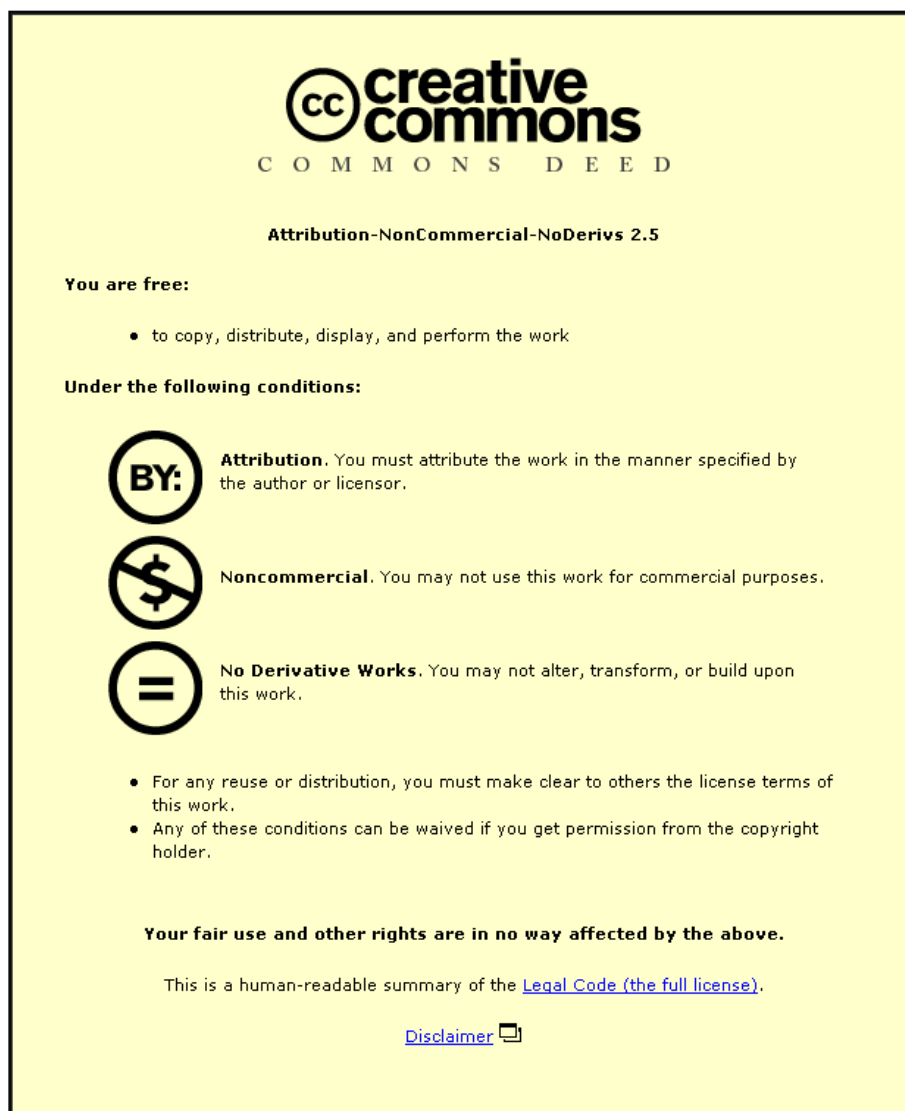


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MELT AND SOLID STATE BEHAVIOUR OF POLYOLEFIN BLENDS

BY

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**A Doctoral Thesis submitted in partial fulfilment
of the requirements for the award of the
degree of Doctor of Philosophy of the
Loughborough University of Technology**

June 1990

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***Dedicated to my parents
and my wife, Tahereh***

ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor professor A. W. Birley for his invaluable advice and guidance throughout this project.

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Finally, I am indebted to my parents and my wife, Tahereh for their moral support and patience.

