MECHANICAL AND THERMAL PROPERTIES OF PHYSICALLY-BLENDED-PLASTIC FILMS

BY

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"Submitted in partial fulfilment of the requirements
for the degree of Master of Science in Physcis,
Faculty of Science, University of Jordan
Amman-Jordan"

October, 1983

بسم الله الرحمن الرحيم

LOVE IS EMOTION

To Those Whom I Love,

To My Parents,

To My Brothers.

The examining committee unanimously considers this thesis satisfactory for the award of the degree of Master of Science in Physics.

Prof. A.M. Hindeleh — Chairman of Committee

Dr. N.A. Halim — Member of Committee

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Date: Oct. 26, 1983.

DECLARATION

None of the material contained in this thesis has been submitted in support of an application for another degree of qualification of this or any other University or Institution of learning.

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ABSTRACT

Low density polyethylene (LDPE) and isotactic polypropylene (PP) blend were produced in film form and have been characterized by a number of techniques such as wide-angle X-ray diffraction, differential thermal analyser (DTA), scanning electron microscope (SEM), and Instron tensile tester.

Results of X-ray and DTA show conclusively that the two components in the blend are incompatible. SEM micrographs indicated that the 60/40 and 40/60 PP/PE blends show approximately fine homogeneous dispersion of the minor component into the matrix of the major component. The mechanical properties of the blend films improved with respect to the PE homopolymer. The improvement was more remarkable with the increase of the PP component in the blend. Results obtained in this work are explained in terms of crystallinity and the crystallite orientation.

الخواص الميكانيكيه والحراريه لأفلام بلاستيكيه مصنّعه من مبلمرين مخلوطين فيزيائيا

ملخّص

لقد تم انتاج أفلام بلاستيكيه مكونه من مادتين مبلمرتين مخلوطتين فيزيائيا وهما البوليبروبلين والبوليإثلين ذو الكثافه المنخفضه. وقد أجريت على الافلام فحوصات متنوعه باستخدام حيود الاشعه السينيه والتحليل الحرارى التفاضلي والمجهر الالكتروني الماسح وأجهزة فحص الخواص الميكانيكيه.

ولقد دلّت نتائج حيود الاشعه السينيه والتحليل الحرارى التفاضلي على أن جزيئات المادتين لم يتحدا سويا في المخاليط. كما أشارت صور الفحص بالمجهر الميكروسكوبي على أن العينتين المكونتين من ٦٠/٤٠ و ٤٠/٦٠ من البوليإثلين/والبوليبروبلين ينتشر فيها العنصر الاقل نسبه بتجانس وسط العنصر الاعلى نسبه. أما نتائج الفحوصات الميكانيكيه فقد أثبتت أن خواص الافلام المنتجه من المخاليط تفوق خواص الافلام المنتجه من مادة البوليإثلين فقط، كما أن هذه الخواص تتحسن كلما زادت نسبة البوليبروبلين. وقد فسرت النتائج بالاشارة الى الحاله البلوريه للمادتين ودرجة ترتيب البلورات.

ACKNOWLEDGEMENTS

I would like to express my sincere gratitude to professor A.M. Hindeleh and Dr. N.A. Halim for their supervision of the work and for their continual advice and encouragement througout the course of the work.

Sincere thanks are also due to:

Mr.T. Abu Eitah the manager of the Jordan Plastic Industrial Company for providing the materials, the plastic division in the Royal Scientific Society for using their extruder machine,and the staff of the mechanical workshop of the university of Jordan for assistance in building up some of the instruments used in this work .

The author wishes to thank:

Mr. K. Tadrus for his help with the scanning electron microscope , and Mr. Said Khawaldeh for typing this thesis.

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CHAPTER TWO : EXPERIMENTAL METHODS

CHAPTER THREE : RESULTS

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1.1 POLYMER BLENDS:

Polyblends are intimate physical mixtures of structurally different polymeric components; the two components must be thoroughly mixed before the final processing. In polyblends, the components are held together through secondary bond forces, such as: Van der Waals forces, dipole interaction or hydrogen bonding.

Polyblends offer a strong analogy to the well established role of copolymerisation as a means of combining the useful properties of different molecular species, but blends allow this to be done through physical rather than chemical means. In copolymers, the components are linked together by strong covalent bonds. Thus, polyblends have been defined [1] as a single entity of material containing within its physical boundary at least two thoroughly mixed polymers which are not linked covalently.

Papero, Kubu and Roldan[2] are the pioneers who first reported the discovery of polyblends in a fiber form containing polyethylene terephthalate and nylon 6 in 1967. The morphological characteristics were examined by optical and electron microscope, the minor component was found to be of fibril form embedded in the matrix of the major component. The fibrils were found to be of 100-200 µm in length with diameter of 0.1 µm. Furthermore, the X-ray diffraction pattern of each blend was found to be simply a superposition of the two individual patterns, indicating that the crystal structure of each component was not disturbed by that of the other.

In a patent literature, Kitao et al.[3] have described the structure and the mechanical properties of melt-spun polyblend fibers consisting of nylon 6 as a basic component and one of the following materials: Nylon6.6, Nylon6.10, Nylon11, Nylon12 and polyethylene terephthalate. They concluded that the physical properties are primarily determined by the state of dispersion of the two components. When the two components were so well dispersed such that an interpenetrating three-dimensional network was generated, the tensile properties of the polyblend filaments were at least equivalent to the values predicted from those of the two components. Kitao et al.[3] also reported that when the minor component is discretely distributed as short fibrils in the matrix of the major component, the polyblend filament has inferior properties. The patent literature also described a marked increase in the tensile strength and the initial modulus of 50/50 nylon 6/nylon 6.10 blend fiber. The most highly drawn 50/50 blend has a tenacity of roughly 12 gm/denier, which is about twice as large as that obtained with either pure homopolymer .

1.2 COMPATIBILITY OF POLYBLENDS:

Two polymers of different structure are said to be compatible if any mixture of the two shows a homogeneous single phase structure[1]. Phenomenologically, compatibility can be described by the degree of homogenity; the finer the size of the dispersed phase, the better is the compatibility. On the other hand, compatibility has been defined in terms of the phase separation in a common solvent[4]; when a polymer mixture does not exhibit a phase separation in a common solvent, the two polymers are said to be compatible. Krause[5] reviewed the concept of compatibility showing that no precise definition exists. It is a qualitative term which can be used with a wide variety of meanings and implications. Some workers define compatibility as miscibility on a molecular scale. To others, compatible polymers are polymer mixtures that have desirable physical properties when blended.

However, from the thermodynamics considerations, the mixing process is governed by the following equation:

$$\Delta F_m = \Delta H_m - T \Delta S_m$$

where ΔF_m = the change in free energy on mixing,

ΔH_m = the change in heat content on mixing,

ΔS_m = the change in entropy on mixing at temperature T.

The sign of ΔF_m depends upon that of ΔH_m and the magnitude of $T\Delta S_m$ which is normally positive. Frith and Tuckett[6], explained the statistical meaning of entropy, and concluded that the increase in entropy during a mixing process is based on the tendency of the molecules to approach the random state. ΔH_m is a measure of the attraction between the molecules to be mixed; its sign depends upon whether the mixing is an endothermic or exothermic process. In the latter case, ΔH_m is negative, thus ΔF_m will be negative and a homogeneous mixture can be obtained. However, in general, the mixing of most polyblends is an endothermic process, which means that ΔH_m is positive. Hence, the sign of ΔF_m will be determined by the absolute value of $T\Delta S_m$. But, usually ΔS_m is small when mixing polymers because the molecular movement will be restricted by the length of the molecules; hence, ΔH_m will be greater than $T\Delta S_m$. Consequently, ΔF_m will be positive, and mixing on a molecular scale will not take place spontaneously, and a heterogeneous mixture will be obtained.

Since the mixing process in polymer is normally endothermic, Flory[7] suggested that incompatibility is the normal state of blends and that compatibility is exceptional. Thus, from the theoretical consideration, it is rare for two chemically dissimilar polymers to be intimately mixed on the molecular level. One, therefore, can conclude that compatibility is a qualitative description of the state of dispersion between two dissimilar polymers. Since the state of dipersion is relative, the compatibility is also relative.

1.3 ADHESION BETWEEN POLYMERS:

Adhesion refers to bonding or joining of dissimilar bodies. Good[8] reported that the bond energy of a chemical bond is typically about 80 kcal/mole, whereas, that of Van der Waals attraction is 2.5 kcal/mole. Thus, interfacial chemical bonds could be utilized effectively to promote adhesion. In polyblends the two components are immiscible and the integrity of a blend emerges through secondary forces which may be Van der Waals forces, dipole interactions or hydrogen bonding. Wu [9], suggested the wetting-contact theory of adhesion; he proposed that Van der Waals forces alone are sufficient to promote adhesion provided that the two phases are in a molecular contact. However, perfect molecular contact is difficult to achieve experimentally. On the other hand, Voyutskii and Vakula [10], critized the above theory on the grounds that the molecular contact at the interface alone is not sufficient to invoke. This interdiffusion clearly invokes some degree of miscibility, or compatibility.

Krause[11], reported that most polymer pairs are mutually incompatible. However, Helfand and Tagami[12], suggested that various degrees of interdiffusion of the segments of polymers must occur in the interfacial layers to minimize the interfacial energy.

However, neither the complete wetting required by the wetting-contact theory, nor the interdiffusion proposed as an alternative have been proved conclusively to achieve experimentally in polyblend systems. Therefore, Wu[9], suggested that a combination of the two is likely; contact must precede interdiffusion. The formation of the adhesive bond should proceed in two stages: The first stage involves wetting to promote interfacial contact, and the second stage involves interdiffusion to form diffuse interfaces.

1.4 CRYSTALLISATION ON SUBSTRATES; EPITAXY AND TRANSCRYSTALLISATION:

Crystallisation on solid substrates has been reviewed by Geil[13] and Wunderlich[14]. The substrate, whether a polymeric or a nonpolymeric surface, will act as a nucleating agent on which the crystals grow in accord with its geometry. Furthermore, crystals nucleated on a substrate tend to grow along that substrate and, therefore, develop as flat lamellae. The crystal growth depends upon whether the substrate is oriented or not. In the former case, oriented epitaxial growth will result, whereas, in the latter case, transcrystallisation will take place.

In a polymer, epitaxial growth on an oriented polymer surface is of particular interest; it is not necessary for the substrate to be of a different polymer. Wunderlich and Milillo[15], showed an epitaxial growth of folded chain polyethylene crystals on the surface of extended chain crystals of the same polymer. They proposed that the extended chain crystal serves as a substrate for chain folded crystallisation. Keller and Machin [16], showed that lamellar crystals of natural rubber could grow epitaxially on a fibrous substrate. Epitaxial growth in the form of lamellar crystals growing on a lamellar substrate was also suggested by Anderson and Carr [17]. They interpreted the bi-modal crystal texture of polypropylene in terms of the epitaxial growth of the a-axis oriented crystals on the surface of c-axis oriented crystals.

In homo-epitaxy, the lattice parameters match perfectly as was shown by Wunderlich and Melillo [15]. However, epitaxy on oligomer crystals which introduces some mismatch has been reported by Macchi, Morosoff and Morzwetz [18]. They have reported the case of epitaxy of nylon 6 on its monomer crystals.

This epitaxy showed a mismatch of about 17%.

Epitaxy of one polymer upon a chemically different polymer has also been reviewed by Wunderlich[14]. The lamellae of epitaxial crystals are aligned at right-angles to the draw direction of the substrate so that the chain axes of the substrate, and the epitaxially grown folded chain lamellae, are parallel.

Where the substrate is unoriented, crystallisation is still enhanced because the interfacial energy is lower than the polymer's surface energy, thus, the interface can provide a heterogeneous nucleation. Furthermore, on cooling the sample, the surface at the substrate will cool to the crystallisation temperature faster than the interior. This also enhances the nucleation on the surface where the nuclei will be crowded. Owing to the nature of the polymer molecule, the surface-nucleated crystal growth should have its chain axis parallel to the surface for maximum reduction of free energy of nucleation. The faster crystal growth direction should be normal to the surface. Such preferential orientation was termed as "transcrystallisation".

1.5 PREVIOUS WORK:

Polymer blends have come to the fore as such a major endeavour. The phase structure of the polyblend systems and the mechanical properties have been reported by several authors[19-22]. Polyethylene and isotactic polypropylene blends, in fiber and film forms have also been studied[19-21]. Coombs, Cannon and Keller[19], have studied polyblend fibers and films prepared by rotor method from mixed solution of polyethylene and isotactic polypropylene. The X-ray diffraction pattern of 50/50 blend composition showed that the two components were highly oriented with the c-axis parallel to the fiber axis. Furthermore, the two polymers were present in their separate crystalline phases with no detectable amorphous scattering. They reported that the differential scanning calorimetry results showed that the crystalline phase of the two constituents are deposited separately without mutual interference between their morphologies. Coombs _et al._[19], also reported that the two-phase nature has no adverse affect on their tensile properties. They concluded that the blended fibers or films from mixed solutions are most probably deposited by the "surface growth" mechanism. To explain the product of the polyblend fibres and films, they suggested that entaglements between polyethylene and polypropylene chains must occur despite their incompatibility both in solution and in the absorbed layer on the rotor surface. These entaglements between dissimilar molecules should occur in the same way as between different molecules of the same polymer.

Extruded unoriented specimens of high density polyethylene and isotactic polypropylene were also mechanically characterized by Greco _et_ _al_.[20]. Wide-angle X-ray diffraction patterns showed random orientation of the crystallites in the extruded specimens of pure polymers as well as in their blends. The wide-angle X-ray diffraction pattern of the polyblend samples showed a superposition of the two pure components, indicating that no co-crystallisation had resulted.

They also investigated the mechanical behaviour of the blends using an instron tensile tester. The young's modulus was found to increase linearly with the increase in polypropylene component in the blend. This linear behaviour was attributed to the similar morphology, spherulitic, for each component in the blend. The yield strength and the yield strain did not show a linear relationship at concentration higher than 25% polypropylene. The polypropylene-rich blends showed a marked reinforcing effect of the polyethylene component. Thus, the presence of small quantities of polyethylene in a polypropylene matrix seemed to decrease the plasticity of the material, whereas small amounts of polypropylene did not provide any reinforcement in a polyethylene-rich blends.

Margon Tang et al.[21] have also investigated the mechanical properties of ultradrawn polyethylene-polypropylene blend fibers at various temperatures. They showed that the blends exhibited a brittle behaviour at room temperature and a ductile behaviour above (40-60)° depending on the blend composition.

1.6 THE PRESENT WORK:

The aim of this work is to study the mechanical behaviour of polyblend films consisting of commercial homopolymers: Low density polyethylene (PE) and isotactic polypropylene (PP). Polymeric blend films were extruded directly after mixing the two homopolymer chips in an extruder machine fully described in the next chapter. Polyblend films with various PE/PP ratios by weight were prepared. An Instron tensile tester was then used to study the mechanical behaviour in two dimensions: the flow direction and the transverse direction. The stress-strain curves were then analysed and discussed.

Differential thermal analyser was also used to study the melting behaviour.

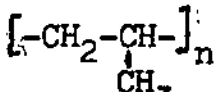
A scanning electron microscope (SEM) was also used to study the fine dispersion of the minor component in the matrix of the major component. Thus, polyethylene component was leached out in p-xylol, and the residual component was examined microscopically.

