SOME STUDIES ON ABS/PVC POLYBLENDS UNDER NATURAL AND AGGRESSIVE CONDITIONS

A Thesis Presented to the Ahmadu Bello University
In Partial Fulfilment for the Degree of:

MASTER OF SCIENCE
IN POLYMER SCIENCE AND TECHNOLOGY

By

GLADYS ENUMA MBAMALI

MARCH, 1979

TO MY BABY SON, CHUKS, WITH LOVE.

ACKNOWLEDGEMENT

I acknowledge, with profound gratitude, the guidance, useful suggestions and constant encouragement of my supervisors, Dr. J. Y. Olayemi and Dr. E. G. Kolawole. I thank them very much for reading through the draft and making necessary corrections.

I appreciate the interest shown by the Head of the Chemistry Department, Prof. U. D. Gomwalk, in the progress of the course.

I am grateful to Dr. W. Werblinski, of the Chemistry Department, for the discussions I had with him.

For his patience and skill I say, 'thank you', to the typist, Mr. J. Omonaiye.

Finally, I thank my husband and children for their understanding, support and encouragement at all times and especially during this course.

G. E. Mbamali
Zaria
March 1979

GLOSSARY

ABS = Acrylonitrile Butadiene Styrene

PVC = Poly vinyl Chloride

Irgastab T290 = Dibutyl tin maleate stabiliser

BHBM = 3,5 - diteriary butyl - 4 - hydroxybenzyl mercaptan

EBHPT = 4 - benzyl - 3 - hydroxyphenyl - 0 - ethylthioglycollate

Synergism = When the effect of a mixture of two or more antioxidants is not additive but greater than would be expected from the additivity law, the observed effect is called synergism.

Antagonism When the effect is less than would be expected from the additivity law.

ABSTRACT

Acrylonitrile Butadiene Styrene (ABS) which has been previously stabilised against heat and UV irradiation has been added in the form of Masterbatches to modify PVC*

The general procedure followed was to compare the effects of these additives, in the RAPRA torque Rheometer at 170 C, with conventional unstabilised ABS (when used to modify the strength) and with conventional PVC stabiliser (when used as a stabiliser).

The samples used for testing were prepared from compression moulded films and were heated in an air oven and also exposed to sunlight for various lengths of time*

Changes in the chemical and physical properties were examined by IR spectroscopy and tensile strength measurements*

It was found that the photooxidation of ABS follows first order kinetics and proceeds through the oxidation of the double bond. Blending ABS with PVC damaged the weatherability of PVC from chemical and physical aspects. It could also be shown that previously stabilised ABS added to PVC| gave no protection to PVC. However, it was found that a combination of commercial stabiliser, Irgastab $T_{2q_}$, and EBHPT (added as Masterbatch) gave a relatively good protection

to PVC during thermal ageing and UV irradiation* The commercial thermal stabiliser proved better **than** 3HBM (added as masterfoatch) for stabilising impact-modified PVC. **Long** processing times did a lot of damage to the polyblend and is therefor© not desirable technically* A blend containing lO-20% A3S and about 80% PVC proved to have the greatest elongation at break*
It was found also that the blending of PVC with A3S led to a decrease in tensile strength, A correlation exists betv/een the embrittlement time of the sample and its mechanical behaviour*

CONTENTS

CHAPTER		Page
1	Introduction and Previous Work	1
2	Studies on Processed Films	16
3	Studies on Cast Films	28
4	Conclusions and Suggestions for Further Work.	32

CHAPTER 1

INTRODUCTION AND PREVIOUS WORK

CONTENTS

		Page
1.1	Introduction	1
1.2	Previous Work	3
1.2.1	On Preparation of ABS	3
1.2.2	On Stabilisation of ABS	4
1.2.3	On Impact Modifiers for PVC	6
1.2.	On Degradation and Stabilisation of PVC	9
1.3	References	14

CHAPTER I

I. Introduction

Polymer scientists are constantly faced with the problem of producing new polymers with 'tailor-made' properties to meet an ever-increasing demand. Whilst the volume production of completely new polymers which have achieved commercial viability in recent years has been small, the development of polyblends has been highly significant.

A polyblend is a material which is composed of two or more polymeric ~~structures~~ compounds. When the polymers are suitably paired, it may be possible to modify or correct the deficiency in one by the other.

Polyblends can be produced by physically mixing two polymers, for example in a processing machine, by coagulation of a mixture of two latexes or by grafting of one polymer onto the backbone of the other, during a chemical reaction.

The present work involves the use of stabilised ABS as impact modifier for rigid PVC and as a high molecular weight lubricant/stabiliser for rigid PVC. Although the mechanism of photodegradation and thermal degradation of ABS is known[1,2] very little is known about its weathering behaviour when it is incorporated into PVC. It is therefore desired to know how the incorporation of photochemically and thermally stabilised ABS into PVC affects,

(i) the impact properties of rigid PVC

(ii) the photochemical and thermal stability of PVC

(iii) the tensile strength and elengation of PVC.

The greatest disadvantages of polyvinyl chloride (PVC) for many applications (e.g. building) are its brittleness at low temperatures, its sensitivity towards notch and its poor resistance to impact.[3]

It has been reported[4,5] that polybutadiene based materials, of which the more important are acrylonitrile-butadiene-styrene (ABS), methyl methacrylate-butadiene-styrene (MBS) and methylacrylate butadiene-styrene (MABS), are widely used as impact modifiers for rigid PVC.

ABS is itself a terpolymer consisting of three polymerised materials - acrylonitrile, butadiene and styrene and each of these components of ABS serves a specific function in PVC. Polybutadiene secures elasticity and absorbs the energy of the external stresses; polyacrylonitrile gives good chemical resistance and rigidity while polystyrene improves thermo-plasticity and processing properties of hard PVC compounds.

The modifier itself represents a two phase system - a rigid continuous phase made by styrene -acrylonitrile copolymer and a disperse phase of rubbery polybutadiene. The continuous phase of modifier is to a great extent soluble in PVC continuous phase and both continuous phases penetrate each other to produce

solid links between PVC and the particles of the modifier. By this way, dispersed polybutadiene particles are 'embedded' in the PVC phase and remain insoluble in the system. When a crack formed by an external stress meets such an embedded rubber particle, it converts the mechanical energy into heat energy and the propagation of fracture is stopped.

The ratio of the modifier's components must be balanced very carefully because all the three components also show adverse effects on PVC properties. For example - an excess of polybutadiene improves impact but decreases fluidity, rigidity and mechanical properties.

- an excess of polyacrylonitrile improves rigidity but decreases fluidity and impact.
- an excess of polystyrene improves fluidity, rigidity and elongation at break but decreases impact strength.

1.2 Accounts of previous works

A lot of work has been done on ABS, on impact modifiers for PVC and on stabilisation of PVC. The author will now give a brief account of some of the previous works.

1.2.1 On preparation of ABS

Various methods have been reported for the preparation of ABS.

Daly[6] in a patent issued in 1948 blended a styrene - acrylonitrile copolymer with a butadiene-acrylonitrile

elastomer on a rubber mill. It was found that when the major proportion was the styrene-acrylonitrile resin, the product was hard, with an Izod impact of 2-3, about eight times that of the base resin.

On the other hand, the product was flexible but leathery when the major component was the elastomer. It is probable that the continuous phase in each case was the polymer present in major proportion.

More recent technology,[7-11] has shown that by polymerizing resin-forming monomers in the presence of butadiene rubbers, graft polymers are formed, in which the resin chains are chemically attached to the rubber.

ABS is now generally made by graft copolymerisation. An advantage of this is that the grafted rubber is more 'efficient' in the sense that higher impact strengths are obtained at low rubber levels[12].

In the 1950's and up to the present time, a large number of patents have appeared using almost every known method for the preparation of ABS graft copolymers. A listing of these patents was published by Rosen.[13]

1.2.2 On Stabilisation of ABS

Although ABS has an excellent all-round combination as an engineering plastic as well as an impact modifier, its outdoor

performance is very poor.

The rubber component is very susceptible to oxidation. Photo-oxidation leads to cross-linking of the rubber phase accompanied by scission of the graft between rubber and matrix, with consequent rapid loss of impact strength[1]. Designs for outdoor use must therefore take account of its weatherability.

In recent years, a lot of work has been done on stabilisation of ABS polymers against[2,5,15-17] environmental degradation mainly thermal and photo-oxidation, since the photo-initiators for photo oxidation are produced during thermal processing.[17,18]

Conventional light stabilisers, for example, peroxide decomposers, give some protection to these polymers during exposure but high concentrations are necessary. This is because the stabilisers are uniformly dispersed through the bulk of the polymer matrix, although it is the rubber component which is sensitive to photo oxidation. Moreover, these additives are readily lost from the polymer by volatilisation and solvent leaching.[1]

It was found[1] that a masterbatch concentration of up to 8g/100g ABS, using a combination of a phenolic antioxidant BHBM, and a thiol UV stabiliser EBHPT, gives a synergistic mixture which has a UV lifetime about five times that of commercially stabilised ABS and over seven times that of the unstabilised product.

1.2.3 On impact modifiers for PVC

The most widely used impact modifiers for PVC are acrylics and acrylates which are close to PVC in refractive index and are readily dispersed, so that phase separation and and stress whitening in transparent articles are minimised.

In general, impact modifiers improve impact strength at the expense of tensile strength whilst softness of the blends remain unchanged[19]. The degree of compatibility between the resin and modifier must also be in the right ratio, for example, when modifier is too compatible, it becomes ineffective in improving impact strength, while highly incompatible product will cause stress whitening and opacity on bending.[19]

Impact modifiers for PVC may be divided into five distinct groups viz:-

(i) Copolymers of acrylonitrile -butadiene-styrene(ABS)

(ii) Copolymers of methylmethacrylate-butadiene-styrene (MBS)

(iii) Copolymers of vinyl chloride and esters of acrylic acid.

(iv) Chlorinated polyethylene.

(v) Copolymers of ethylene and vinyl acetate.

Werblinski[19] in his recent work has compared the effectiveness of various polymers used as impact modifiers for PVC as regards impact strength, tensile strength, clarity,

cost of production, thermal and photodegradation stability etc. His results could be summarized as follows:

ABS modifiers

These modifiers are historically the first impact modifiers developed by the USA firm, Marbon Resin, and exist under the trade name BLENDEX. They give opaque products.

MBS modifiers

These modifiers are produced by Japanese firms under the trade names KUREHA and KANE ACE and by U.S.A firm under the trade name PARALOID with appropriate indices.

In general, they are more efficient than ABS modifiers in that they give products with excellent transparency and much better light stability. They also aid processing of PVC.

Vinyl Chloride and Acrylate Copolymers

This type of modifiers is produced by a German firm under the trade name SOLVIC 602. Application include blow moulded products with low permeability for gases and very good light stability.

Chlorinated polyethylene

This modifier is produced by a German firm under the trade name HOSTALITZ and by U.S.A firm under the trade name PLANSKON. The limited application of these modifiers is caused by their

good mechanical and thermal properties and low cost, they are widely used for the production of building carpentry. They have excellent processing properties.