SYNOPSIS

Polymer-Polymer blends are rapidly growing as an important resource for obtaining new and improved polymeric materials; and polyolefins are among the most widely used thermoplastics in the polymer industries due to their low cost, desirable physical properties and wide range of applications. For this reason several polyolefin polymers were melt blended and different experimental techniques were used to investigate their characteristics and their properties. The blends under investigation are reported in four chapters, following a literature survey and a description of experimental techniques.

Chapter three compares the copolymer of ethylene-vinyl acetate with melt blends of ethylene-vinyl acetate and low density polyethylene. The results obtained by DSC show that blends of ethylene-vinyl acetate/low density polyethylene are immiscible and give poorer mechanical properties than EVA copolymer.

Chapter four investigates the binary blends of linear low density polyethylene/high density polyethylene and ternary blends of linear low density polyethylene/high density polyethylene/low density polyethylene. The binary blend showed some improvement in mechanical properties, due to compatibility of linear low density and high density polyethylene.

Chapter five deals with the binary blend of linear low density polyethylene and low density polyethylene. It was found that these blends are miscible in the melt and do not segregate in the solid state provided that they are cooled quickly. Blown films and injection

moulded samples were made at different cooling rates and their mechanical properties compared.

Chapter six studies the blends of linear low density polyethylene and polypropylene. These blends were found to be immiscible; but unusual and interesting results were detected by DSC when small amounts of LLDPE were added to polypropylene. The last part of this chapter discusses three processing techniques which might reasonably be expected to benefit from the presence of small amounts of LLDPE.

Finally, the last chapter discusses the overall conclusions and commercial exploitation of polyolefin blends.

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CHAPTER 1

INTRODUCTION

1.1 POLYMER BLENDS

1.1.1 Background

The concept of appropriately combining together two or more different polymers to obtain a new material system with the desirable features of its constituents is not new. Over the years, numerous systems based on the chemical combination of different monomers through random, block and graft copolymerisation methods have been developed with this objective⁽¹⁾. The list of new concepts in polymer synthesis has not been exhausted. However, it has become clear that new chemical structures or organisation are not always needed to meet new needs or to solve old problems⁽²⁾.

More recently, the concept of physically blending two or more existing polymers to obtain new products has attracted widespread interest and commercial utilization⁽²⁾. The high cost of developing new reactor grades is most likely the reason for the recent success of blends. Other factors impacting on the further growth of blends are⁽³⁾:

1. blends may offer a cost-effective means to fill the gap in performance of existing materials;
2. blends may often improve the critical properties required for a particular end-use;

3. blends may result in increased revenue/sales without major expenditure or capital expansions;
4. blends may often represent an easy way for commodity plastic producers to enter the lucrative specialty segment of the business.

Commercial thermoplastic blends have been known for over twenty years-the first patents on polyolefin blends were granted in the late fifties⁽⁴⁾. B.F. Goodrich introduced ABS/PVC (Cycovin) blends in 1960. G.E.C started the commercial production of PPO/PS (Noryl) in 1965⁽⁵⁻⁷⁾. Before 1980, some poly(vinyl chloride), polypropylene and polystyrene were blended commercially for commodity applications⁽³⁾. However, it was not until the introduction of linear low density polyethylene(LLDPE) that interest became focussed on the modification of low density polyethylene(LDPE). In addition to the aspect of material saving, greater consideration was given to property enhancement.

