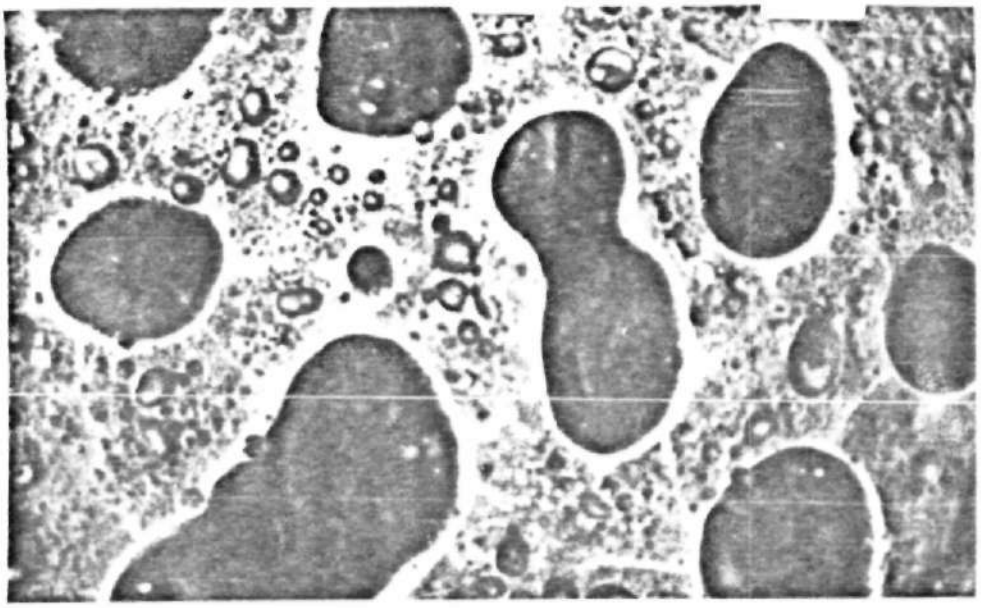
6.1 RESULTS AND DISCUSSION

6.11 Compatibility studies

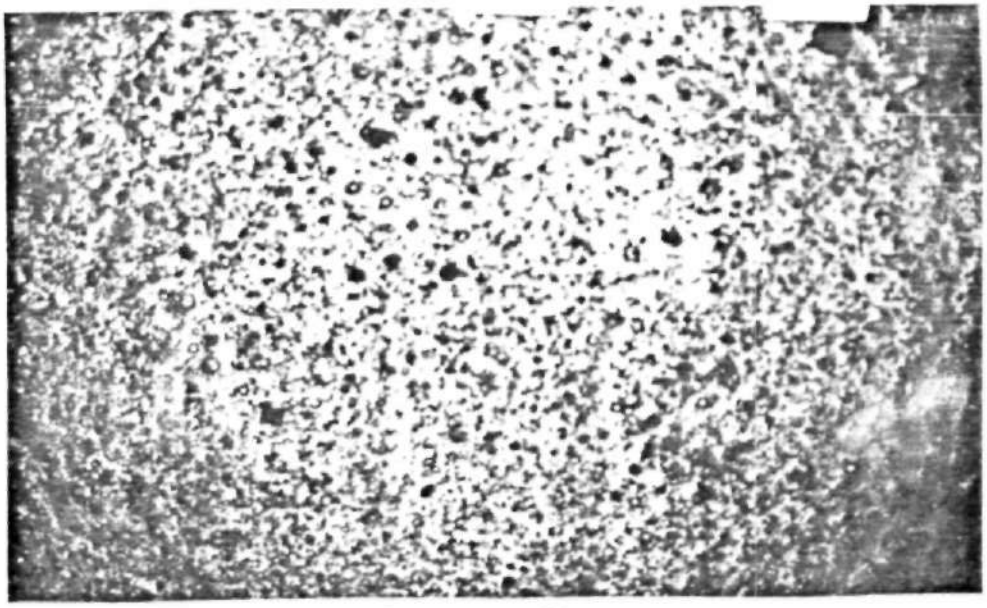
Compatibility studies were effected through calculations and measurement of densities of the homopolymers and their blends and taking the light micrographs of the 30:70, 50:50 and 80:20 PVA:PS blends. In the calculation of densities, the additivity of volumes was assumed. Figure 6.1 shows the plots of the measured and calculated densities. The disagreement between these two values suggests the incompatibility of the two polymers (4, 5, 14). Plate 2, shows the light micrographs of the 30:70, 50:50 and 80:20 PVA:PS blends. The films were opague, with opacity increasing with increase



30:70 PVA:PS



50:50 PVA:PS



80:20 PVA:PS

Plate 2: Light micrographs of PVA:PS blends; magnification x 30

in PS concentration in the blend. This indicates phase separation in the blends (3). With these observations, it is logical to conclude that PVA and PS are incompatible at all levels of blend composition. In the micrographs, PS forms the continuous phase, in whose metrix is embedded PVA.

6.12 Outdoor weathering

Figure 6.2 shows the stress-strain curves of PVA, PS and the PVA:PS blends at zero hour. The shapes of the curves show PS to be a typically hard and brittle polymer while PVA is typically soft and tough. Rigidity is observed to increase with increase in the PS component of the blend. At 2% elongation PVA had under its curve an area of 4.6 sq cm At the same strain, 90:10 PVA:PS had an area of 10.60 sq cm 50:50 PVA:PS had an area of 16 sq cm, 20:80 PVA:PS had 24 sq cm while PS had 40 sq cm. The films showed stress whitening and little necking.

Figure 6.3 shows the dependence of modulus, tensile strength and percentage elongation of PVA, PS on composition at both zero hour and after 20 days outdoor weathering. At zero hour, both modulus and tensile strength showed similar trends. The two increased with increase in PS in the blend and neither showed a minimum. Percentage elongation, on the other hand decreased with increase in the PS component of the blend and showed minima at 10:90, 20:80 and 30:70 PVA:PS. This suggests that at those blends compositions PVA causes deterioration of mechanical properties. After 20 days outdoor weathering, much improvement was produced in modulus, particularly at the compositions 40:60-70:30 PVA:PS, where

the value was highest and virtually the same. Tensile strength showed minimum at 30:70 PVA:PS composition. The increase in rigidity indicated by the high values of modulus and tensile strength at this point in the outdoor weathering is compensated for by the sharp drop in percentage elongation. Among the blends the 30:70 blend showed the lowest tensile strength, lowest modulus and at the same time lowest percentage elongation.

Figures 6.4(a) and (b) show the dependence ~~the~~ of percentage elongation of PVA, PS and the PVA:PS blends on outdoor exposure time. The unmixed PVA reached a plateau and then dropped. The same behaviour is observed for the 50:50, 40:60, 30:70, 20:80 and 10:90 PVA:PS blends. The rest of the blends and the unmixed PS showed continuous decrease in percentage elongation on exposure to outdoor weathering.

Figure 6.5 shows the dependence of tensile strength of PVA, PS and PVA/PS blends on outdoor weathering time. Some of the blend curves are omitted to make for clarity. For each of the blends and the homopolymers, tensile strength increased to a maximum and then decreased. It is observed that the time to attain a maximum in tensile strength increased with increase in PVA in the blend; although the 30:70 PVA/PS showed the steepest fall in tensile strength and reached its maximum before any other blend. This, along with the earlier observation that the 30:70 PVA/PS blend showed the lowest tensile strength, lowest modulus and lowest percentage elongation, tends to suggest that PVA produces deterioration in the mechanical properties of PS, and then is highest at this composition.

Figure 6.6 shows the dependence of modulus of PVA/PS

blends on outdoor weathering time. Except for the unmixed PS, which showed an initial decrease, then increased to a maximum and finally dropped, all the blends showed the same trend. Like the unmixed PVA, they all showed an increase to a maximum and then decreased. The time to attain a maximum increased with increase in PVA in the blend, reached a maximum at 50:50 and 60:40 PVA/PS and then decreased again. This trend suggests that some degree of interaction could be taking place at the phase boundaries, thus resulting in a reinforcement in property at near 50:50 PVA/PS blend composition.

Changes in the microstructure of the blends and the unmixed polymers were monitored using their infra-red spectra. Table 1 shows the induction and embrittlement times of PVA, PS and PVA/PS blends on outdoor weathering.

Table 1

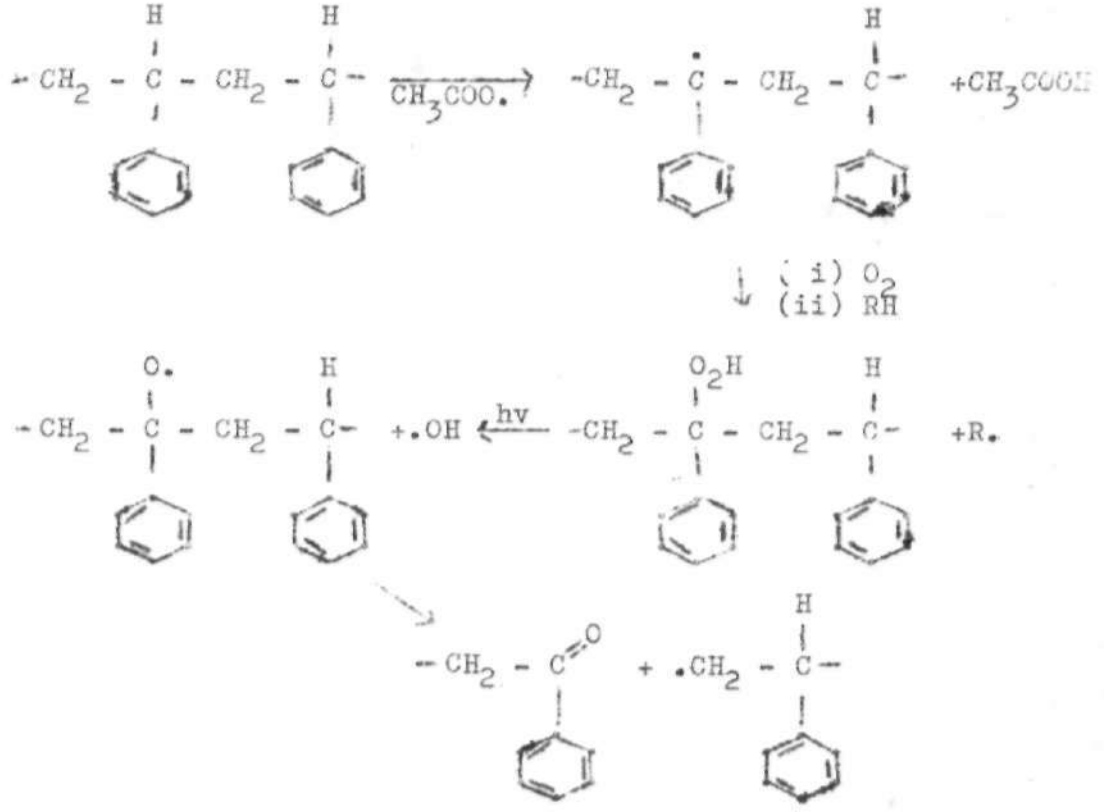
Induction and embrittlement times for PVA/PS blends on outdoor weathering

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PS	360	634
10:90 PVA:PS	340	802
20:80 PVA:PS	325	802
30:70 PVA:PS	210	802
40:60 PVA:PS	80	802
50:60 PVA:PS	250	1294
60:40 PVA:PS	-	641
70:30 PVA:PS	-	1294
80:20 PVA:PS	120	1294
90:10 PVA:PS	110	1440
100% PVA	240	1440

Figure 6.7 shows the indices of carbonyl absorption peaks of PVA/PS blends on outdoor weathering. All the blends and the homopolymers showed induction periods. PS showed the longest induction period and embrittlement soon after. PVA showed the steepest growth in indices of carbonyl absorption peaks. The decrease in induction period as PS decreased in the blend up to 40:60 PVA/PS suggests increased vulnerability to oxidative degradation on outdoor weathering as result of blending the two homopolymers. It is observed that the higher the PS in the blend the slower the rate of carbonyl growth.

From the induction period, it appears the degradation of PVA started before that of PS. There is reduction in induction time with increase in PVA concentration in the blend and above 20% PVA in the blend, the induction period falls below those of both homopolymers. This implies that the oxidizability of PS and PVA is increased on blending. This suggests interaction at least at the phase-boundaries. The breaking of the PS component and its subsequent oxidation would therefore occur readily if small radicals from PVA diffused into the PS phase to abstract a tertiary hydrogen atom. This should then leave a polystyryl radical which can be radily attacked by atmospheric oxygen to initiate the oxidative degradation of PS.

For the unmixed PS exposed for outdoor weathering, ultraviolet rays from the incident sun rays can induce the formation of macroradicals via the abstraction of a hydrogen atom. The following mechanism is therefore proposed for the degradation of PS in the blend.



The rate of hydrogen abstraction from the PS main chain must be accelerated by the diffusion of acetate radicals into the PS phase to account for the increased rate of carbonyl growth with increase in PVA in the blend. Since the polymers are incompatible (3) these interactions must be taking place at the phace boundaries to explain the reinforcement in mechanical properties as observed in modulus and tensile strength on outdoor weathering of the blends.

Figure 6.8 shows the dependence of intrinsic viscosity of PS on outdoor exposure time. The continuous decrease in molecular weight suggests that chain scission started soon on exposure. From the graph it may be assumed that cross-linking does not take place when unmixed PS in degraded by outdoor weathering.

6.3 Thermal oxidative degradation

Changes in the microstructure of PVA/PS blends exposed to oven aging were monitored using their infra-red spectra. Changes in mechanical properties were followed by calculating changes in tensile strength, modulus and percentage elogation. Figure 6.9 shows the dependence of tensile strength, modulus and percentage elongation on oven aging time. It is observed that the higher the PVA in the blend, the greater the fall in percentage elongation on heating. For PS and 20:80 PVA:PS blend, there was little or no change in percentage elongation on heating. For any given composition, modulus and tensile strength are observed to show similar trends. For PS these properties decreased on heating up to 48 hours, showed a small increase on the third day and finally decreased on the fourth day. For 80:20 PVA:PS blend, the properties increased, reached a maximum and then decreased.

The unmixed PS showed continuous decrease in tensile strength until after 72 hours of heating when a small increase in property was recorded. Reiner (48) noted that the thermal degradation of PS results in depolymerization giving rise to decreasing amounts of monomer, dimer, trimer, tetremer and pentamer. Jellinek (58) accounted for the features of thermal degradation of PS in terms of formation and subsequent decomposition of hydroperoxides. Stromberg, Stratus and Achhammer (38) established that benzaldehyde, formaldehyde, formic acid, carbon dioxide, carbon monoxide and water were the products of thermal oxidative degradation of PS. These indicate that there should be rapid degradation of PS on thermal aging as is reflected in the decrease in tensile

strength and modulus on heating.

For the blends it is observed that tensile strength and modulus increased, got to a maximum and then decreased. The initial increase in these properties can be accounted for in terms of increased rigidity as a result of a probable build up in carbon-carbon double bond formed during the deacetylation of the PVA component of the blends and the possibility of cross-link formation among the microradicals formed during degradation.

Figure 6.10 shows the dependence of carbonyl index of PVA, PS and PVA/PS blends on oven aging time. Table 2 shows the induction and embrittlement times for the same system.

Table 2

Induction and embrittlement times for PVA, PS and PVA/PS blends on oven aging

Polymer/blend	Induction times (hrs)	Embrittlement time (hrs)
100% PS	120	367
10:90 PVA:PS	150	418
20:80 PVA:PS	140	960
30:70 PVA:PS	127	291
40:60 PVA:PS	140	418
50:50 PVA:PS	160	418
60:40 PVA:PS	100	351
70:30 PVA:PS	70	208
80:20 PVA:PS	-	57
90:10 PVA:PS	-	291
100% PVA	12	29

PVA had an induction period of 12 hours after which it decomposed rapidly, resulting in a rapid decrease in carbonyl index. The 90:10 and 80:20 PVA/PS blends showed no induction periods. This suggests that at these blend compositions the PVA destabilizes PS. This also accounts for the low induction period of the 70:30 PVA:PS blend. This can only occur via the diffusion of acetate radicals into the PS phase as explained in section 6.3. It could be seen that for all the blends, except for the 50:50 PVA:PS blend, induction period decreased with increase in PVA content of the blends. PVA concentrations exceeding 50% caused reduction in both induction and embrittlement times while concentrations below this value caused increases in both. This was found to be highest at equal proportion of both homopholymers in the blend. This is cooperative stabilization.

Only PS, 10:90 and 20:80 PVA:PS blends showed continuous increase in indices. The rest were found to show an initial increase after which they showed sudden decrease and in most cases fell below the initial carbonyl index. The decomposition of PVA was accompanied by sharp decreases in the carbonyl and reference methylene group absorptions.

6.4 Ultraviolet degradation

Films of the blends and unmixed polymers were irradiated with UV light. Changes in macrostructure were monitored using both their infra-red and ultraviolet spectra.

Table 3 shows the induction and embrittlement times for the carbonyl absorption peaks and Figure 6.11 shows the dependence of indices of carbonyl absorption of PVA, PS and

PVA/PS blends on ultraviolet irradiation time PVA is observed to be very stable to ultraviolet irradiation. PS, on the other hand, is very vulnerable to UV degradation. The table reveals that as little as 10% PS in a blend with PVA causes marked destabilization of PVA, the induction period of most of the blends being the same as that of the unmixed PS. All of them showed continuous increase in indices immediately after the induction period.

Table 3

Induction and embrittlement times of PVA, PS and PVA/PS on ultraviolet irradiation

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PS	330	775
10:90 PVA:PS	330	1263
20:80 PVA:PS	330	818
30:70 PVA:PS	330	916
40:60 PVA:PS	360	1263
50:50 PVA:PS	330	1358
60:40 PVA:PS	330	1263
70:30 PVA:PS	360	1263
80:20 PVA:PS	300	818
90:10 PVA:PS	480	1358
100% PVA	1052	2826

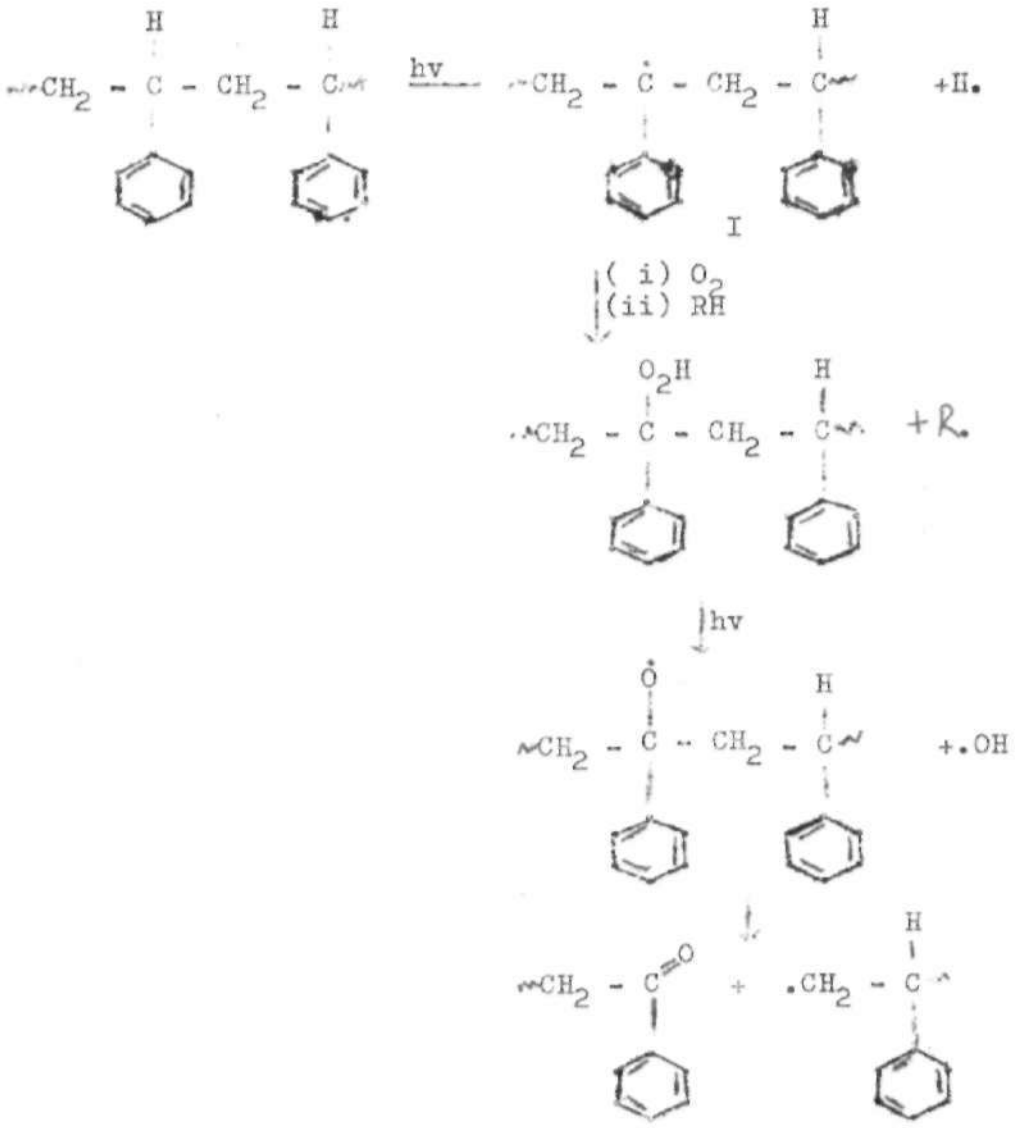
Grassie and Weir (55) observed that PS on photolysis gave off hydrogen gas and the polystyryl radicals formed resulted in crosslinking and unsaturation in the main chain.

They were of the opinion that crosslinking was concurrent with hydrogen evolution. They noted that insolubility and embrittlement of PS occured after short period of irradiation.