Preliminary structural investigation has been made using wide-angle X-ray camera.

Chapter two discusses the experimental techniques that have been used in this investigation. The results are reported in Chapter three, while Chapter four interprets the results and presents the conclusions.

2.1 SAMPLE PREPARATION

2.1.1 Material

Two homopolymers, low density polyethylene (LDPE), $[-CH_2-CH_2-]_n$, and isotactic polypropylene (PP),  $[-CH_2-\underset{CH_3}{CH}-]_n$ have been used in this study. Both polymers have a melting index of 4.0 and manufactured by the Dow Chemical Company.

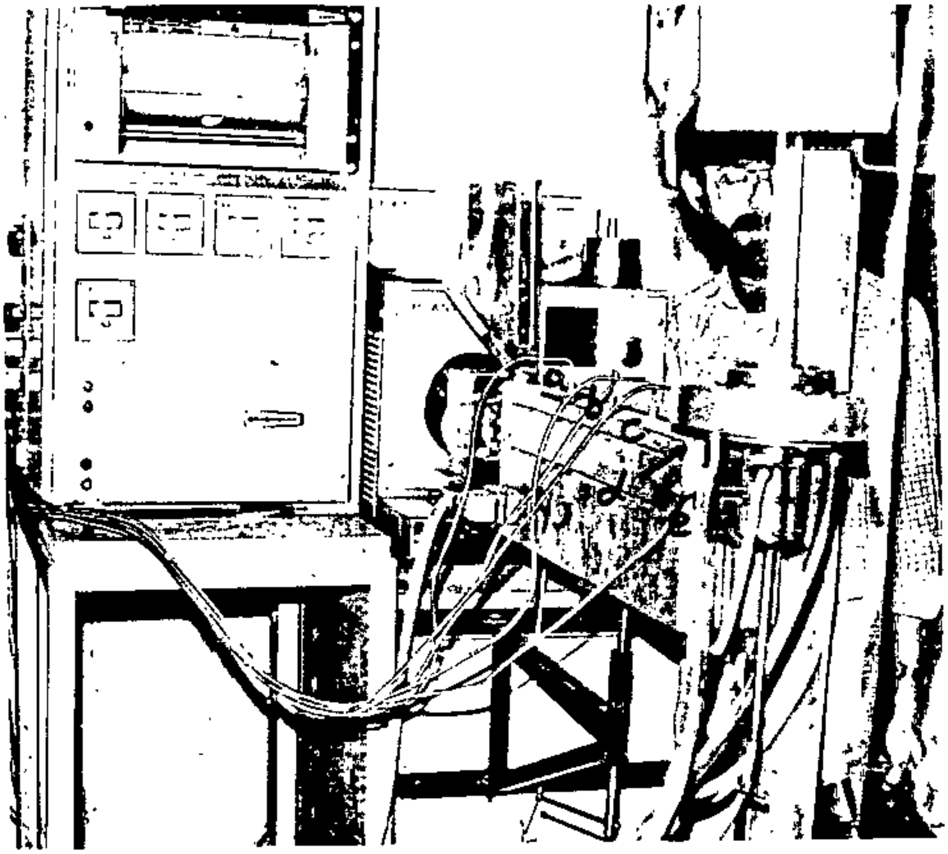
Mixtures of the following composition by weight were prepared by mixing the two polymer chips to produce blend films:

PE(%)	100	80	60	40	20	0
PP(%)	0	20	40	60	80	100

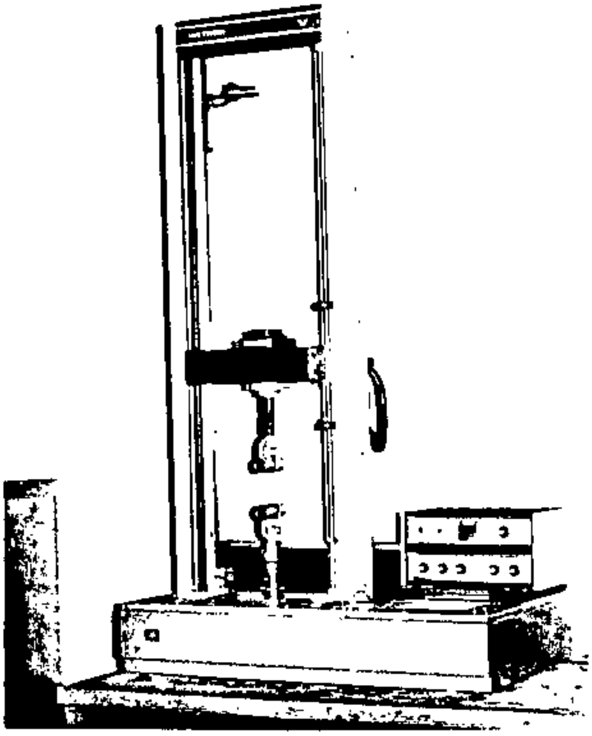
The chips were then oven dried at 100°C for 24 hours. Drying was essential for avoiding air moisture which may cause a fail in the subsequent extrusion process.

2.1.2 Extrusion

Polymer - blend films were then produced by an extrusion process. A research extrusion rheometer, Brabender type 827000, shown in Figure 2.1 was used for the production of blown films. The molten polymer after leaving the die was



Fig(2.1): Extruder machine .



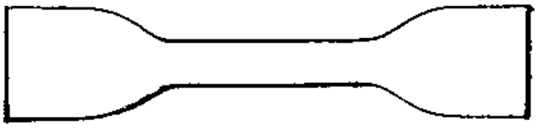
Fig(2.2): Instron tensile tester.

inflated to the required diameter by air pressure. The extrusion velocity of the rheometer was set at 15 rev. min^{-1}. The extruder incorporates five heaters labelled a to e in Figure 2.1. The temperatures of the heaters were set up such that the flow is viscous. The extrusion pressure ranged between 13 to 16 Nm^{-2} depending on the blend ratio [see table 3.1].

2.2 MECHANICAL PROPERTIES:

The mechanical properties of the extruded films were determined at room temperature, 22°C, and a relative humidity of 50% using an Instron tensile tester model 1026 shown in Figure 2.2. A load cell type 2512-117 having a load range of 0-50 Newtons on the full scale width of the chart was employed. The analysis was carried out as follows: Samples were cut into a dumble shape [see Figure 2.3] using a ZWICK cutting device type 7102. The gauge length of the sample is 2 cm and the width is 0.4 cm. Ten determinations of each extruded film were made. Both the cross head speed and the recorder chart speed were adjusted at 20 cm/min.

The mechanical properties were characterized in terms of Young's modulus, yield stress, yield strain, breaking stress, and breaking strain.



Figure(2.3): Sample shape used for mechanical properties test.

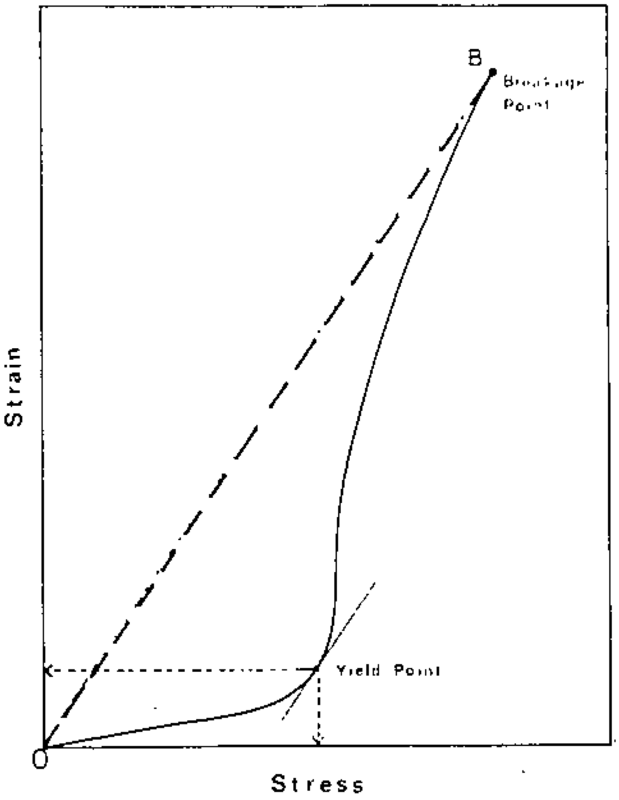


Fig. 2.4 Yield Point .

The Young's modulus (Y) is defined as

$$Y = \text{stress/strain} = \frac{F/A}{\Delta L/L} \qquad (1)$$

where F is the load, A is the cross-sectional area, L is the gauge length, and ΔL is the change in length. F and ΔL were determined from the initial part of the load-extension curve.

The yield point is defined as the point at which the tangent to the stress-strain curve is parallel to the line joining the origin (O) and the breaking point (B) as shown in Figure 2.4[23]. The yield point is known as the point of elastic limit[24], at which permanent deformation starts to take place and below the yield point the polymer has a good elastic recovery. Hence an increase in the yield stress suggests that the material can stand a bigger load before it starts to deform, and an increase of the value of the yield suggests that the region of plastic recovery has increased. It is clear from Figure 2.4 that the strain increases rapidly at smaller increments of stress than before the yield point.

The breaking stress is defined as the maximum stress at the moment of the sample rupture, while the breaking strain is the maximum percentage extension of the sample at the moment of rupture[25].

2.2.1 Plastic Recovery:

Elasticity is defined as the property of a body by virtue of which it tends to recover its original size and shape after deformation. Deformation is classified into two **categories** : elastic and plastic. The former is recovered when the stress is removed while the latter is permanent.

Plastic recovery, which is the behaviour of a material when the stress is removed, is quantitatively defined as:

$$\text{Plastic Recovery}(\%) = \frac{L_o - L}{L_o} \times 100 \qquad (2)$$

where L_o is the extension of the sample caused by an applied force, and L is the residual extension length after removing the load.

Samples were drawn to different draw ratios which are 3:1, 4:1, 5:1, 6:1 and 8:1 using the Instron tensile tester. The gauge length was chosen to be 2 cm. Each sample was extended at a constant rate of 5 cm/min to a fixed strain, holding it for 3 minutes to allow stress relaxation, then allowing the sample to contract at the same rate of extension. After that the final length was measured.

2.3 THERMAL SHRINKAGE:

Samples were drawn to various ratios ranging between 5 and 8 at room temperatures using the Instron tensile tester. A gauge length of 2 cm and an extension rate of 5 $cm.min^{-1}$ were applied. Then the sample was held for 3 minutes at a fixed strain to allow stress relaxation. Finally the load was decreased at the same rate of extension.

A portion of the drawn sample was cut and transferred to a shrinkage testing apparatus were the sample was clamped at one end only. The apparatus was then admitted into an oven where the sample was annealed in air for 30 minutes at temperature levels ranging between 70 and 150°C. The sample was then air-quenched at room temperature and its final length was measured.

The shrinkage ratio is defined as:

$$S.R(\%) = \left(\frac{L_o - L}{L_o}\right) \times 100 \qquad (3)$$

where L_o and L are the sample lengths before and after annealing respectively.

2.4 THERMAL ANALYSIS:

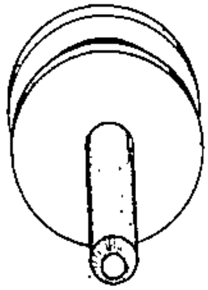
Thermal analysis of the blended films were carried out using differential thermal analyser (DTA) type Perkin Elmer. The sample weight was 10 mg, it was placed in the aluminum sample pan and the lid was fixed in a pan crimper, an empty pan was used in the reference holder, the scan speed was 10°C/min.

When a phase transition such as melting or crystallization occur in the sample material, an endothermic or exothermic change takes place. Because the input of electrical energy to the sample holder is constant, the same as that to the reference holder during transition, a difference of temperature is established between the two, this is recorded as a peak or trough in the DTA chart. The chart abscissa gives the transition temperature and the area under the peak indicates the total energy transfer to or from the sample.

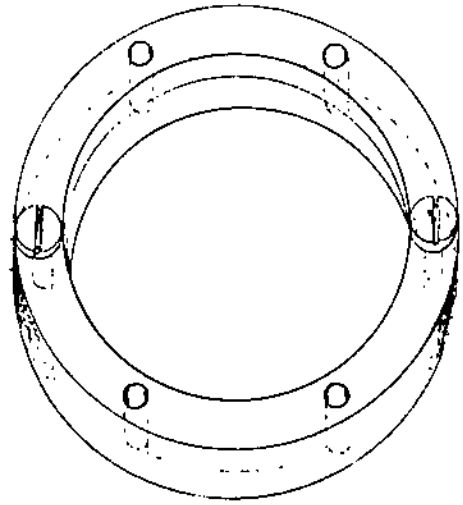
2.5 ELECTRON MICROSCOPY:

2.5.1 Surface Topography of Blend Films:

The surface topography of the blend films was monitored in a scanning electron microscope (SEM) type AMR 1000A, manufactured by Ernst Leitz Wetzlar GMBH company. The sample was mounted on an appropriate sample holder see Fig.2.5 and gold coated under vacuum of about 0.1 torr using SEM,E5000 coating unit. The scanning was carried out at 10 KV and



Figure(2.5): Scanning electron microscope sample holder.



Figure(2.6): Sample holder used for leaching PE Component from the blend.

and 150 mA. A set of sample drawn mechanically to the same ratios were also tested in the same way. Four sets of samples were tested: the first set comprised samples as produced from the extruder. The second comprised extruded samples drawn to a ratio of 4:1. The third set was for samples from which the PE component was leached out, while the last set was for the drawn samples from which the PE component was leached out after drawing.

2.5.2 Chemically-Treated(Leached) Blend Films:

The polyetylene component in the extruded blend films was leached out in a pure p-xylol, $C_6H_4(CH_3)_2$, liquid which dissolved the polyetylene within 3 minutes at a temperature of 70°C. A special sample holdre shown in Fig. 2.6 was specially designed to prevent the shrinkage of the polypropylene component at this temperature.

2.6 WIDE-ANGLE X-RAY DIFFRACTION:

The wide-angle X-ray diffraction patterns of the polymer blend films were recorded on photographic films using a constant output Philips X-ray generator at 35 KV and 30 mA. A wide-angle X-ray camera having a fine collimator and a flat film cassette was used. The specimen to film distance was 4 cm. An exposure time of 30 minutes was adequate.

3.1 SAMPLE PRODUCTION:

The extrusion process depends mainly upon the temperature, rheometer speed and pressure. These parameters differ from one polymer to another depending on its molecular weight and its melting point. A successful extrusion of films consisting of the two homopolymers, PE and PP individually, as well as PE/PP blend films was obtained by choosing the parameters shown in Table 3.1. It can be seen that higher extrusion temperatures were necessary for PP films. This increase in temperature was found to be associated with the increase in the PP proportion in the blend. At constant rheometer speed, 15 rev. min^{-1}, the pressure was varied between 13-16 Nm^{-2}. Table 3.1 shows the extrusion conditions, the thickness and the transparency of the extruded films.

3.2 MECHANICAL PROPERTIES:

The mechanical properties of the extruded films were measured in the axial (flow) direction as well as in the transverse direction of the film. Figure 3.1 illustrates typical load-elongation curves. Whenever the PP was the major component in the blend, a well-defined yield point was

Table 3.1: Extrusion conditions, film thickness and transparency.