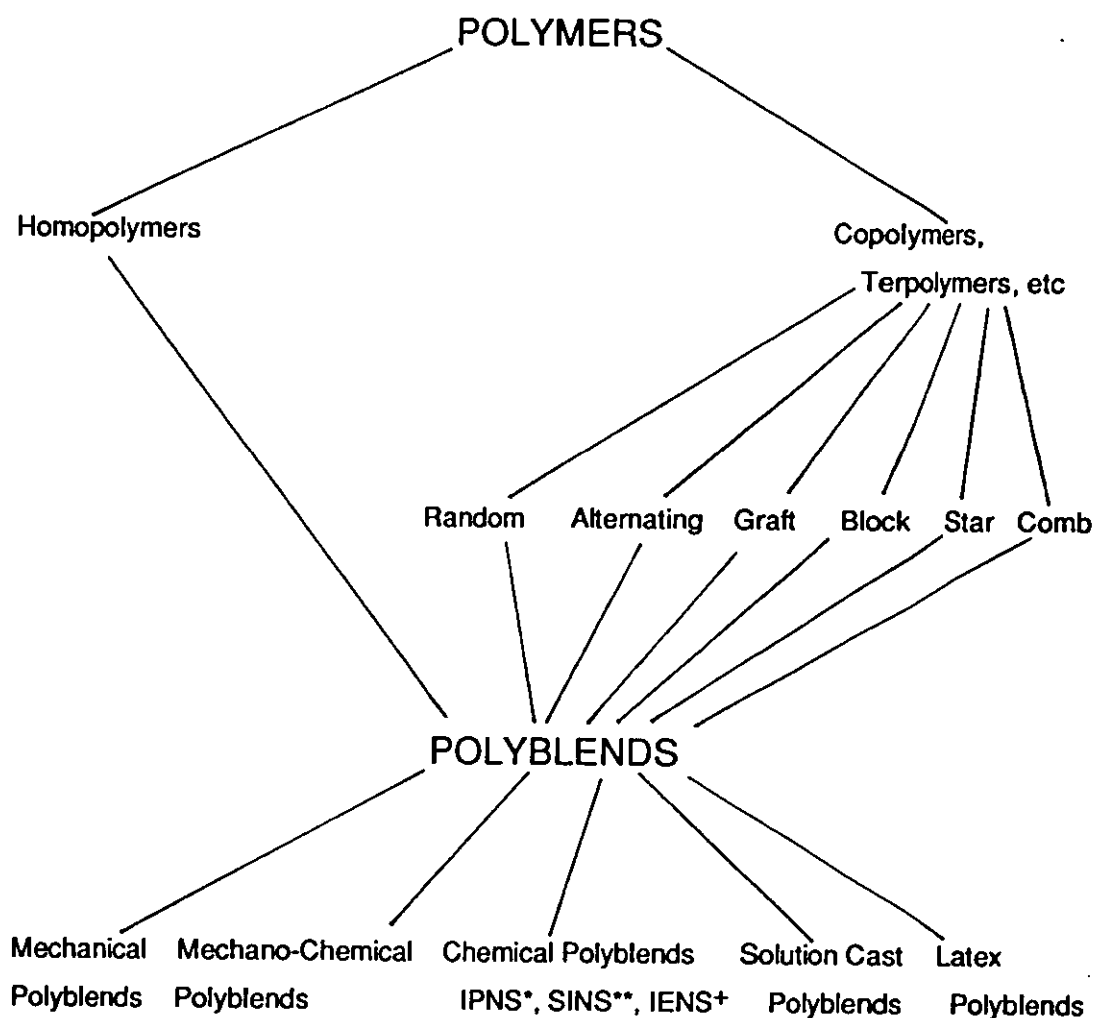
1.1.2 Definition of Polymer Blends

Polymer blends are physical mixtures of chemically different polymers and/or copolymers⁽⁸⁾; they are often referred to by the contraction "polyblend" and sometimes as "alloy" to borrow a term from metallurgy⁽²⁾.

1.1.3 Classification of Polymer Blends

Polyblends may be classified in terms of their method of preparation⁽⁹⁾ Fig. 1.1. Commercially available polyblends are almost exclusively mechanical polyblends. Usually they are prepared either on an open roll, in an extruder, or in suitable internal

mixer(10). The processing temperature must be well above the melting temperature(T_m) of each of the constituent polymers for mixtures containing semi-crystalline polymers and above the glass transition temperatures(T_g) for mixtures containing amorphous polymers(9).