EVA modifiers

Ethylene-vinyl acetate copolymers are the most recent PVC modifiers. Produced by a German firm under the trade name LEVAREN, it has a combined thermoplastic and elastic properties. It's glass transition temperature is -22°C, therefore it gives PVC blend having excellent impact strength. Due to its excellent overall properties and weatherability, it is the preferable material for modifying PVC for building carpentry.

Because the polychloroprene latex is chemically more stable than that of polybutadiene, Lahlouh and Tahan[2] produced a new type of impact modifier for PVC, Acrylonitrile-Neoprene - Styrene (ANS). They found[2] that although ANS was more stable than ABS, it possessed inferior physical properties as an impact modifier for PVC due to its inability to preserve the desired size and shape of the rubber component in the matrix.

In a recent communication, Hardt[20] modified PVC by graft polymerizing the monomer onto a backbone of Ethyl vinyl acetate containing 45% vinyl acetate (EVA-45). He found that incorporating 5-7% by weight of this EVA into PVC gave an optimum effect in terms of mechanical properties and impact modification. It is

also reported[21,22] that graft polymers with high EVA content (30-50%) could be used as non-migrating flexible PVC.

Hardt[20] compared the ageing behaviour of PVC/EVA-45 system with other existing impact modified PVC systems, and found that the PVC/EVA-45 system was superior to others. This system can thus be used under extreme climatic conditions[23]

1.2.4 On degradation and Stabilisation of PVC

PVC is very unstable to heat and when heated at temperatures above 70°C, thermal degradation takes place. The first physical manifestation of degradation is colour change. Initially white, on heating, PVC changes in sequence to yellow, orange brown and black. At processing temperatures used in practice (150 - 200°C) sufficient degradation may take place during standard processing operations to render the product useless. In addition, the photoinitiators for photooxidation are produced during thermal processing.

For these reasons, PVC needs to be adequately stabilised against thermal and photooxidative degradation.

In a recent study on colour formation in exposed PVC samples, Scott[5] found that the intensity of colour formed increased with an increase in carbonyl. This result is in accord with the findings of Martin and Tilley[24] who related

the discolomation of PVC to oxidation and formation of carbonyl groups.

Scott's evidence suggests that colour formation is more pronounced in processed films than in cast films. This is due to the presence of unsaturation at the beginning of the exposure as a result of the thermal degradation in processed samples of PVC. He also observed that cast PVC films containing a synergistic combination of thermal stabilisers showed good colour stability on exposure to UV light; the effect of processing on the same system, however, was to cause a marked reduction in the induction period followed by a rapid discoloration . The sample containing dienophilic tin stabiliser showed very little discoloration due to the ability of this stabiliser to destroy the unsaturation without affecting the carbonyl group.

Physical and mechanical properties of PVC are also affected by photodegradation. It has been reported[17] that the glass transition temperature (Tg) which occurs at above 80°C in unirradiated PVC, shifts to slightly lower temperatures on prolonged irradiation. There is also a reduction of the intensity of the Transition at -20°C on irradiation of PVC. These changes could be due to plasticisation of the PVC by lower molecular weight photodegradation products since it had

been established from previous studies[25] that there is a reduction in molecular weight (both Mn and Mw) of PVC on exposure.

Commercially available stabilisers for PVC can be divided into thermal and light stabilisers.

PVC degrades by dehydrochlorination to give polyene structures. Thermal stabilisers react with the HCl produced. Degradation is thus prevented since HCl propagates further degradation. The following are the more common stabilisers used for protecting PVC during processing:

1. Lead compounds
2. Organic salts of barium, cadmium, calcium, zinc and tin
3. Organic nitro bases
4. Chelators and epoxy compounds.

Werblinski[19] in his recent work compared the merits of these compounds as follows:

Lead compounds

These are the most important class of stabilisers. In general they give rise to products of varying opacity; they are toxic and turn black in a contaminated environment due to the contents of sulfur; they are good heat stabilisers.

Cadmium-Barium Stabilisers

A wide range of metal stearates, ricinoleates, palmitates and octeates are now available commercially. These are

compounds of cadmium, barium, calcium and zinc. The most important are cadmium-barium coprecipitates because they show synergistic effect.

Organotin Compounds

These are the most universal and the best PVC stabilisers. They are very good heat and light stabilisers and they give crystal-clear transparent products which are odorless. They are very expensive but may be used in much less amounts.

Organic Nitro bases

They are mostly used for pre-stabilised emulsion polymers. They are weak heat and light stabilisers but they have no adverse effects on the system.

Chelaters

These react with the metal chlorides from the stabilisers to form complexes. Additionally they act as antoxidants and light stabilisers.

While thermal stabilisers prevent PVC degradation in a chemical way, light stabilisers act as an optical filters, which absorb UV rays energy and transform it into heat energy or long wave radiation. They are generally named UV absorbers. The most important are 2-hydroxybenzo-phenone, esters of salicylic acid and derivatives of 2-hydroxyphenyl-benatrizoles.

In their work, Burchill and Pinkerton[26] described a method of photostabilization of PVC by surface screening on the polymer. The surface screen was obtained by graft copolymenization of a polymerizable hydroxybenzophenone UV absorber such as 2-hydroxy-4(3-methacryloxy-2-hydroxypropoxy) benzophenone (HMB). They showed that cast PVC films could be protected by this grafting technique, even after 500 hr. continuous exposure in an MBTF lamp assembly.

1.3 References

1. Scott G., International Conference on Toughening of Plastics (1978)

2. Lahlouh J., and Tahan M.,) Private Communications
   Oo M., and Tahan M.,)

3. Gormley J., Reg. Tech. conf. Soc. Plastics Eng. Inc. (1970)

4. Keskkula H., App. Pol. Sym. 1 (1968)

5. Scott G., Europ. Pol. J. 13, 989 (1977)

6. U. S. Pat., 2,439, 202 (1948)

7. Amos J. L., McCurdy J. L., and McIntire, U.S. Pat. 2,694,692 (1954).

8. Hayes R. A., U.S. Pat. 2,802,808 (1957)

9. Childers C. W. and Fisk C. F., U. S. Pat. 2,820,773 (1958)

10. Fremon G. H., and Stoops W. N., U.S. Pat. 3,168,593 (1965)

11. Calvert W. C., U.S. Pat. 3,238,275 (1966)

12. Bergen R. L., 7 42 (1968)

13. Rosen S. L., Pol. Eng. Sci. 7 (1967)

14. Scott G., and Tahan M., Europ. Pol. J., 13, 981 (1977).

15. Fernando W. S. E., Ph.D. Thesis. University of Aston (1977).

16. Kolawole E. G., Univ. of Aston (1978)

17. Scott G., ACS Symposium Series 25, 340 (1976)

18. Glaffar A., Scott A., Scott G., Europ. Pol. J. 13, 83 (1977)

19. Werblinski W., Private Communication

20. Hardt D., International Conference on Toughening of Plastics (1978).

21. Brit. Pat., 027 710.

22. Belg. Pat., 927175

23. Mentel G., Hundertmark G., Plastverarbeifer 7, 397 (1973)

24. Martin K.G., Tilley R. I., Br. Pol. J. 1, 213 (1969)

25. Scott G., and Tahan M., Europ. Pol. J. 11, 535 (1975)

26. Burchill P. J., and Pinkerton D.M., J. Pol. Sci. 55, 185-193 (1976)

CHAPTER 2

STUDIES ON PROCESSED FILMS

CONTENTS

		Page
2.1	Experimental	16
2.2	Formulation of the Materials	16
2.3	Film Pressing of the Processed Samples	16
2.4	Testing	17
2.4.1	Outdoor Exposure	18
2.4.2	Thermal Oxidative Degradation.. ..	19
2.4.3	Embrittlement Test	19
2.5	Results	20
2.5.1	General Features of the IR Spectra..	20
2.6	Discussion	21
2.7	References	27

CHAPTER 2

2.1 EXPERIMENTAL

Studies on processed Polymer blends

Changes in chemical properties due to degradation of ABS, PVC and ABS/PVC polyblend were followed by measurement of carbonyl index from Infra Red spectra of the samples and by embrittlement tests on the samples.

For these studies, processed films were used.

2.2. Formulation of the Materials

Nine samples of different formulation as shown in the table belowwere processed in the R.A.P.R.A. torque rheometer at 190°C using fast speed of mixing. (The processed samples were kindly supplied by Dr. E. G. Kolawole). Samples 1 - 5 and 9 were processed for 3 minutes each.

Sample 6 was processed for 5 minutes.

Sample 7 was processed for 7½ minutes

Sample 8 was processed for 10 minutes.

2.3. Film pressing of the processed samples

Pressing films of ABS/PVC polyblend was carried out in two stages.

i. Pre-pressing

About 8 g of impact modified PVC was placed between glazing

from 4000cm^{-1} to 650cm^{-1} were recorded on the chart paper using medium speed. The peak at 2910cm^{-1} corresponding to methylene peak was used as reference. In each case, the observed growth of the carbonyl and hydroxyl absorption peaks and the observed decay of the trans 1, 4 polybutadiene were expressed as indices. The indices were expressed as the ratio of the absorbance of the growing or decaying peaks to that of the reference peak.

Three types of measurements were carried out viz.

(i) Stability of the films to UV irradiation when exposed to sunlight.

(ii) Stability of the films to thermal oxidative degradation using an air oven at 100^{o}C.

(iii) Embrittlement tests on the exposed samples.

2.4.1 Outdoor Exposure

The outdoor weathering of the films were carried out by exposing the films outside Chemistry Department A.B.U. Zaria. For this exposure, the samples were mounted between two plywood sheets in which nine holes of appropriate dimensions were cut. The samples were then placed centrally over the holes on one sheet before placing the other on top. The system was then clamped to hold the sheets in position. Degradation was followed by IR measurement and time to embrittlement was recorded, the average temperature at this time of the year was 25^{o}C.

2.4.11 Thermal Oxidative degradation

Oven Ageing Studies

Accelerated thermal oxidation of the films was carried out by mounting the sample films on specially prepared cardboard holders as described above (2.3.1) and were suspended by copper wires in the air oven. Ageing was carried out at 100°C. The degradation was followed by running the IR spectra at regular intervals.

2.4.111. Embrittlement Test

The embrittlement test was carried out on all the specimens. This test was carried out by bending the specimen twice at 180°. The first bending was performed towards the unirradiated surface and the second was carried out next, but towards the irradiated surface. This procedure was carried out at regular time intervals and the results obtained from such tests have been tabulated in Tables 2 and 3.