Sample Type		Extrusion Temperature (^{o}C)					Rheometer Speed (Rpm)	Pressure (Nm^{-2})	Av. Film Thickness (μm)	Film Transparency*
PE (%)	PP (%)	A	B	C	D	E				
100	0	170	185	210	200	195	15	15	46.6	Tr
80	20	175	190	215	205	200	15	16	63.8	T/O
60	40	175	190	215	205	200	15	16	32.5	T/O
40	60	185	215	230	225	215	15	15	50.0	T
20	80	185	220	240	235	225	15	14	70.0	O
0	100	180	210	215	210	210	15	13	28.0	O

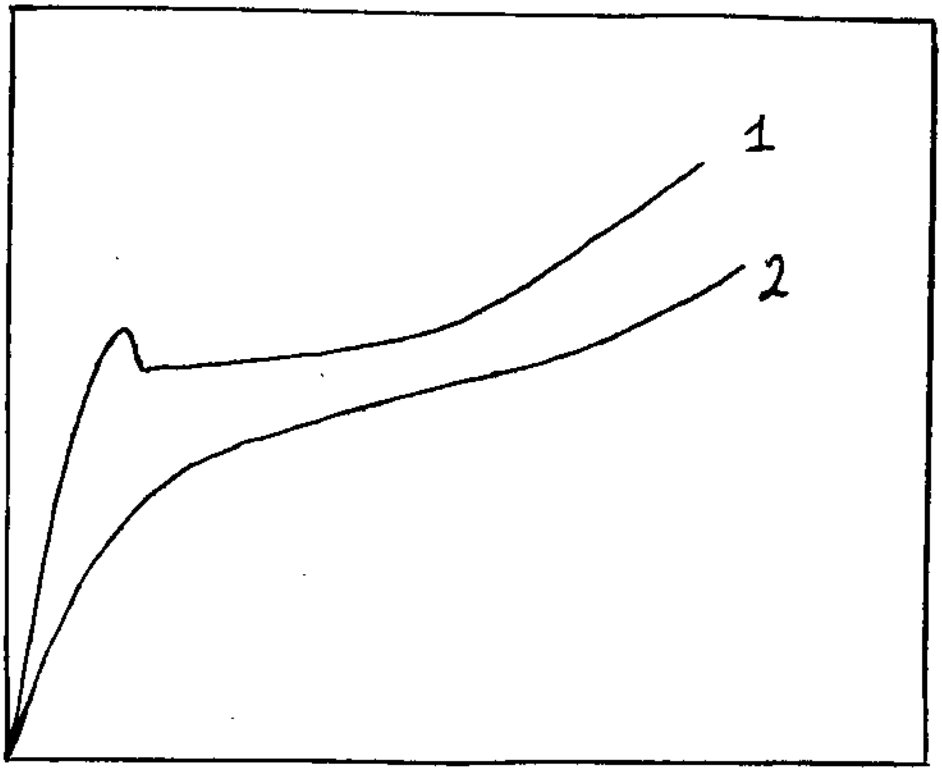
* Tr = transparent; T = transluscent ; O = Opaque

obtained as shown in Figure 3.1. However, when the PP was the minor component in the blend, a less well-defined yield point was obtained as shown in Figure 3.1. Figures (3.2-3.6) show the mechanical properties in both directions. Table 3.2 shows the results of the mechanical properties.

3.2.1 Initial Young's Modulus:

Figure (3.2a) shows the relation between the initial Young's modulus in the axial direction and the blend composition. For the two homopolymer samples, PE and PP, the modulus of PP (3.44×10^8 Nm^{-2}) is twice as that of PE (1.67×10^8 Nm^{-2}). All the other blend samples show an increase in the modulus higher than that of the pure PE films; this increase is directly proportional to the increase in PP content.

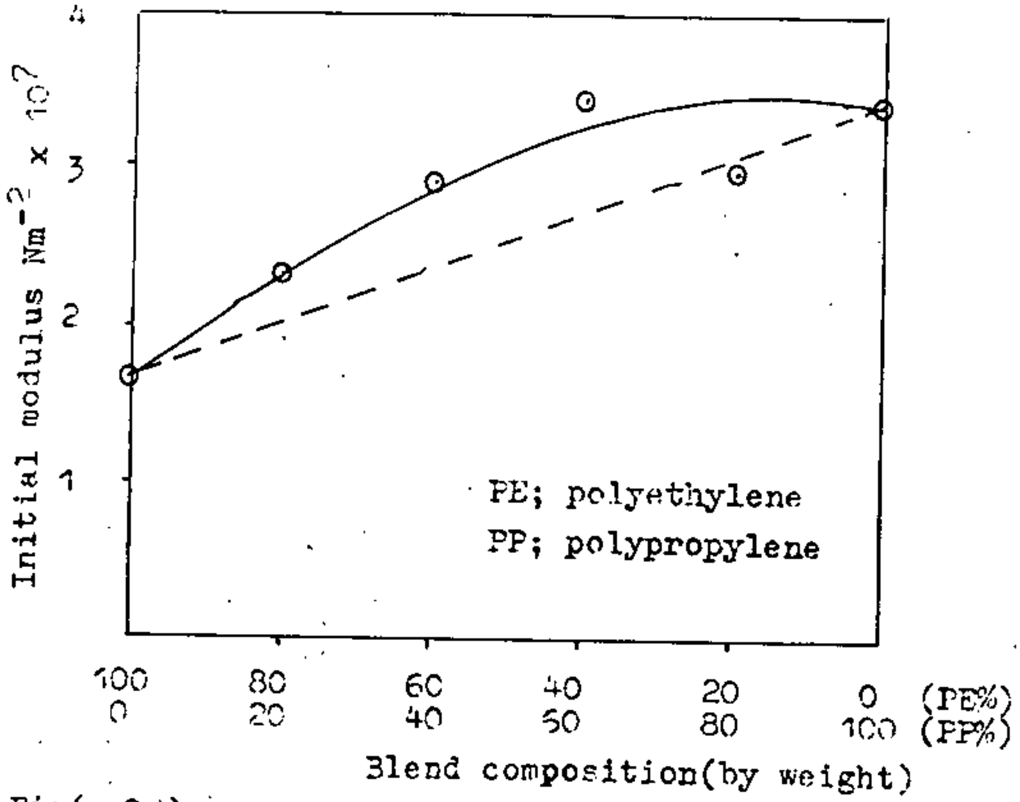
The initial modulus in the transverse direction is plotted against the blend composition in Figure (3.2b). This Figure shows that the initial modulus of the PP film has a magnitude of 3.2×10^8 Nm^{-2} which is greater than that of PE film by approximately 130%. There is practically no change in the modulus by a 20% addition of PP to PE , but all other blends showed a considerable increase in the initial modulus directly



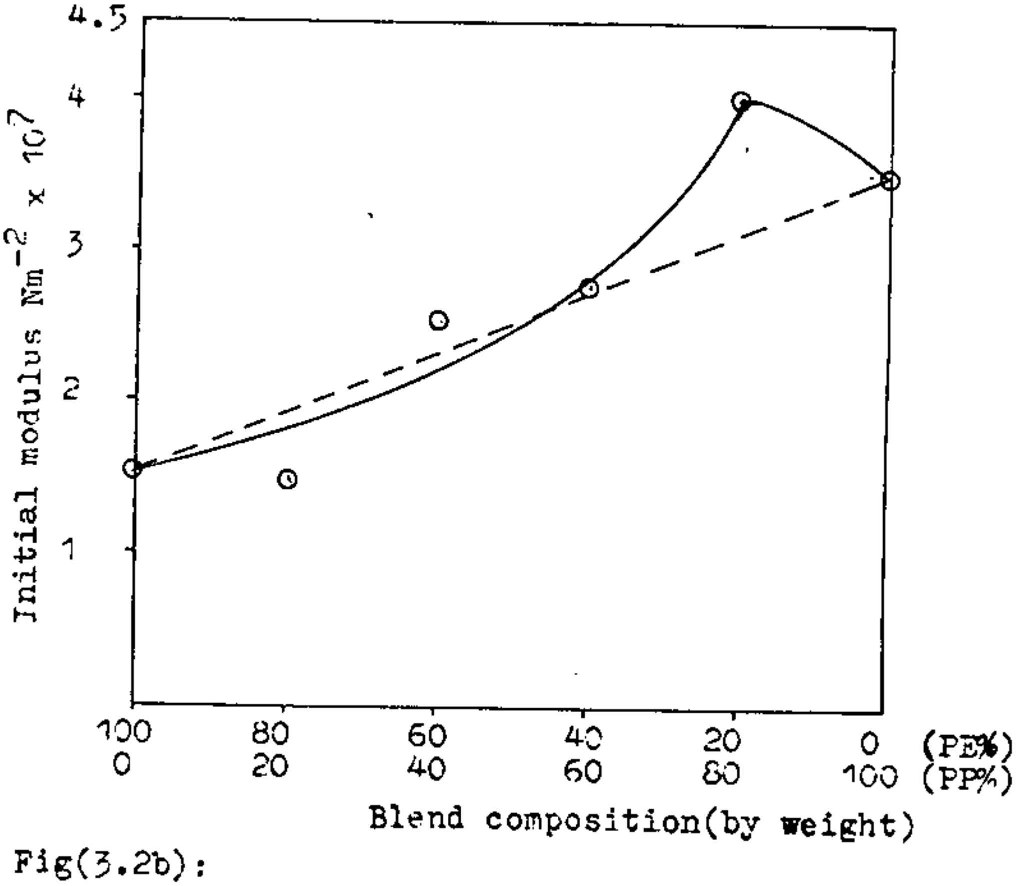
Fig(3.1): A typical load elongation curves showing a well defined yield point in 1 whereas in 2 the yield point is not well defined.

Table 3.2: Mechanical properties of the extruded films.

Blend ratio		Direction of analysis	Breaking stress Nm^{-2}	Breaking Strain %	Yield stress Nm^{-2}	Yield strain %	Initial Young's modulus Nm^{-2}
PE%	PP%						
100	0	axial	1.62×10^{7}	629	0.96×10^{7}	5.8	1.67×10^{8}
80	20	"	2.30×10^{7}	824	1.48×10^{7}	6.4	2.34×10^{8}
60	40	"	2.69×10^{7}	673	1.88×10^{7}	6.4	2.92×10^{8}
40	60	"	4.25×10^{7}	850	3.43×10^{7}	9.1	3.48×10^{8}
20	80	"	3.68×10^{7}	787	2.94×10^{7}	9.9	3.00×10^{8}
0	100	"	3.56×10^{7}	579	2.99×10^{7}	8.6	3.44×10^{8}
100	0	transverse	1.74×10^{7}	560	0.90×10^{7}	5.9	1.52×10^{8}
80	20	"	2.06×10^{7}	716	1.45×10^{7}	11.0	1.49×10^{8}
60	40	"	2.59×10^{7}	636	1.75×10^{7}	6.8	2.54×10^{8}
40	60	"	3.20×10^{7}	745	2.39×10^{7}	8.7	2.75×10^{8}
20	80	"	3.34×10^{7}	763	2.90×10^{7}	7.3	4.00×10^{8}
0	100	"	3.29×10^{7}	592	2.45×10^{7}	7.9	3.50×10^{8}



Fig(3.2a):



Fig(3.2b):

Fig(3.2): Initial modulus versus the blend composition:-

(a):In the flow direction.

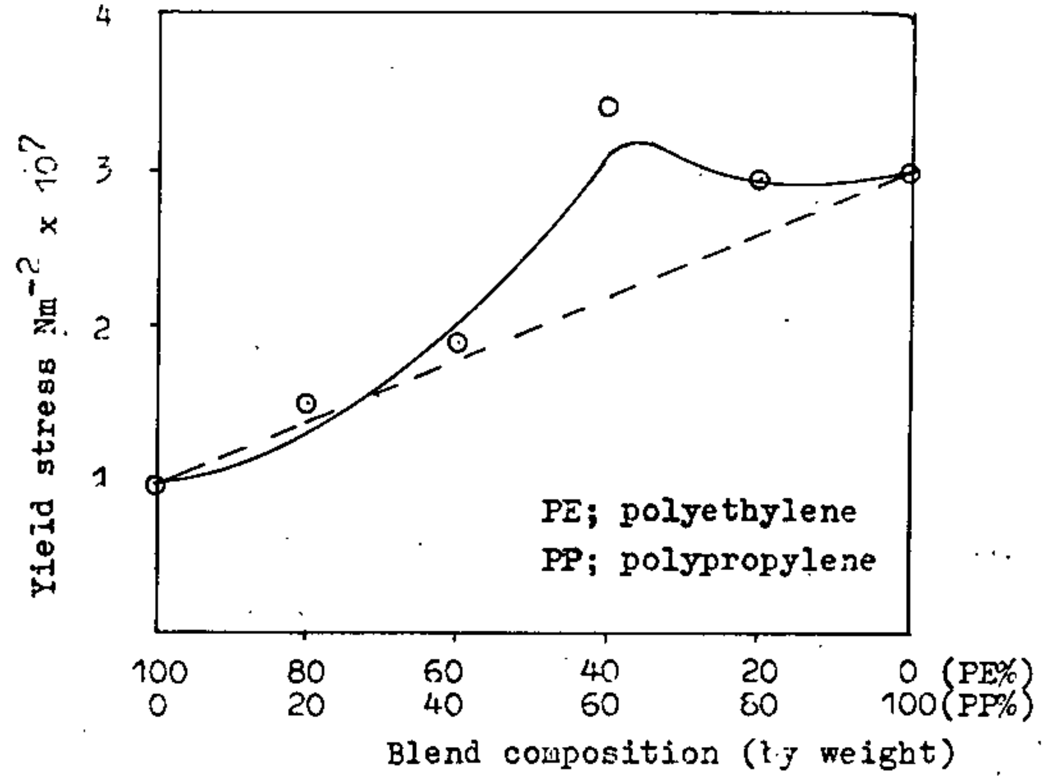
(b):In the transverse direction.

proportional to the increase in PP content.