* interpenetrating polymer networks **simultaneous interpenetrating polymer networks
+ interpenetrating elastomeric networks.

Fig. 1.1 Classification of Polymer blends by the method of preparation(9)

Depending (9,10) on the thermal stability, the high shear involved during processing can initiate polymer reactions due to formation of free radicals. The free radicals can react with structurally different polymer present resulting in true chemical grafts and such mixtures are referred to as mechano-chemical polyblends. A chemical polyblend is made by in-situ polymerisation and cross linking of the constituent polymer and the result is interpenetrating cross-linked polymer networks of structurally different polymers. The three main categories are interpenetrating polymer networks (IPN's), simultaneous interpenetrating polymer network (SIN's), and interpenetrating elastomeric networks (IEN's) (9,11). In general, the IEN's are made by mixing and coagulating two different kind of polymer latices, and cross linking of the coagulum to form a three-dimensional mosaic structure. If the latex coagulum is not cross-linked, the resulting product is called a latex polyblend.

Solution cast polyblends are prepared by dissolving the constituent polymers in a common solvent such that the solutions have about the same viscosity and mixing the solutions thoroughly. The resulting solution could be film-cast, coagulated, spray dried or freeze-dried to form polyblend (9).

1.1.3.1 Additivity Rule (9,10)

Generally, blending technology rests on the premise of property additivity, although strictly, the additivity principle is valid for miscible polyblends only. For these systems, such properties as T_g , density, refractive index, dielectric constant, thermal conductivity, heat capacity, thermodynamic properties,

elastic moduli, viscosity of liquid mixtures, and surface tension of liquid mixtures follow the dependence (12)

$$P = P_1 \phi_1 + P_2 \phi_2 + I \phi_1 \phi_2 \quad (1.1)$$

Where P is the property of interest, ϕ is the composition (by volume), and I is an interaction term which can be positive, negative, or zero. If I is zero, the rule of mixtures (additivity principle) is obeyed, if it is positive, the polyblend property would be better than the weighted average of the constituent polymers and the polymers are said to be synergistic with each other; if I is negative the polyblend property would be below what one would expect from sample averaging and the system could be referred to as non-synergistic. The behaviour is illustrated in Fig. 1.2.

In the case of immiscible polymer blends another semi empirical mixing rule is obeyed for such properties as elastic moduli, electrical conductivity, thermal conductivity, dielectric constant, thermal expansion coefficient, diffusion coefficient, and the viscosity of suspension (12)

$$P/P_1 = 1 + AB \phi_2 / 1 - B \psi \phi_2 \quad (1.2)$$

where ϕ_2 is the composition (by volume) of dispersed phase constituent, A (between zero and infinity) depends on the shape and orientation of the dispersed phase and the nature of the interface, B depends on the values of properties P_1 , P_2 , and A , and ψ is a reduced concentration term that is a function of the maximum packing volume fraction ϕ_m . However, for immiscible blends, the additivity rule has been applied, in a

crude sense, to calculate such properties as moduli, impact strength, thermal and oxidative resistance, processability, environmental weatherability, colour, hardness, heat resistance, flame retardance, domain morphology, thermal expansivity thermal conductivity, compressibility and refractive index. In all the applications involving immiscible polyblends, one polymer phase is always the continuous phase in contrast to the application involving miscible polyblends where the property additivity principle is often possible over the entire composition range.