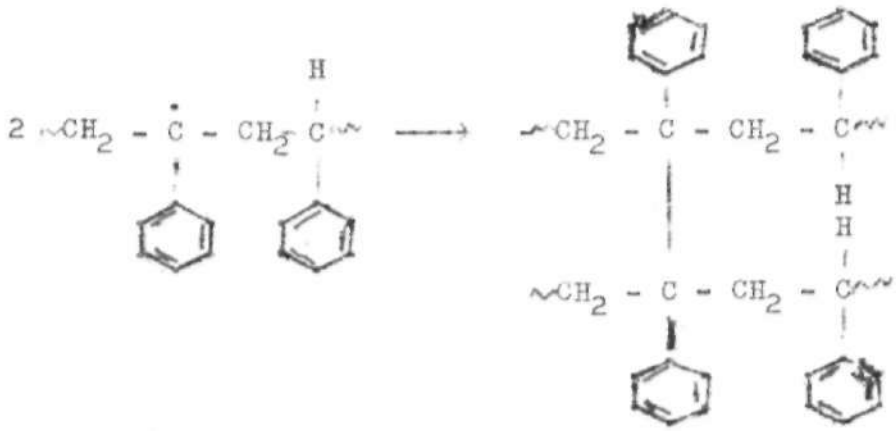
Rabek and Randy (62) observed that the mechanism of PS photolysis in the solid state depended on the mobility of the free radicals in the polymer matrix and their recombination. Free hydrogen radicals diffuse readily through the polymer matrix and recombine in pairs or abstract hydrogen atoms from PS chains. On the other hand the polystyryl radicals have limited mobility. They may abstract hydrogen atoms from neigbouring polystyrene chains or combine with other polystyryl radicals in the vicinity, thereby giving rise to crosslinking. They could also react with oxygen to give oxidative products. The main reactions involved in the photolysis of PS are chain scission, crosslinking and oxidative degradation (65).

Kolawole and Agboola (67) made similar observations in this laboratory on the photolysis of PS.

The following mechanism is hereby proposed for the ultraviolet degradation of PS.

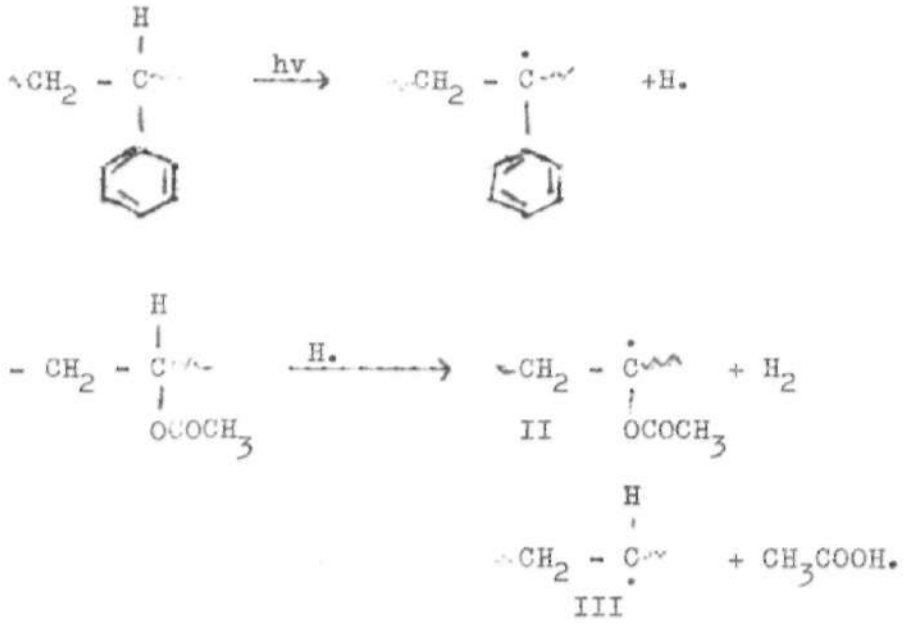


Macroradical (I) could also undergo crosslinking

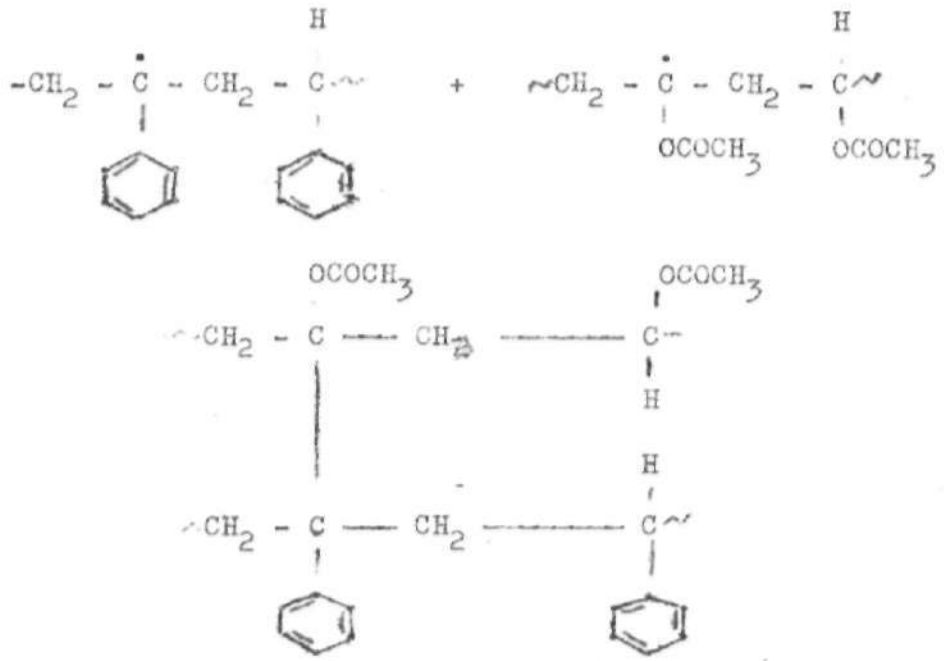


The destabilizing effect of PS on PVA towards UV degradation arises from the migration of hydrogen radicals into the PVA phase and the subsequent abstraction of hydrogen atoms and or the acetate radicals. The abstraction of these radicals, should produce macroradicals which can either undergo oxidative degradation or crosslink with polystyryl radicals:

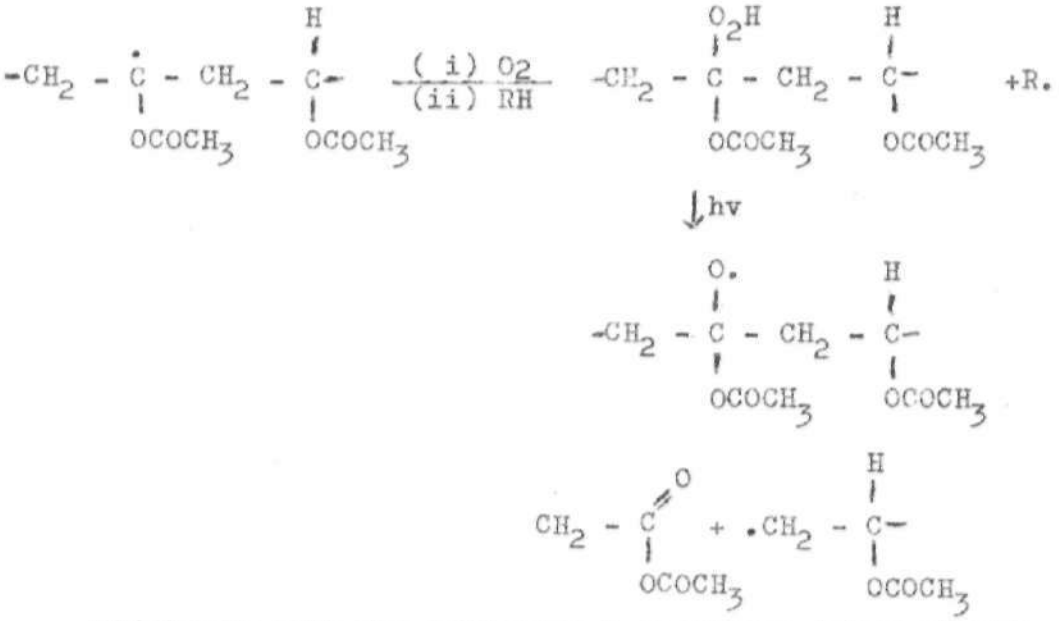
The following mechanism is therefore proposed for the ultraviolet degradation of PVA in the blend.



Matroradical (II) can undergo crosslinking with the polystyryl macroradical (I).



The macroradicals (II) and (III) can undergo oxidative degradation.



Whichever path the oxidative degradation takes should result in an increase in carbonyl absorption.

There should be considerable interaction between PVA and PS in the system. It must be emphasized that this interaction is limited by the immiscibility of the two homopolymers in the

blends, but once the reaction is initiated, it propagates fast throughout the phases.

6.2 CONCLUSION

The two polymers are incompatible. On oven aging PS stabilizes PVA at PS concentrations above 50% in the blends. Cooperative stabilization is observed at the 50:50 blend composition. Thus this blend exhibited the greatest structural stability, although it does not offer the best mechanical properties. The blends offer better mechanical properties than both PVA and PS on oven aging. PS destabilizes PVA against ultraviolet degradation. None of the blends has an induction or embrittlement time half that of the unmixed PVA. On outdoor weathering, it is observed that the 50:50 PVA:PS blend offers the best compromise in structural stability. There was considerable destabilization of PVA by PS at PS concentrations exceeding 50%.