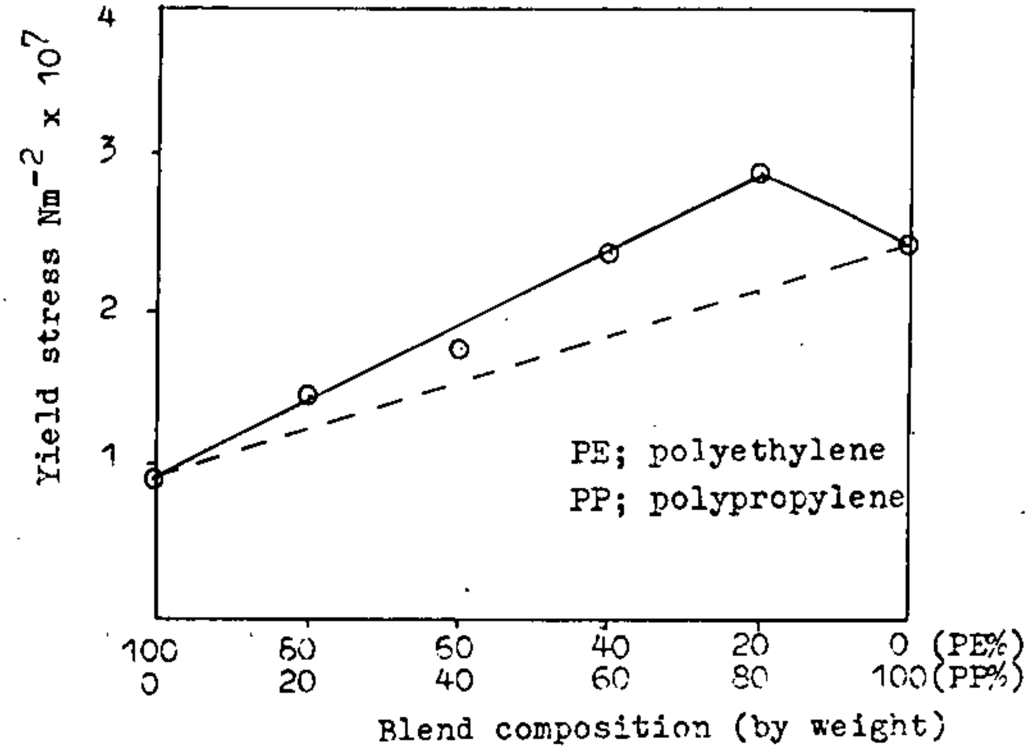
3.2.2 Yield Stress:

The yield stress in the flow direction is plotted against the blend composition in Figure (3.3a). This figure shows that the yield stress of PP film which has a magnitude of 2.99×10^7 Nm^{-2} is greater than that of PE film by approximately 210%. All the blended polymer films showed a considerable increase in the yield stress with respect to the PE film which has a magnitude of 0.96×10^7 Nm^{-2}. The increase in the yield stress for all blends is more than expected from the additivity of properties. The optimum yield stress was obtained at the 40/60 of PE/PP blend.

The yield stress in the transverse direction is plotted against the blend composition in Figure (3.3b). It can be seen that the yield stress of PP film which has a magnitude of 2.45×10^7 Nm^{-2} is greater than that of PE film by approximately 180%. All the blended-polymer films showed a considerable increase in the yield stress with respect to that of PE film; PE film has a yield stress of 0.9×10^7 Nm^{-2}. By increasing the proportion of the PP component in the blend the yield stress increased gradually and obtained



Fig(3.3a):



Fig(3.3b):

Fig(3.3): Yield stress versus the blend composition:-

(a):In the flow direction.

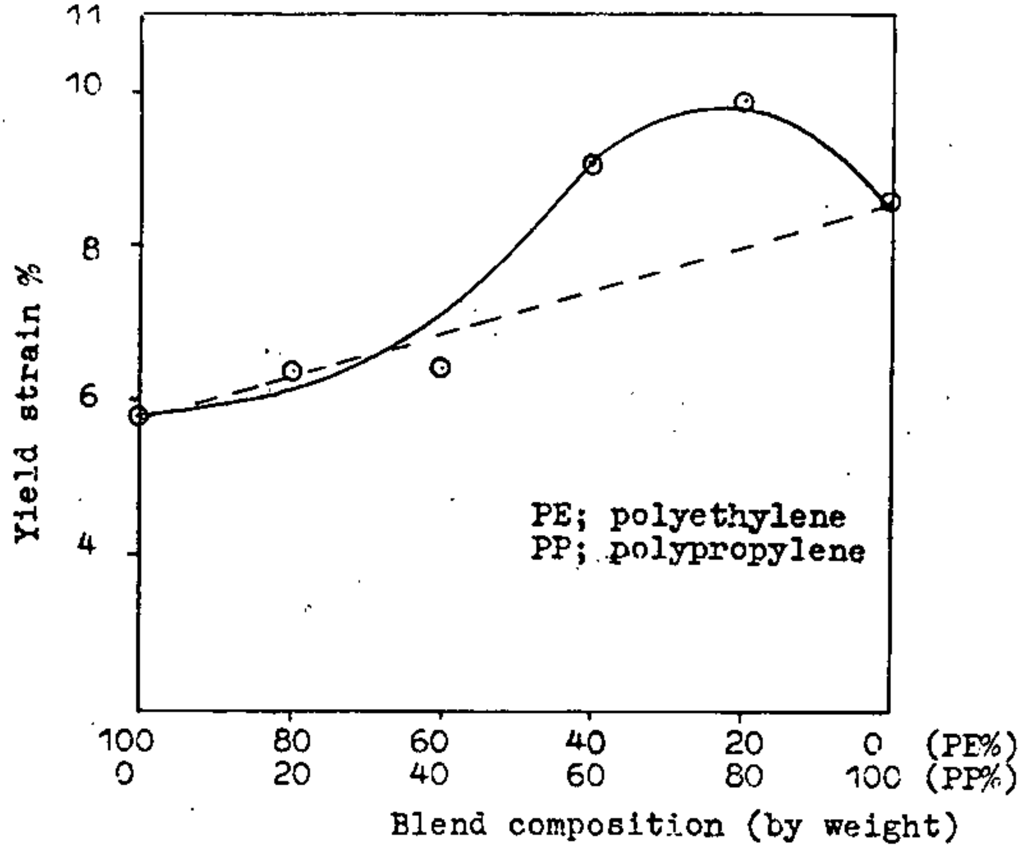
(b):In the transverse direction.

its optimum value (2.9×10^7 Nm^{-2}) at a blend ratio of 20/80 PE/PP. The increase in the yield stress is more than expected from the additivity of properties.

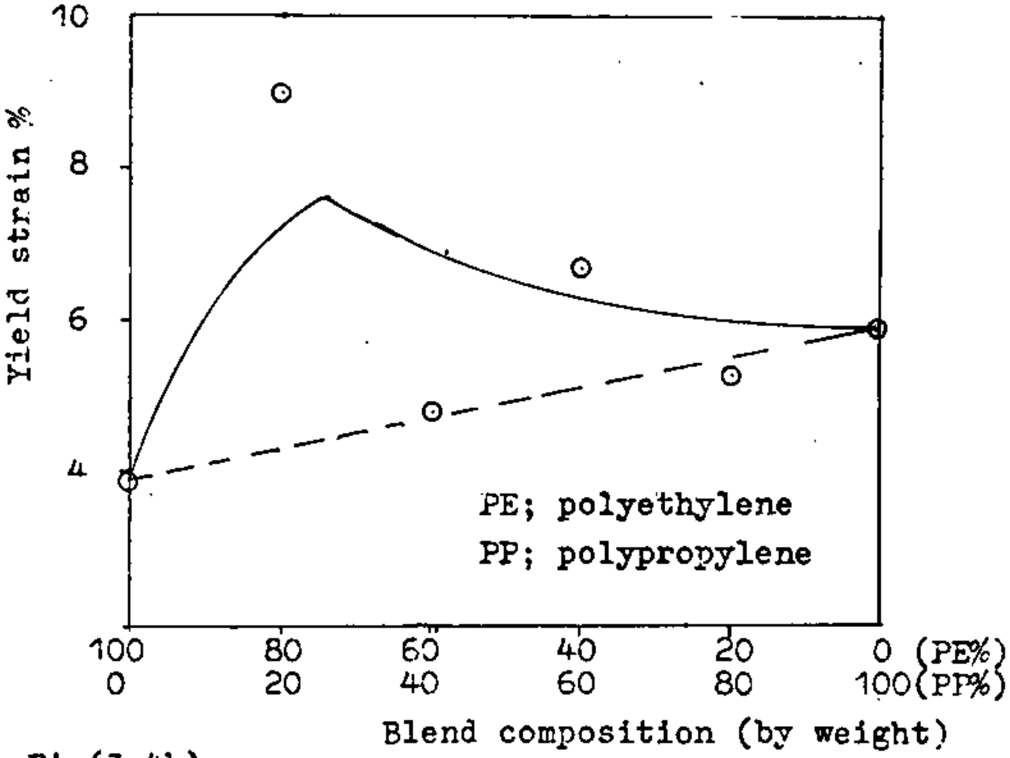
3.2.3 Yield Strain:

The yield strain in the flow direction of the tested sample is plotted against the blend composition in Figure (3.4a) which shows that the yield strain of the PP film which is equal to 8.6% is greater than that of **PE** film by approximately 30%. Until a **40%** PP component in the blend the increase in the yield strain over that of PE is unappreciable. Further increase in the PP content caused a remarkable increase in the yield strain with a maximum at 20/80 of PE/PP blend. The increase in the yield strain is more than expected from the additivity of properties except for that of 80/20 and 60/40 of PE/PP which can nearly satisfy this principle.

The yield strain in the transverse direction is plotted against the blend composition in Figure (3.4b). It can be seen from this Figure that the yield strain of PP film which is equal to 7.9% is greater than that of PE film by approximately 25%. The 80/20 PE/PP blend exhibits an increase in the yield strain which is higher than that of its



Fig(3.4a):



Fig(3.4b):

Fig(3.4): Yield strain versus the blend compostion:-
(a);In the flow direction.
(b);In the transverse direction.

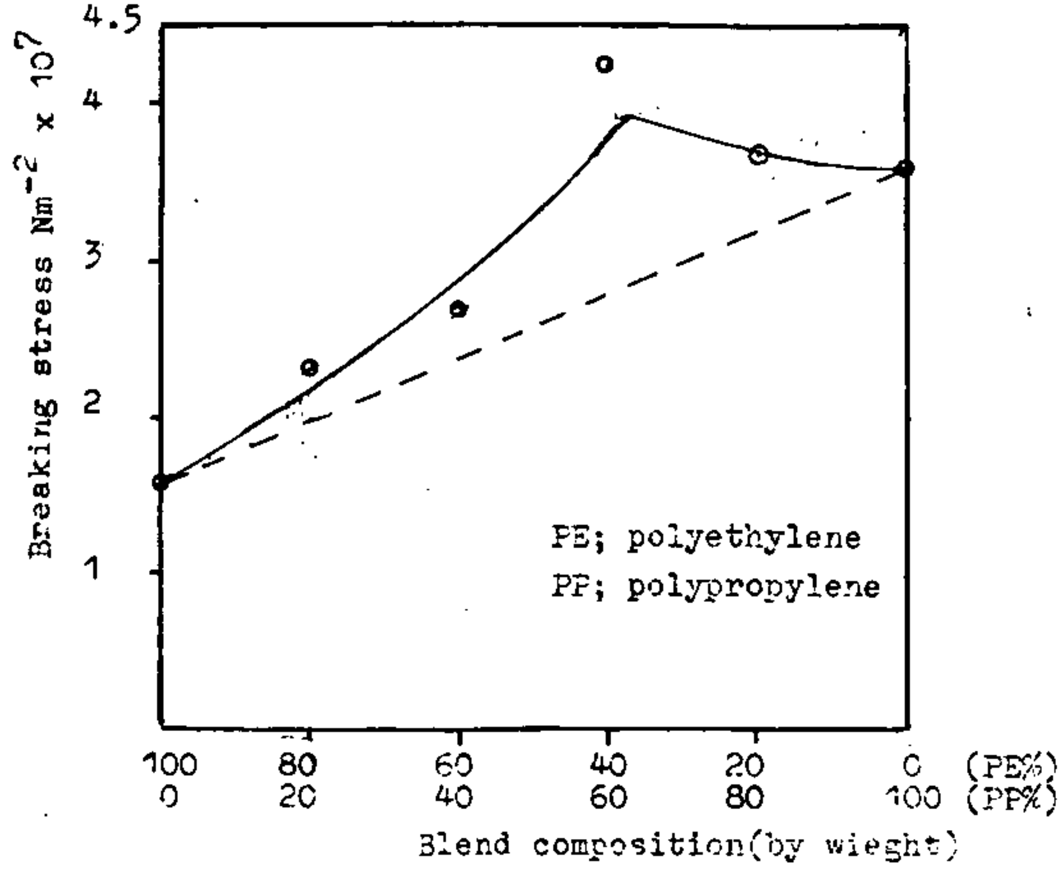
both components; 45% higher than that of PE and 28% higher than that of PP. By increasing the proportion of PP by 20% and 60% , these blends show an increase in the yield strain which is more than expected from the additivity of properties. However, by increasing the proportion of PP by 40% and 80% , these blends show an increase in the yield strain which satisfies the principle of additivity of properties.

3.2.4 Breaking Stress:

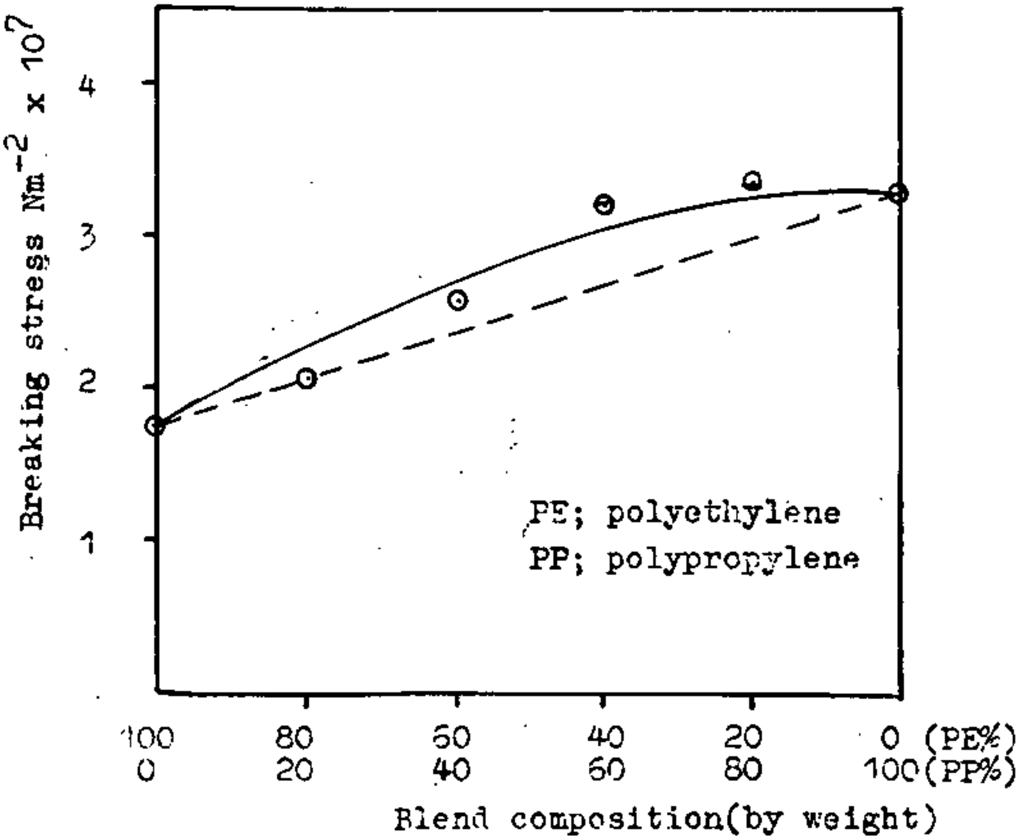
Figures (3.5a) and (3.5b) show the breaking stress in the flow and in the transverse directions of the films respectively. In both directions the breaking stress of PP is greater than that of PE by a factor of approximately 2. In the blended-polymer films the breaking stress increased appreciably with the increase in the PP component, and attained optimum values at 20/80 of PE/PP blending ratio in the transverse direction and at 60/40 of PE/PP blending ratio in the axial (flow) direction.