TABLE 2

OUTDOOR EXPOSURE

SAMPLE	MATERIAL	ANTIOXIDANT/STABILISER	PROCESSING TIME (MINUTES)	INDUCTION PERIOD(h)	TIME TO EMBRITTLEMENT(h)
1	PVC	-	3	None	1050
2	PVC/ABS	IRGASTAB T_{290}/	3	260	Not Yet
3.	PVC/ABS	BHBM/	3	130	980
4	PVC/ABS	IRGASTAB T_{290},/ EBHPT	3	130	Not Yet
5	PVC/ABS	BHBM/EBHPT	3	100	980
6	PVC/ABS	BHBM/EBHPT	5	None	840
7	PVC/ABS	BHBM/EBHPT	7½	None	840
8	PVC/ABS	BHBM/EBHPT	10	None	840
9	ABS	-	3	None	30

TABLE 3 CVEN AGEING STUDIES

SAMPLE	MATERIAL	ANTIOXIDANT/STABILISER	PROCESSING TIME (MINUTES)	INDUCTION PERIOD(h)	TIME TO EMBRITTLEMENT(h)
1	PVC	-	3	None	882
2	PVC/ABS	IRGASTAB T_{290}/	3	Over 800	Not Yet
3	PVC/ABS	BHBM/	3	80	642
4	PVC/ABS	IRGASTAB T_{290} EBHPT	3	200	Not Yet
5	PVC/ABS	BHBM EBHPT	3	130	600
6	PVC/ABS	BHBM EBHPT	5	100	550
7	PVC/ABS	BHBM EBHPT	7½	80	500
8	PVC/ABS	BHBM EBHPT	10	80	500
9	ABS	-	3	None	25

2.5 Results

The stability of each of the nine samples towards outdoor weathering and accelerated thermal oxidation were studied by IR spectra. These studies were made in triplicate.

2.5.1 General Features of the IR spectra

Fig. 1 shows one of the IR spectra of PVC containing ABS (M_1) and ABS(M_2), processed for 10 minutes. The general features of all the spectra are similar. In all spectra in this work, the regions of greatest interests are areas relating to the double bonds centred at 965 cm^{-1}, the ketonic band around 1720cm^{-1} and the hydroxyl band around 3500 - 3400cm^{-1}. It is clearly seen that after a certain length of time, that the poly trans-1,4-butadiene at 965cm^{-1} is destroyed as evidenced from the diminishing bands. It is clear also that the bands at 1720 and 3450-3500 cm^{-1} also grow (Fig. 1).

Fig.2 shows the variation of the different indices with exposure time. The -C=C- index at 965cm^{-1} decreases and then levels off after a certain time. The -O-H at 3450cm^{-1} increases and then reaches a sort of 'plateau'. The point at which the -O-H stops to increase corresponds to the point when the diminishing -C=C- levels off. The C=O index at 1725 cm^{-1} continues to grow even after the -OH and the -C=C- indices have levelled off.

Figs. 3, 5,6,8 show the plots of the carbonyl index of the various samples as a function of time when samples were heated in an air oven at 100°C while Figs. 4,7,9 show the carbonyl index of the samples as a function of time when the samples were exposed outdoor at an average temp. of 25°C. Fig.10 is a plot of the initial hydroxyl index against processing time of the various samples.

2.6. Discussion

On measurement of the indices of an exposed sample, it is found that the hydroxyl index increases and it may level off after a certain time; this increase represents the production of hydroxyl groups. As the degradation of the sample starts, there is a growth of the carbonyl index. The slope of the growing carbonyl index indicates the extent of the degradation. In the presence of a stabilising additive, an induction period may be observed. As the hydroxyl groups are produced, they are consumed by the additive before they can initiate the degradation of the polymer. Once the additive is destroyed, the hydroxyl group produced is converted first to acid and then to the carbonyl; this leads to the growth of the carbonyl peak at the end of the induction period.

The embrittlement time gives an idea of the length of time that

the sample can be exposed under the same condition, before it fails. (the useful life of the sample under the same condition).

Fig.3 & 4 compare the carbonyl index of ABS, PVC and ABS/PVC polyblend on exposure.

No induction period was observed for all the three samples. From the slopes of their carbonyl index, it is obvious that at any particular time, PVC was the least degraded and ABS was the most degraded. This shows that unstabilised PVC is more stable to thermal and photooxidative degradation than either unstabilised ABS or unstabilised ABS/PVC polyblend.

It will appear that ABS degrades in the polyblend as if it were on its own. Hence, incorporation of unstabilised ABS into PVC, reduces the stability of PVC. Fig. 5 shows the carbonyl index for the nine samples and again it can be seen that unstabilised ABS is the least stable. This is confirmed by Tables 2 & 3 where the time to embrittlement is seen to be least for ABS.

Figs 6 and 7 compare the efficiencies of the commercial thermal stabiliser, Irgastab T_{290} with ABS (M_1) containing the antioxidant BHBM. From the respective values of the carbonyl index and from the shapes of the curves, it could be said that PVC containing thermal stabiliser T_{290}, performs better than impact modified PVC containing BHBM.

This indicates that at any time during the exposure, the sample containing ABS(M_1) was more degraded than that containing T_{290}. Hence T_{290} is more effective for stabilising PVC. Now from tables 2 and 3, on outdoor exposure, sample 2 containing T_{290} has an induction period of 260 h and after 1000 h the sample was still not brittle. On thermal exposure, the inducti period for this sample was more than 1000 h and after this length of exposure, the sample was still not brittle. The corresponding lengths of time for sample 3 are much less. The combined performance of both T_{290} and BHBM are better when used to stabilise PVC against thermal degradation than against photooxidative degradation.

In this work on stabilisation of ABS, Kolawole[1] established that a mixture of 1% ABS(M_1) containing anti-oxidant BHBM and 2% ABS(M_2) containing UV stabiliser EBHPT gives a synergistic mixture which is very satisfactory for stabilising ABS. It has also been established[2] that a mixture of Irgastab T_{290} and EBHPT is a very good system for stabilising PVC.

In Figs. 8 and 9, a comparison of the efficiency of these two systems, when used to stabilise PVC, has been made. The slopes of the index (Fig 8 & 9) for sample 4 containing T_{290} and EBHPT are lower than those for sample 5 containing the synergistic

mixture. This indicates that sample 5 was more degraded than sample 4 at any period during the exposure of the samples.

Tables 2 and 3 show that on thermal exposure, the induction period for sample 4 was 200h while that of sample 5 was 130 h. Also, sample 4 was still not brittle after 1000 h exposure outdoor and in an air oven at 100°C. On thermal exposure, sample 5 embrittled after about 600h and on outdoor exposure, the time to embrittlement was 900h. These figures confirm that the mixture containing T_{290} and EBHPT is a better system than ABS(M_1) and ABS(M_2) containing BHBM and EBHPT respectively, for stabilising PVC. Since EBHPT and BHBM both contain sulphur, it is probable that in PVC they show an antagonistic effect in contrast to their synergistic effect in ABS. It is clear also that the two systems are better for stabilising PVC against thermal degradation than for photooxidative degradation.

Fig. 5 shows that PVC stabilised by the ABS synergistic mixture ABS(M_1) and ABS(M_2) and processed for different lengths of time, has different values of the carbonyl index.

Polymers being bad conductors of heat are susceptible to damage by overheating PVC polymers in particular are very unstable to heat hence processing temperatures and times should be carefully selected.

Samples 5 & 8 have been processed for various lengths of time varying from three to ten minutes. From tables 2 and 3

it can be seen that there is no direct relationship between the processing time and the IP = induction period and ET = embrittlement time. At the same time, it is obvious from the values of IP and ET that those samples for shorter periods appear to be relatively more stable than those processed for onger periods. When the values for IP & ET for samples 5-8 are compared for the thermal weathering and outdoor exposure, one would see that the samples are more stable to heat than to UV irradiation from the sun. From the ET obtained, it is suggested that the long term outdoor performance at low temp. will be better than use of these blends at high temperature operations. It is however very clear that the additives are very unstable to UV light. The higher ET obtained may be due to the fact that they act as screeners. It is also suggested that a measure of initial hydroperoxide concentration produced may be a better way of estimating the effect of processing time on the samples. (It could be seen from visual observation of the processed polymers that some of the samples are almost carbon black due to damage done during long processing times.) In the presend study, it has been found that a plot of initial hydroperoxide index against processing time passes through a maximum. (Fig 10). It has been shown[3] that there is a linear relationship between hydroperoxide index measured

spectrophotochemically and hydroperoxide concn. measured chemically by iodometric titrations.

Therefore it can be concluded that a maximum concentration of hydroperoxide is produced at five minutes. The greatest damage to the polymer is done during the period of thermal processing.

TABLE 2

OUTDOOR EXPOSURE

SAMPLE	MATERIAL	ANTIOXIDANT/STABILISER	PROCESSING TIME (MINUTES)	INDUCTION PERIOD (h)	TIME TO EMBRITTLEMENT (h)
1	PVC	-	3	None	1050
2	PVC/ABS	IRGASTAB T_{290}/	3	260	Not Yet
3	PVC/ABS	BHBM/	3	130	980
4	PVC/ABS	IRGASTAB T_{290},/ EBHPT	3	130	Not Yet
5	PVC/ABS	BHBM/EBHPT	3	100	980
6	PVC/ABS	BHBM/EBHPT	5	None	840
7	PVC/ABS	BHBM/EBHPT	7½	None	840
8	PVC/ABS	BHBM/EBHPT	10	None	840
9	ABS	-	3	None	30

TABLE 3 OVEN AGEING STUDIES

SAMPLE	MATERIAL	ANTIOXIDANT/STABILISER	PROCESSING TIME (MINUTES)	INDUCTION PERIOD(h)	TIME TO EMBRITTLEMENT(h)
1	PVC	-	3	None	882
2	PVC/ABS	IRGASTAB T_{290}/	3	Over 800	Not Yet
3	PVC/ABS	BHBM/	3	80	642
4	PVC/ABS	IRGASTAB T_{290} EBHPT	3	200	Not Yet
5	PVC/ABS	BHBM EBHPT	3	130	600
6	PVC/ABS	BHBM EBHPT	5	100	550
7	PVC/ABS	BHBM EBHPT	7½	80	500
8	PVC/ABS	BHBM EBHPT	10	80	500
9	ABS	-	3	None	25

2.7 References

1. Kolawole E.G., Univ. of Aston (1978)

2. Cooray B. B.,

3. Khirud B., Chakraborty and Scott G., Europ. Pol. J. 13, 731-737.

CHAPTER 3

STUDIES ON CAST FILMS

Contents

		Page
3.1	Casting of Films	28
3.2	Testing	28
3.3	Results	29
3.4	Discussion	29
3.5	References	31

CHAPTER 3

EXPERIMENTAL

3. Studies on Cast films

Changes in physical properties due to degradation of ABS, PVC and ABS modified PVC were followed by mechanical tests. For these studies, cast films were used.

3.1. Casting of films

A cast film of ABS was obtained by dissolving 2g ABS powder in dichloromethane. The solution was cast over a mercury surface, in a dessicator. On evaporation of the solvent, a film of fairly even thickness was obtained.

PVC cast film was obtained in a similar way, using PVC powder and tetrahydrofuran as the solvent.