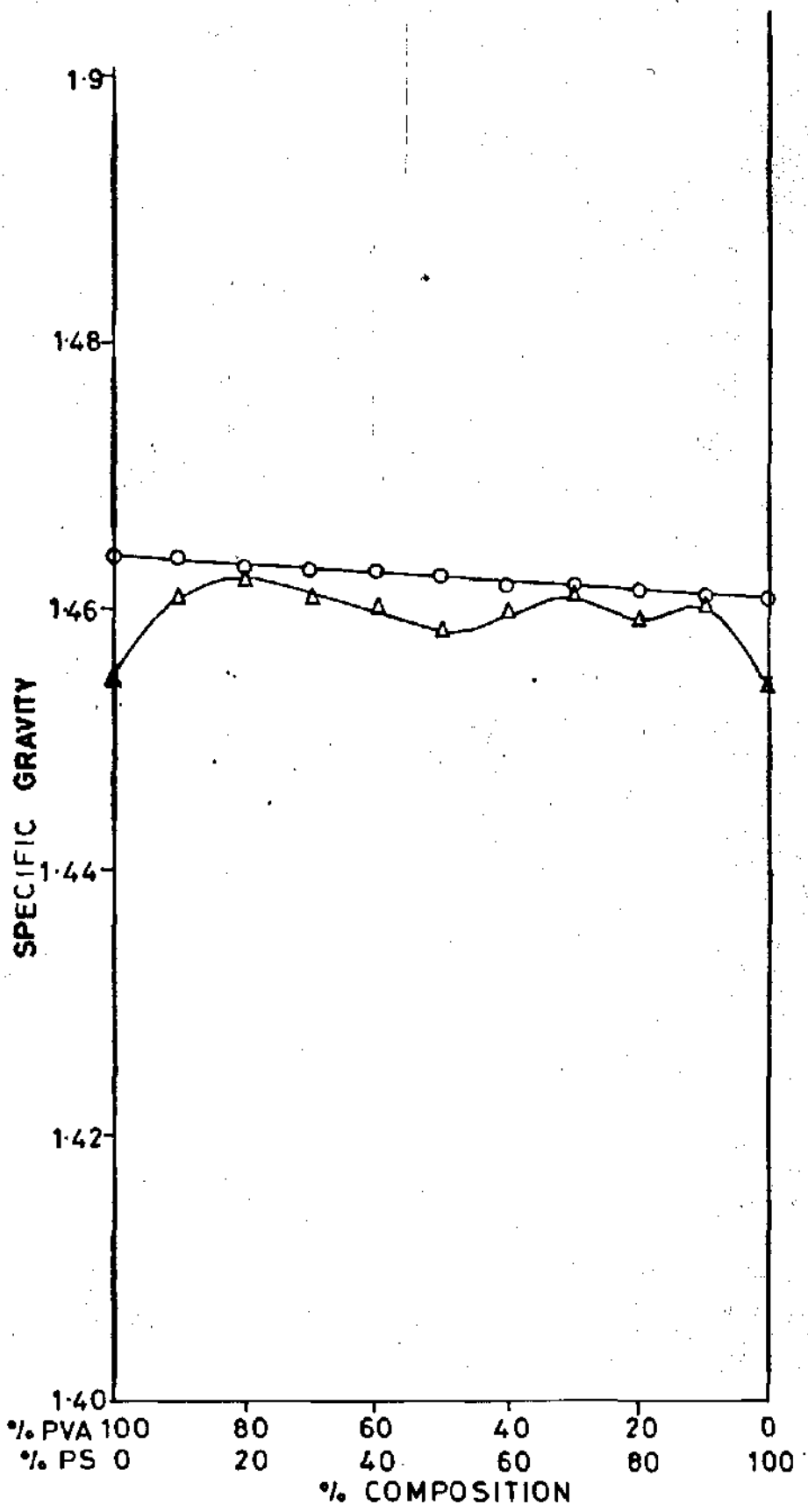


FIG. 6·1 DEPENDENCE OF SPEEIFIC GRAVITIES OF PVA/PS BLENDS ON % COMPOSITION

o THEORETICAL Δ PRATICAL

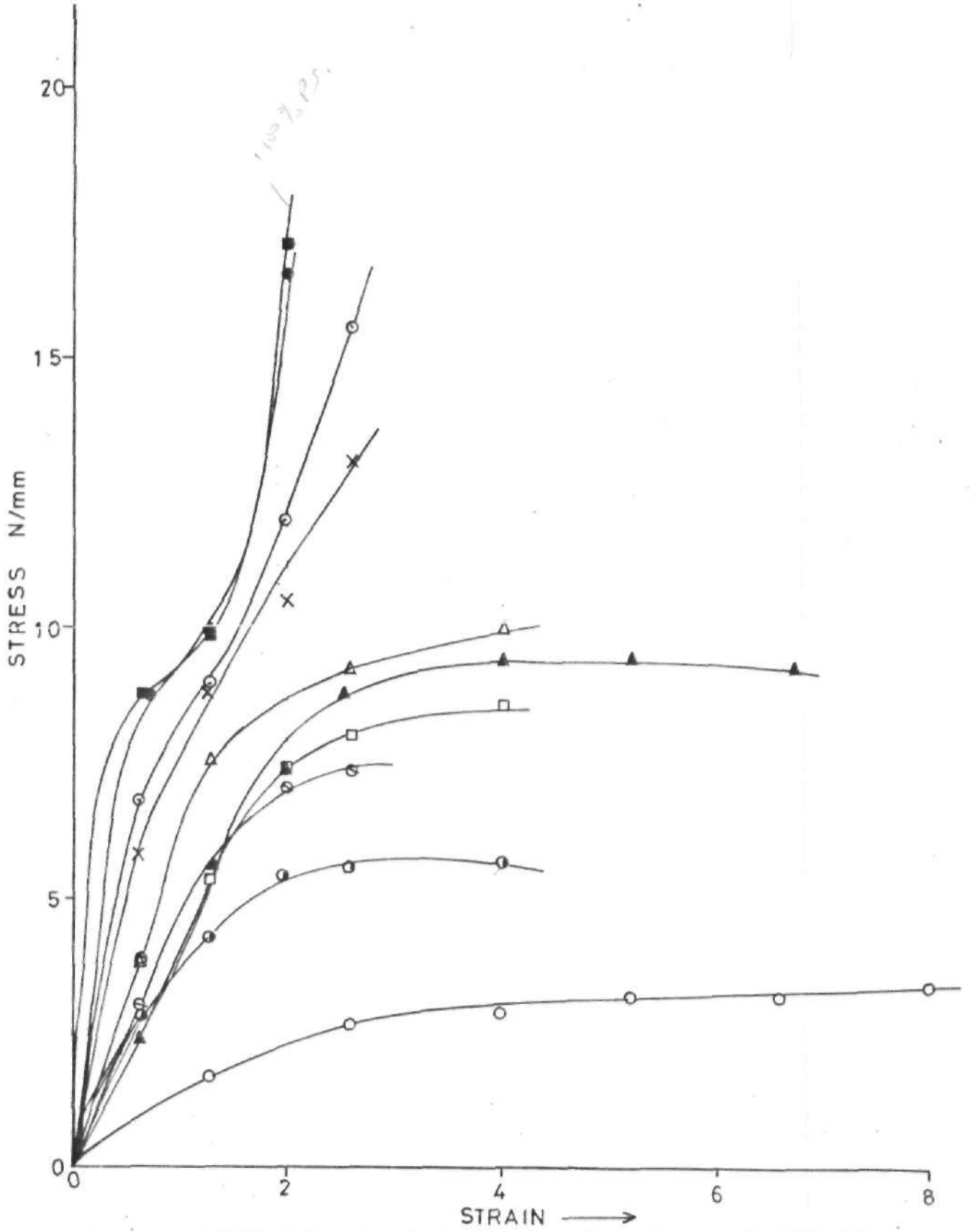


FIG. 6·2 STRESS-STRAIN CURVES OF PVA, PS AND PVA/PS BLENDS AT ZERO TIME

○ 100% PVA ● 10:90 PVA:PS ◎ 20:80 PVA:PS × 30:70 PVA:PS

△ 40:60 PVA:PS ▲ 50:50 PVA:PS ◔ 60:40 PVA:PS □ 70:30 PVA:PS

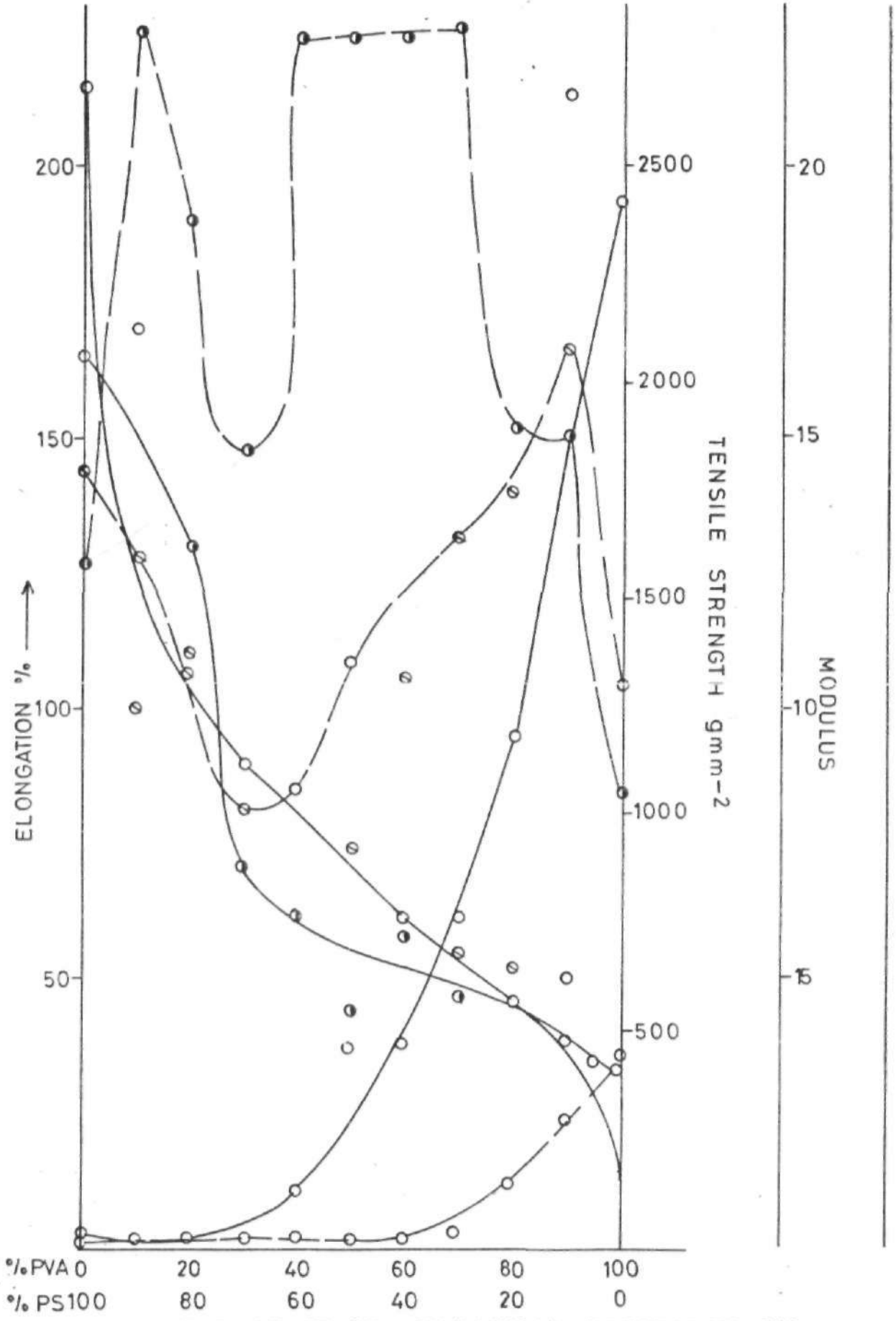


FIG. 6·3 DEPENDENCE OF MECHANICAL PROPERTIES ON COMPOSITION OF PVA/PS BLENDS

◑ MODULUS, o% ELONGATION ——— AT ZERO HOUR

⊖ TENSILE STRENGTH — — — AT 20 DAYS

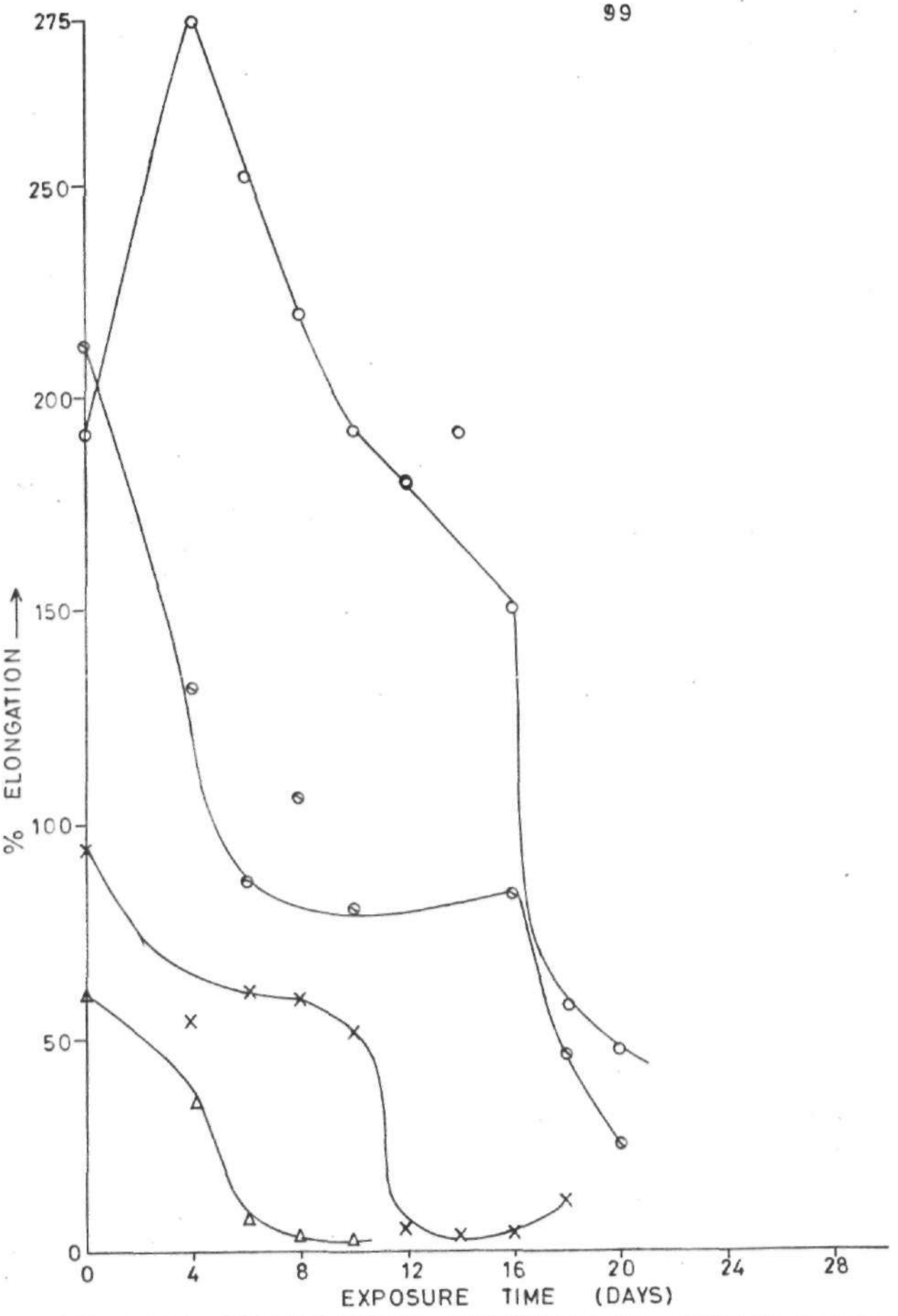


FIG. 6·4 (a) DEPENDENCE % ELONGATION ON OUTDOOR EXPOSURE TIME FOR PVA:PS BLENDS

○ 100 % PVA ⊖ 100 % PS ◑ 90:10 PVA:PS × 80:20 PVA:PS

△ 70:30 PVA:PS

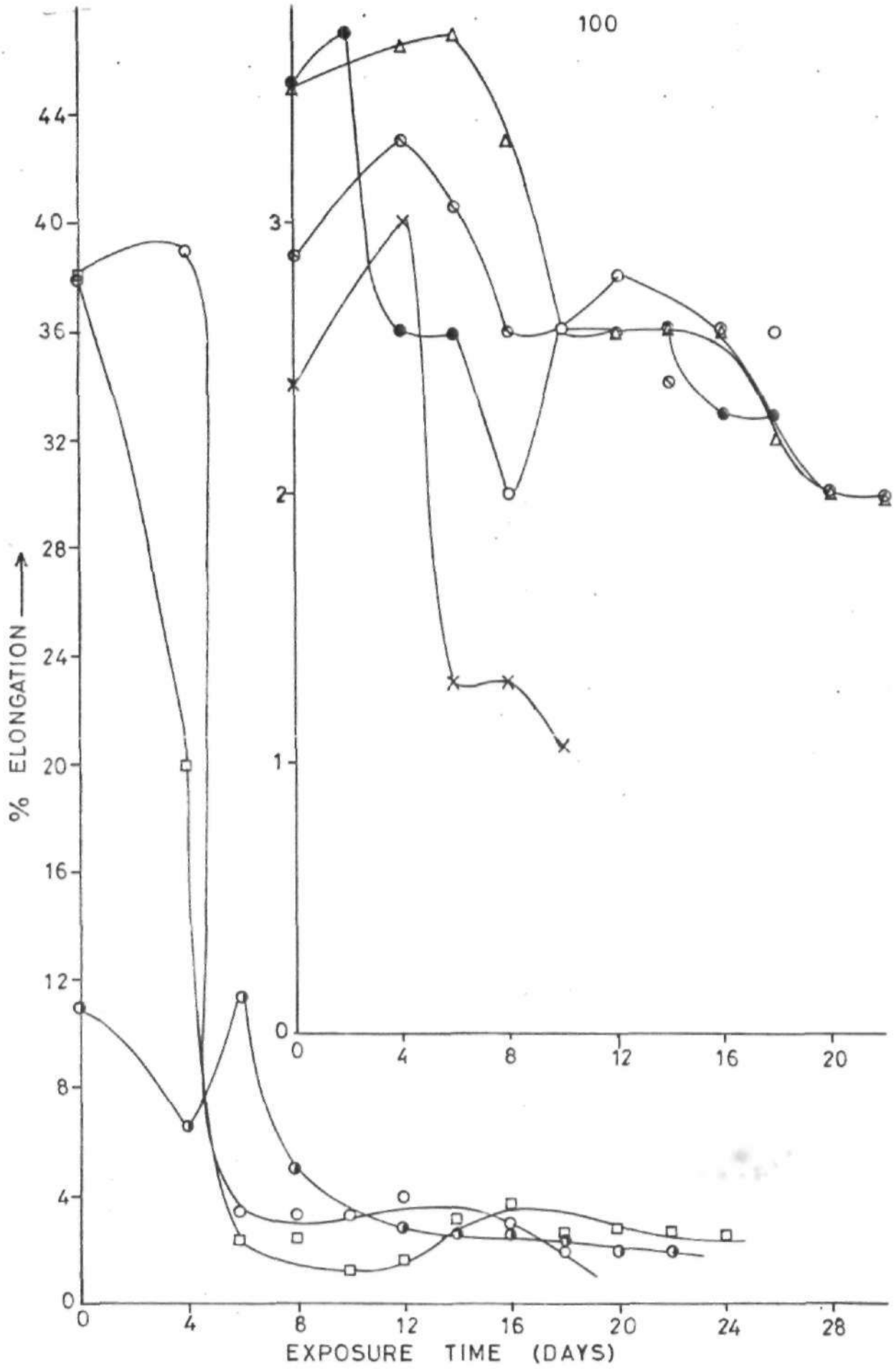


FIG. 6·4(b) DEPENDENCE OF % ELONGATION ON EXPOSURE TIME FOR PVA/PS BLENDS

○ 60:40 PVA:PS ◻ 50:50 PVA:PS ◐ 40:60 PVA:PS △ 30:70 PVA:PS
⊘ 20:80 PVA:PS × 10:90 PVA:PS ● 100% PS

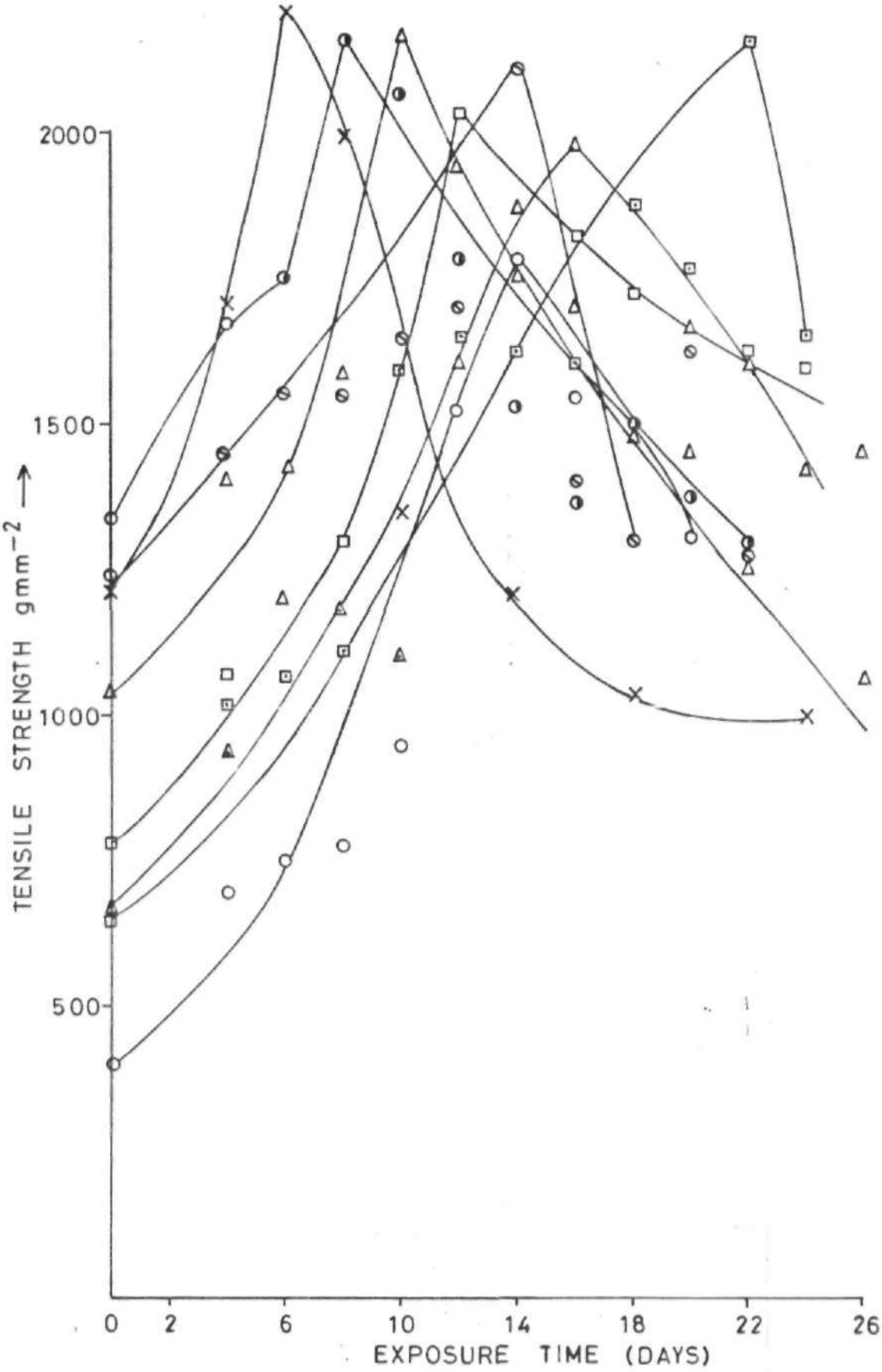


FIG. 6·5 DEPENDENCE OF TENSILE STRENGTH OF PVA/PS BLENDS ON OUTDOOR EXPOSURE TIME

○ 100 % PVA ◔ 10: 90 PVA: PS ◑ 20: 80 PVS: PS × 30: 70 PVA: PS

△ 40: 60 PVA: PS □ 60: 40 PVA: PS ▲ 70: 30 PVA: PS

⊡ 80: 20 PVA: PS

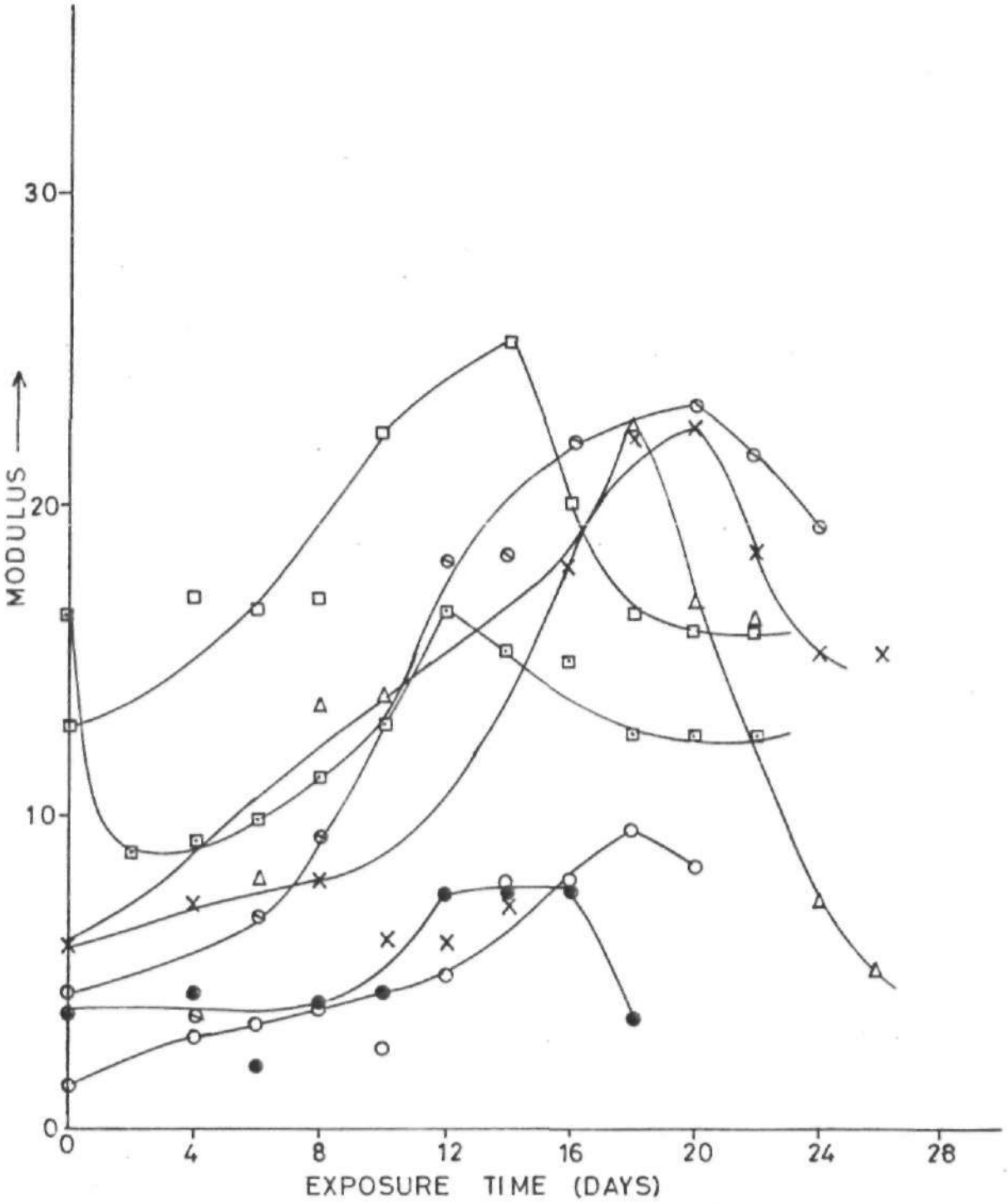


FIG.6-6 DEPENDENCE OF TENSILE MODULUS OF PVA/PS BLENDS ON OUTDOOR WEATHERING TIME

○ 100 % PVA ● 90:10 PVA:PS × 60:40 PVA:PS ⊙ 50:50 PVA:PS

△ 40:60 PVA:PS □ 20:80 PVA:PS ⊡ 100 % PS

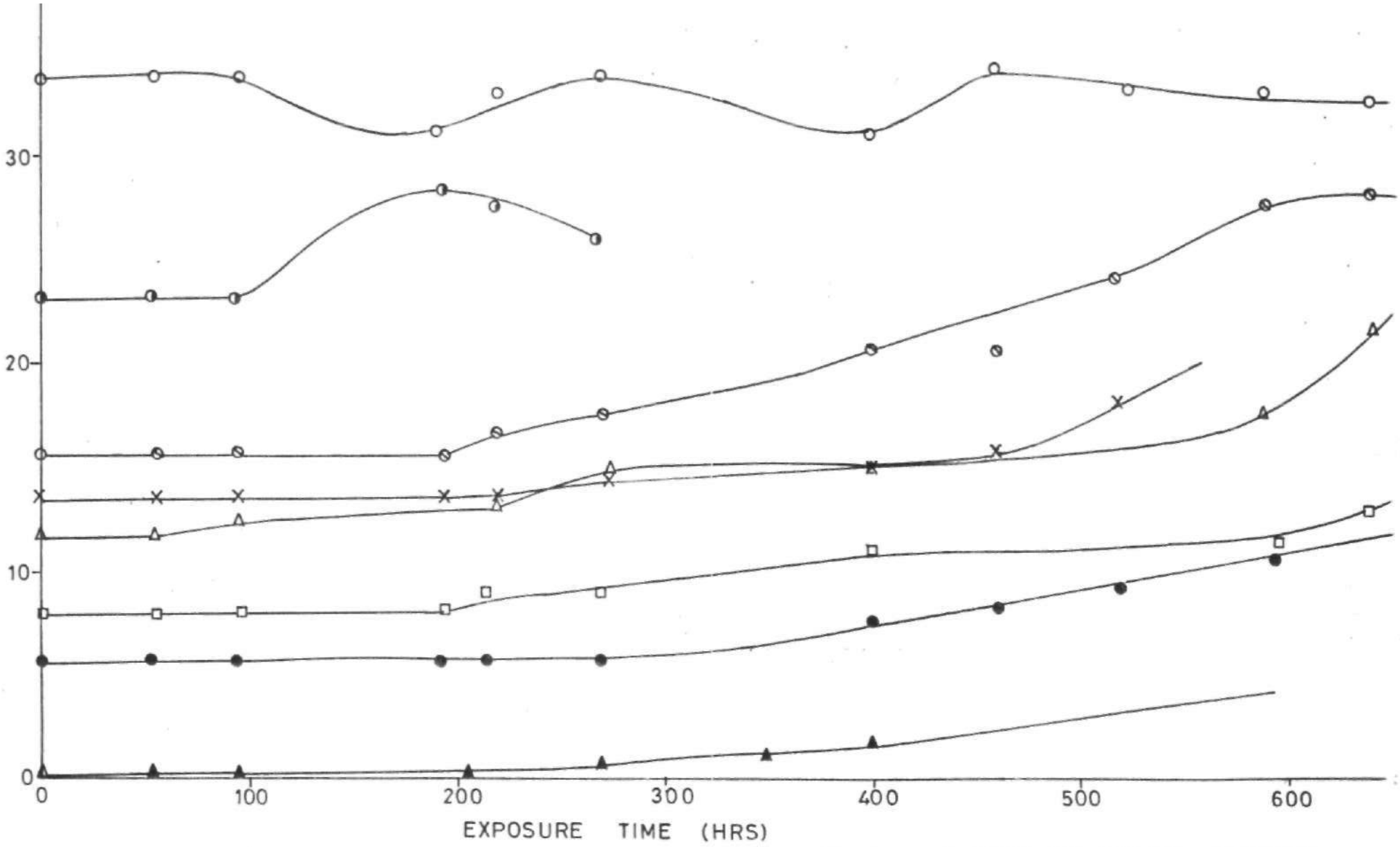


FIG. 6·7 DEPENDENCE ON CARBONYL INDEX ON OUTDOOR EXPOSURE TIME OF PVA/PS BLENDS

○ 90:10PVA:PS ⊘ 100% PVA ◑ 80:20PVA:PS × 50:50PVA:PS △ 40:60PVA:PS □ 30:70PVA:PS ● 20:80PVA:PS
○ 10:90PVA:PS ▲ 100% PS

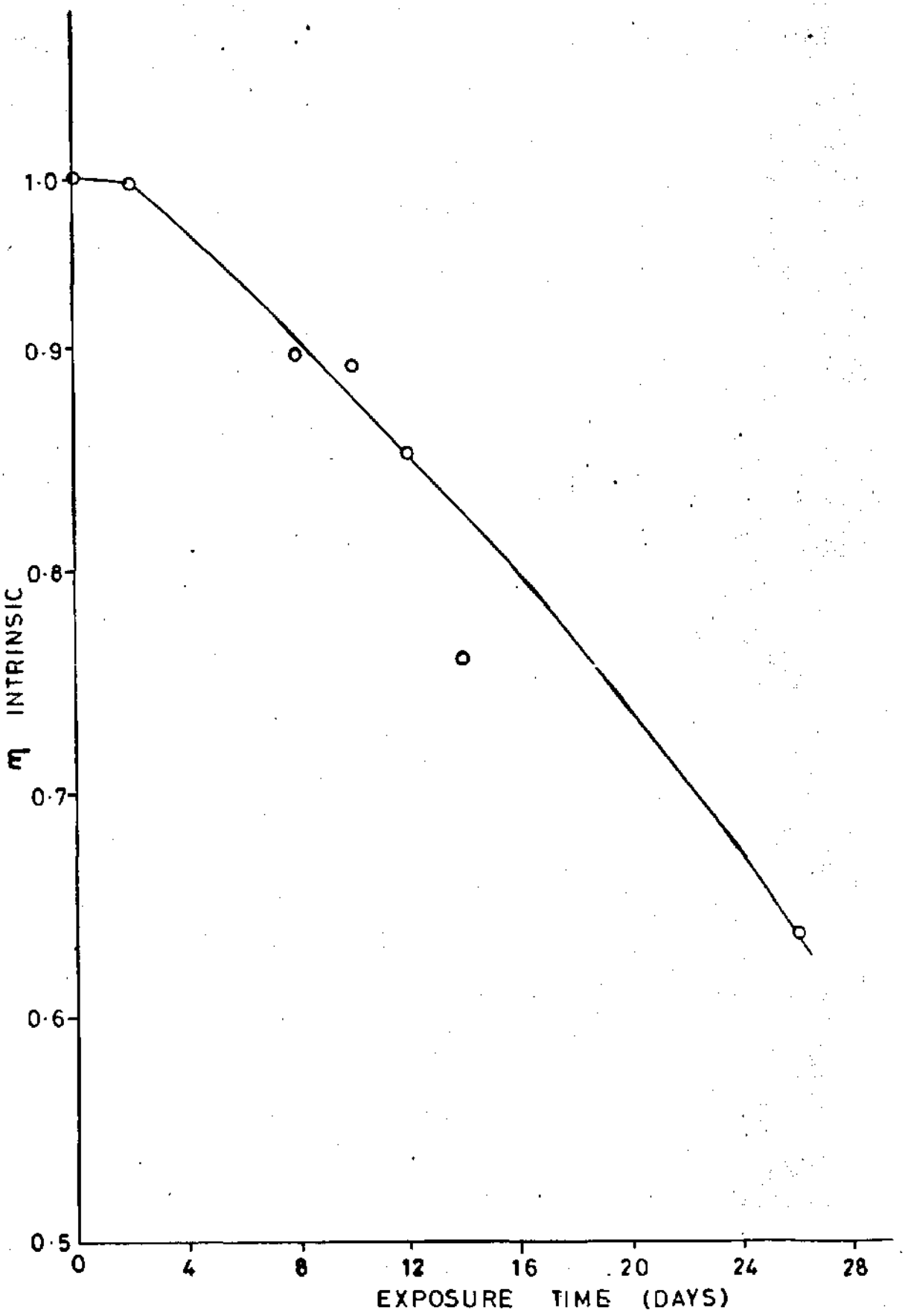


FIG. 6·8 DEPENDENCE OF INTRINSIC VISCOSITY OF PS ON EXPOSURE TIME

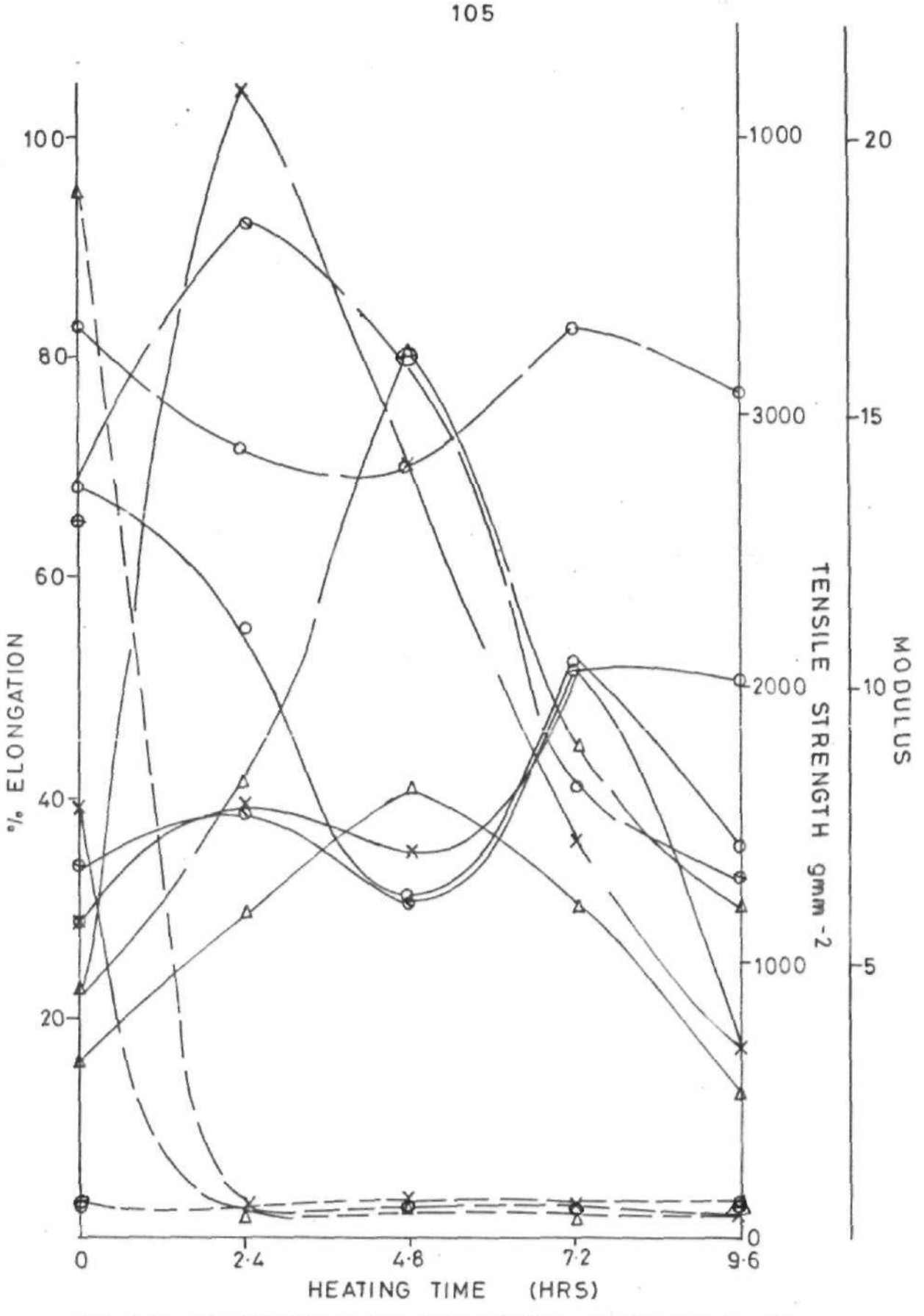


FIG. 6·9 DEPENDENCE OF MECHANICAL PROPERTIES ON HEATING TIME OF PVA/PS BLENDS

o 100% PS o 20:80 PVA:PS × 50:50 PVA:PS △ 80:20 PVA:PS

——— TENSILE STRENGTH —— —— MODULUS

— — — — % ELONGATION

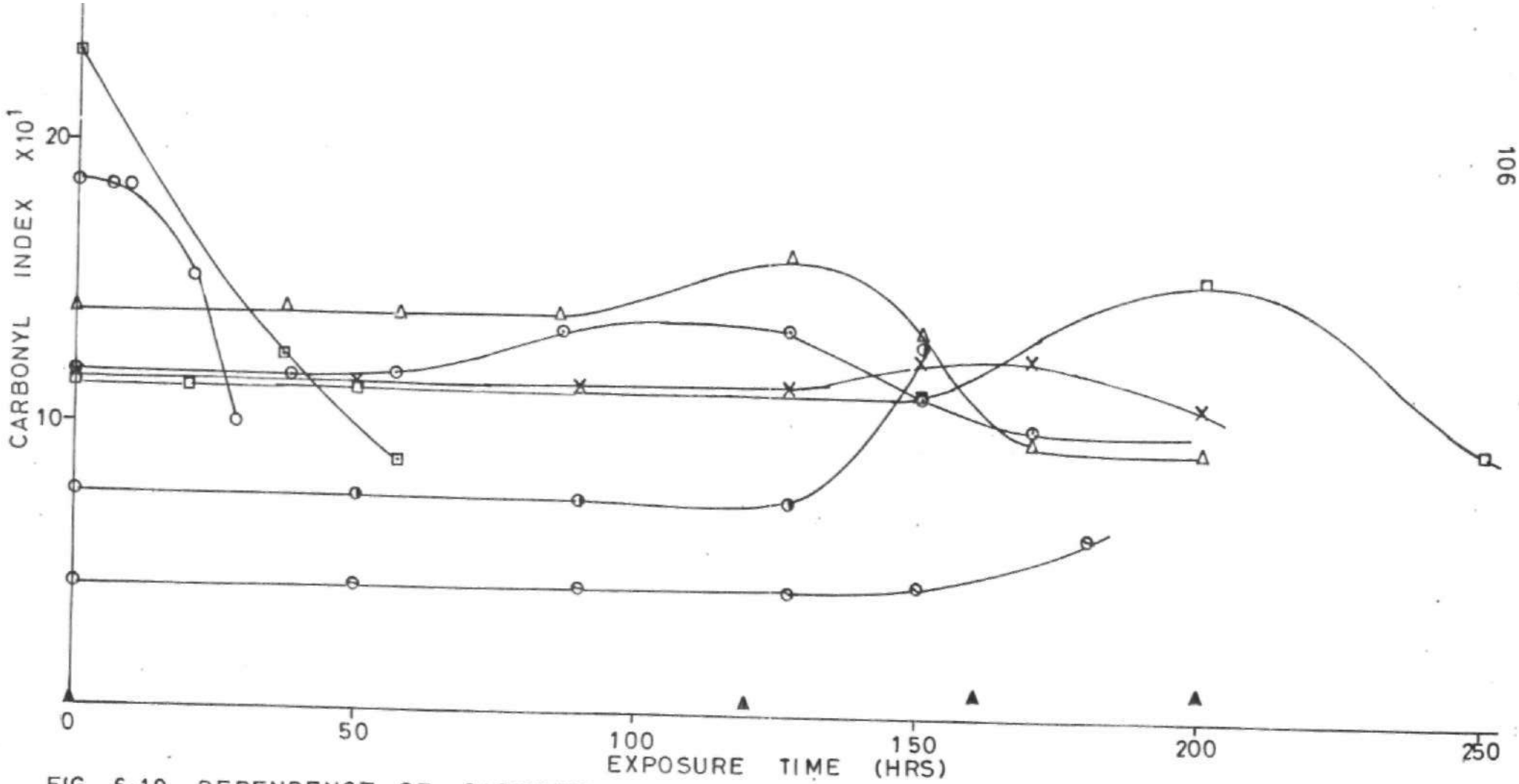


FIG. 6·10 DEPENDENCE OF CARBONYL INDEX FOR PVA/PS BLENDS ON HEATING TIME

○ 100% PVA ⊘ 10:90 PVA:PS ◐ 20:80 PVA:PS X 40:60 PVA:PS □ 50:50 PVA:PS △ 60:40 PVA:PS

⊙ 70:30 PVA:PS ⊡ 80:20 PVA:PS ▲ 100% PS

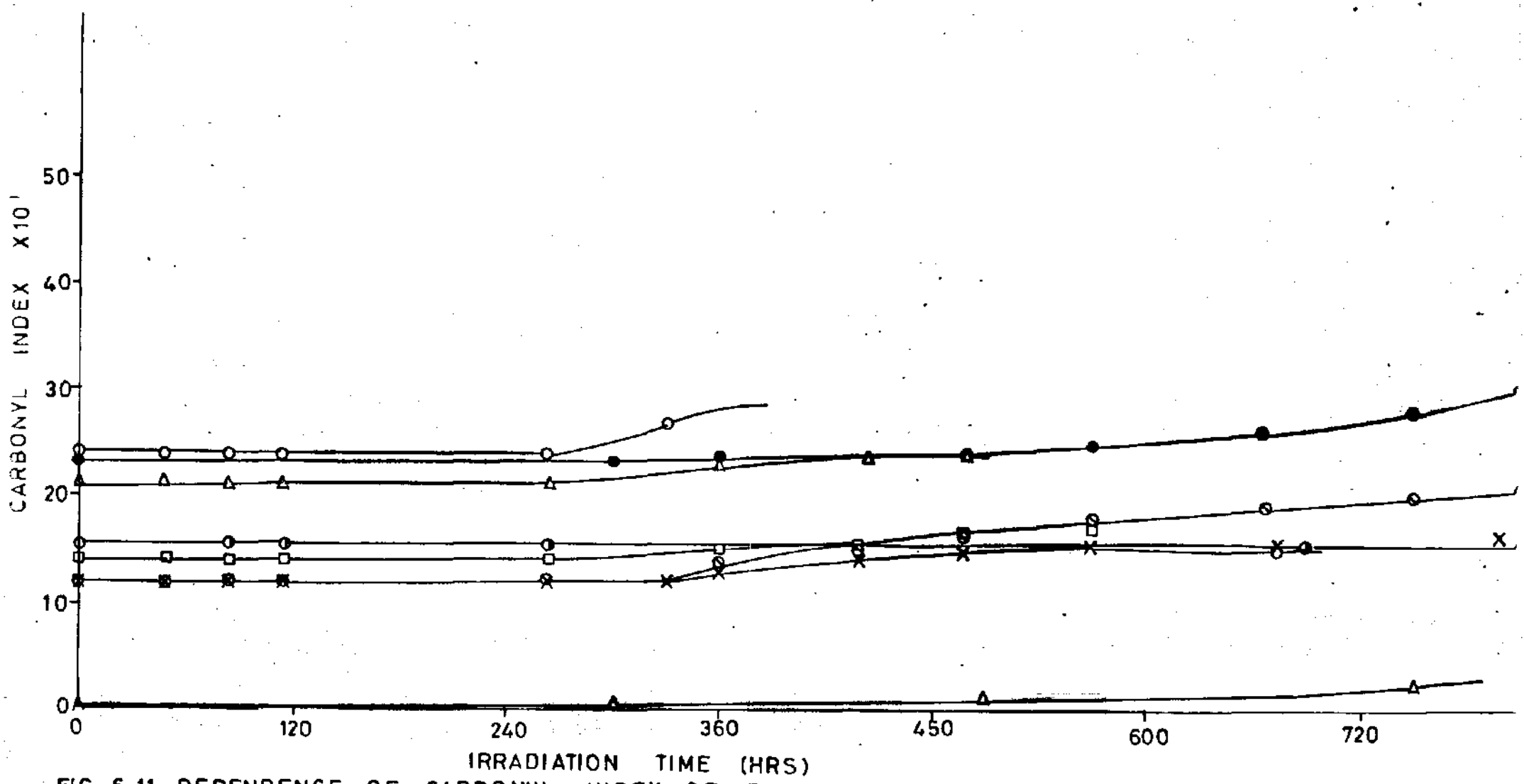


FIG. 6·11 DEPENDENCE OF CARBONYL INDEX OF PVA/PS BLENDS ON UV IRRADIATION TIME

o 80:20 PVA:PS ⊙ 70:30 PVA:PS Δ 60:40 PVA:PS □ 50:50 PVA:PS X 40:60 PVA:PS ◐ 100% PVA ▲ 100% PS ● 90:10

CHAPTER 7

STUDIES ON PS/PMMA BLENDS

In this work studies were carried out on density, morphology, mechanical and chemical properties of the unmixed polymers and their blends. For mechanical properties tensile strength, tensil modulus and percentage elongation were calculated. Changes in microstructure were monitored using the ir spectra of the homopolymers and their blends on exposure to outdoor weathering, thermal oxidative degradation and ultraviolet irradiation.

7.1 RESULTS AND DISCUSSION

7.11 Compatibility studies

Figure 7.1 shows the plots of measured and calculated densities of the unmixed polymers and their blends. The calculated densities, assuming the additivity of volumes, agree well with the measured densities. The light micrographs of the 20:80, 50:50 and 80:20 PS:PMMA blends were very clear. Since these are fairly representative of the spectrum of blends, it may be assumed that the blend films were completely amorphous and showed no heterogeneity. In the absence of crystallinity, the agreement between the calculated and measured densities suggests the miscibility of the polymers,

resulting in closer-packing which may be due to increased interaction between PS and PMMA in the blends. Shun and Randy (4, 5) noted that evidences such as above would suggest the compatibility of the polymers. But Grassie, McNeill and Cooke (61) noted the absence of interaction between the two polymers when degraded as thin film. This would, to the contrary, indicate incompatibility. In light of the above contradiction a reinvestigation of the system using different degradation methods was necessitated. Hence the present study on the system.