3.2.5 Breaking Strain:

Figure (3.6a) shows the relation between the breaking strain in the axial direction and the blend

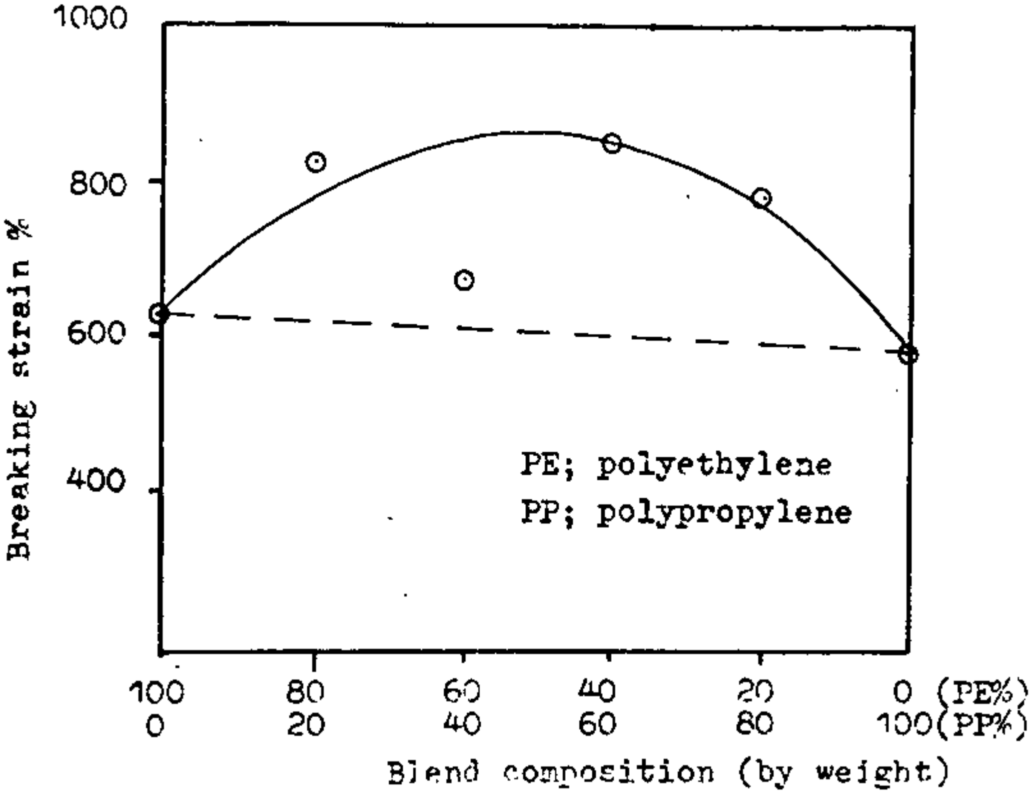


Fig(3.5a)

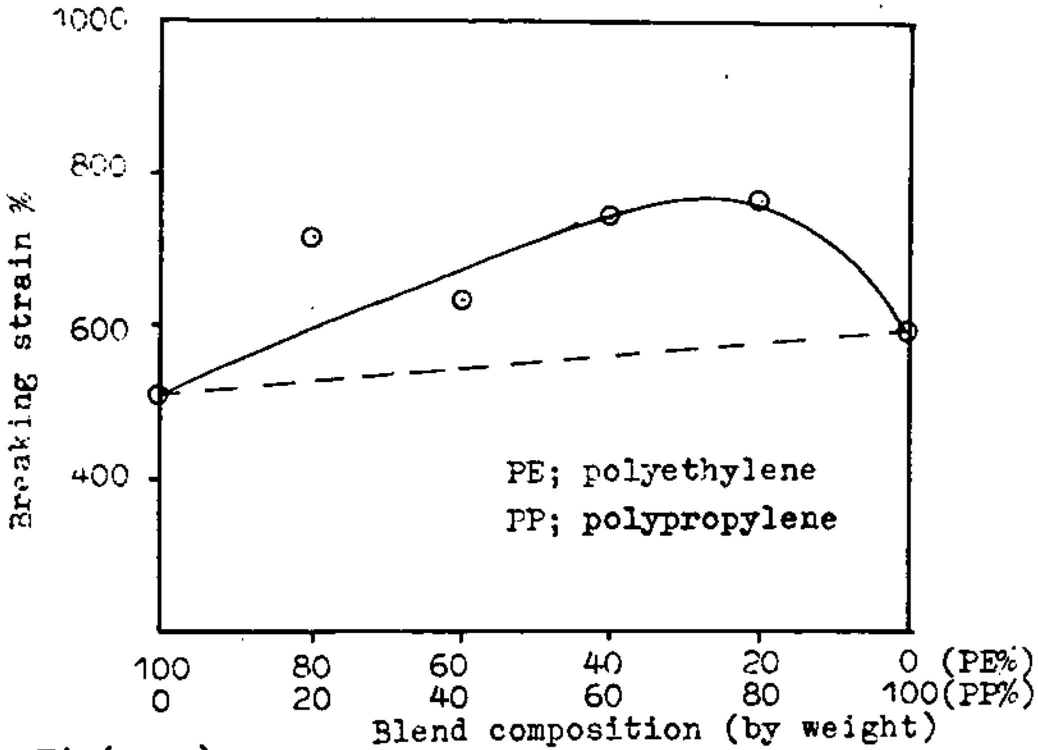


Fig(3.5b):

Fig(3.5): Breaking stress versus the blend composition:-
(a):In the flow direction.
(b):In the transverse direction.



Fig(3.6a):



Fig(3.6b):

Fig(3.6): Breaking strain versus the blend composition:-

(a): In the flow direction.

(b): In the transverse direction.

composition. The breaking strain of PE is 630% while that of PP is 580%. Figure (3.6b) shows the breaking strain in the transverse direction versus the blend composition. The breaking strain of PE film is 560% and for PP films is 590%. It is remarkable in both directions that blending the two polymers caused an increase in the strain specially for the blend ratio 40/60 of PE/PP films. The breaking strain of this blend (40/60 PE/PP) is 850% in the axial direction and 745% in the transverse direction. These values are considerably higher than those of the films produced from either PE or PP.

3.2.6 Plastic Recovery:

Table (3.3) gives the plastic recovery at draw ratios ranging between 3 and 8, against the blend composition. It is clearly seen that at all draw ratios, the plastic recovery of PE is greater than that of PP. Hence, as would be expected, the plastic recovery decreased as the PP content increased in the blend. It is also clearly seen that for the homopolymers, as well as for the blends, the plastic recovery decreased when the draw ratio was increased.

Table 3.3: Plastic recovery percentage versus blend composition.

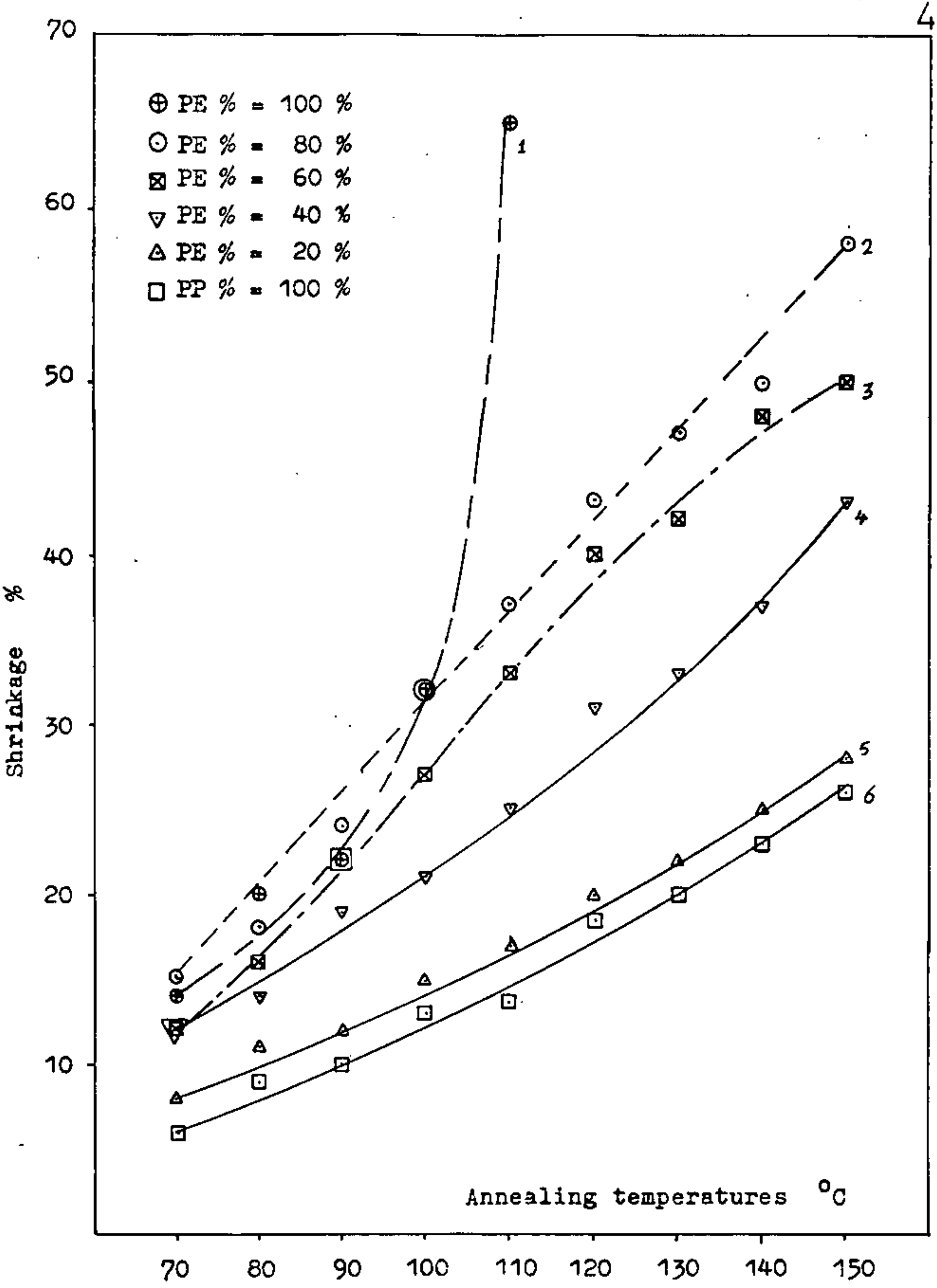
ratio		Draw Ratio				
PE%	PP%	3:1	4:1	5:1	6:1	8:1
100	0	25.8	20.0	14.2	13.3	11.4
80	20	18.4	16.3	15.0	12.8	9.4
60	40	11.7	15.6	12.0	11.3	9.9
40	60	9.2	9.4	13.0	9.0	8.1
20	80	8.8	8.8	8.8	8.7	7.4

3.3 THERMAL SHRINKAGE:

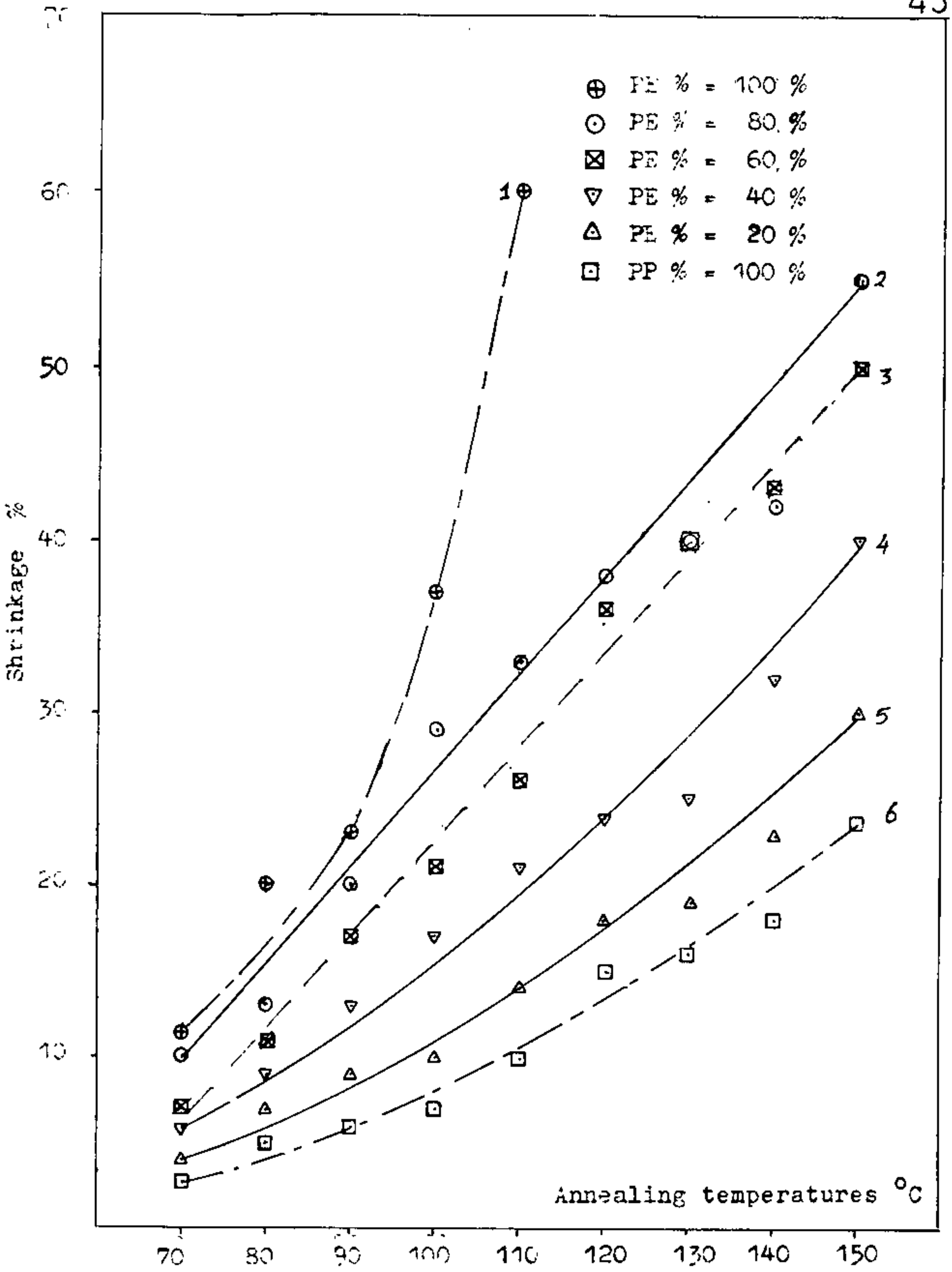
Figure 3.7a contains six curves related to the six samples with draw ratio 8:1, and shows the relation between the shrinkage property and the annealing temperature in the temperature range from 70°C to 150°C. Cruve number 1 indicates that PE had melted after 110°C, so its shrinkage test was terminated at 110°C where the shrinkage amounted to approximately 70%. It can be clearly seen from these curves that the shrinkage increases with the increase in annealing temperature. By comparing the six curves at any fixed temperature, it can be seen also that PP is less shrinkable than PE, hence all the blends show intermediate shrinkage property between those of the two homopolymers. Figure (3.7b) and (3.7c) show the shrinkage property for draw ratios of 6:1 and 5:1 respectively. The Figures suggest similar observations as those obtained from Figure (3.7a).