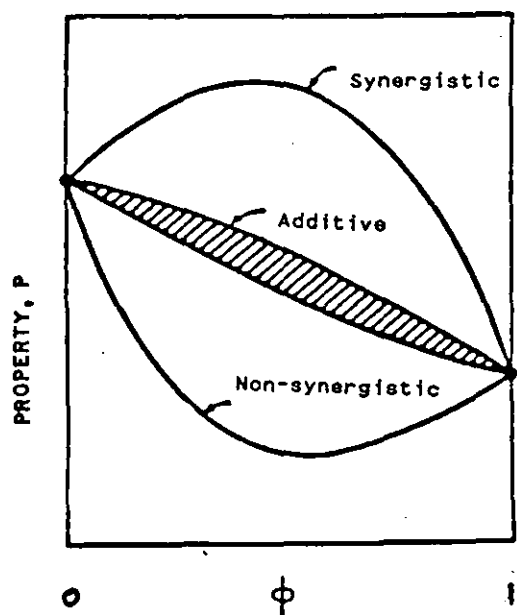


Fig.1.2. (9) Property-composition dependence for miscible polyblend.

1.2 WHY BLEND POLYOLEFINS?

1.2.1 Materials Characteristics

Ethylene and propylene from petroleum refining operations or from natural gas are the cheapest raw materials for polymer production⁽¹³⁾, and for this

reason polyolefins form the largest group of commercial thermoplastics.

They constitute a group of polymers of complex macromolecular structure⁽¹⁴⁾: wide molecular weight distributions that are diverse in shape, can have substantial short and long chain branching, and high crystallinity, coupled with a multitude of spherulitic forms and orientability. Their density is the lowest among polymers and strongly influences performance characteristics.

The characteristics pertinent for melt mixing (blending) are⁽¹⁴⁾: excellent dielectric properties, water repellency, nonpolarity, high melt viscosities that respond weakly to temperature changes but strongly to shear rate or stress changes coupled with inherently high melt elasticity and melt strength. Polyolefin glass transition temperatures, with the notable exception of polypropylene, are low.

1.2.2 Why Blend Linear Low Density Polyethylene With Other Polyolefins?

Linear low density polyethylene (LLDPE), is a new thermoplastic⁽¹⁵⁾. For many applications, its properties are superior to those of low density polyethylene (LDPE). In comparison to LDPE, LLDPE has⁽³⁾:

- better stiffness
- better tensile strength
- better elongation
- better puncture resistance
- better environmental stress-crack resistance
- higher energy requirements for extrusion

easier melt drawability

Linear low density polyethylene⁽¹⁵⁾ is produced by process which also produced high density polyethylene(HDPE). In the case of gas-phase technology, the investment cost for greenfield plants is the lowest of all polyethylene processes, and the operating costs to produce pellets are as low as the best of the rival technologies. The ability to use a range of comonomers such as butene, octene, hexene etc gives same flexibility of product properties. The largest share of LLDPE is used in blends with other polymers to obtain an averaging of physical properties and/or benefit on processing properties and/or material cost⁽³⁾.

1.2.2.1 Structural Comparison of LDPE, HDPE and LLDPE

Low density polyethylene made in high pressure plants is branched, with both long and short chain branching, and gives rise to polymers in the density range 0.916-0.930 gm/cm³, whereas high density polyethylene has essentially linear molecules with little side chain branching, lying in the density range 0.950-0.965 gm/cm³. Linear low density polyethylene has a significantly higher level of short side chain branching brought about by the copolymerisation of α -olefins such as butene, octene, etc, at levels ranging from around 8-10% for low density and around 1-2% for high density copolymers⁽¹⁶⁾.

1.2.3 Recent Advances in Application of Polyolefin Blends

Probably, the most prominent new blends are LLDPE/LDPE, and LLDPE with HDPE⁽¹⁷⁾. At present, more than 60% of LLDPE for commercial application is blended with other polymers⁽³⁾. Adding small amounts of LDPE to LLDPE results in reduced haze and better stability (tubular film extrusion) with a sacrifice in machine direction tear strength⁽¹⁷⁾. Plastic grocery sacks are presently made by using LLDPE/LDPE-70/30 blend, or a small amount of HDPE is added to LLDPE. The advantage of these blends over the original LDPE sacks is the ability to produce thinner gauge sack while retaining acceptable properties.