7.12 Outdoor weathering

Figure 7.2 shows the stress-strain curves of the unmixed polymers and their blends before exposure to outdoor weathering. It shows PS and PMMA as typically hard and brittle polymers and the blends 10:90 and 80:20 as harder and more brittle than the homopolymers while the blends 20:80 and 60:40 appear to be softer and tougher than the homopolymers.

Figure 7.3 shows the dependence of percentage elongation of PS/PMMA blends at zero time and after 16 days outdoor weathering. At zero time both tensile strength and percentage elongation showed similar trends. All the blends had these properties lower than those of the homopolymers. But all of them had modulus greater than those of the homopolymers, suggesting increased rigidity on blending. Usually increase in tensile strength goes with increase in modulus. This deviation observed with the blends and the fact that tensile strength and percentage elongation showed minima throughout the blend compositions tend to suggest loss of property on

blending.

The same trend is observed after 16 days outdoor weathering. Tensile strength and percentage elongation showed greatest minima at 30:70, 70:30 and 80:20 PS:PMMA compositions. This spread of minimum over the blend composition range suggests that the presence of PS in the blend produces loss in the mechanical properties of PMMA and vice versa.

Figure 7.4 shows the dependence of tensile strength on outdoor exposure time. Figure 7.5 and 7.6 show the dependence of modulus and percentage elongation respectively on outdoor weathering time for the unmixed polymers and their blends. In tensile strength, except for the 50:50 PS:PMMA blend which showed continuous decrease in property and the 100% PS which initially showed a decrease, followed by an increase up to a maximum the rest showed continuous increase, up to a maximum and then decreased. Unmixed PMMA had the highest tensile strength at any given time and showed a maximum on the 20th day, by which time all the blends and PS had become too brittle for instron testing.

In the plot of percentage elongation, it is observed that for most of the blends percentage elongation initially fell, then increased up to a maximum and finally dropped. PS showed the same trend as in tensile strength, a continuous decrease in property. This would suggest that chain scission sets in early during outdoor weathering of PS. Generally, the time to attain a maximum increased with increase in the PS component of the blend, despite the fact that PMMA, as for its tensile strength, showed its maximum percentage

elongation on the 22nd day, when most of the blends had become too brittle for instron testing.

Table 1 shows the induction and embrittlement times and Figure 7.7 shows the dependence of index of carbonyl absorption peaks of PS, PMMA and PS/PMMA blends on out door weathering time.

Table 1

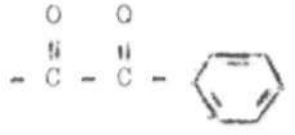
Induction and embrittlement times for carbonyl absorptions of PS, PMMA and PS/PMMA blends on outdoor exposure time

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PMMA	150	946
10:90 PS:PMMA	170	575
20:80 PS:PMMA	280	624
30:70 PS:PMMA	150	575
40:60 PS:PMMA	90	575
50:50 PS:PMMA	150	624
60:40 PS:PMMA	-	575
70:30 PS:PMMA	-	624
80:20 PS:PMMA	80	624
90:10 PS:PMMA	-	575
100% PS	220	634

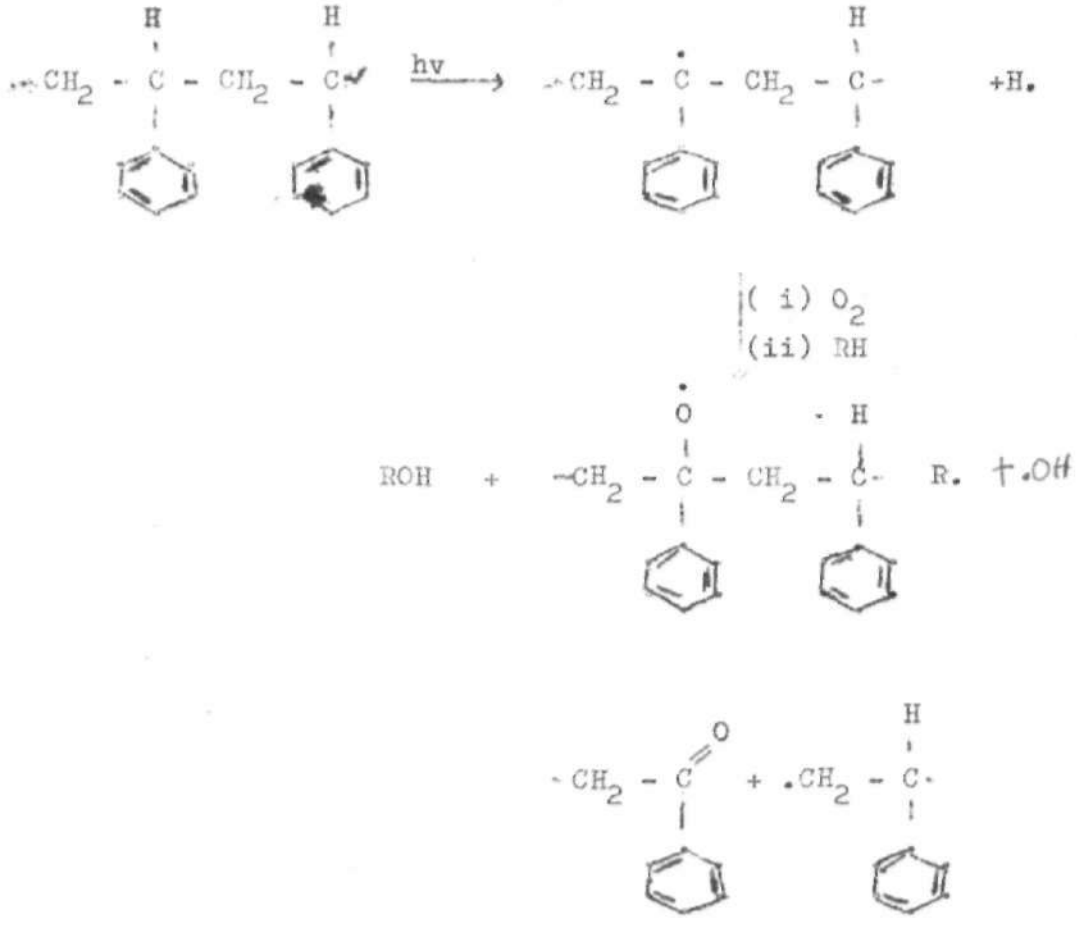
Figure 7.7 shows PS as less vulnerable to oxidative degradation than PMMA, judging from the induction times and slopes of curves after induction. Both homopolymers and the blends, except 60:40, 70:30 and 90:10 PS:PMMA, showed

induction periods. The induction periods are, however, observed to decrease with increase in the PS component of the blend. The embrittlement time showed no particular trend. It is however noteworthy that none of the blends had an embrittlement time higher than either homopolymer. All the blends and homopolymers showed continuous growth in indices of carbonyl growth immediately after the induction period, with the most rapid growth observed for 50:50, 60:40, 70:30 PS/PMMA blends; while the 20:80 showed the least growth in property. The embrittlement times indicate that there is loss of oxidative stability on blending the two polymers.