3.4 THERMAL ANALYSIS:

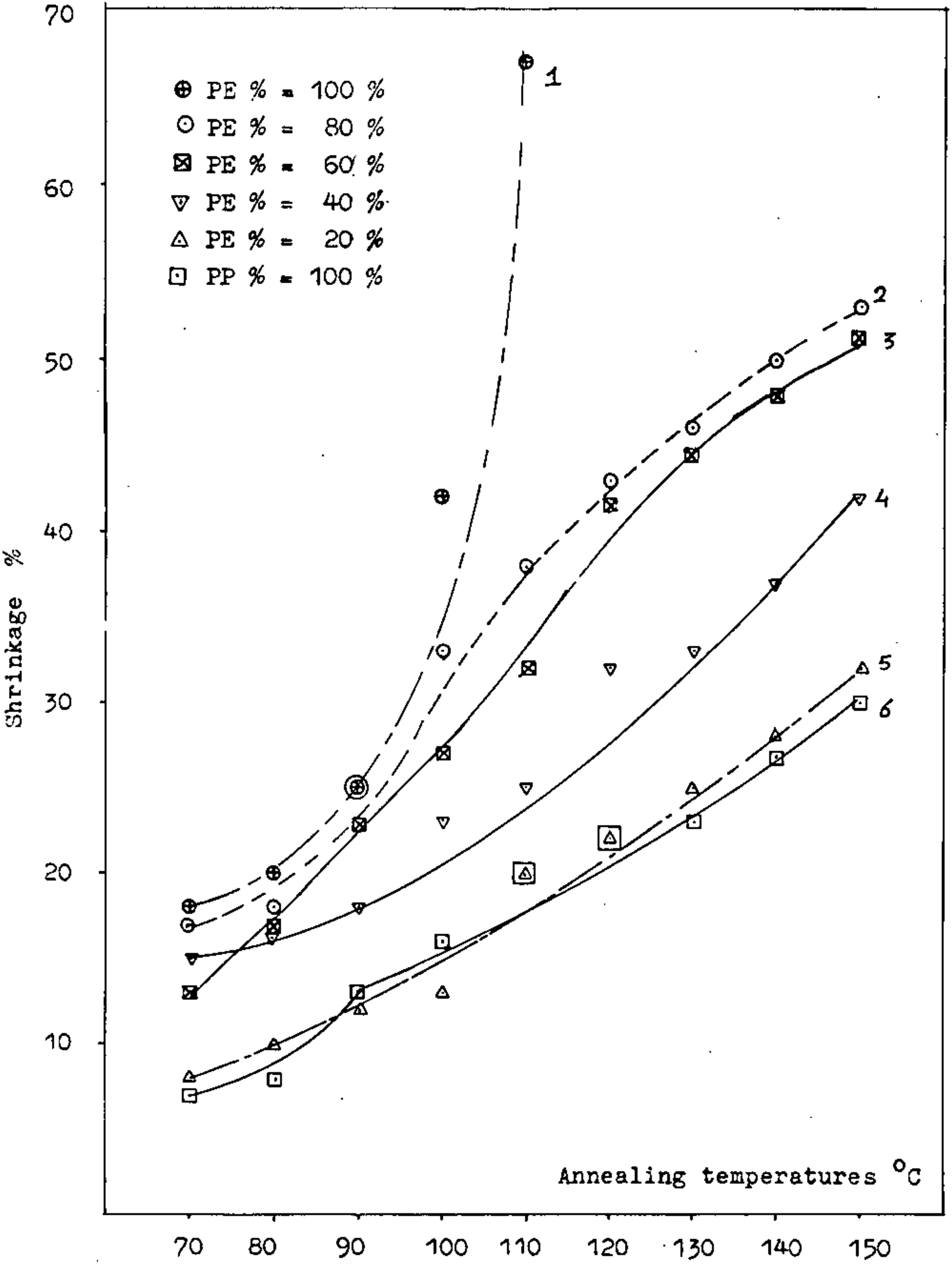
Figures 3.8(a-f) show differential thermal analysis scan (DTA) in the temperature range from 310°K to 480°K. Figure 3.8a shows one peak only related to the homopolymer PE, and a melting point equal to 385°K. Figure (3.8b) relates to the



Fig(3.7a): Shrinkage % of drawn polyblend films (D.R.= 8:1) versus annealing temperatures.



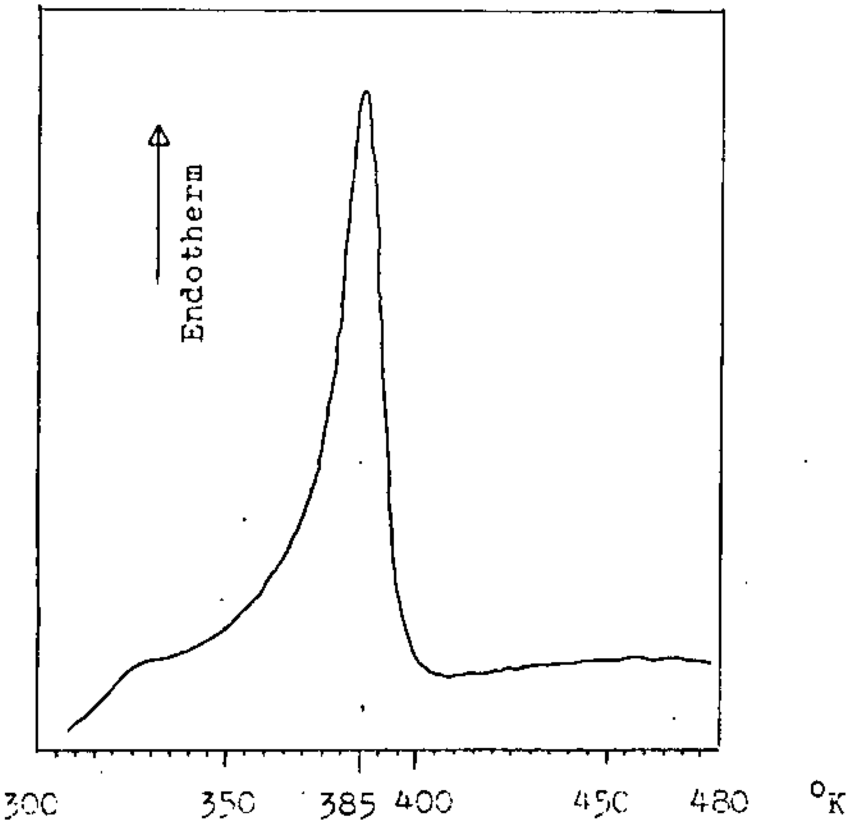
Fig(33.7b): Shrinkage % of drawn polyblend films (D.R.=6:1) versus annealing temperatures.



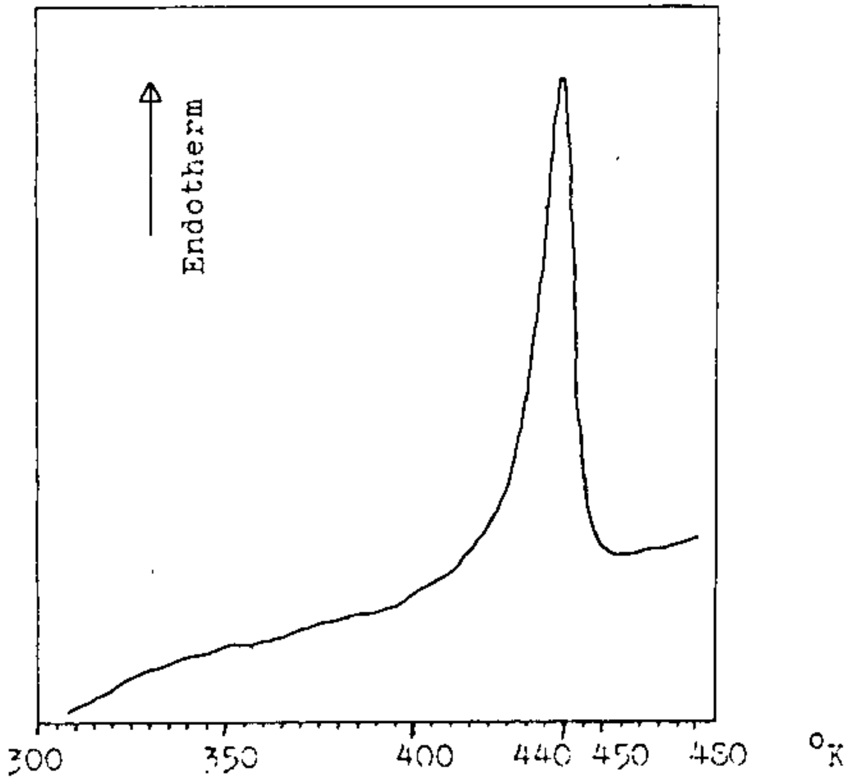
Fig(3.7c): Shrinkage % of drawn polyblend films (D.R.= 5:1) versus annealing temperatures.

Table 3.4: Shrinkage percentage versus blend composition.

Blend ratio		Draw ratio	Temperatures °C								
PE%	PP%		70	80	90	100	110	120	130	140	150
100	0	8:1	14	20	22	32	65	Melted			
80	20	"	15	18	24	32	37	43	47	50	58
60	40	"	12	16	22	27	33	40	42	48	50
40	60	"	12	14	19	21	25	31	33	37	43
20	80	"	8	11	12	15	17	20	22	25	28
0	100	"	6	9	10	13	14	19	20	23	26
100	0	6:1	11	20	23	37	60	Melted			
80	20	"	10	13	20	29	33	38	40	42	55
60	40	"	7	11	17	21	26	36	40	43	50
40	60	"	6	9	13	17	21	24	25	32	40
20	80	"	4	7	9	10	14	18	19	23	30
0	100	"	3	5	6	7	10	15	16	18	22
100	0	5:1	17	20	25	42	67	Melted			
80	20	"	17	18	25	33	38	43	45	50	53
60	40	"	13	22	23	27	32	42	45	48	52
40	60	"	15	17	18	23	25	32	33	37	42
20	80	"	8	10	12	13	20	22	25	28	32
0	100	"	7	8	13	17	20	22	23	26.7	30



Fig(3,8a)



Fig(3.8f)

Fig(3.8a-f): DTA thermogram of extruded polyblend films; rate of heating 10°C/min:-
(a); PE = 100%. (f); PP = 100%

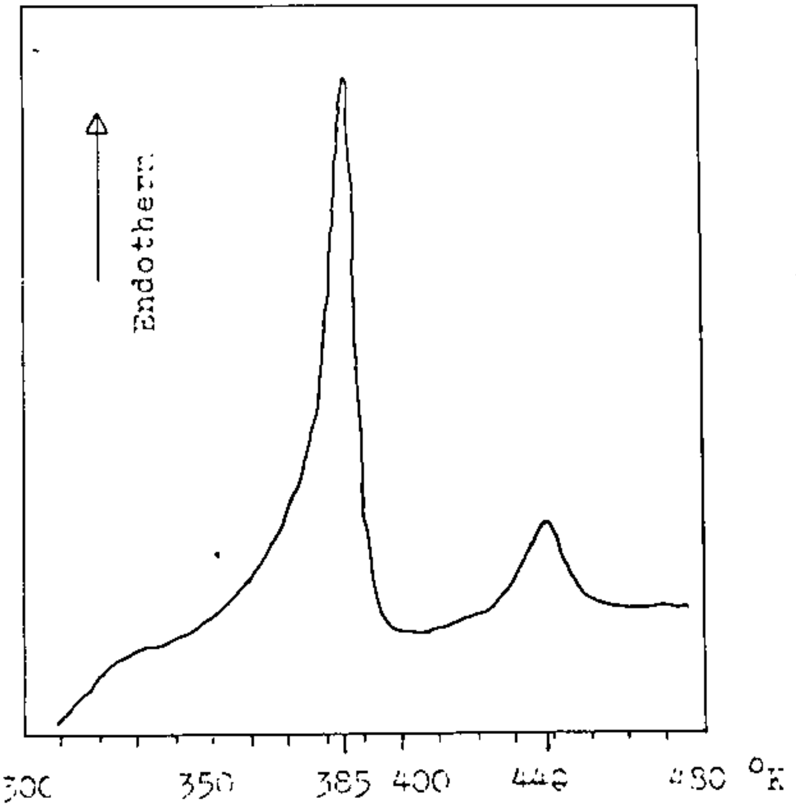
80/20 of PE/PP blend, and shows two peaks of unequal size where the larger peak corresponds to the major component PE in the blend. Hence the melting points are 385^{o}K for PE and 440^{o}K for PP. This Figure suggests that the two polymers are incompatible in the blend.

Figures 3.8(d-e) show a decrease in the size of the peak related to PE as the PE component in the blend was decreased. However, in all cases the two polymers remained incompatible and the two melting points did not vary.

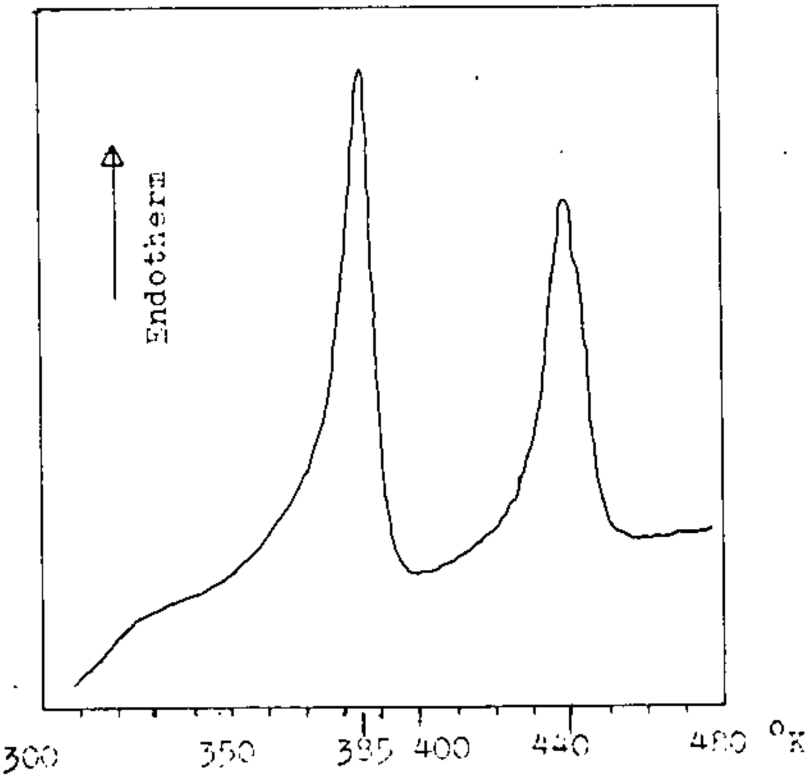
Figure (3.8f) shows the melting behaviour of pure PP, it is seen that the PP melts at 440^{o}K. It is seen from Figures 3.8(b-e) that the blend ratio is approximately proportional to the areas under the peaks.