Cast films of ABS/PVC polyblends were similarly obtained using various ratios of ABS and PVC powders. Tetrahydrofuran was used as solvent.

3.2. Testing

For each sample, specimens were cut out and mounted on a cardboard for outdoor exposure.

The tensile property of each sample was tested before and at in ervals during exposure, using an Instron tensile Machine Model TM-M, under a full scale load of 2000g, crosshead speed of

0.51cm/min and a chart speed of 10cm/min. Several specimens were tested for each sample.

3.3. Results

Figs. (3.1 - 3.3) show the effect of photooxidative degradation on the tensile strength, elongation and Modulus of the test samples.

Figs (3.4 - 3.6) show the effect of composition of the polyblends on tensile strength, elongation and modulus of the samples.

Fig (3.7) show the stress-strain profiles for different composition of the blend.

3.4 Discussion

It could be observed from fig. 3.1 that the elongation at break decreases with increase in the time of exposure; it also decreases with an increase in the amount of ABS in the polyblend, that is 100% PVC gave the maximum elongation at break while 100% ABS gave the minimum elongation at break, on outdoor exposure. On incorporation of ABS into PVC, values of elongation, between those for pure PVC and pure ABS, were obtained.

It was observed that for all the samples Ultimate Tensile strength increases with exposure of the materials until a

maximum is reached. (fig.3.1). It was also observed that the time required to reach the maximum varied from one sample to another, depending on the composition of the blend. Once the maximum is reached, the graph levels off. For example, as shown in Fig. 3.2, the maximum is reached after 25 hours. From a measurement of embrittlement time, it could be shown that the time required to reach the maximum, correspond to the embrittlement time of these samples.

In Fig. (3.4) it is clearly seen that the extensibility of PVC is reduced on the addition of ABS. The graph passes through a maximum for a blend of about 20% PVC.
This seems to be the optimum blend in terms of extensibility of the material. It was expected that due to the rubber content of ABS, that this material should have a higher extensibility than PVC. However, it was shown that the elastic properties of ABS is highly temperature dependent. At low temperatures, ABS has a higher elongation than PVC. As the temperature increases however, it begins to lose its extensibility, PVC being thermoplastic, has better extensibility at these higher temperatures. These tests were carried out at temperatures above $25^{\circ}C$, hence the lower values obtained for the elongation of 100% ABS.

It was observed that on outdoor exposure of the samples, (Fig.3.5) there was an increase in Young's Modulus. It is

therefore suggested that the samples become more rigid.

A marked increase in Young's Modulus was also observed (Fig. 3.6) with an increase in the amount of ABS in the polyblend. Thus it can be said that the presence of ABS in PVC weakens the structure of PVC but it also increases the rigidity of PVC. This blend tends to behave in a similar way to Polyethylene/ PVC blend.

Fig (3.7) shows the typical stress-strain profiles obtained for three samples. It is observed that the amount of elastic region increases as the amount of PVC in the blend increases; in other words, maximum elastic region is obtained with 100% PVC.

Finally the degradation of ABS cast film was followed by measurement of $^{-}OH, >C = O$ and $C = C$ indixes. From Fig. 8 it could be seen that the degradation proceeded by a first order reaction.