High density polyethylene or polypropylene is added to LLDPE for increased stiffness as compared to pure LLDPE, which is particularly important when reducing film thickness. These applications include garment film, grocery sacks, merchandise bags and refuse bags. If the material cost is not a predominant factor, the addition of an EVA copolymer to LLDPE can be considered as a means of improving toughness⁽³⁾.

1.3 PREPARATION OF POLYOLEFIN BLENDS

1.3.1 General

The preparation of a blend is important both from the point of view of its properties and its economics⁽¹⁸⁾. The objective of mixing during the preparation of blend is to bring the component materials into close proximity, facilitating the relaxation of any non-equilibrium concentration gradients. Generally, mixing

is aided by solvent, heat or both. In addition, shearing of the mixture is required.

Several mixing methods are available for blending polymers. Such methods are melt mixing, casting from common solvents, freeze drying, emulsions and mixing via reaction. Here only the melt mixing will be discussed, because of its advantages over the other methods and as being the most common method used in the polymer industry.

1.3.2 Melt Mixing (18)

Mixing in the melt state is often the method of choice for the preparation of polymer blends. It offers the advantage of introducing no foreign components (e.g. solvents) into the blend. For this reason and because of the simplicity and speed of melt mixing, it has economic advantages which make it the primary commercial blending method. It is possible to obtain excellent mixing of the components by using the appropriate equipment. Temperature, time and environment for the mixing can usually be carefully controlled. The primary disadvantage of melt mixing is that both the components must be in the molten state, which can mean that temperatures may be high enough to cause degradation.

1.3.3 Methods of Manufacturing Polyolefin Blends (19)

To improve blending, heavy mixing equipment capable of producing high shear is necessary for promoting dispersion of the components and mechanochemistry, which could lead to graft copolymers. In addition, the equipment should control the temperature and the melt,

limit its exposure to oxygen, and provide some extensive mixing to ensure uniformity.

The Banbury mixer is often cited as being the standard piece of equipment for blending. It is a batch mixer with counter rotating rotors turned at different speeds in the 100 rpm range. In the Farrel continuous mixer (FCM) (20), the Banbury has been adapted to continuous processing which transfers the mix into the Banbury-like paddle section by two screws. The speeds are generally high, e.g 250-300 rpm. Temperature of the melt and degree of mixing are controlled both by the rotor speed and by the volume. The out put from the discharge port is most often fed to a single-screw extruder for pelletizing.

Two popular devices for blending polyolefins are single and twin screw extruders. The single-screw extruders employed for compounding are usually equipped with one of a large variety of equipments to enhance mixing, with the objective of greatly improving the mixing action. The twin screw extruder with interlocking, co-rotating screws with a kneading section gives intensive mixing. These machines can be tailored for almost any compounding operation by fitting together various screw sections.

1.4 PHASE SEPARATION MECHANISM

1.4.1 General Aspects of Phase Behaviour

A blend of two or more polymers may exist in a completely homogeneous state where their segments are mixed at the most intimate level or it may segregate into distinct phases (21). Fig. 1.3 classifies phase

separation behaviour and mechanisms for phase diagrams of polymer mixtures, where UCST and LCST are the upper and lower critical solution temperatures respectively(22). Phase segregation may be the result of incomplete miscibility between two molten polymers or more components from an otherwise homogeneous melt mixture. Obviously, both modes of phase segregation may exist simultaneously.

A homogeneous amorphous phase upon cooling will eventually become a glass at a single temperature intermediate between the glass transitions of the pure components(21). The glass transition of the blend will depend on composition and reflect the mixed environment of the segments. This will be so even if phase segregation by crystallisation has occurred provided there remains a homogeneous amorphous phase albeit of a different composition than the overall blend. On the other hand, blends comprised of separate amorphous phase will exhibit glass transition characteristics of each phase. Thus, glass transition behaviour can be a powerful tool for identifying the amorphous phase structure of blends.