3.5 SURFACE TOPOGRAPHY OF THE EXTRUDED AND DRAWN FILMS:

Figure (3.9) show the SEM surface topography of two sets of films; the first set comprises four samples with blend ratio PE/PP equal to 80/20, 60/40, 40/60 and 20/80, as they are produced. Whereas set 2 comprises the same samples but after drawing them on the Instron tester to draw ratio of 4:1. The SEM micrographs of the first set show a randomly distributed

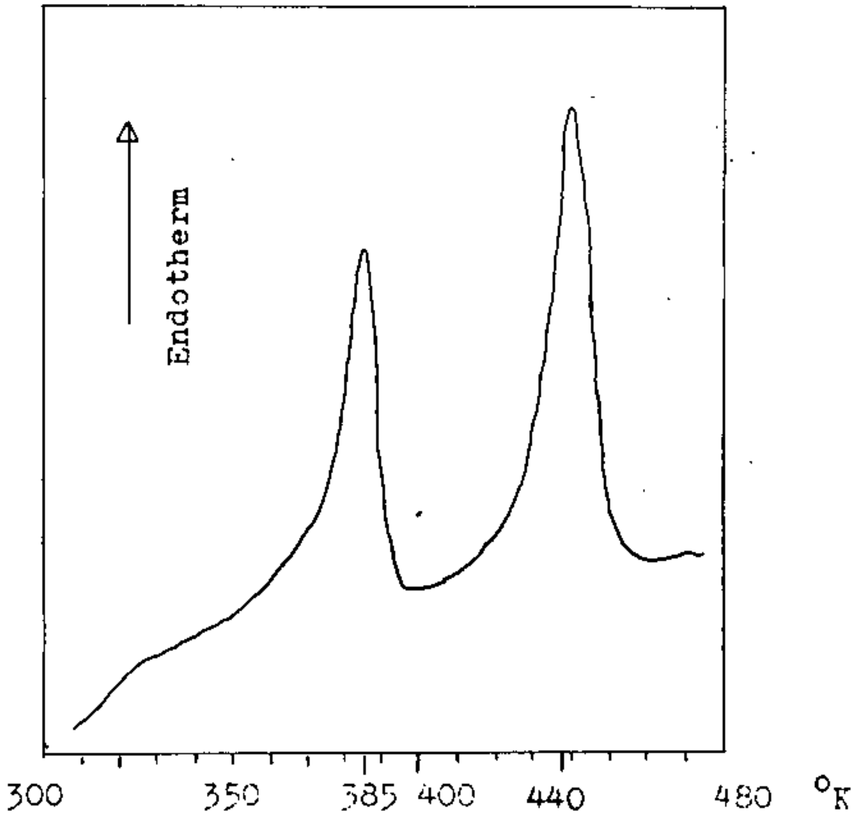


Fig(3.8b)

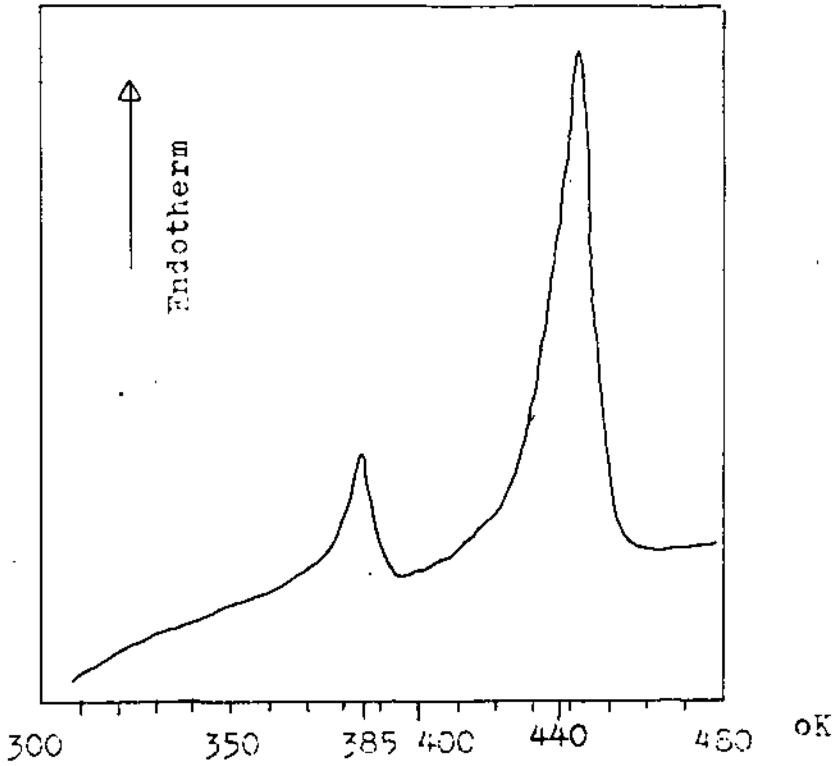


Fig(3.8c)

Fig(3.8b,c): DTA thermogram of extruded polyblend
films, rate of heating 10C/min:-
(b); PE/PP=80%/20%.
(c); PE/PP=60%/40%.



Fig(3.8d)



Fig(3.8e)

Fig(3.8d,e) : DTA thermogram of extruded polyblend
films, rate of heating 10C/min:-
(d); PE/PP = 40%/60%.
(e); PE/PP = 20%/80%.

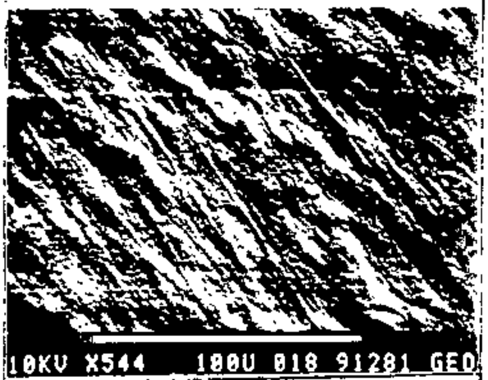
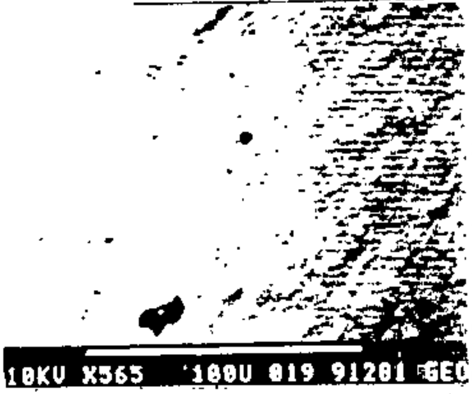
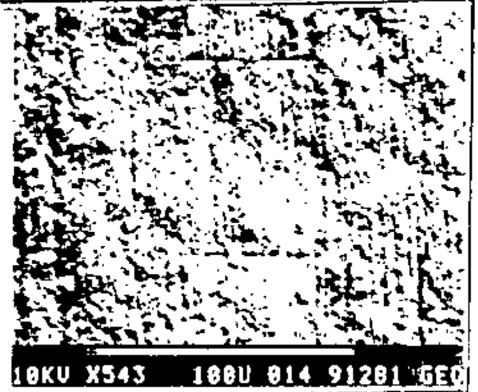
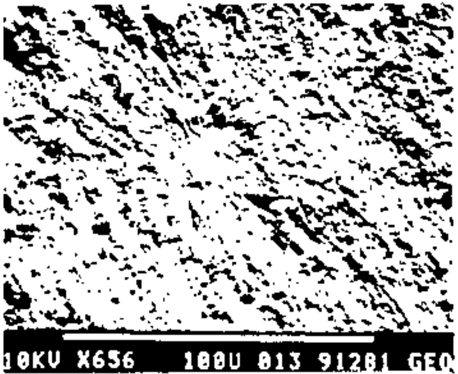
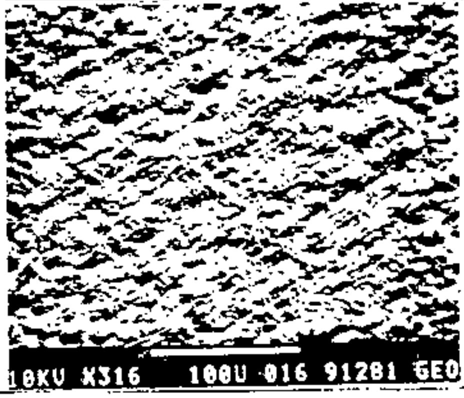
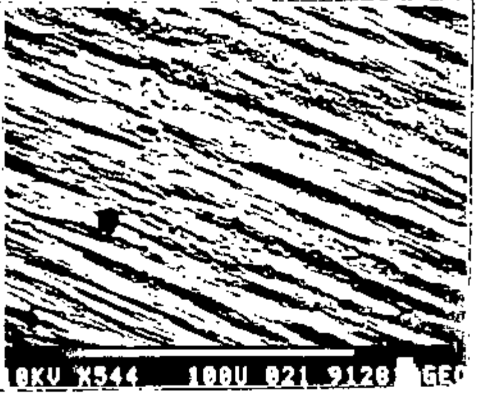
Blend Ratio			
PE%	PP%	Undrawn Samples (set1)	Drawn Samples (set 2)
80	20		
60	40		
40	60		
20	80		

Fig (3.9): Scanning electron micrgrph showing the effect of drawing on the surface topography of blended polymer films.

roughness of the surface consistent with the wide-angle X-ray diffraction, which indicated that the crystallites are randomly oriented in these samples. In set No. 2 the micrographs show surface striations suggestion a crystallite orientation in the drawing direction. This phenomenon was also exhibited in the X-ray diffraction pattern of the drawn samples.

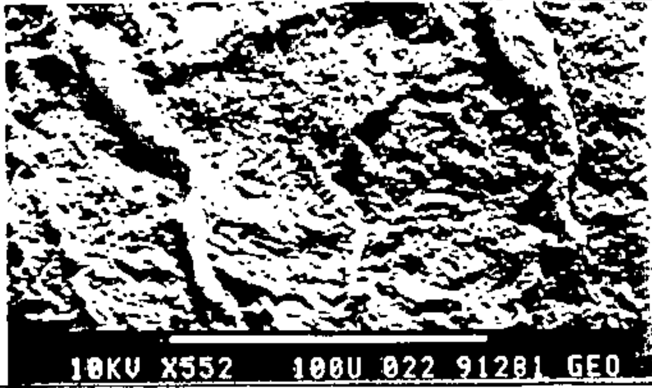
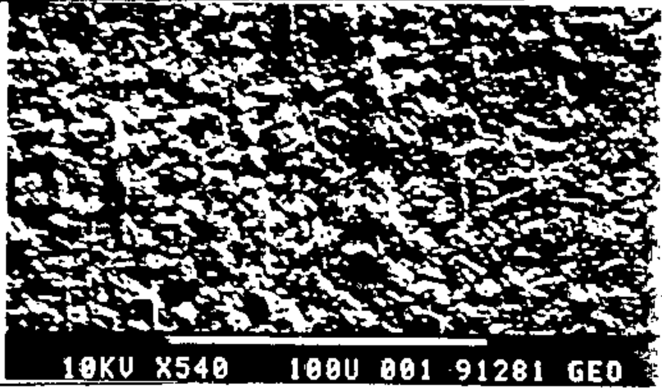
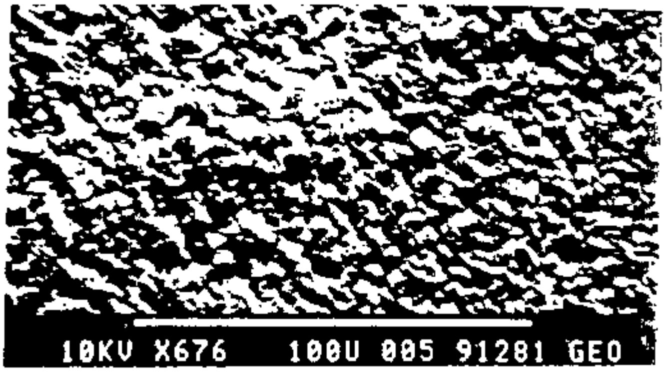
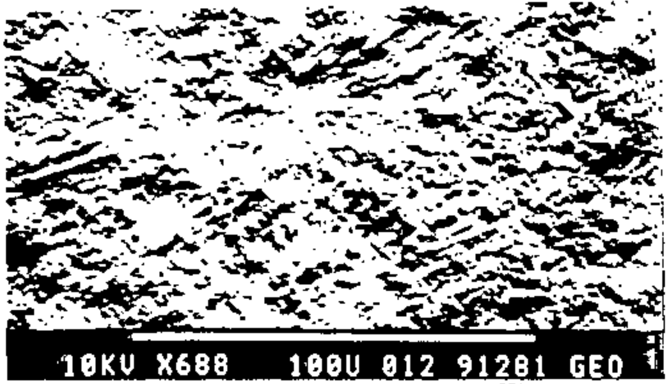
Figures (3.10a) and (3.10b) relate to the above mentioned samples but after leaching out the polyethylene component as discussed in Chapter 2. It is clearly seen that:

(a) The remaining PP component (see Fig. 3.10a) is randomly distributed in set No.3. This phenomenon suggests that both PE and PP components are randomly distributed in the blend.

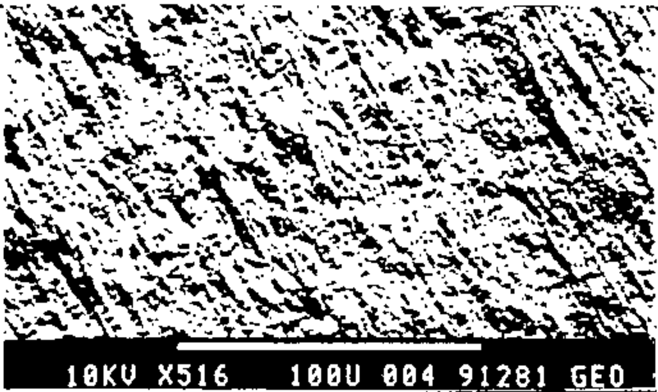
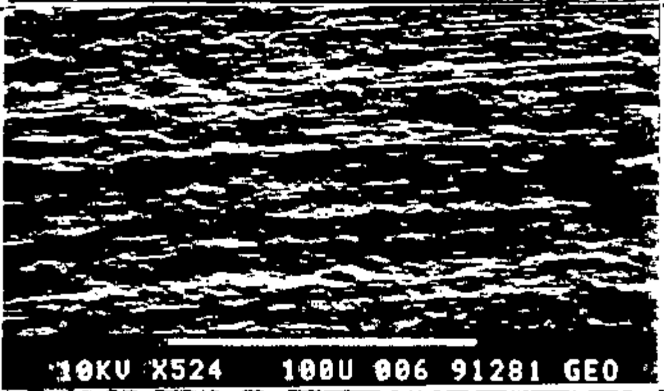
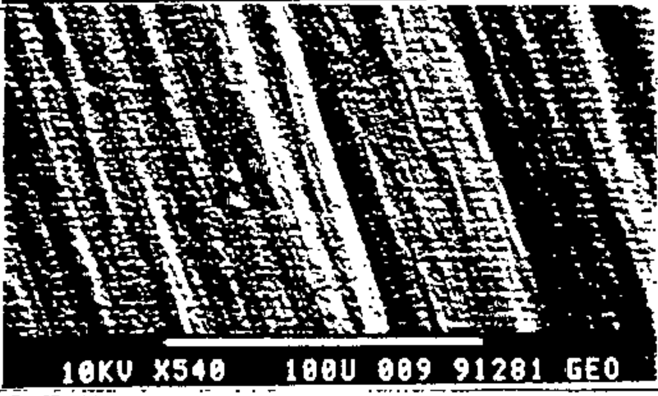
(b) The remaining component, PP, in set No.4 (see Fig. 3.10b) remained oriented in the drawing direction.