3.5 References

3.5.1 Werblinski W., Private Communications.

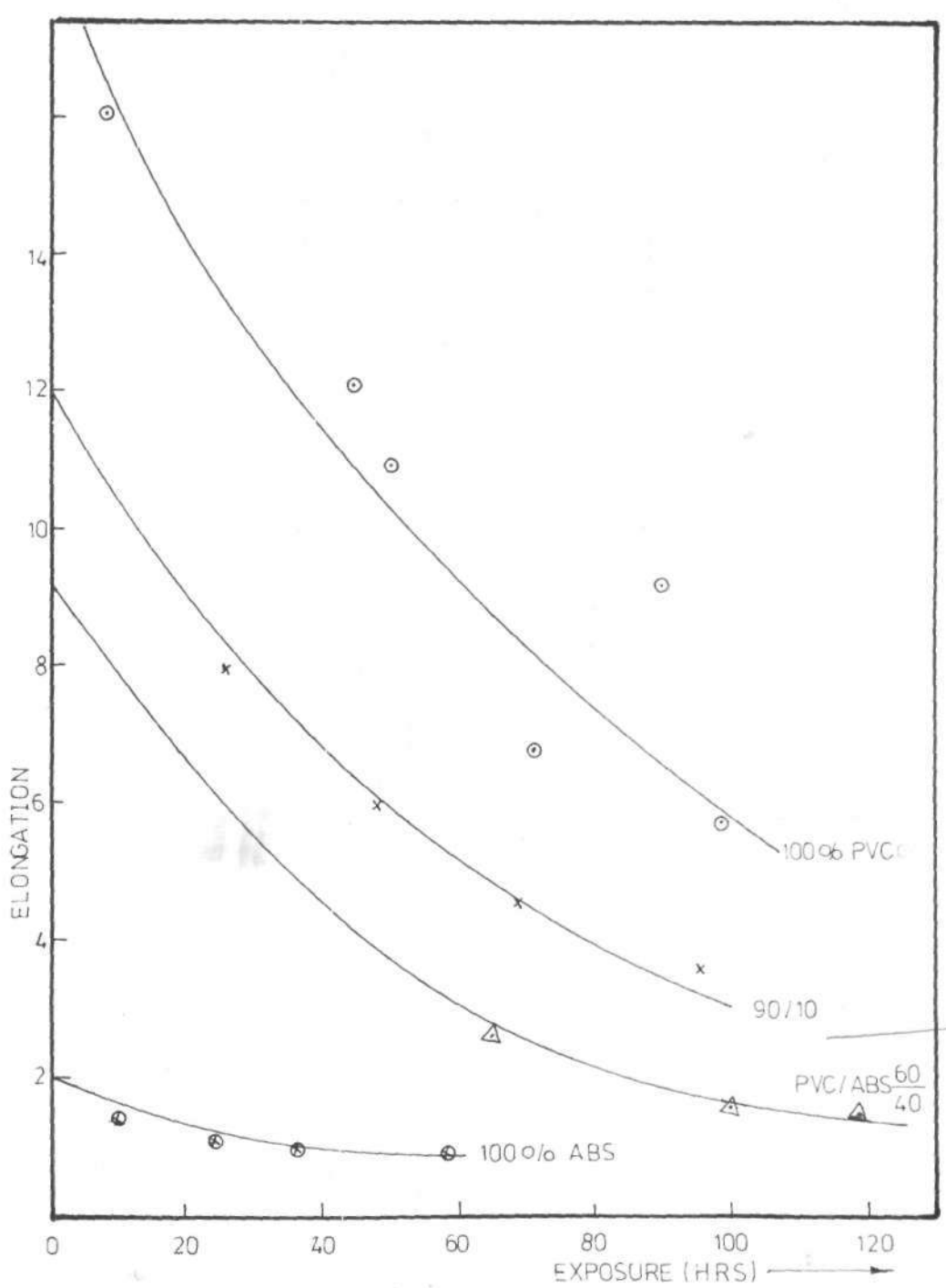


Fig. 3.1 DEPENDENCE OF ELONGATION ON EXPOSURE

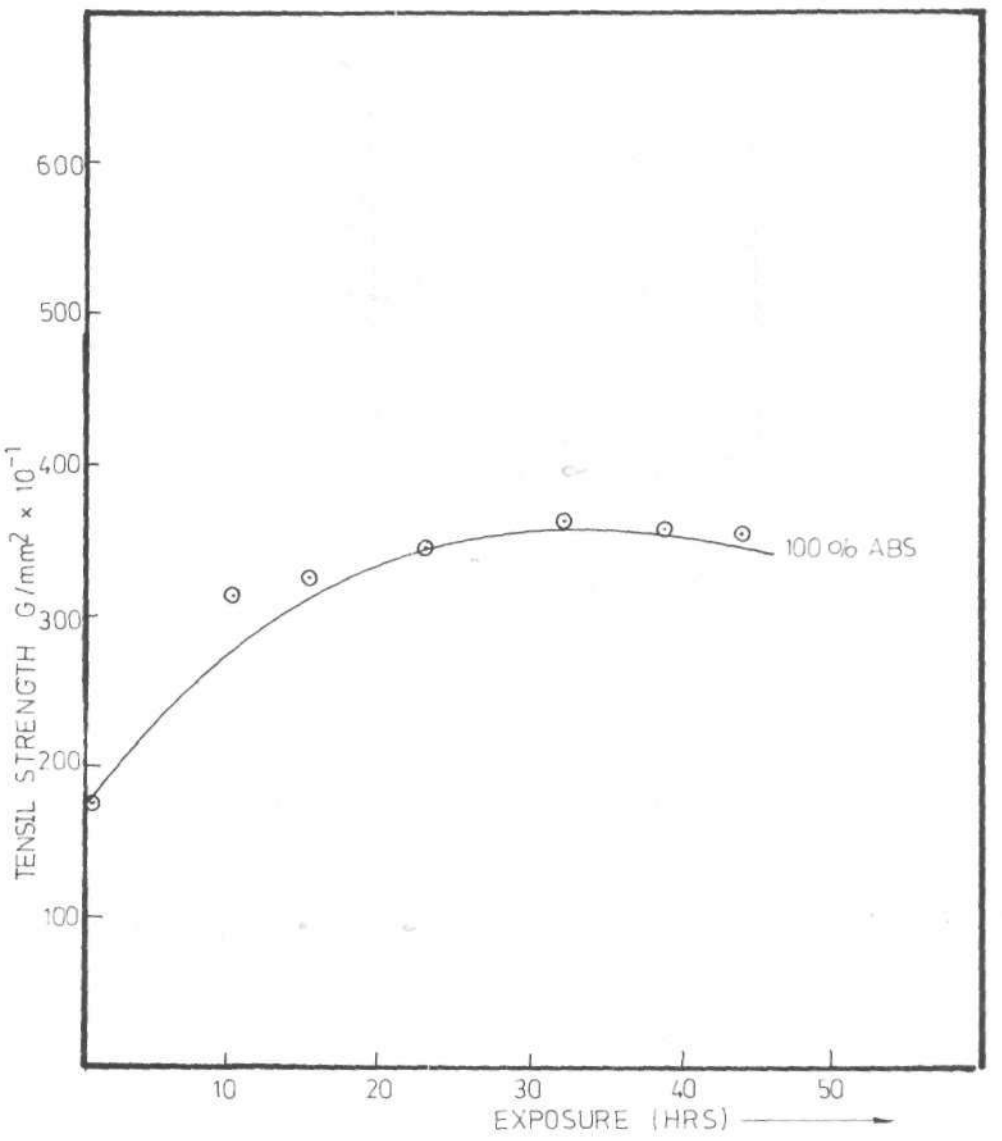


Fig. 3.2 DEPENDENCE OF TENSILE STRENGTH ON EXPOSURE

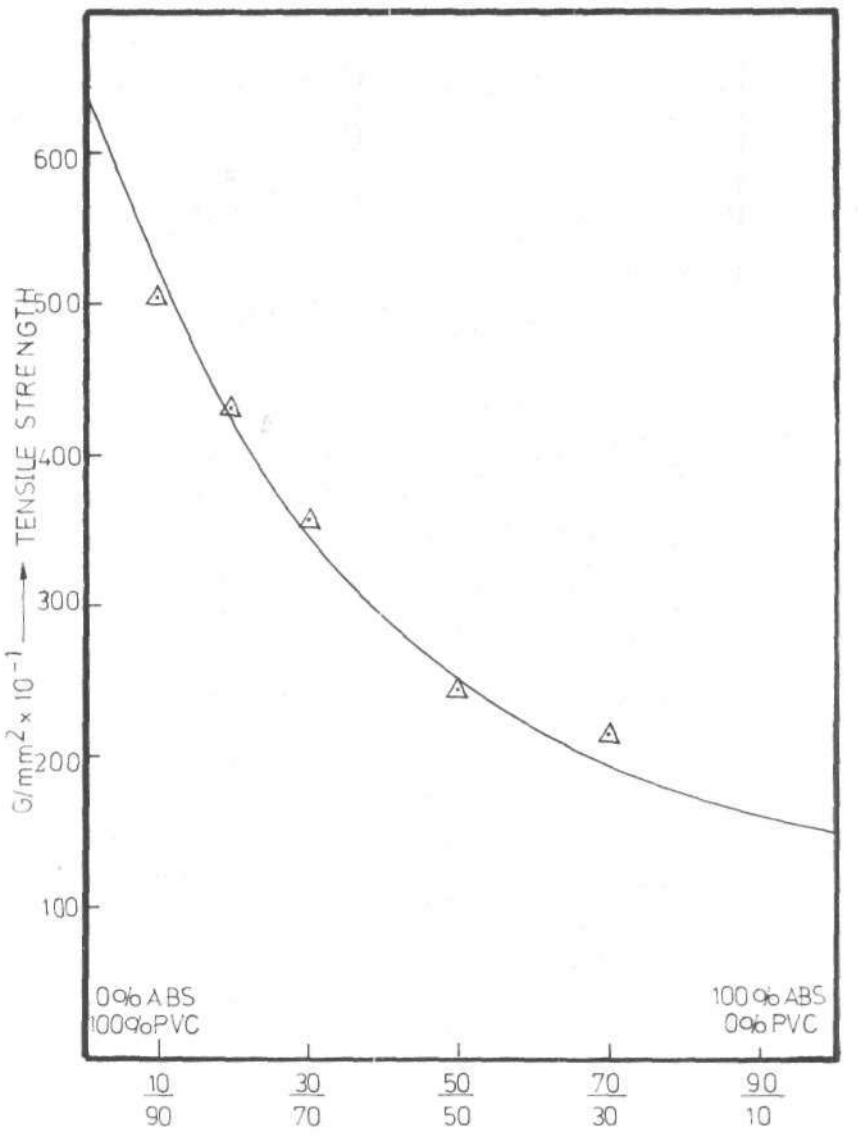


Fig.3.3 DEPENDENCE OF TENSILE STRENGTH ON COMPOSITION OF ABS/PVC POLYBLEND

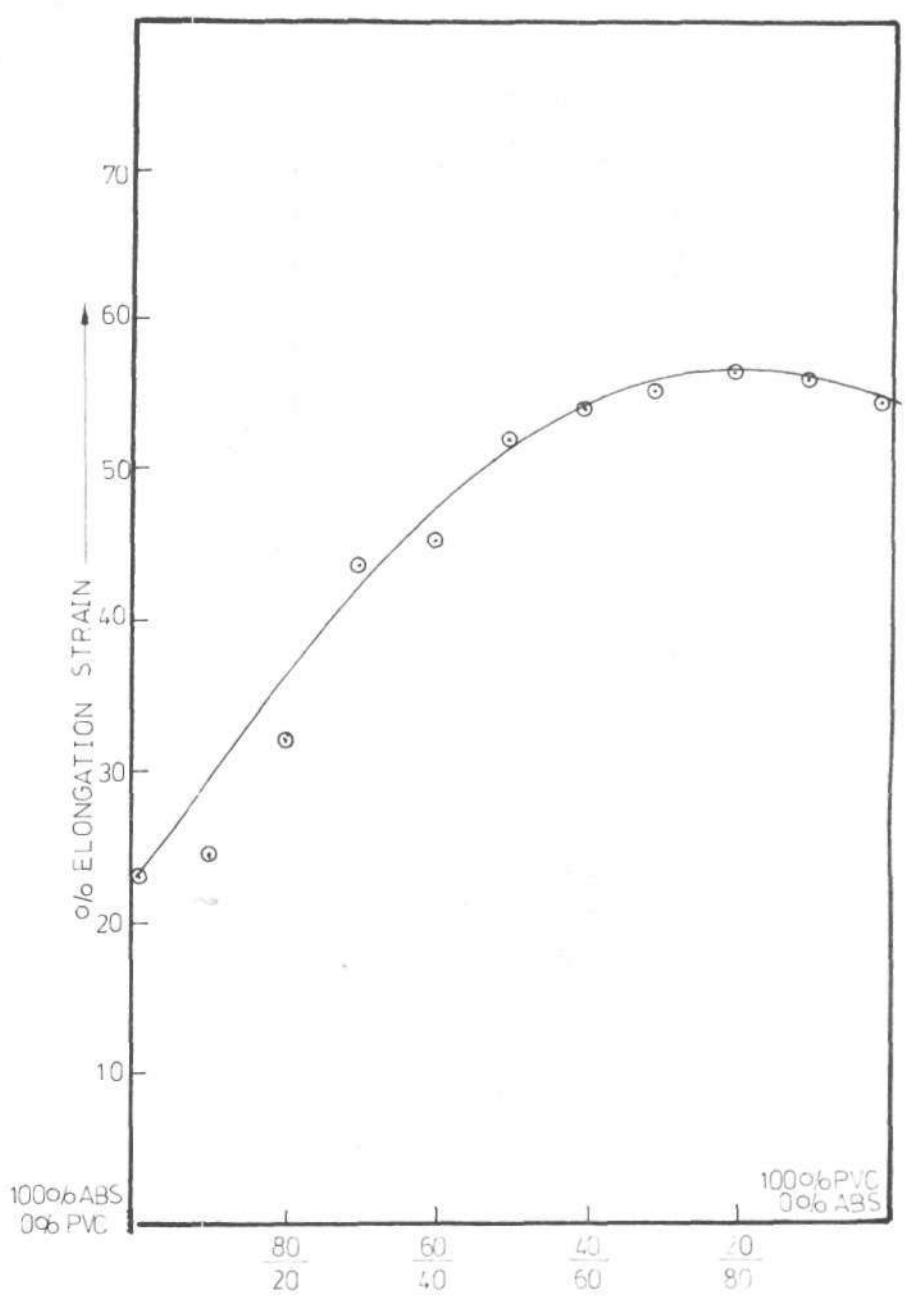


Fig. 3.4 DEPENDENCE OF % ELONGATION ON COMPOSITION OF ABSIPVC POLY-BLEND

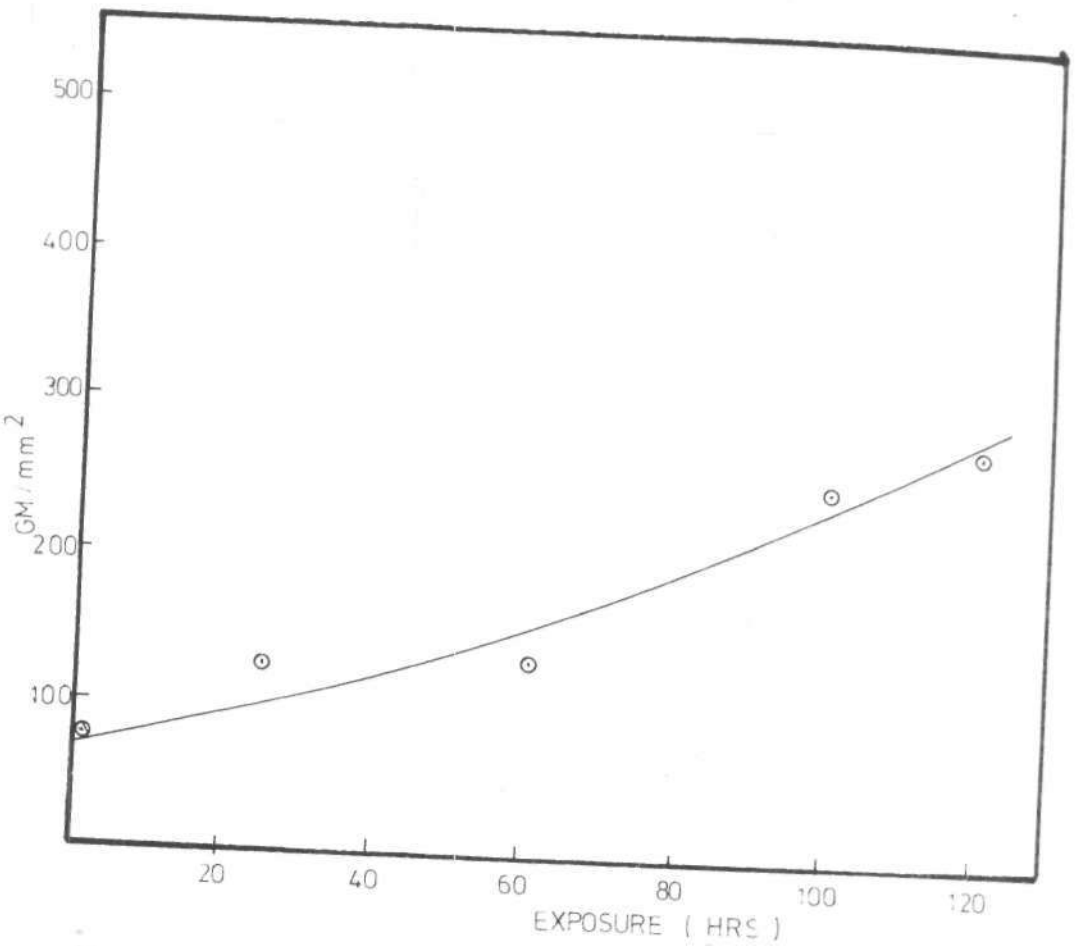


Fig. 3.5 DEPENDENCE OF MODULUS ON EXPOSURE OF ABS/PVC POLYBLEND 40/60

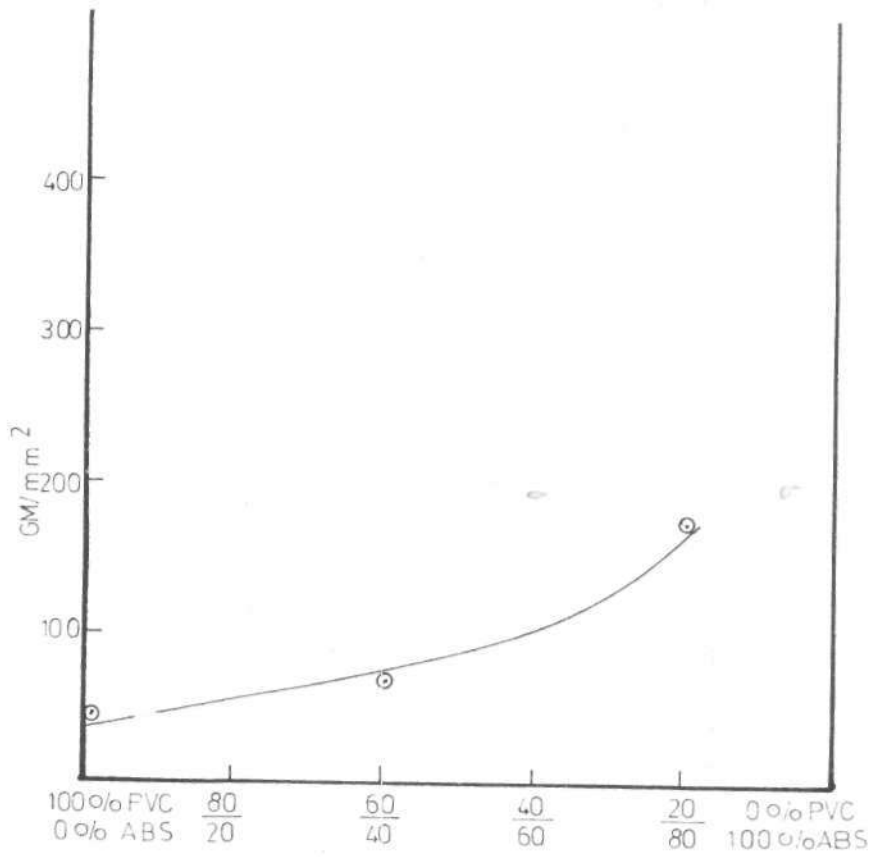
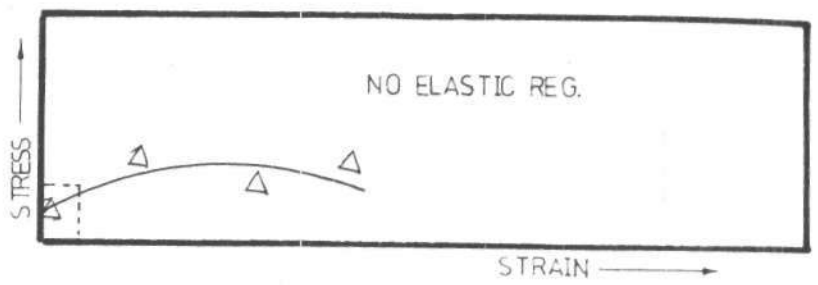
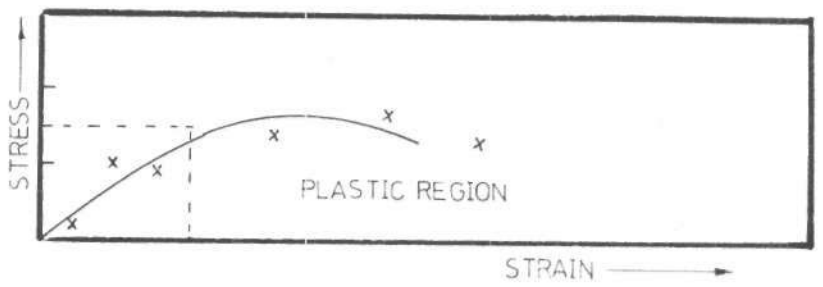


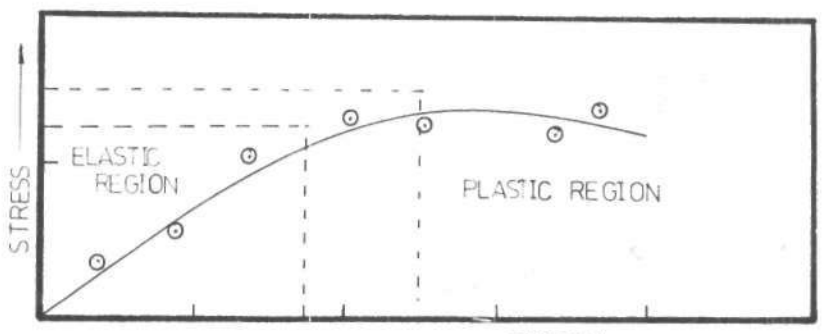
Fig. 3.6 DEPENDENCE OF YOUNG'S MODULUS ON COMPOSITION



STRESS-STRAIN FOR 100% ABS



STRESS-STRAIN FOR POLYBLEND 50/50



STRESS-STRAIN FOR 100% PVC

Fig. 3.7

⊙ = C=O AT 1725cm^{-1} Δ = -O-H AT 3450cm^{-1}

x = C=C AT 965cm^{-1}

CHAPTER 4

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

Contents

		Page
4.1	Conclusions	32
4.2	Suggestions for further work	32

4. Conclusions and Suggestions for future Work

4.1 Conclusions

(1) Incorporating unstabilised ABS into PVC, damages the chemical and physical properties of the impact-modified PVC.

(2) Synergistic stabilisers bound to ABS are not efficient in stabilising impact modified PVC against thermal and photooxidative degradation.

(3) Irgastab T_{290} is an efficient thermal stabiliser for unmodified PVC.

(4) A mixture of Irgastab T_{290} and a UV stabiliser bound to ABS, is an efficient stabilising system for impact-modified PVC.

(5) Processing times should be as low as possible.

(6) At about 25°C, 10-20% ABS is the optimum amount for blending with PVC.

(7) A corrleation exists between embrittlement time and the mechanical behaviour of the blends.

4.2 Suggestion for further Work

It will be desirable to investigate the concentration of ABS (M) in ABS which gave the most satisfactory thermal

and photooxidative performance, as a high molecular weight lubricant/stabiliser for rigid PVC.

When impact testing machine is available, it will be very desirable to measure the impact strength of the samples reported in this work.

Since the combination of T_{290} and the UV stabiliser gave an induction period, it would be interesting to investigate the effects of synergism of the UV absorber and the thermal stabiliser on the impact modifier and impact modified PVC.

It would also be desirable to prepare a compound which could act as a thermal stabiliser and a UV absorber for PVC and which could also give a synergistic effect in situ.