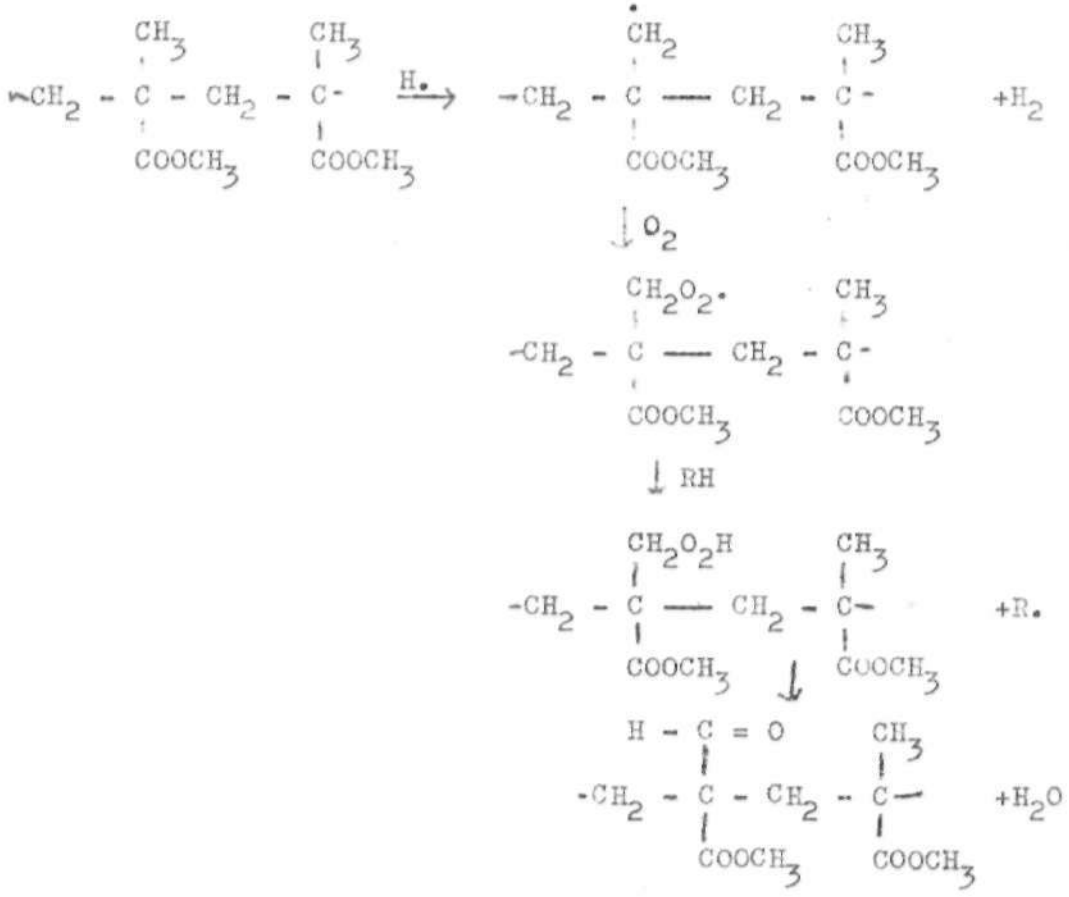
McNeill and Neill (51) observed that PMMA degrades via depolymerization, giving quantitative amounts of monomer, dimer, trimer, etc. Beachell and Smiley (52) observed that during the oxidative degradation of polystyrene, oxygen preferentially attacks the α-hydrogen atom formed on the backbone of the polystyrene chain. Using ir, nmv and uv spectra he concluded that the products formed were aromatic carbonyl structures, similar to acetophenone, benzyl acetophonone and a dicarbonyl compound.



For the outdoor degradation of polystyrene the following mechanism is hereby proposed:



Grassie and McNeill (61) noted since the tertiary hydrogen atoms of PS are vulnerable to reactions and intramolecular transfor reactions occur extensively in PS degradation. In the present work, it is observed that the 20:80 PS:PMMA showed the greatest stability towards outdoor weathering than any other blend. The induction and embrittlement times shown by the blends suggest interaction between the homopolymer, contrary to the observations of Grassie and McNeill (61). These interactions account for the destabilization of PMMA in the blends. Degraded as a blend, a hydrogen atom can be abstracted from the PMMA chain by either the polystyryl radical or by the hydrogen atom abstracted from the polystyrene chain.



This could well account for the increase in carbonyl absorption during the environmental degradation of PMMA in the blend.

7.13 Thermal oxidative degradation

Figure 7.8 shows the dependence of tensile strength, modulus and percentage elongation of PS, PMMA and PS/PMMA blends on oven heating time. There is no particular trend shown in any of these properties. 100% PS showed continuous decrease in modulus, a decrease up to a minimum and then a small increase and undulations in the percentage elongation. The 80:20 and 50:50 PS:PMMA blends showed the same trend in all the properties; continuous decrease in tensile strength and percentage elongation and undulations in modulus. For the 20:80 PS:PMMA blend, there were initial increases in tensile strength and percentage elongation before continuous decreases

were observed, but in modulus it showed a continuous decrease.

Figure 7.9 gives a comparative picture of the effect of outdoor weathering and oven heating times on the tensile strengths of the 20:80, 50:50 and 80:20 PS:PMMA blends. The 20:80 PS:PMMA blend showed on initial increase, up to a maximum and finally a gradual decrease under both conditions. The 50:50 and 80:20 PS:PMMA blends showed continuous decrease in property under both conditions. The most remarkable decrease occured for the 80:20 PS:PMMA. Generally the decrease in tensile strength was more pronounced for the oven-heated blend films and the greater the PS component in the blend the higher the decrease. The trend reveals the destabilizing effect of PS on PMMA.

Figure 7.10 shows the dependence of indices of carbonyl peak absorption on oven-heating time for PS, PMMA, and the PS:PMMA blends. Table 2 shows the induction and embrittlement times for the same systems.

Table 2

Induction and embrittlement times for the indices of carbonyl absorption of PS, PMMA and the PS:PMMA blends on heating

Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PMMA	No changes in absorption	1337
10:90 PS:PMMA	75	367
20:80 PS:PMMA	120	1110
30:70 PS:PMMA	75	531
40:60 PS:PMMA	110	550
50:50 PS:PMMA	110	550
60:40 PS:PMMA	75	367
70:30 PS:PMMA	175	367
80"20 PS:PMMA	120	367
90:10 PS:PMMA	115	367
100% PS	300	367

The table reveals that the blending results in increased vulnerability of the polymers to oxidative degradation and destabilization of PMMA by PS. The blends containing higher proportions of PS all had the same embrittlement times as PS, while 20:80 PS:PMMA blend showed the greatest stability, among the blends to thermal degradation. From Figure 7.10 it is observed that the 10:90, 20:80, and 40:60 and 50:50 showed steeper growths in carbonyl index than the higher PS containing blends, with the steepness decreasing in that order. This shows that PS has a disproportionate destabilizing

effect on PMMA as observed by Grassie and McNeill (61). McNeill and Neil (50) observed that PMMA is stable up to 250°C when heated alone. Grassie and McNeill (61) observed that thermal stability of PMMA is extremely sensitive to nature of the end groups, initial molecular weight and the presence of comonomers, even in quite low concentrations. It may then be argued that the degradation of the PMMA and PS in the blends is due to the sensitivity of PMMA to the presence of PS in the blends and the vulnerability of the α-hydrogen of PS to oxidative attack.

7.14 Ultraviolet degradation

Figure 7.11 shows the dependence of indices of carbonyl absorption peaks on ultraviolet irradiation time. Table 3 shows the induction and embrittlement times of PS, PMMA and PS:PMMA blends on uv irradiation.

Table 3

Induction and embrittlement times of PS, PMMA and PS:PMMA blends for the carbonyl absorption on ultraviolet irradiation

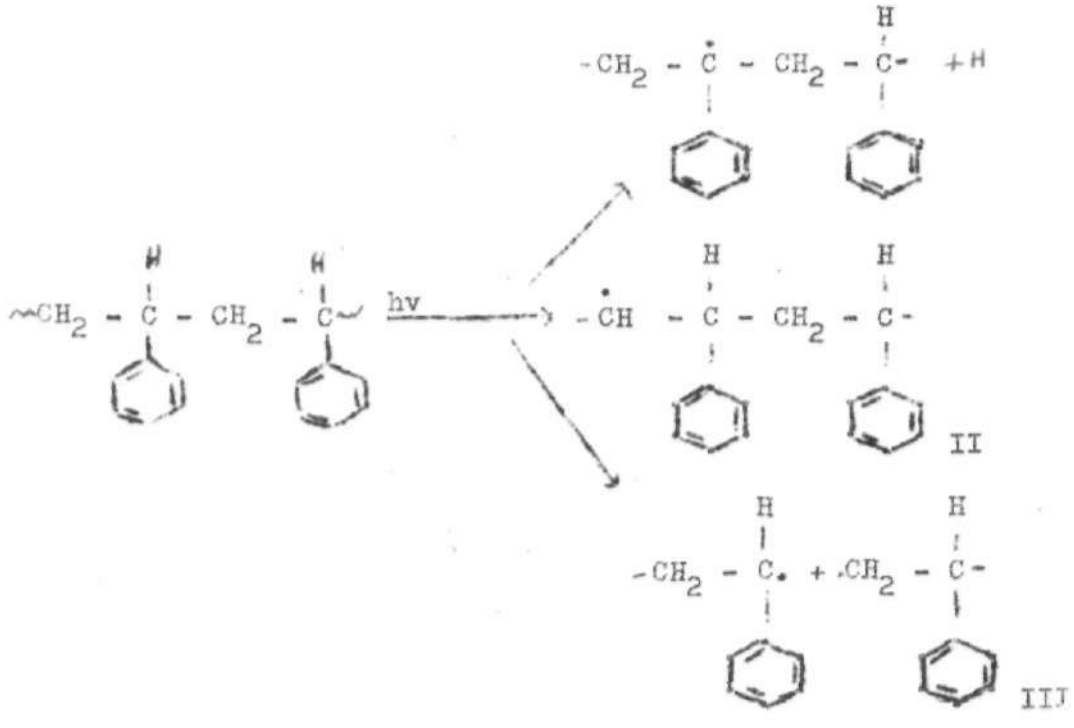
Polymer/blend	Induction time (hrs)	Embrittlement time (hrs)
100% PMMA	360	2000
10:90 PS:PMMA	180	775
10:80 PS:PMMA	250	775
30:70 PS:PMMA	250	775
40:60 PS:PMMA	320	775
50:50 PS:PMMA	170	775
60:40 PS:PMMA	170	775
70:30 PS:PMMA	100	775
80:20 PS:PMMA	170	775
90:10 PS:PMMA	250	775
100% PS	330	775

The graphs show almost the same trend as observed for the films heated in the oven; that is, the steepness of the graph decreased with increase in PS component of the blend. There is destabilization of PMMA in the blend as shown by the embrittlement times.

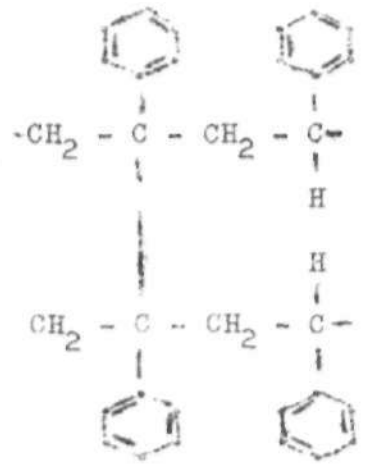
Grassie and Weir (55), observed on ultraviolet irradiation of PS, that molecular hydrogen was liberated and the polystyryl radicals formed gave rise to crosslinking and noticed a general increase in carbonyl absorption and suggested the presence of carbon-carbon double bond absorptions. Rabek and Ranby (62) noted that the mechanism of PS photolysis

in the solid state (film) depends upon the mobility of the free radicals in the polymer matrix and their molecular recombination and that the photo-oxidation of the PS film is dependent on the rate of diffusion of oxygen into the polymer. The free radicals produced on irradiation can abstract hydrogen atoms from the surrounding or combine with polystyryl radicals or hydrogen in the vicinity. The main reactions involved in PS photolysis are chain scission and crosslinking.

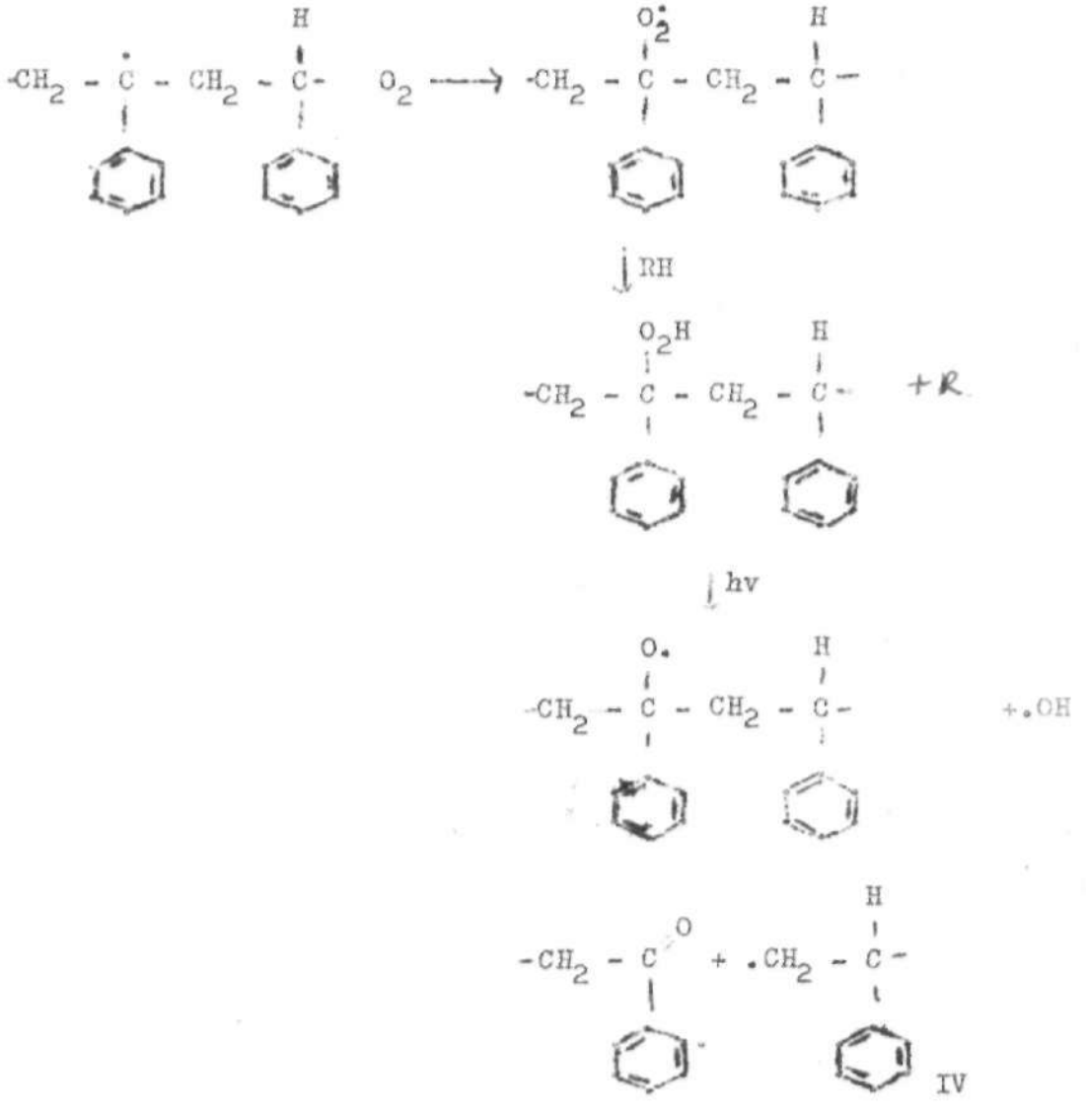
The following mechanism is hereby proposed to the photo-degradation of PS.



Macroradical (I) can (i) combine in pairs to give crosslinks.



(ii) abstract a hydrogen atom from a polystyrene chain to form a similar radical and (ii) be attacked by oxygen to give an oxidative product.

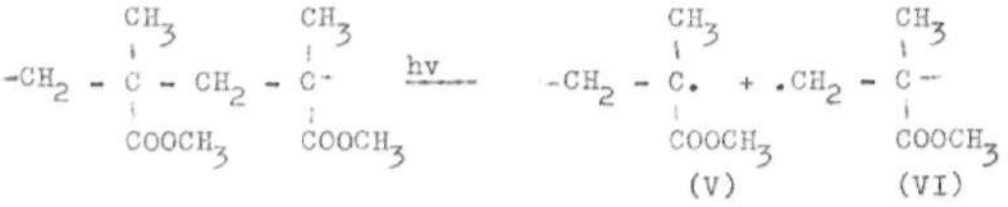


The macroradical (IV) can undergo oxidative attack to give a benzophenone as observed by Beachell and Smiley (52).

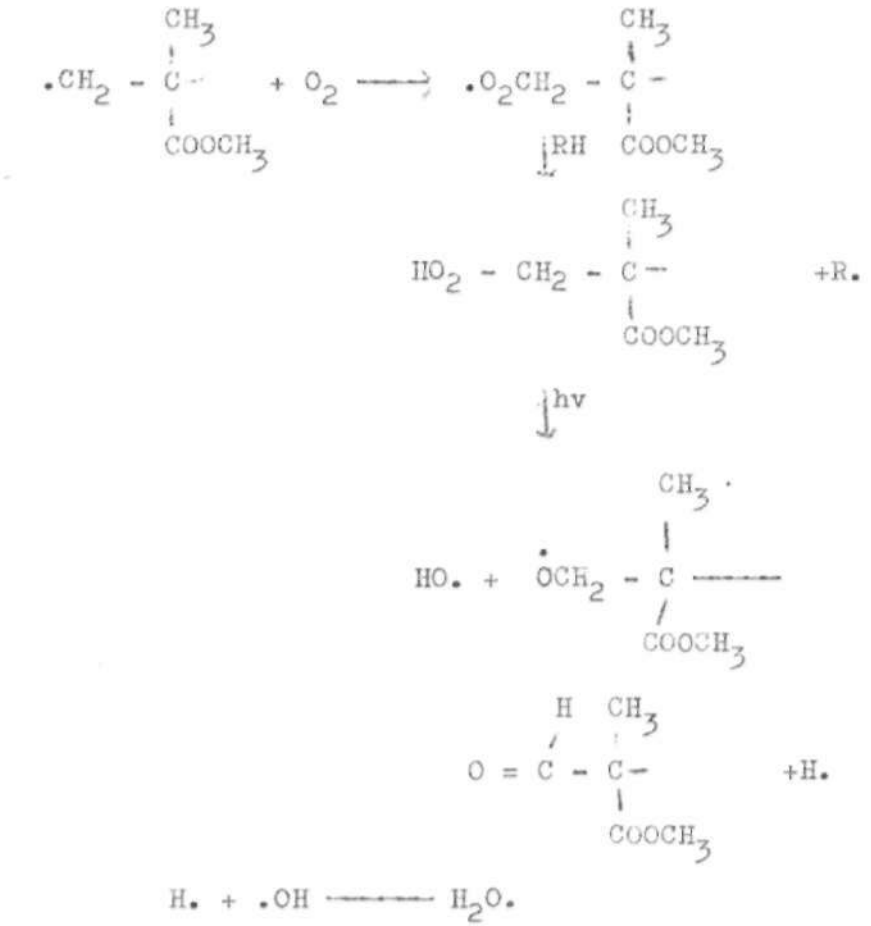
Macroradicals (II) and (III) can undergo similar reactions to give oxidative products.

On ultraviolet irradiation, PMMA can show any of the following reactions (i) random homolytic scission of main chain carbon-carbon bonds (ii) scission of the side chain ester groups and (iii) scission of methyl side groups.