A homogeneous crystalline phase upon cooling shows a single crystallisation temperature and upon heating shows a single melting temperature. The crystallisation temperature and the crystalline melting temperature are influenced by their heat history, experimental time-scale and condition. On the other hand, blends with a separate crystalline phases exhibit two crystallisation temperatures upon cooling and two crystalline melting temperatures upon heating. Therefore crystalline melting temperature and crystallisation temperature are powerful tools for identifying the miscibility of crystalline-crystalline polymer blends.

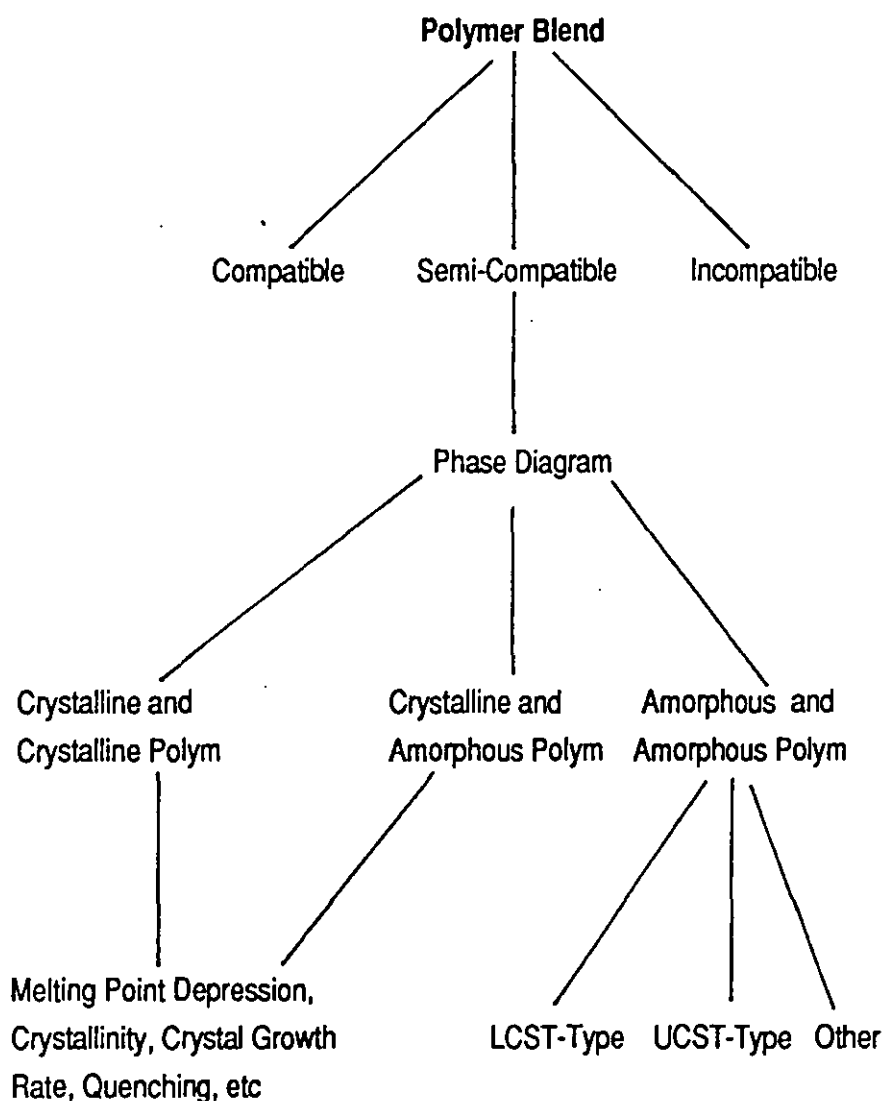


Fig. 1.3(22) Classification of phase separation behaviour of polymer mixtures.