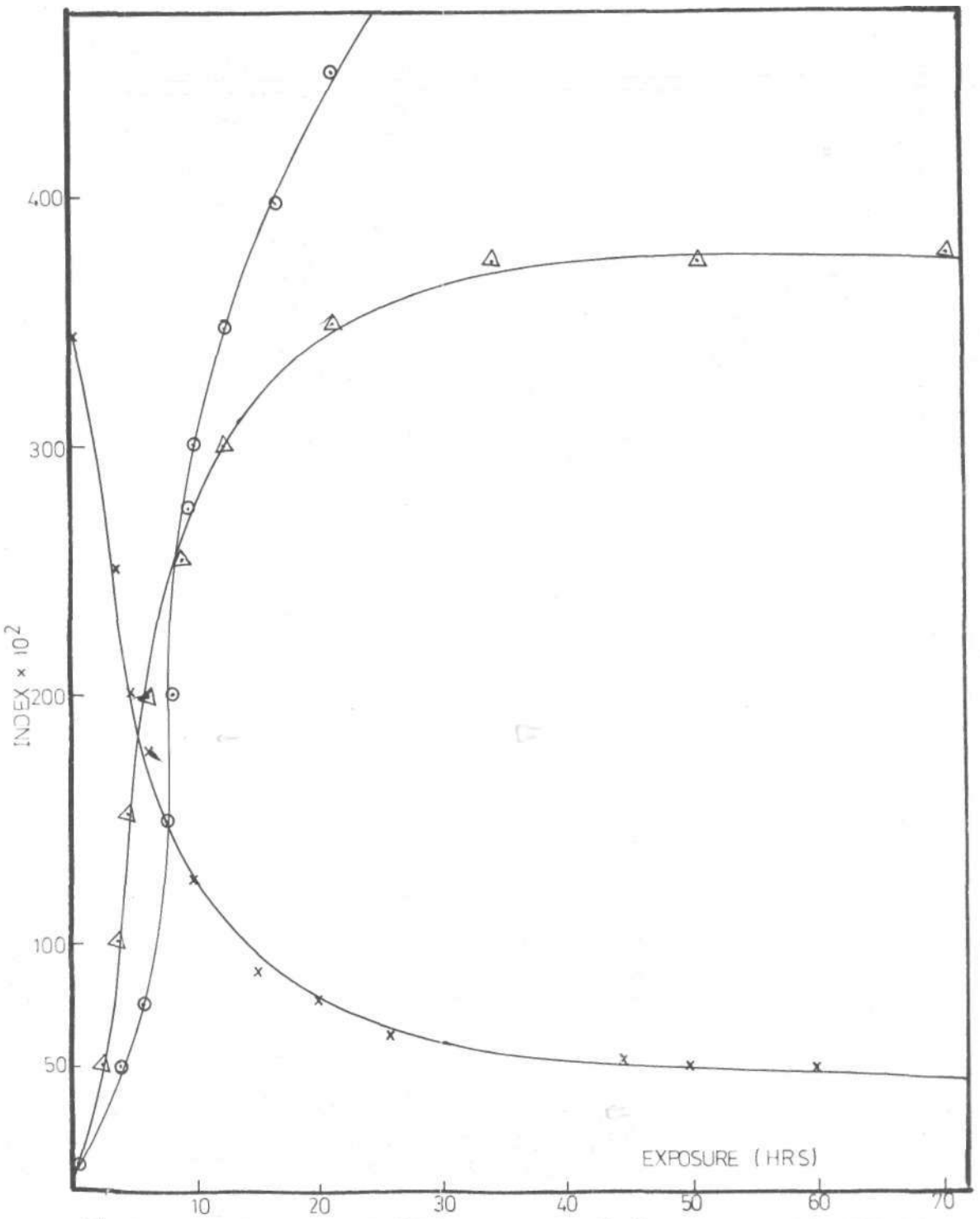


Fig. 2.2 DEPENDENCE OF INDICES ON OUTDOOR EXPOSURE OF UNSTABILISED ABS FILM

⊙ = C=O AT 1752 cm^{-1} × = -C = C- AT 965 cm^{-1} △ = -O-H AT 3450 cm^{-1}

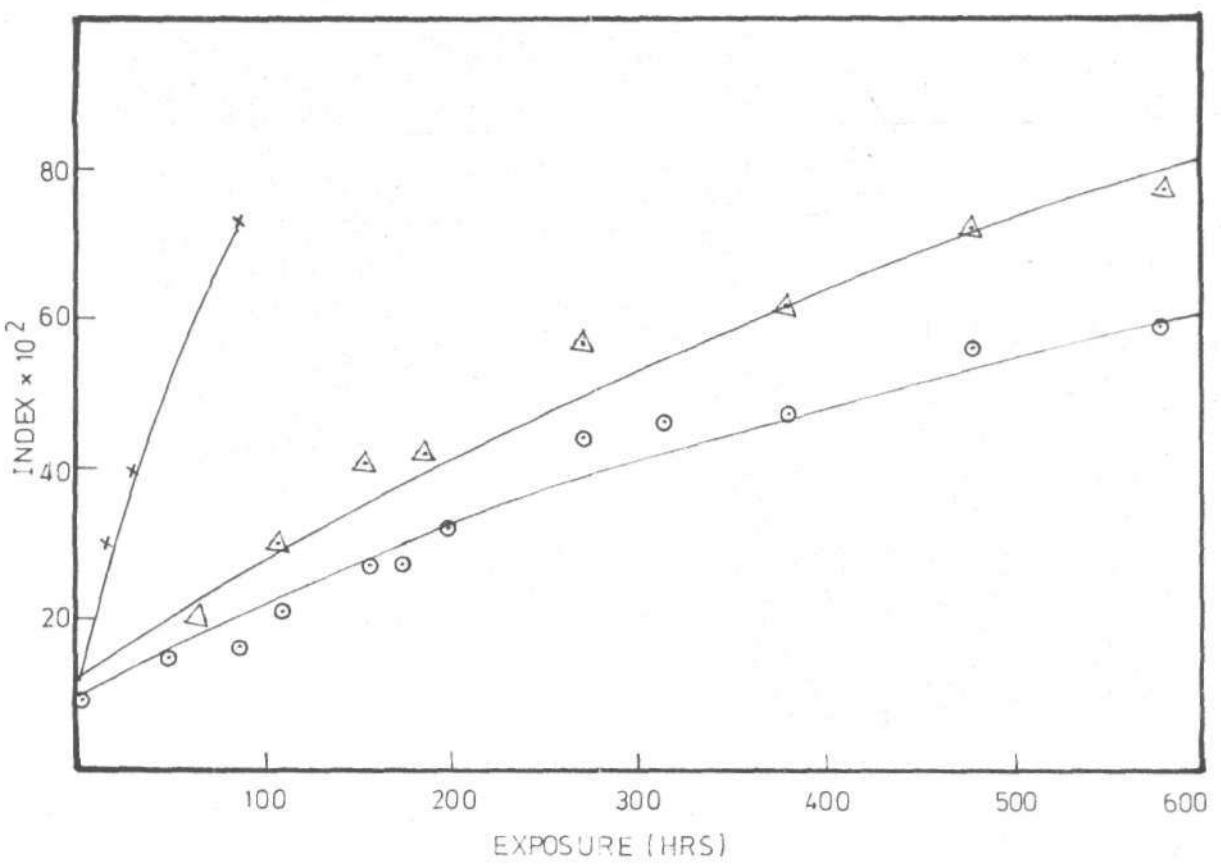


Fig. 2.3 DEPENDENCE OF INDICES OF CARBONYL AT 1725cm⁻¹ ON THERMAL EXPOSURE

⊙= PVC
× = ABS
△= ABS/PVC

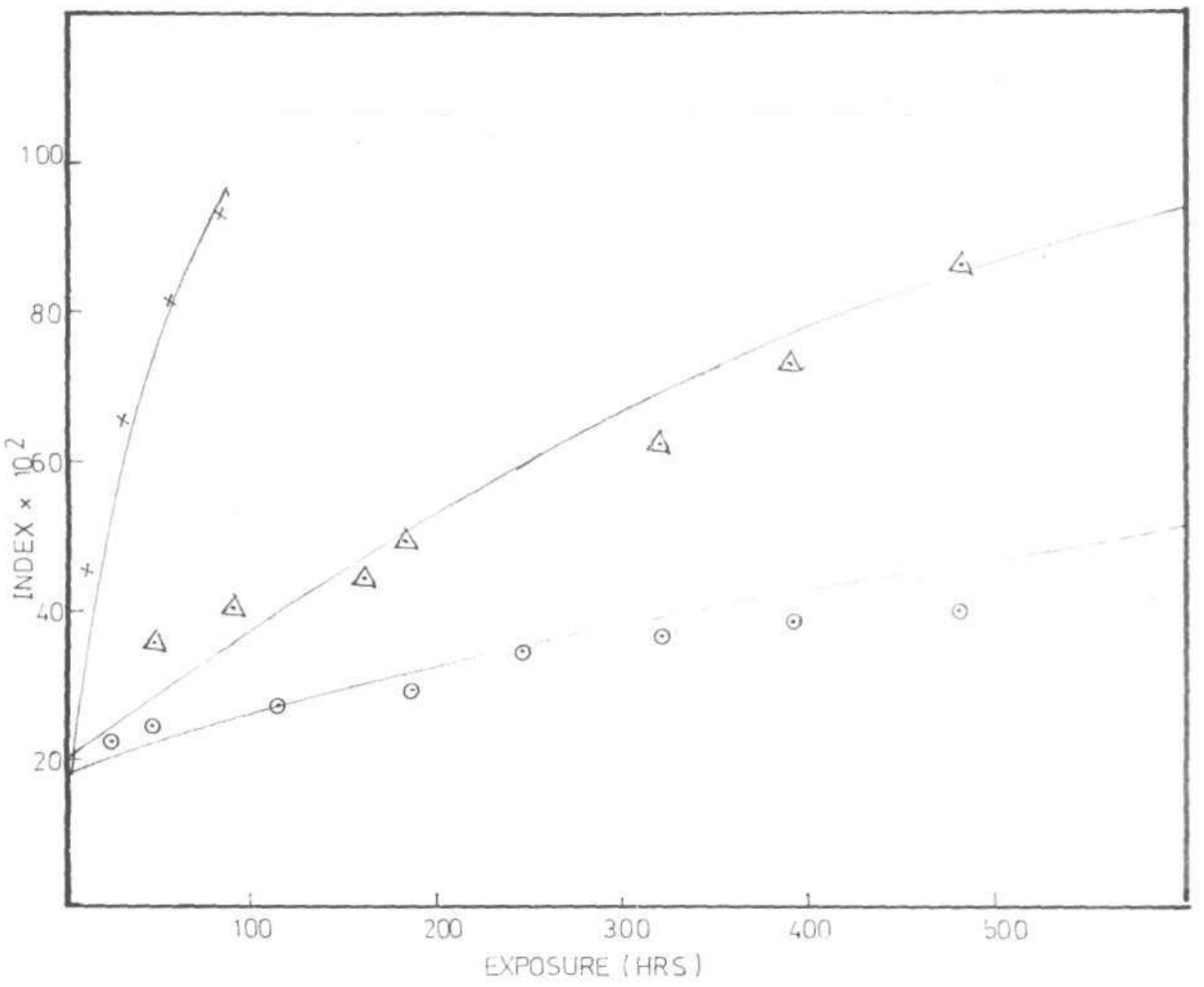


Fig. 2. 4 DEPENDENCE OF INDICES OF CARBONYL (AT 1725cm^{-1}) ON OUTDOOR EXPOSURE

⊙ = PVC
× = ABS
△ = ABS/PVC

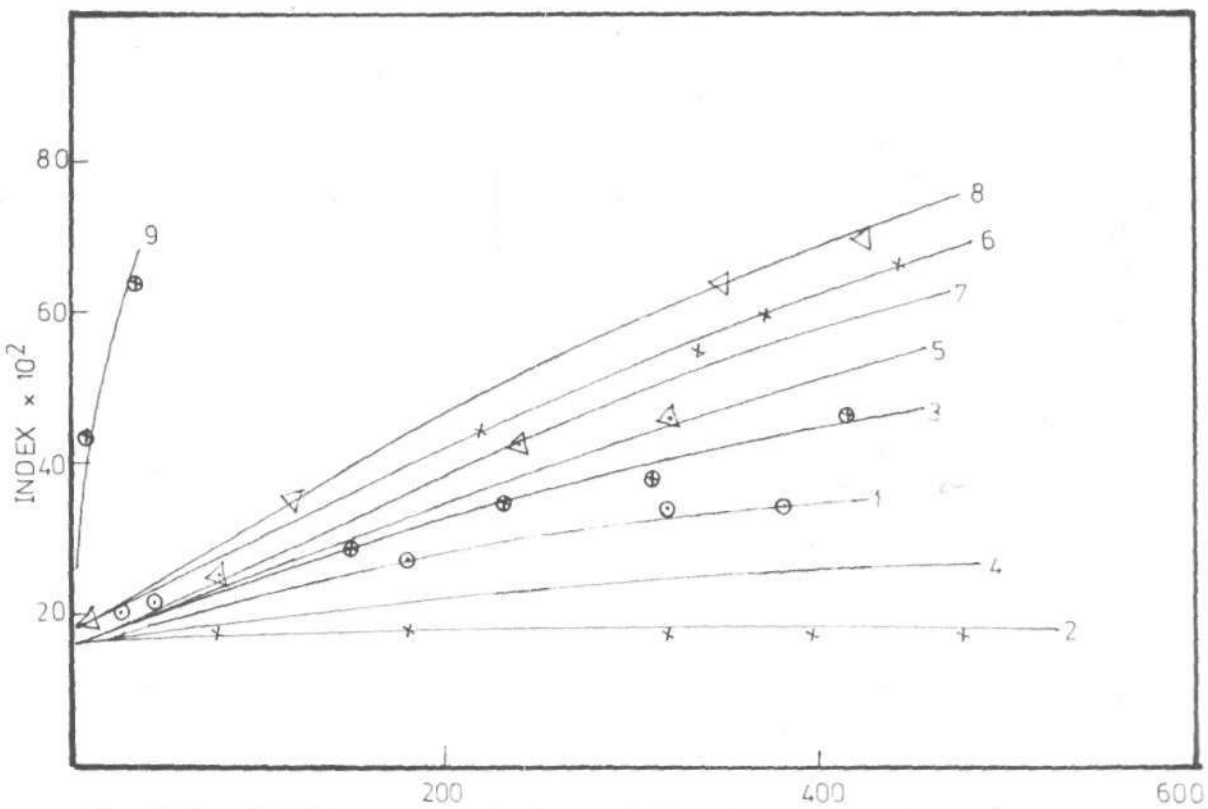


Fig.2.5 DEPENDENCE OF INDEX OF CARBONYL (AT 1725cm^{-1}) ON THERMAL EXPOSURE

1 = PVC ONLY