Scission of the main chain carbon-carbon bonds could take place as follows:

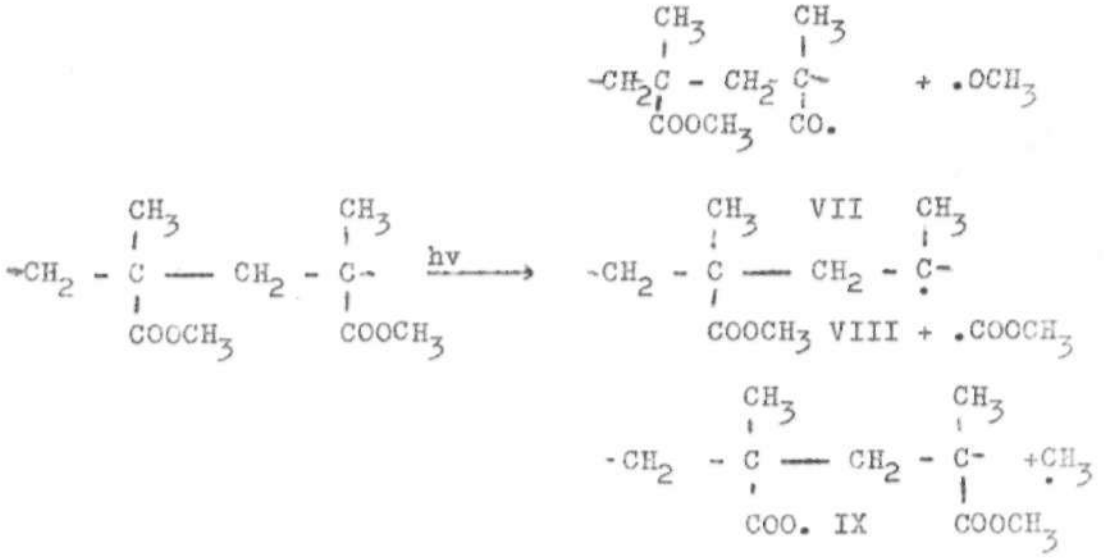


Macroradical (VI) can undergo oxidative degradation

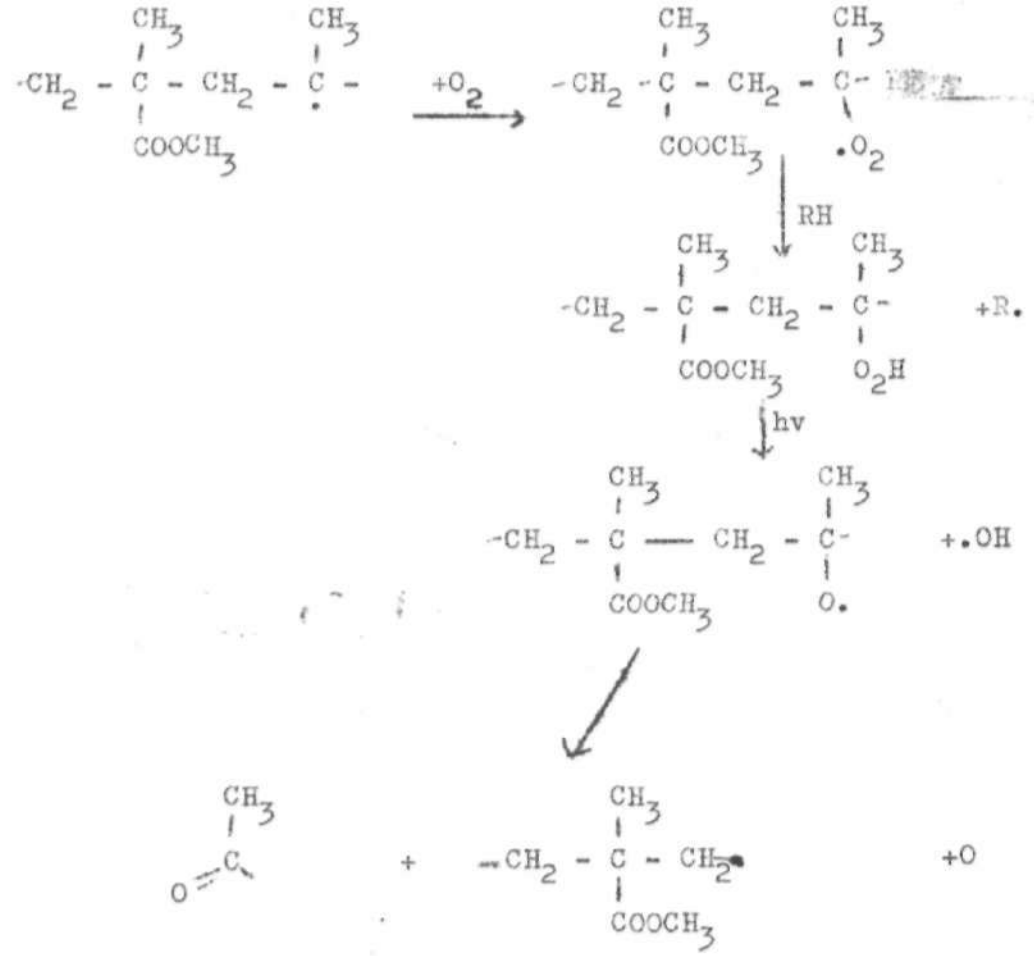


The stability of the hydroxyl and peroxy groups must be very low to account for the seemingly complete absence of changes in hydroxyl absorption in the ir spectra of the homopolymers and their blends.

Scission of side chain ester groups may take place as follows:



Macroradical VIII can undergo an oxidative attack to give a ketone:



Degraded as a blend, there could be extensive interactions at the phase boundaries among the macroradicals to accelerate the incidence of oxidative photodegradation, as is shown by the lower induction periods of the blends relative to those of the homophlymers.

7.2 CONCLUSION

Studies on density and morphology indicate that the system is compatible. Studies on structural stability and mechanical properties show that extensive interaction occurs between PS and PMMA in the blends. The lower concentrations of PS have greater destabilizing effect on the PMMA.component thereby indicating that PS has a disproportionate destabilizing effect on PMMA. Generally there is increased vulnerability to oxidative degradation and loss of mechanical properties on blending. From these observations, the blending of PS with PMMA should be seen as purely an academic exercise and of no industrial applications.

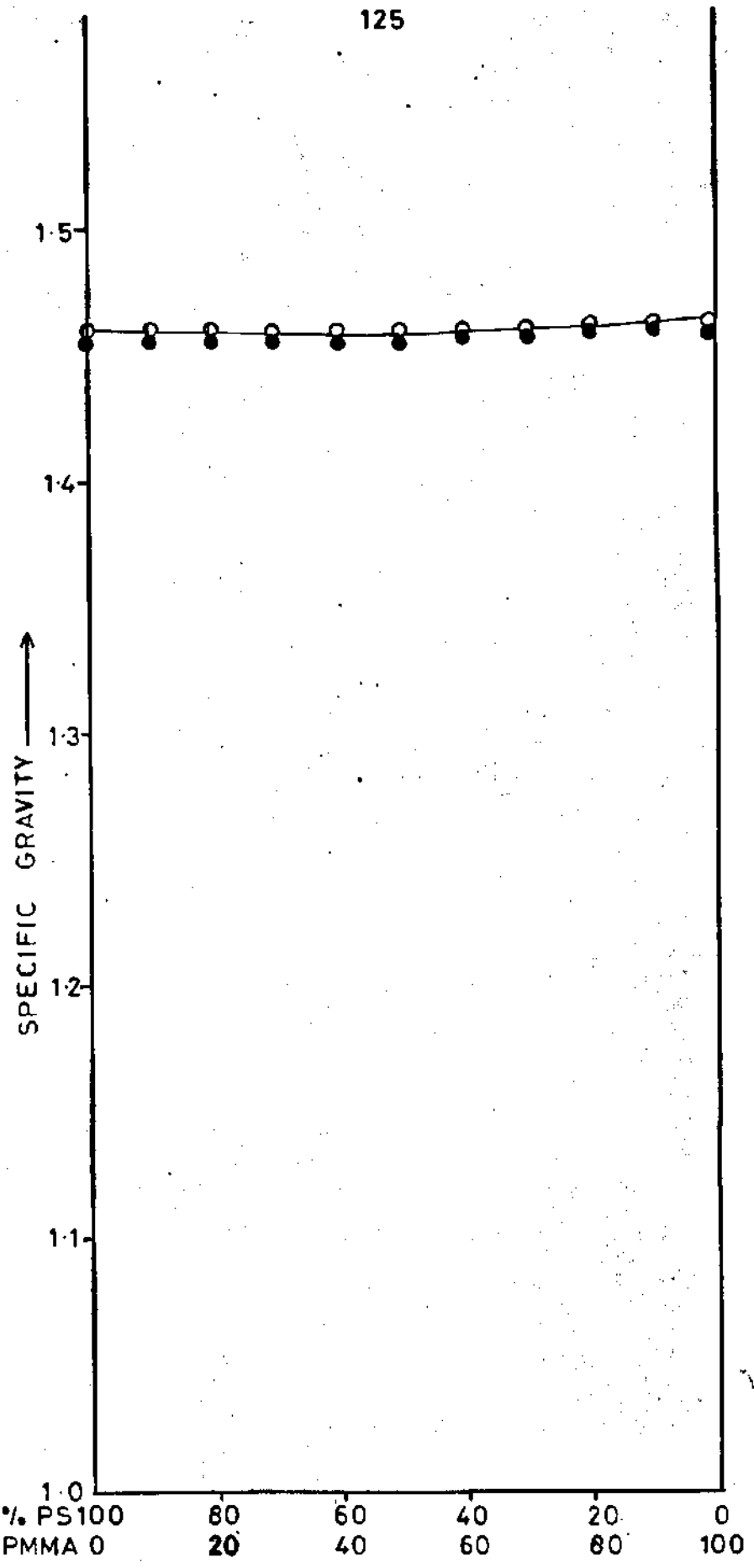


FIG. 7·1 DEPENDENCE OF SPECIFIC GRAVITY ON % COMPOSITION OF PS/PMMA BLENDS
o PRACTICAL ● THEORETICAL

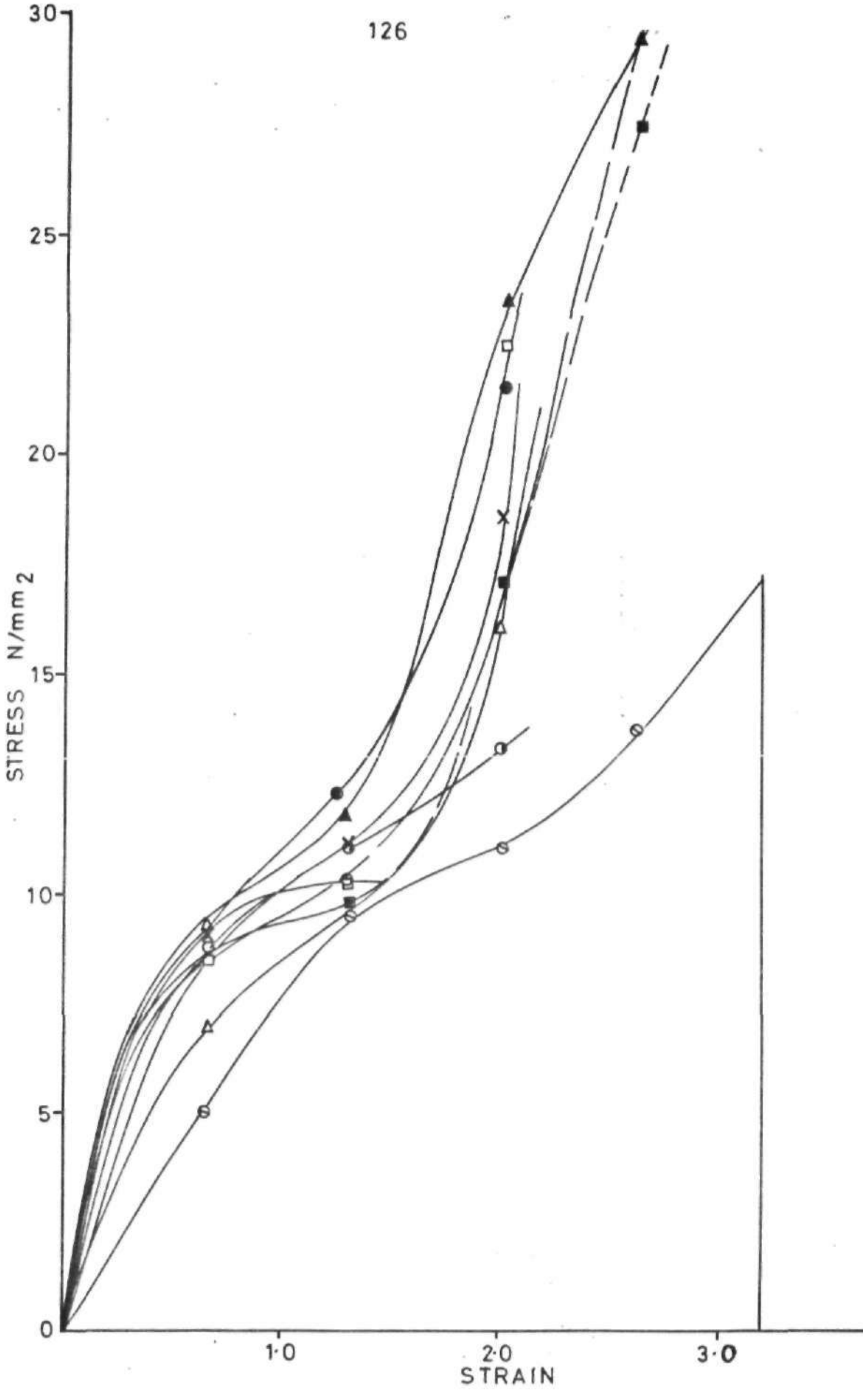


FIG. 7·2 STRESS–STRAIN CURVES FOR PS PMMA AND PS/PMMA BLENDS AT ZERO TIME

○ 90:10 PS:PMMA ● 80:20PS:PMMA ◑ 70:30PS:PMMA
⊖ 60:40PS:PMMA × 50:50PS:PMMA △ 20:80PS:PMMA
▲ 10:90PS:PMMA ■ 100% PS □ 100% PMMA