3.6 WIDE ANGLE X-RAY DIFFRACTION:

Figure (3.11a-f) show the wide-angle X-ray diffraction photographs of extruded polymer-blend films. Figures a and f relate to the two homopolymer films, PE and PP respectively. The photographs show sharp rings which suggest a good degree of crystallinity and random orientation of crystallites. Figure (3.11b-4) relate to the blend films with PE/PP composition

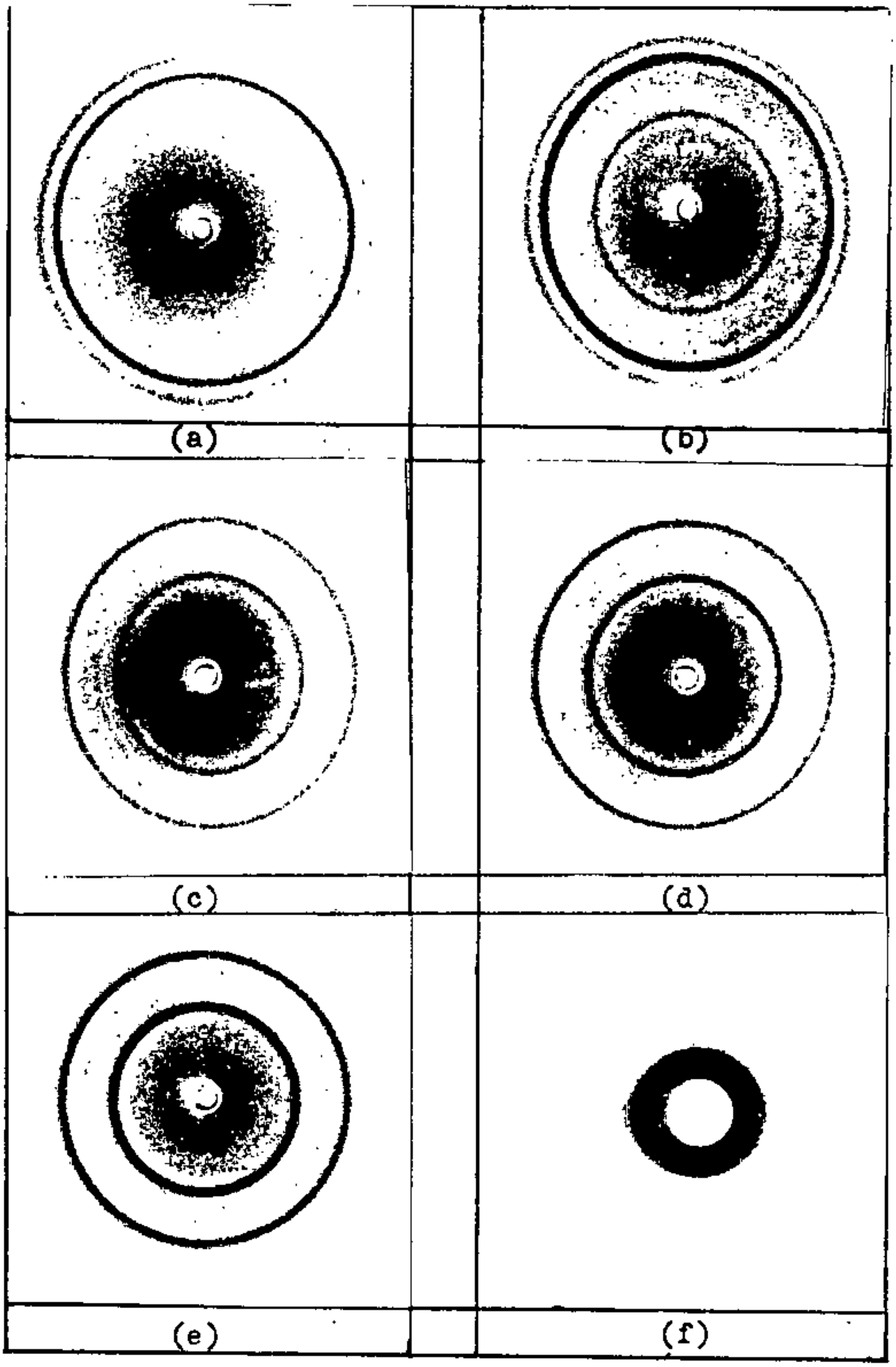
Blend Ratio		
PE %	PP %	Leached Samples (set 3)
80	20	
60	40	
40	60	
20	80	

Fig(3.10a): Scanning electron micrograph showing the effect of leaching out the polyethylene component from the undrawn blended polymer films.

Blend Ratio		
PE %	PP %	Drawn and Leached Samples (set 4)
80	20	
60	40	
40	60	
20	80	

Fig(3.10b): Scanning electron micrograph showing the effect of leaching out the polyethylene component from the drawn blended polymer film.

of 20/80, 40/60, 60/40 and 80/20 respectively. The four figures show rings relevant to PE as well as to PP. In Figure (3.11b) the PE rings are relatively more intense than those of PP. As the ratio of PP in the blend was increased, the PP rings became more intense. However, one can conclude from the whole set of photographs that both the PE and PP components in the blend are crystalline with random distribution of crystallites. Further X-ray diffraction investigation done recently in this laboratory has indicated that both components have acquired a good degree of crystallite orientation upon drawing the film to a ratio of 4:1.



Fig(3.11a-f): Wide angle x-ray photographs of extruded films quenched at room temperature:-
(a); PE = 100%. (b); PE/PP= 80%/20%.
(c); PE/PP= 60%/40%. (d); PE/PP= 40%/60%.
(e); PE/PP= 20%/80%. (f); PP =100%.

4.1 SAMPLE PRODUCTION

Commerical homopolymers, low density polyethylene and isotactic polypropylene were deliberately choosen to produce polyblend films. Usually, the structure, morphology and mechanical properties of polyblends are strongly affected by several factors among which are the molecular weights of the component in the blend, their melting points, viscosities, their ratios by weight, the mixing process and the extrusion conditions. Since all the factors were fixed in the present work by using the same batch of homopolymers and similar extrusion conditions for all the produced sample, the major and very important factor that had been considered is the effect of the blend ratio on the X-ray diffraction pattern, the compatibility of the components, the possible variation in the melting behaviour, the transparency, the mechanical properties of the produced films and the advantages of using blended homopolymers in industrial production. As it was shown in Chapter Two, a simple procedure was adopted for mixing the components. This was accomplished through manual mixing of the chips from the two components, followed by melt blending in the cylinder of the extrusion machine during the production of the films.

The transparency of the films decreased as the PP content increased; this might serve as an indication of the beginning of spherulitic structure [26].

4.2 MECHANICAL PROPERTIES:

The mechanical properties of the polyblend depend on several factors among which are the following:

(a) the original properties of the components,
(b) the blend ratio,
(c) effect of each component on the other,
(d) the mixing process, and
(e) the extrusion conditions.

4.2.1 Initial Young's Modulus:

The initial modulus of the blend relative to that of the PE component increased as the PP component was increased, and attained a maximum value at a blend ratio of 40/60 PE/PP. This increase is shown in Figure (3.2a) to be greater than the expectation of the additivity of properties. This could be due to the fine dispersion of PP component in the matrix of PE component as will be discussed later in this chapter (Section 4.5). However, the initial modulus in the transverse direction does not behave in a similar trend. The 20/80 and 80/20 PP/PE blends showed respectively a remarkable increase and decrease relative to the additivity of properties as was shown in Figure (3.2b). The increase in the initial modulus can be accounted for the increase in crystallinity or orientation or both. Since the PP component will solidify first, the PE component would crystallize on the surface of a solid substrate. Relative to the PE component, the crystallinity would increase which in turn will lead to an increase in the initial modulus. The behaviour of 80/20 and 20/80 PP/PE blends in the transverse direction could be attributed to the crystallite orientation; the PE component in the 80/20 PP/PE blend could be well oriented in the transverse direction of the film. This was not investigated because of the lack of X-ray facilities.

4.2.2 Yield Stress:

The increase in the yield stress in the transverse direction indicates that the increase in the crystallinity enhances with the crystallite orientation in this direction (transverse direction). This explains the behaviour of the yield stress in the longitudinal direction where the crystallinity of PE increases with the increase in PP component in the blend. The 80/20 PP/PE blend may indicate that the crystallite orientation in the flow direction is poor. This is consistent with what has been proposed above; the 80/20 PP/PE blend in the transverse direction has a magnitude of initial modulus greater than both components.

4.2.3 Yield Strain:

The yield strain results in both, the flow and the transverse direction could be explained in a similar manner as above, the increase in crystallinity due to PP component will lead to a decrease in the yield strain. Since the orientation in the transverse direction is much better than that of the flow direction thus, one would expect that the yield strain in the transverse direction will be less than that of the flow one as was shown in Figure (3.4a,b).

4.2.4 Breaking Stress:

Results of breaking stress in both directions of the film can also be explained in terms of crystallinity increase in PE component on the surface of PP component. The difference in the breaking stress behaviour in Figure (3.5) could be due to the above hypothesis; the crystallinity enhance with good orientation in the transverse direction rather than in the flow direction.

4.2.5 Breaking Strain:

The results of breaking strain in both directions of the film shown in Figure (3.6a,b) are consistent with what has been proposed above; the breaking strain in the flow direction of each blend is greater than that in the transverse direction. This means that the orientation in the transverse direction is better than that in the flow direction. The behaviour of 60/40 PE/PP may indicate that the orientation in the flow direction is better than that in the transverse direction which is consistent with the results of the initial modulus (see Fig. 3.2.a,b).

4.2.6 Plastic Recovery:

The results of plastic recovery shown in Table (3.3) suggest that the plastic recovery of each film individually decreases with the increase in the draw ratio.[27] The decrease in plastic recovery of polyblend film relative to the PE component can be attributed to the increase in crystallinity, this is consistent with what has been proposed above.

4.3 THERMAL SHRINKAGE:

Shrinkage results can be explained in terms of:

(a) the characteristics of each component in the blend, and

(b) the blend ratio.

The greater shrinkage of PE relative to the PP is simply due to the fact that shrinkage is strongly temperature dependent. Since the melting points of PE and PP are 112° and 167°C respectively as was determined by DTA (Section 3.4), thus ,up to the temperature of 100°C the effect of heat on the PE film will be much higher than that of PP; the temperature range is high for PE whereas for PP is the low range.[28] The increase of shrinkage ratio with the increase in draw ratio is simply due to the fact that the shrinkage is the reversible process of drawing.

In the polyblend films, the increase in shrinkage with the increase in the PE component above 100°C is due to the surface tension and breakage of interfacial forces between the component which will lead to an increase in the mobility of PP component as a result of the melting of PE component.

4.4 THERMAL ANALYSIS:

The results of the DTA showed that the melting points of the PP and PE are 167 and 112°C respectively. The two endothermic peaks indicate that both the films were crystalline.

The thermogram of polyblend films showed two separate endothermic peaks indicating that the two polymers are incompatible. However, although the mixing was roughly done; the mixing took place in the cylinder of the extruder, there was no premixing, still the dispersion was satisfactory as measured by the area under the curve of the endothermic peak. The ratio of the two areas under the peaks characteristic of each component in the blend was consistent with the blend ratio.

4.5 SURFACE TOPOGRAPHY OF THE EXTRUDED AND DRAWN FILMS:

Except for the 40/60 PP/PE polyblend film surface, the film surface of all other polyblends was found to be rough as was shown in Figure (3.9), Set 1. However, the drawn samples show the surface where the orientation direction was clear as shown in the same Figure, Set 2. A more or less dispersion of one component into the matrix of the other was clear in blends of 60/40 and 40/60 PP/PE films as was shown in Figure (3.10a). However, since the leaching treatment at 70°C is considered also as a thermal treatment then, one would expect a high shrinkage ratio of the residual component. Thus to prevent this expected shrinkage a sample holder shown in Figure (2.6) was built. Hence the residual component was shown in Figure (3.10b) to be drawn. Figure (3.10b) suggested that the dispersion of 60/40 and 40/60 PP/PE blend is less fine than expected. This could be attributed to the mixing process which took place during the extrusion. Although the 20/80 PP/PE blend film showed a well dispersion of PP into the matrix of PE, however, the 80/20 PP/PE blend film on the other hand does not show this fine dispersion. This may serve to explain the difference in the mechanical properties in both the flow and transverse direction as discussed in section 4.2.

4.6 WIDE-ANGLE X-RAY DIFFRACTION:

The wide-angle X-ray photographs of the extruded films in the flow direction showed conclusively that both homopolymers are crystalline but unoriented. Unfortunately, the crystallite orientation in the transverse direction due to the air pressure was not examined because of the lack of X-ray facilities.

The polyblend films also exhibited a superimposed diffraction pattern in a ring form indicating that:

(a) the two polymers are incompatible,

(b) both components in the blend are well crystalline but unoriented.

The unorientation of the crystallite was expected since the pull out force was very small.

The 220 and 040 reflections belonging to the PE and the PP homopolymers respectively were shown to be the more intensive reflections. This is an indication to the preferential crystallite growth directions belonging to the two polymers respectively.

An extra X-ray studies for these polyblend films is of great interest.

4.7 CONCLUSION

Although there was no thorough premixing of the two homopolymers used in this work, satisfactory blend films were obtained. The mechanical properties of the blend films were found to improve with respect to the PE polymer; the more the PP proportion in the blend the better are the mechanical properties. This could be attributed to an increase in the crystalline part; since the PP component will solidify first, the solid surface will serve as a nucleating agent for the PE component to crystallize on. Hence an increase of crystallinity will be expected. The difference in mechanical properties in both directions of the film; transverse and flow direction, may be attributed to the better crystallite orientation in the transverse rather than in the flow direction. This could be because the air pressure effect on the crystallite orientation was more than the take-up finish.

The two supperimposed X-ray diffraction patterns belonging to the two components in the blend, beside the two endothermic peaks given by each blend in DTA technique are satisfactory evidence that the two polymers are incompatible.

Finally, it is to be remarked that the results obtained in this work, specially with respect to the ultimate properties, are quite different from those reported by other authors. This can be attributed to the different processing conditions used for obtaining the present blend specimens. Such conditions are certainly important in determining particular blend morphology which will in turn determine the properties of the analysed samples.

SUGGESTIONS FOR FURTHER WORK

1. Quantitative determination of the crystalline state of the films namely the crystallinity, crystallite size and orientation of each component in the blend.
2. Shrinkage and plastic recovery in the transverse direction.
3. Optical studies on the surface topography by means of Two-Beam Interferometry.
4. Determination of the absorption bands in the Ultra-Violet (U.V) and visible regions of the spectrum.
5. The effect of U.V. dose on the structure and properties.
6. The effect of other production parameters on the structure and properties.
7. Production of blends from polypropylene and high-density polyethylene.

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