2 = PVC + IRGASTAB T290
3 = PVC + ABS (M1)
4 = PVC + IRGASTAB T290 + ABS M2

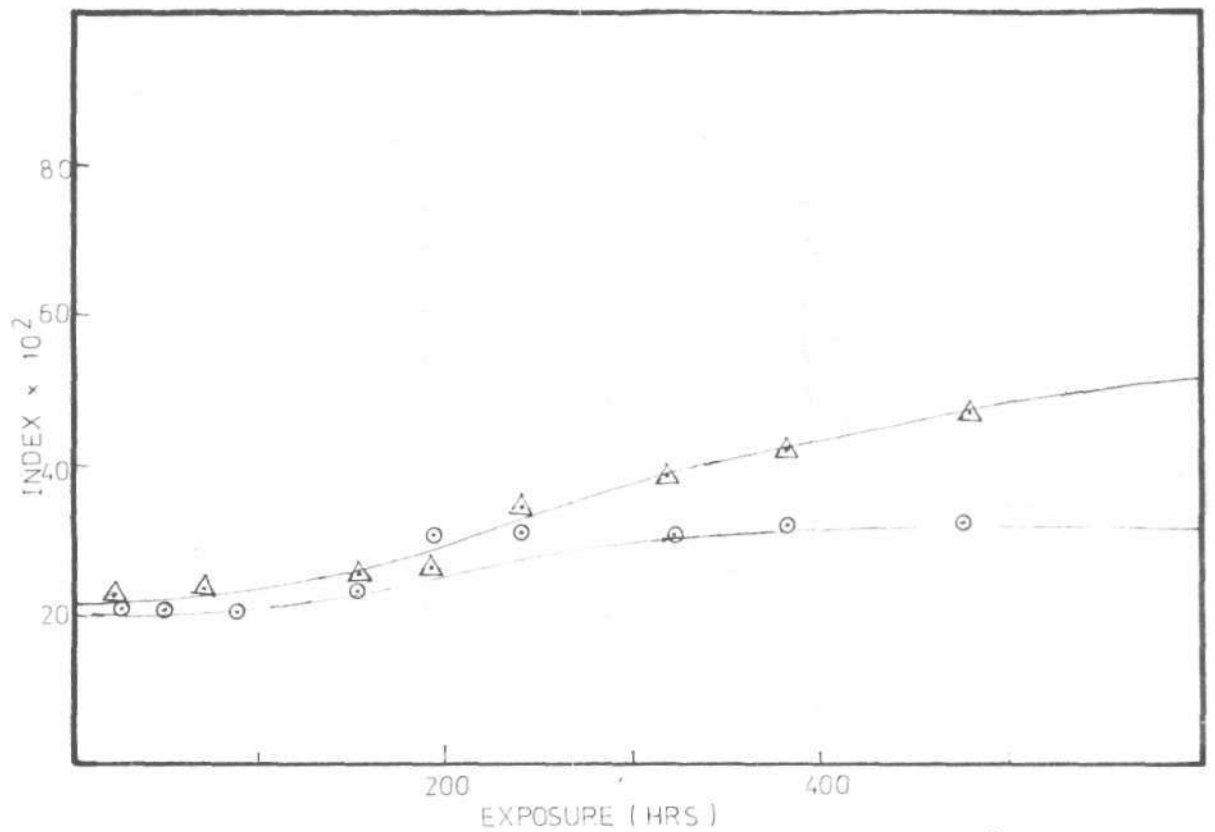


Fig. 2.8 DEPENDENCE OF CARBONYL (AT 1725cm^{-1}) ON THERMAL EXPOSURE

⊙ = PVC + ABS (M2) + IRGASTAB T290

△ = PVC + ABS(M2) + ABS(M1)

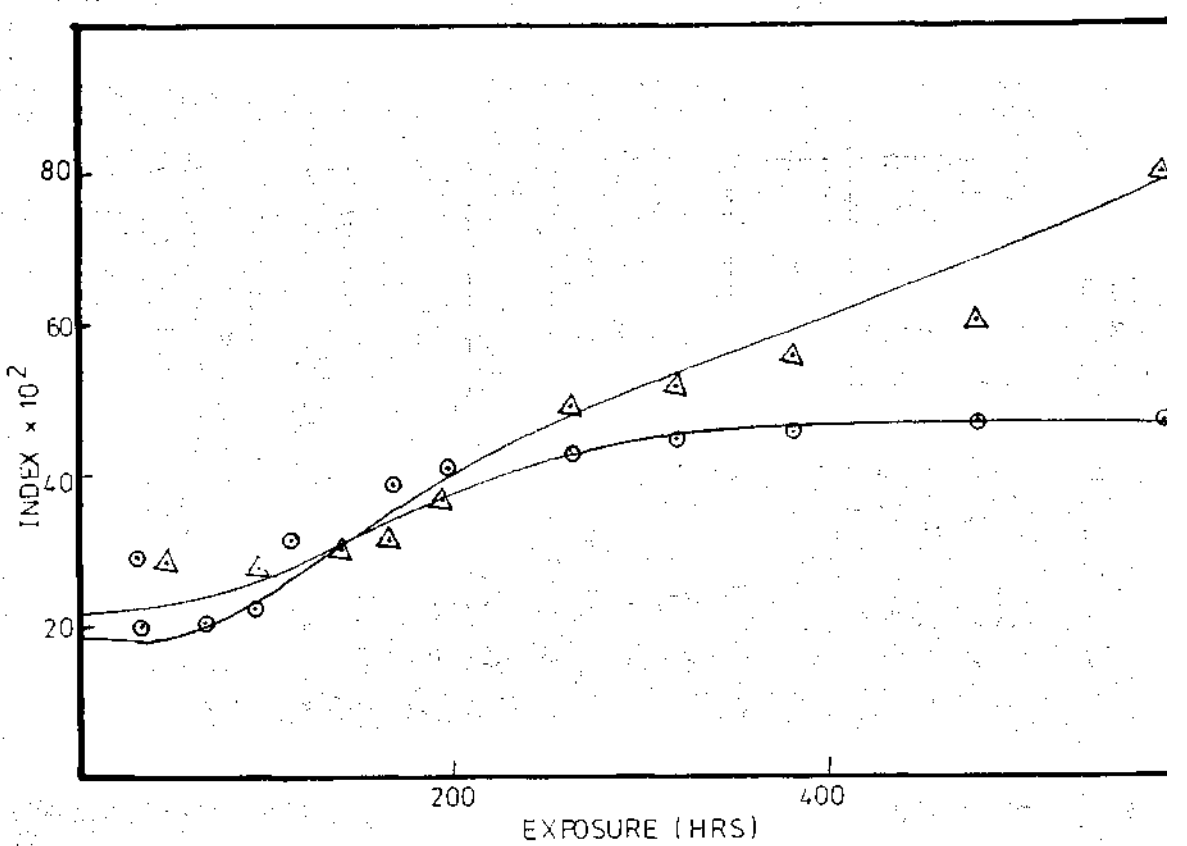


Fig. 2.9 DEPENDENCE OF INDICES OF CARBONYL (AT 1725cm⁻¹) ON OUTDOOR EXPOSURE

⊙ = PVC + ABS (M2) + IRGASTAB T 290
△ = PVC + ABS(M2) + ABS(M1)

(1)

REMARKS PVC S - Thermal green. 181 hrs

ORIGIN

PURITY

PHASE

CONCENTRATION

THICKNESS

DATE

OPERATOR

PERKIN-ELMER

SPECTRUM NO.

SAMPLE 1

SAMPLE 2

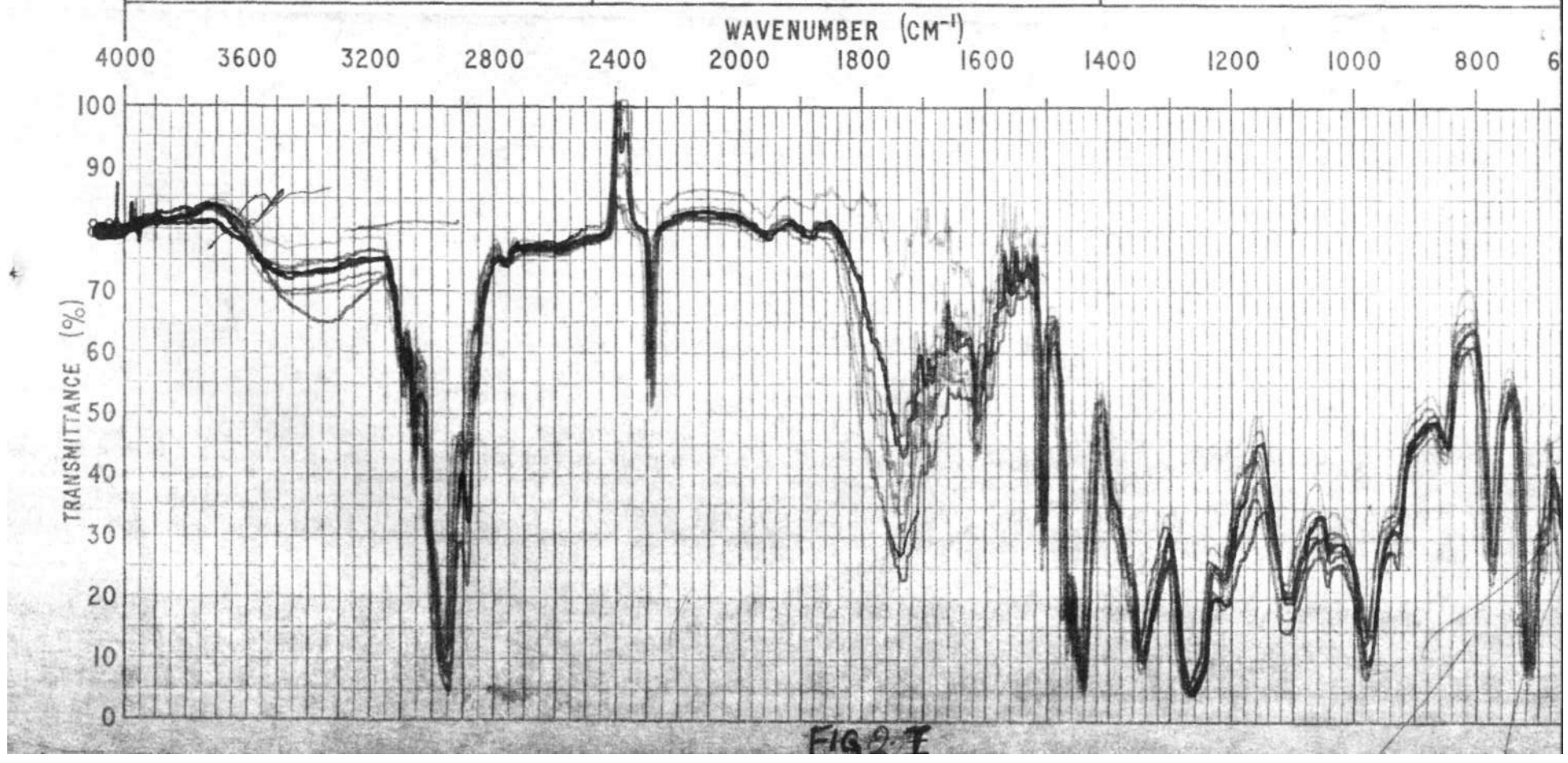


FIG 9-F