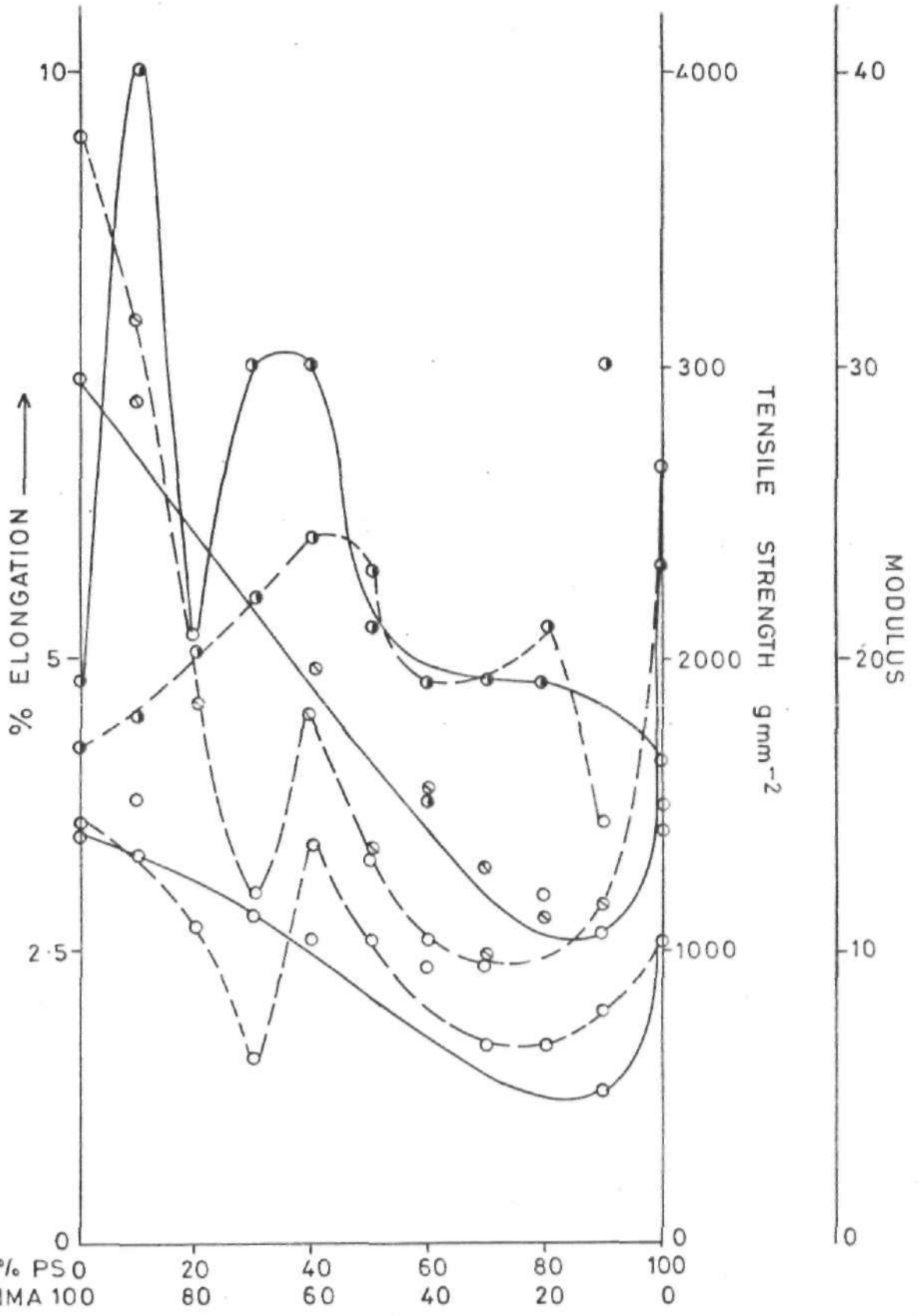


FIG. 7·3 DEPENDENCE OF MECHANICAL PROPERTIES ON THE COMPOSITION OF PS/PMMA BLENDS

o % ELONGATION ——— BEFORE EXPOSURE
⊖ TENSILE STRENGTH – – – – AT 16 DAYS
◑ MODULUS

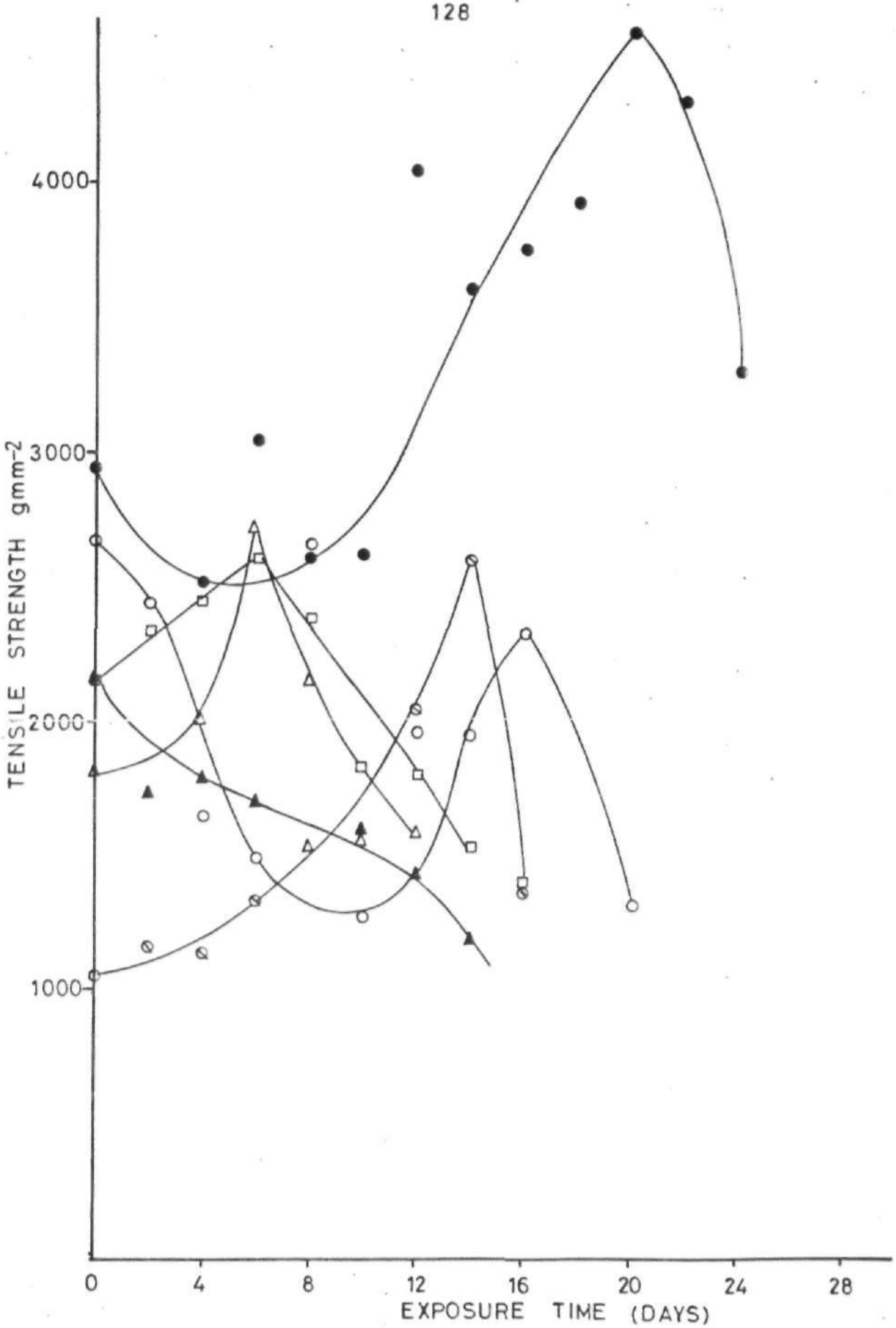


FIG. 7·4 DEPENDENCE OF TENSILE STRENGTH ON OUTDOOR EXPOSURE TIME FOR PS/PMMA BLENDS

○ 100 % PS ● 100 % PMMA ⊘ 90:10 PS:PMMA ▲ 50:50 PS:PMMA
△ 40:60 PS:PMMA □ 20:80 PS:PMMA

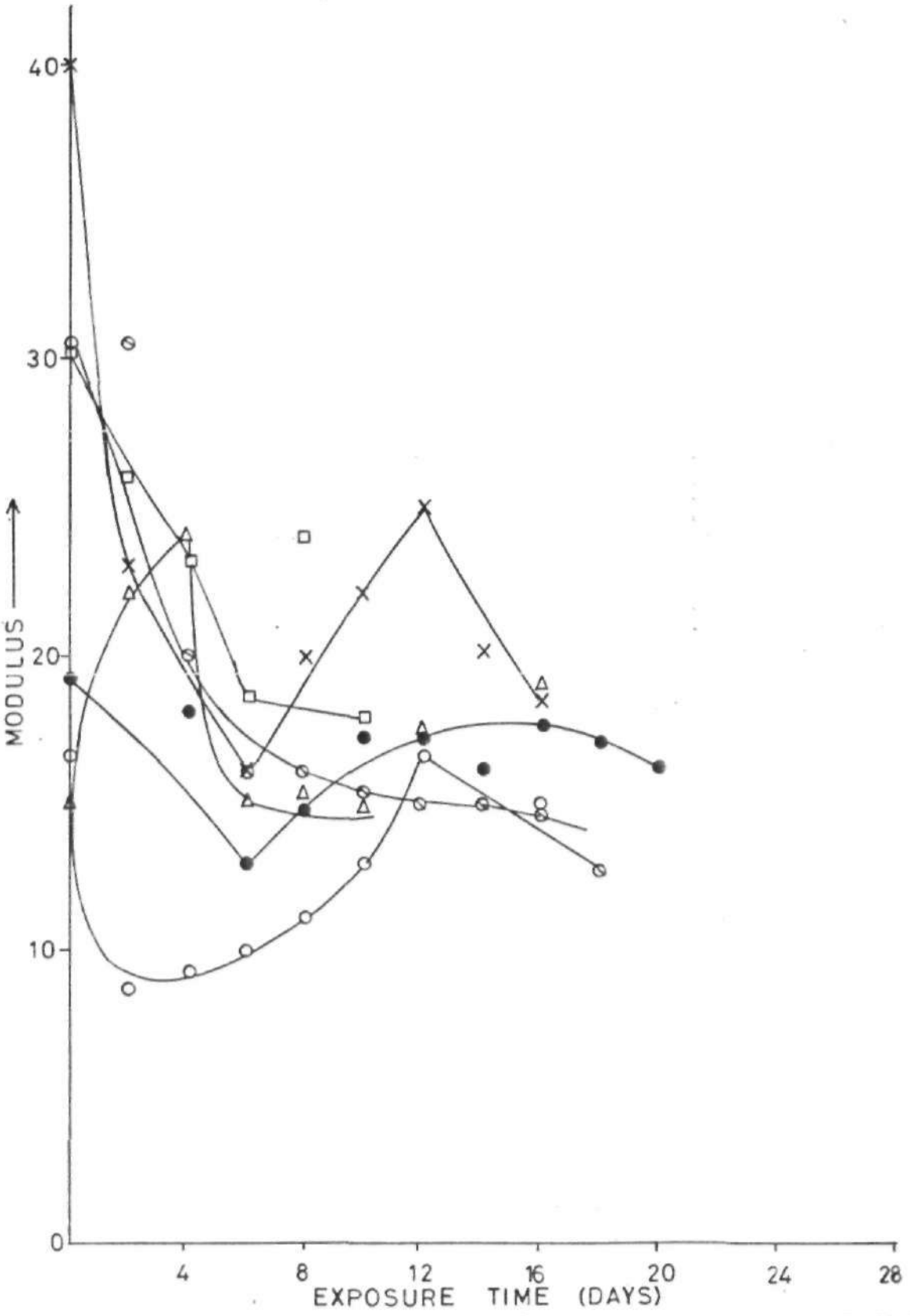


FIG. 7·5 DEPENDENCE OF MODULUS ON OUTDOOR WEATHERING TIME FOR PS, PMMA AND PS/PMMA BLENDS

○ 100 % PS ● 100 % PMMA ◔ 90:10 PS:PMMA

△ 60:40 PS:PMMA □ 40:60 PS:PMMA × 10:90 PS:PMMA

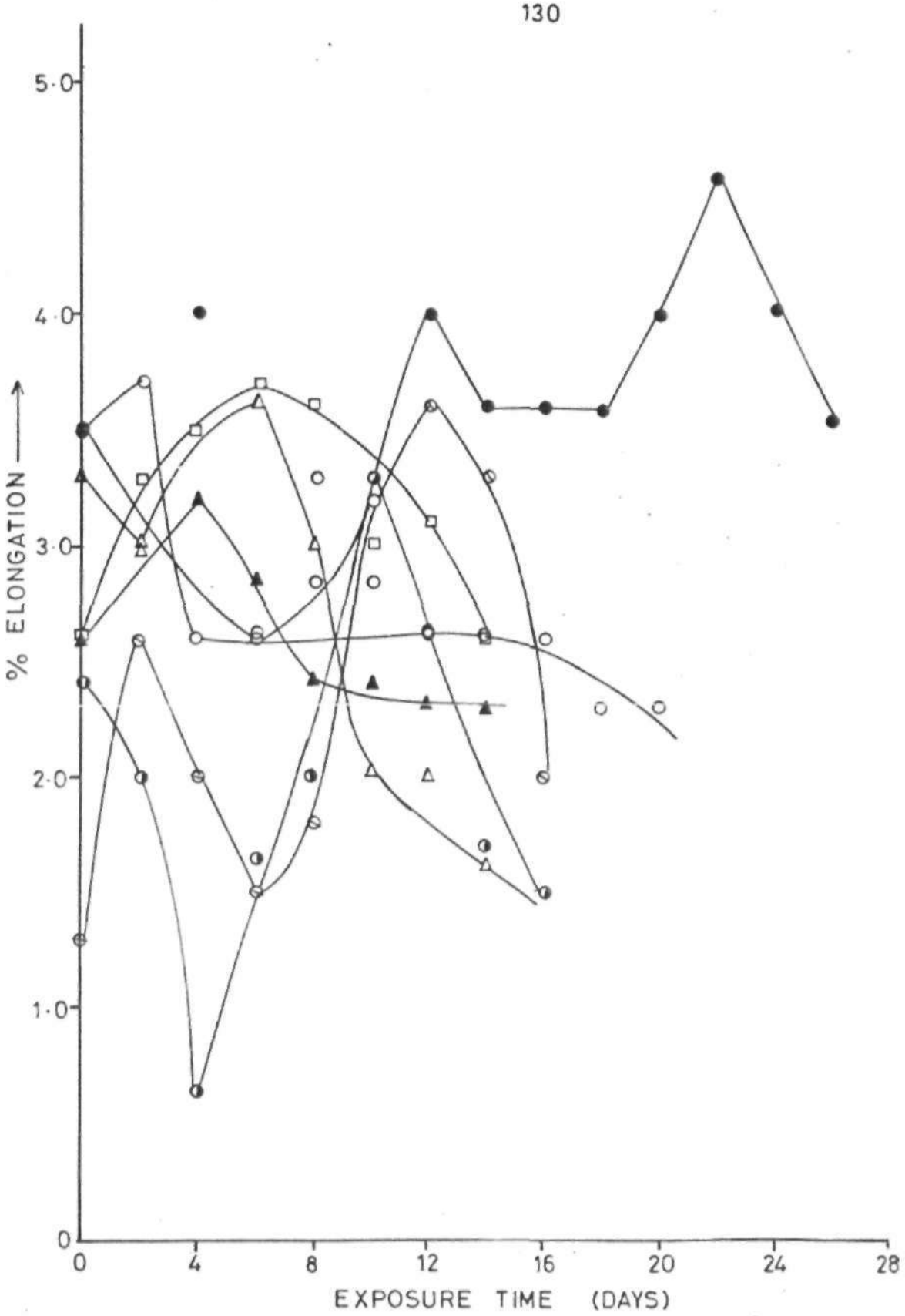


FIG. 7·6 DEPENDENCE OF % ELONGATION ON OUTDOOR WEATHERING TIME FOR PS PMMA AND PS/PMMA BLENDS
○ 100 % PS ● 100 % PMMA ⊘ 90:10 PS:PMMA ◑ 70:30 PS:PMMA
△ 50:50 PS:PMMA ▲ 40:60 PS:PMMA □ 20:80 PS:PMMA

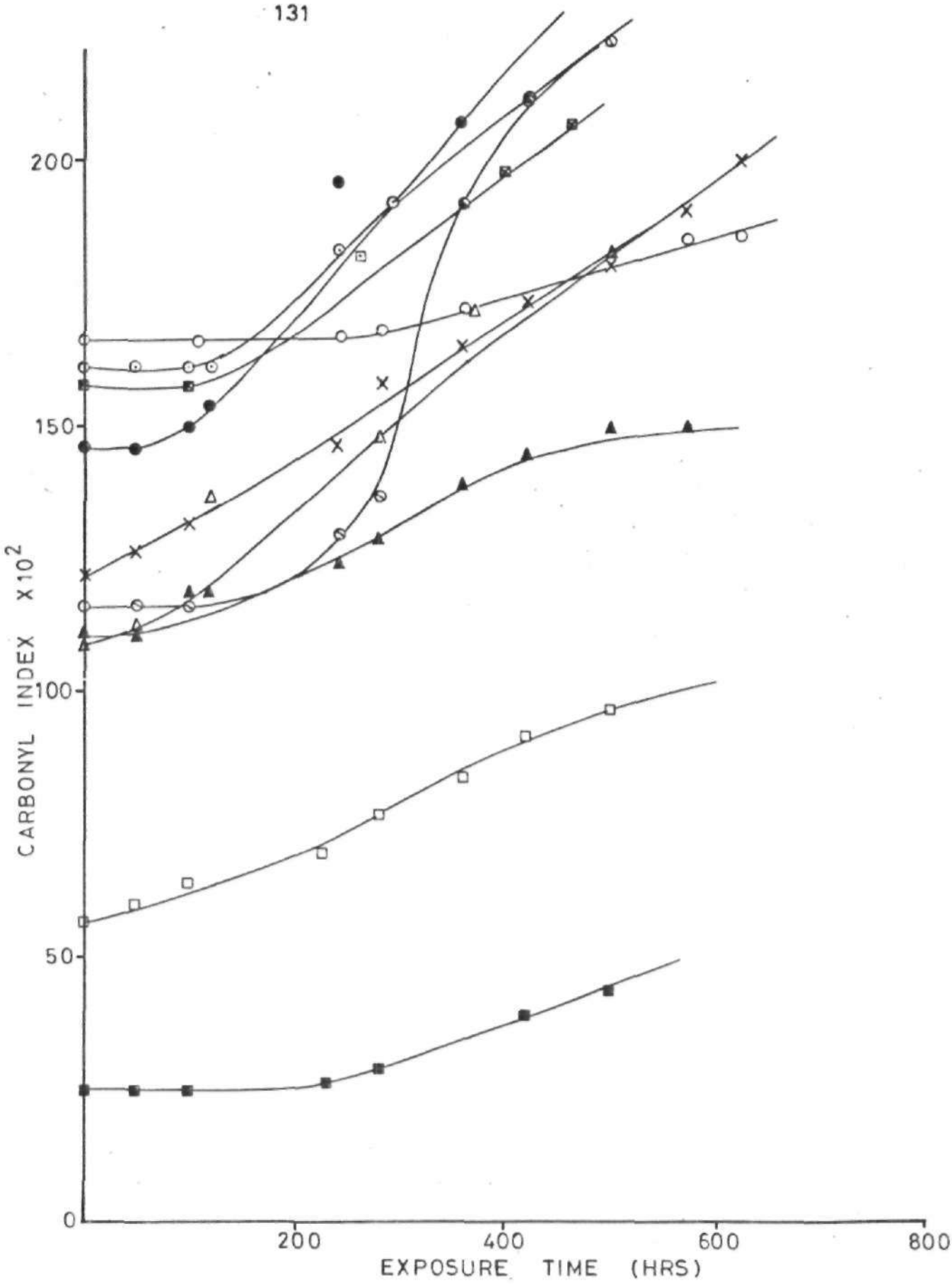


FIG. 7.7 DEPENDENCE OF CARBONYL INDEX ON OUTDOOR EXPOSURE TIME FOR PS PMMA AND PS/PMMA BLENDS

○ 20:80PS:PMMA ◎ 30:70PS:PMMA ● 40:60PS:PMMA
⊘ 50:50PS:PMMA × 60:40PS:PMMA △ 70:30PS:PMMA
▲ 80:20PS:PMMA □ 90:10PS:PMMA ■ 100% PS ⊠ 100% PMMA

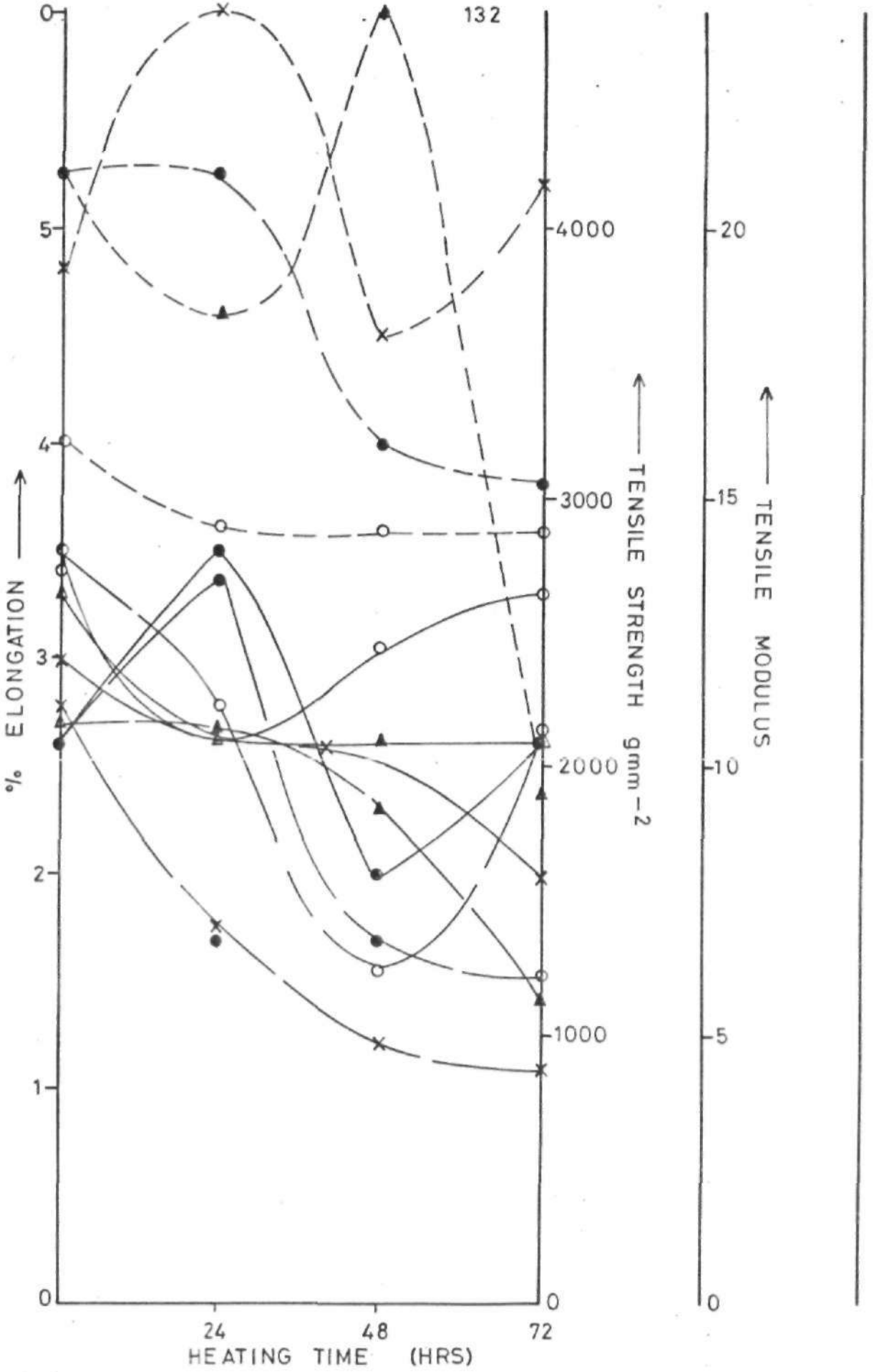


FIG. 7·8 DEPENDENCE OF MECHANICAL PROPERTIES ON HEATING TIME FOR PS PMMA AND PS/PMMA BLENDS

○ 100% PS ◑ 100% PMMA ● 20:80PS:PMMA ▲ 50:50PS: PMMA

× 80:20PS PMMA ——— % ELONGATION

– – – – MODULUS —— —— TENSILE STRENGTH

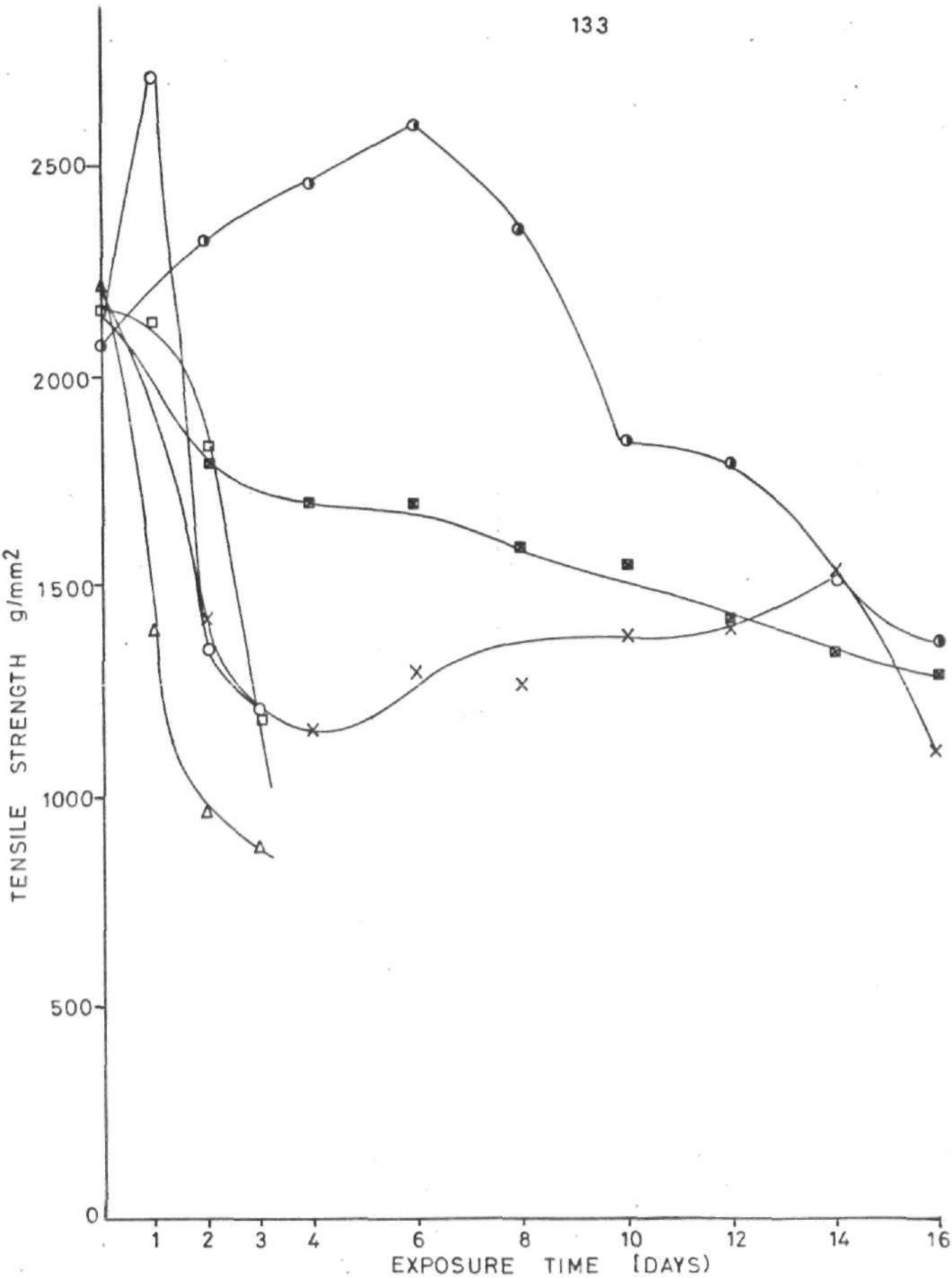


FIG. 7.9 DEPENDENCE OF TENSILE STRENGTH OF PS/PMMA BLENDS ON METHOD OF DEGRADATION

o 20:80PS:PMMA HEATING ◐ 20:80PS:PMMA OUTDOOR

□ 50:80PS:PMMA HEATING ◙ 80:20PS:PMMA OUTDOOR

△ 80:20PS:PMMA HEATING × 80:20PS:PMMA OUTDOOR

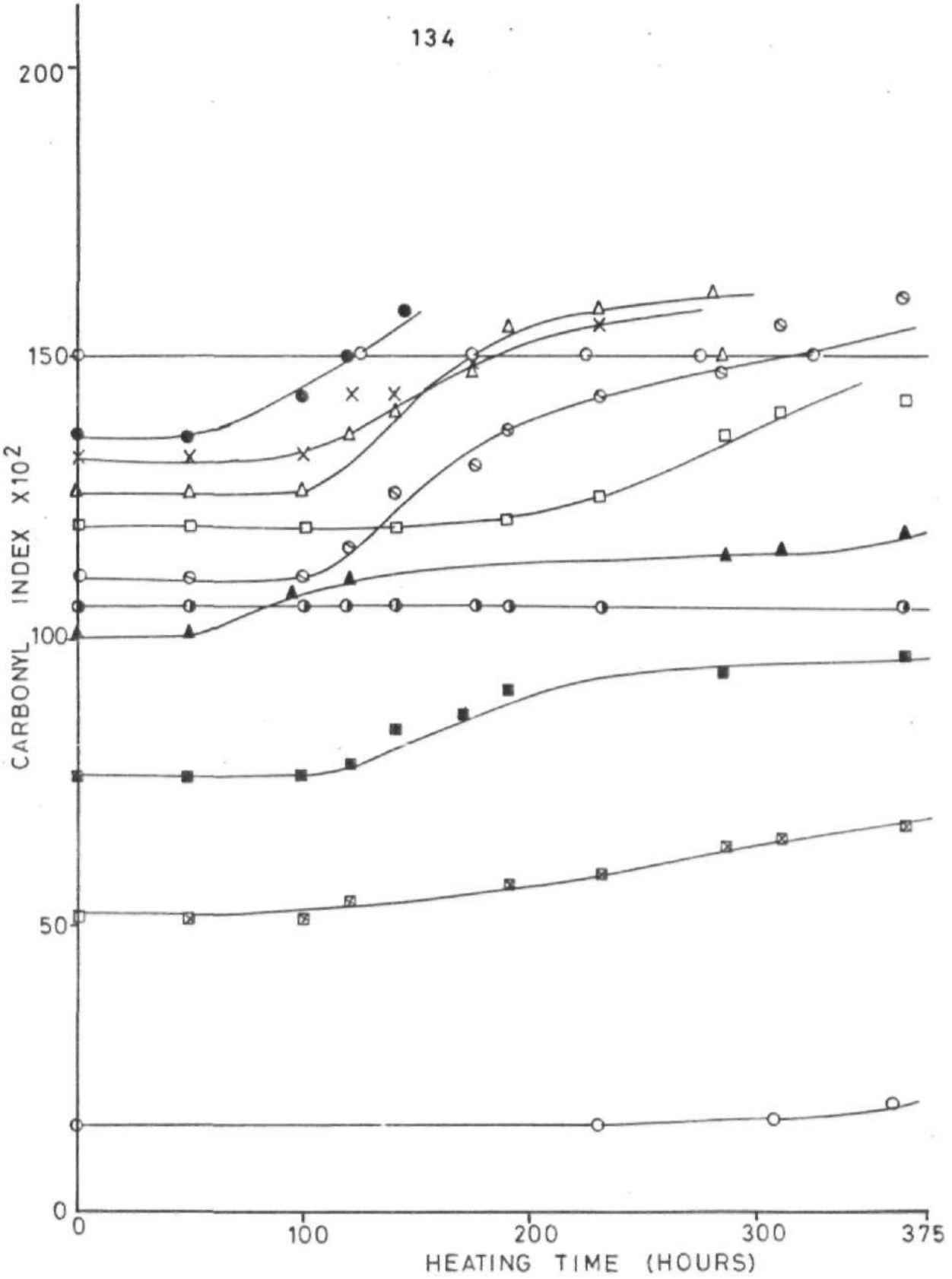


FIG. 7·10 DEPENDENCE OF CARBONYL INDEX ON HEATING TIME FOR PS, PMMA AND PS/PMMA BLENDS

○ 100 % PS ◐ 100 % PMMA ● 10:90 PS:PMMA ⊘ 20:80 PS:PMMA
⊘ 30.70 PS:PMMA × 40:60 PS:PMMA △ 50:50 PS:PMMA
▲ 60:40 PS:PMMA □ 70:30 PS:PMMA ■ 80:20 PS:PMMA
⊠ 90:10 PS:PMMA

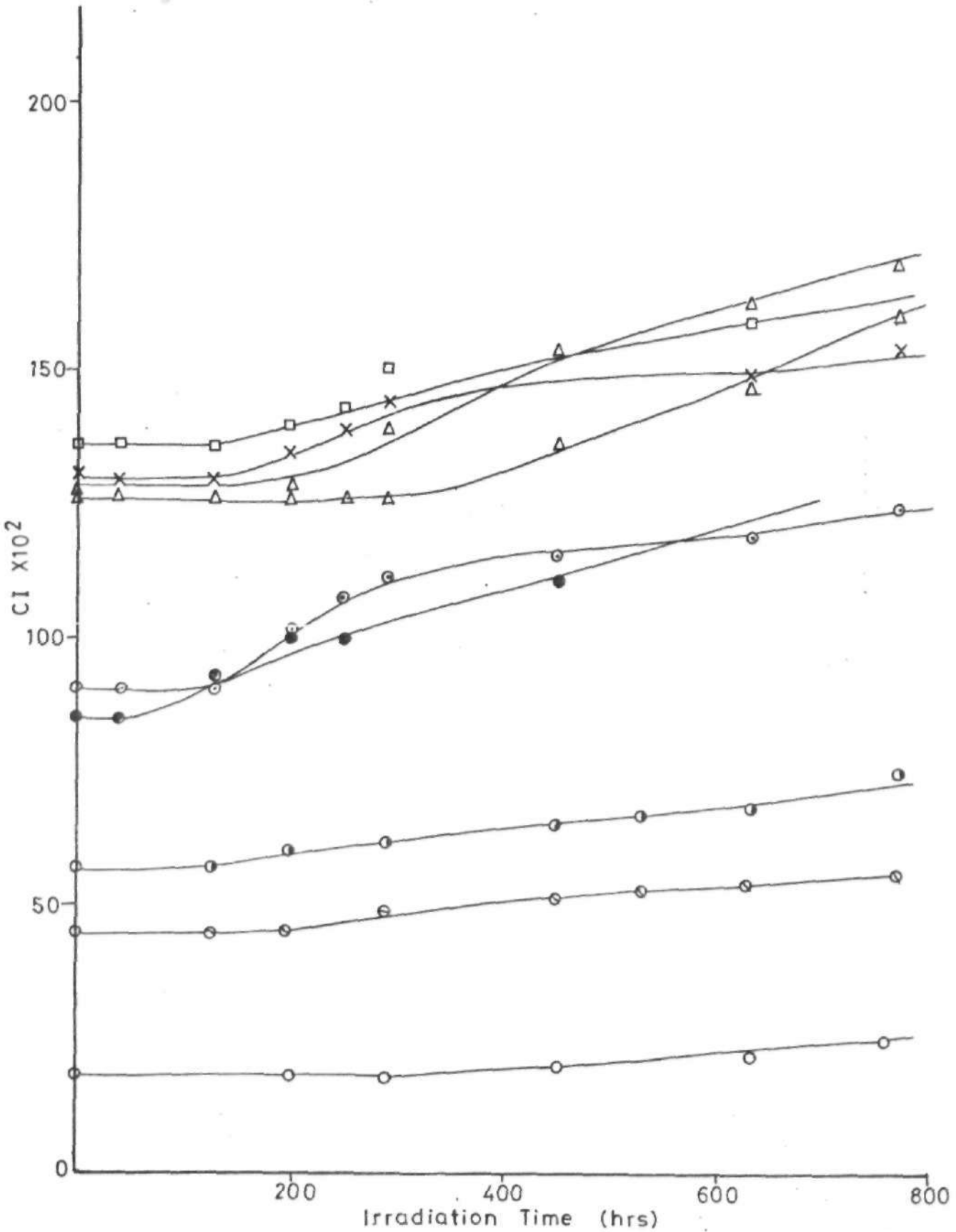


FIG. 7·11 DEPENDENCE OF CARBONYL INDEX ON UV IRRADIATION TIME FOR PS, PMMA AND PS/PMMA BLENDS

o 100% PS ⊙ 90:10 PS:PMMA ◐ 80:20 PS:PMMA ● 70:30 PS:PMMA
⊙ 60:40 PS:PMMA × 50:50 PS:PMMA △ 40:60 PS:PMMA
△ 30:70 PS:PMMA □ 10:90 PS:PMMA

CHAPTER 8

COMPARATIVE ANALYSIS OF RESULTS

Chapters 4, 5 and 6 were devoted to studies on the degradability of the blends of PVA with PVC, PMMA and PS respectively while Chapter 7 was devoted to studies on PS/PMMA blends. All the blends were subjected to similar weathering conditions namely outdoor weathering, heating in a Wallace air-oven at 100°C and irradiation with ultraviolet rays.

The work on each chapter entailed studies on compatibility of the system under investigation. Studies on density and morphology suggest that two of systems namely PVA/PMMA and PS/PMMA could be compatible.

The studies have revealed that PMMA, of all the homopolymers blended with PVA in this work, is the only one capable of improving the structural stability by reducing the oxidizability of PVA in the system and improving the mechanical properties on outdoor weathering and oven aging of the blends.

Figure 8.1 gives plots of tensile strength of PVA/PVC, PVA/PMMA and PVA/PS as a function of blend composition at zero time. All of them showed the same trend in property. Tensile strength decreased with increase in PVA in the blend. It is observed that for PVA/PMMA despite the minimum shown at

90:10 PVA:PMMA composition, the values above this point are relatively high while for the PVA/PS, there was remarkable drop in tensile strength as a result of blending. Only PVA/PMMA shows a maximum in property. This shows the stabilizing effect of PMMA on PVA.

A comparison of Figures 4.3 to 4.6, with 5.4-5.7, 6.3-6.6 and 7.3-7.6, all of which deal with changes in mechanical properties as a function of exposure time shows that for the PVA/PVC system, the higher the PVA component of the blend, the shorter the time to attain a maximum in tensile strength, modulus and percentage elongation and the lower the value at these points. In each case there was an increase in property up to a maximum and then a decrease. For the PVA/PMMA blends, there was in most cases an initial decrease in mechanical property, followed by a rise to a maximum and finally a decrease in property. Figure 5.4 shows there was generally an improvement in mechanical properties as a result of blending. For the PVA/PS, the presence of PVA was observed to cause general deterioration in mechanical properties. On exposure a minimum was observed in modulus, tensile strength and percentage elongation at 30% PVA in the blend. Thus showing that the greatest deterioration in mechanical properties was at this blend composition. Figure 7.3 shows that all the PS/PMMA blends had lower tensile strength and lower percentage elongetion than the homopolymers. Although all the blends had higher modulus than the homopolymers, the spread of minimum over the blend composition range suggests general deterioration of mechanical properties as a result of blending.

Growth in carbonyl index has normally been used to access the vulnerability of a polymeric system to oxidative degradation. A comparison of Figures 4.7 and 5.9 which deal with the carbonyl indices of PVA/PVC and PVA/PMMA respectively on outdoor weathering indicate that all the blends of PVA/PVC showed no induction period. The shapes of the curves indicate that the blends probably degraded in two stages with the degradation of PVC preceeding that of PVA. This in turn is in conformity with the observed incompatibility of the blends, since with two phases interaction should take place only at the phase boundaries. On the other hand, Figure 5.7 shows the PVA/PMMA blends as having high induction and embrittlement times with the highest values occurring at 40-60% PVA in the blend. PVA is observed to stabilize PMMA against outdoor weathering while the presence of PMMA had no effect on the embrittlement time of PVA. Figure 6.7 shows that for the PVA/PS blends induction period decreased with decrease in PS in the blends. This suggests increased vulnerability to oxidative degradation and interaction between the dissimilar molecules in the blends. Figure 7.7 shows that PMMA destabilizes PS against outdoor weathering. All the blends showed continuous growth in carbonyl indices immediately after the induction period.

The PVA/PMMA blends also showed the best stability to thermal degradations. In mechanical properties, it is observed that although PMMA had the highest tensile strength at zero time but showed the lowest values in property throughout the heating time and although PVA soon embrittled on heating, the blends showed increases in modulus and tensile

strength on heating. This suggests cooperative stabilization as a result of blending. For all the blends involving PVA, it was however observed that the higher the PVA in the blend, the steeper the fall in percentage elongetion on heating. The PVA/PVC blend curves showed initial decrease in carbonyl index followed by an increase on heating. The curves of their hydroxyl indices are observed to level off at about 330 hours in each case. This levelling off suggests the stabilization of PVA by PVC, since at about this time most of blends containing higher concentrations of PVA had embrittled. PVA is observed to destabilize PS to thermal oxidative degradation. Hence except for the 50:50 PVA/PS blend, induction period decreased with increase in PVA, with PVA concentrations higher than 50% there was reductions in both embrittlement and induction periods, while its concentration less than 50% caused increases in both and this was found to be highest at 50:50 blend composition. This trend suggests cooperation stabilization at this composition. Only the low PVA containing blends showed continuous growth in indices. The others were found to show an initial increase after which they showed sudden decrease and in most cases fell below the initial carbonyl index. Figure7.10 reveals that blending PS and PMMA results in increased vulnerability to oxiductive degradation. All the blends had lower induction periods than the homopolymers. Pg destabilizes PMMA to thermal degradation.

Exposed to ultraviolet irradiation, the PVA/PVC blends degraded fast, with the blends showing embrittlement times almost the same or less than that of PVC. It is observed that the higher the PVC component of the blend the steeper the

carbonyl index curve as is seen from Figure 5.12. For the PVA/PMMA, it is also the PVA that is destabilized by PMMA. Figure 6.11 and Table 3 of Chapter 6 show that PVA is also destabilized by PS. All the PVA/PS blends showed continuous increase in carbonyl indices immediately after the induction period. For the PS/PMMA blends destabilization of PMMA by PS was observed but since PS is less susceptible to oxidative degradation and since the polystyryl radical can stabilize itself by resonance, it is observed that the steepness of the curves of carbonyl indices decreased with increase PS in the blend.

From the above, it is clear that the most structurally stable and mechanically compatible blends are the PVA/PMMA blends. For PVA/PS, although cooperative stabilization was observed at 50:50 blend composition on heating, there is general deterioration of properties on blending. For the PVA/PVC there is cooperative destabilization and general loss of property. For the PS/PMMA, the blends showed general loss of property as a result on blending.

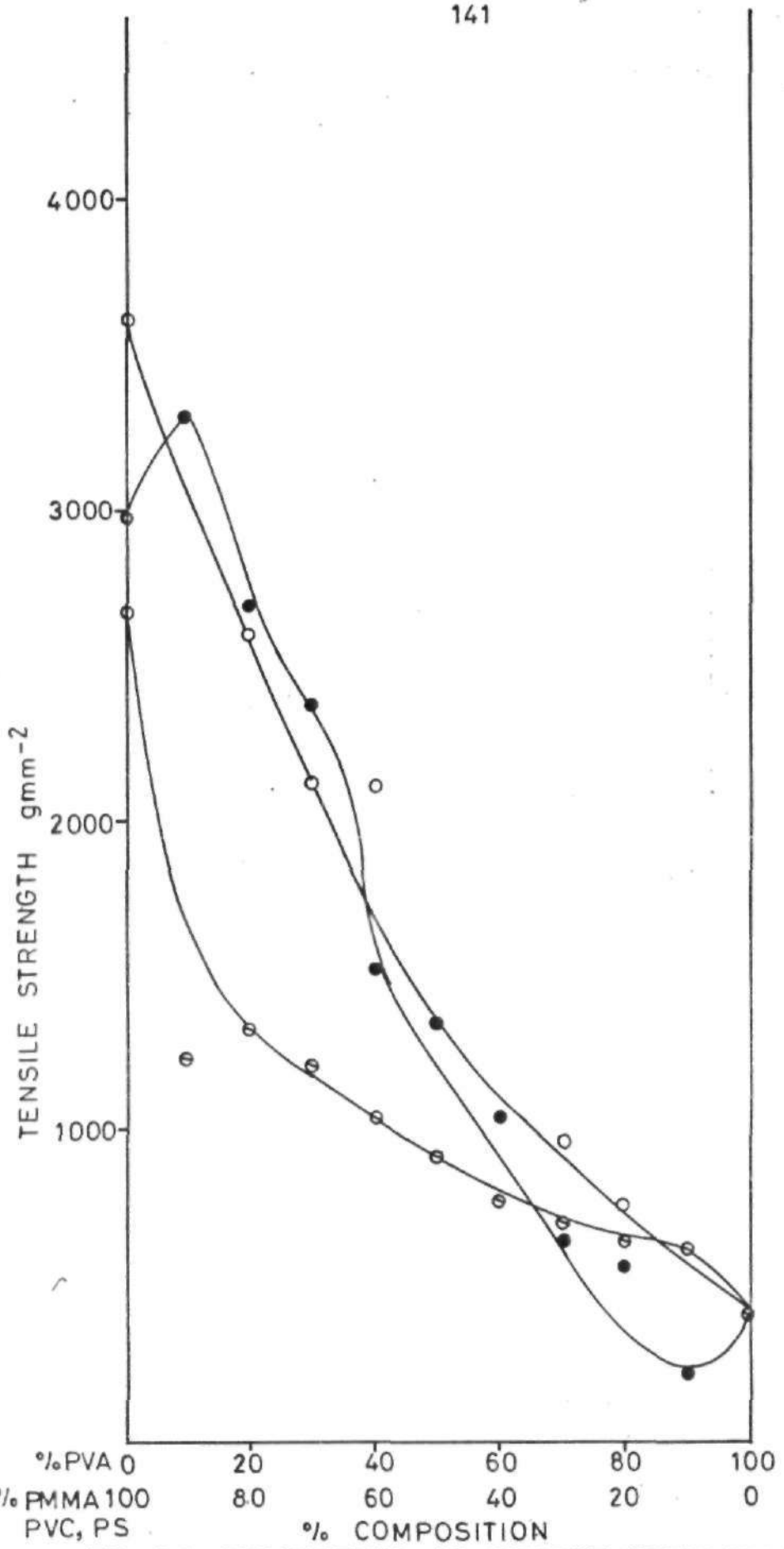


FIG. 8·1 DEPENDENCE OF TENSILE STRENGTH OF FRESHLY PREPARED BLENDS WITH PVA ON TYPE OF SECOND POLYMER AND COMPOSITION

○ PVA:PVC ● PVA:PMMA ⊖ PVA:PS

REFERENCES

1. Paul, D. R.; Newman, S., "Polymer blends", Academic Press Inc., 1978, Vol. 1, P.2.

2. Olabisi, O.; Robeson, L. M. Shaw, T. M., "Polymer-polymer Miscibility", Academic Press Inc., 1979, Chaps. 1 and 2.

3. McNeill, I. C., "Developments in Polymer Degradation", Editor N. Gressie, Applied Sci. Publishers, 1977, Vol. 1, P.121.

4. Shun, J. Y., Randy, B., J. Appl. Polym. Sci. 1975, 19, 1337.

5. Shun, J. Y., Randy, B. J. Appl. Polym. Sci. 1975, 19, 2143.

6. Hughes, L. J.; Brown, G. L., J. Appl. Polym. Sci. 1961, 5, 580.

7. Shultz, A. R., Beach, B. M., Macromolecules 1974, 7, 902.

8. Flory, P. J., "Principles of Polymer Chemistry", Cornell Univ. Press, Ithaca, New York, 1953, Chaps. 7 and 10.

9. Kribgaum, W. R.; Flory, P. J., J. Am. Chem. Soc. 1953, 75, 1975.

10. Flory, P. J., "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York, 1953, Chap. 12.

11. McMaster, L. P., Macromolecules, 1973, 6, 760.

12. Olabisi, O.; Robeson, L. M.; Shaw, T. M., "Polymer-Polymer Miscibility", Academic Press, 1979, P.48.

13. Kwei, T. K.; Nishi, T.; Roberts, F., Macromolecules 1974, 7, 667.

14. Seymour, R. C.; Westrood, A. R., Eur. Polym. J. 1977, 13, 419.

15. Gupta, V. P., Pierre, L. E., J. Polym. Sci. (Polym. Chem. Editor), 1979, 17(13, 797.)

16. Suetly, J.; Lukas, R.; Kolinsky, M., Malcromol Chemie, 1979, 180, 1363.

17. Alman, E. J., J. Polym. Sci. 1954, 12, 543.

18. Alman, E. J., J. Polym. Sci., 1954, 12, 547.

19. Talamini, G.; Pezzin, G., Makromol. Chimie, 1960, 39, 26.

20. Winkler, D. E., J. Polym. Sci., 1959, 35, 3.

21. Baum, B., Wartman, L. G., J. Polym. Sci. 1958, 28, 537.

22. Geddes, W. C., Eur. Polym. J., 1967, 3, 267.

23. Geddes, W. C., Eur. Polym. J., 1967, 3, 747.

24. Matlack, J. D., Metzger, A. P., J. Appl. Sci., 1968, 12, 1945.

25. Gupta, V. P.; Pierre, L. E., J. Polym. Sci., 1970, 8, 37.

26. Gupta, V. P., Pierre, L. E., J. Polym. Sci., 1973, 11, 1841.

27. Gupta, V. P.; Pierre, L. E., J. Polym. Sci., 1979, 17(3), 931.

28. Scott, G.; Tahan, M., Eur. Polym. J., 1977, 13, 989.

29. Chapiro, A. J., Chem. Physics, 1956, 53, 895.

30. Miller, A. A., J. Physical Chem., 1959, 63, 1955.

31. Bengough, W. I.; Sharpe, H. M., Makromol Chimie, 1963, 26, 45.

32. Kwei, K., J. Appl. Polym. Sci. 1968, 12, 1543.

33. Kwei, K. Kwei, T. K., J. Appl. Polym. Sci., 1968, 12, 1551.

34. Charlesby, J. Polym. Sci., 1953, 10, 201.

35. Grassie, N.; McNeill, I. C., Eur. Polym. J., 1970, 6, 865.

36. Grassie, N.; McNeill, I. C., Eur. Polym. J., 1970, 6, 1437.

37. Bengough, W. I.; Sharpe, H. M., Makromol Chemie, 1963, 66, 31.

38. Stromberg, R. R.; Stratus, S.; Achhammer, B. G., J. Polym. Sci., 1959, 35, 355.

39. Braun, D.; Bender, R. F., Eur. Polym. J., (Supplementary Edition), 1969, 5, 269.

40. Jamieson, A., McNeill, I. C., J. Polym. Sci., (Polymer Chemistry Editor) 1974, 12, 387.

41. Gardner, D. L.; McNeill, I. C., Eur. Polym. J., 1971, 7, 569.

42. Gardner, D. L.; McNeill, I. C., Eur. Polm. J., 1971, 1 593.

43. Gardner, D. L.; McNeill, I. C., Eur. Polym. J., 1971, 7, 603.

44. Grassie, N. McLaren, I. F.; McNeill, I. C., Eur. Polym. J., 1970, 6, 367.

45. Grassie, N.; McLaren, I. F.; McNeill, I. C., Eur. Polym. J., 1970, 6, 865.

46. Mbamali, G. E., M.Sc. Thesis, , A.B.U., Zaria.

47. Seymour, R. C.; Westwood, A. R., Eur. Polym. J., 1971, 7, 419.

48. Reiner, R., "Encyclopedia of Polymer Sci. and Technology", 1966, Vol. 4, P.647.

49. Gardner, D. L.; McNeill, J. C., Eur. Polym. J., 1971, 7, 63.

50. McNeill, I. C.; Neill, D., Eur. Polym. J., 910, 6, 143.

51. McNeill, I. C.; Neill, D., Eur. Polym. J., 1970, 6, 569.

52. Beachell, H. C.; Smiley, L. H., J. Polym. Sci., A-1 5, 1935.

53. Grassie, N.; Weir, N. A., J. Appl. Polym. Sci. 1965, 9, 963.

54. Lawrence, J. B.; Weir, N. A., J. Polym. Sci. 1965, 9, 975.

56. Lawrence, J. B., Weir, N. A., J. Polym. Sci., 1965, 9, 987.

57. Lawrence, J. B., Weir, N. A., J. Polym. Sci. (Polymer Chemistry Editor), 1973, 11, 103.

58. Jellinek, H. H. G., J. Polym. Sci., 1949, 4, 1.

59. Jellinek, H. H. G.; Lipovac, S. N., Macromolecules 1980, 3, 237.

60. Jellinek, H. H. G.; Lipovac, S. N., Macromolecules 1980, 3, 231.

61. Grassie, N.; McNeill, I. C.; Cooke, I. J. Appl. Polym. Sci., 1968, 12, 831.

62. Rabek, J. F., Randy, B., J. Polym. Sci., 1974, 12, 273.

63. Kolawole, E. G.; Agboola, M. O., J. Appl. Polym. Sci. 1982, 27, 2317.