Homogeneous blends may experience liquid-liquid phase separation as the result of either raising or lowering the temperature as suggested in Fig.1.4(21). Generally UCST behaviour is characteristic of systems which mix endothermically while LCST behaviour is characteristic

of exothermic mixing and associated entropy effects. LCST behaviour is rather common in polymer blends while UCST behaviour is usually limited to cases where miscibility is the result of the low molecular weight of the compound, e.g mixtures of oligomers.

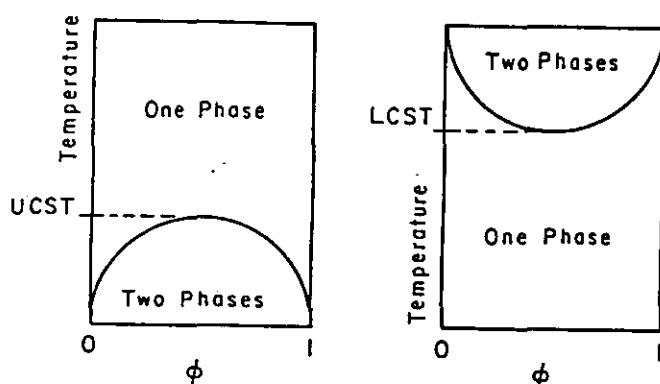


Fig. 1.4(21) Liquid-Liquid Phase behaviour for binary mixtures illustrating systems with an UCST(left) and LCST(right). (MMI Press. Copyright 1982).

1.4.2 Melting Point Depression

Thermodynamic considerations predict that the addition of low molecular weight soluble compounds to crystalline polymers results in melting point depression(23).

The general equation for melting point depression is:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = - \frac{R}{\Delta H_2} \left[\ln \phi_2 + \frac{1}{m_2} - \frac{1}{m_1} \right] + \chi_{12} (1 - \phi_2)^2 \quad (1.3)$$

where

χ_{12} is the interaction parameter
 T_m is the experimental melting point
 T_{m0} is the equilibrium melting point
 ΔH_2 is the heat of fusion of 100% crystalline polymer per mole of repeat unit

V_1 is the molar volume of diluent
 V_2 is the molar volume of polymer repeat unit
 ϕ_2 is the volume fraction of crystalline polymer.

The melting point depression for the above mixture can be determined if we let $m_1 = 1$ and $m_2 \rightarrow \infty$ (m_1 and m_2 are the degree of polymerisation of constituents (1 & 2)). The equation (1.3) reduces to :

$$1/T_m - 1/T_{m0} = -R V_2 / \Delta H_2 V_1 \{ (1 - \phi_2) - \chi_{12} (1 - \phi_2)^2 \} \quad (1.4)$$

Melting point depression data for polymer-diluent systems blends are used to determine the heat of fusion for the crystalline portion of semicrystalline polymers. Heat of fusion of polymer (ΔH_f) can be obtained from the calorimetric data; thus, with the ΔH_2 data of the polymer-diluent systems from equation (1.4) the degree of crystallinity can be determined. For polymer mixtures, m_1 and m_2 both are very large compared with 1, equation (1.4) therefore reduces to:

$$1/T_m - 1/T_{m0} = -R V_2 / \Delta H_2 V_1 \chi_{12} (1 - \phi_2)^2 \quad (1.5)$$

The utility of melting point depression to calculate the interaction parameter was demonstrated by Nishi et al (24, 25). This method, which provides for calculation of χ_{12} can be summarised here.

Equation(1.5) indicates that a negative χ_{12} will yield a melting point depression. With a positive interaction parameter, theory predicts that a melting point elevation would result, as pointed out by Nishi and Wang⁽²⁴⁾. A positive χ_{12} will most probably result in phase separation due to the unfavourable thermodynamic situation of high molecular weight polymer mixtures.

The ratio of χ_{12} and ΔH_2 in equation(1.5) can not be determined simultaneously from calorimetric measurements. Nishi and Wang suggested the following approach to alleviate this experimental problem. The interaction parameter χ_{12} was assumed to be of the form

$$\chi_{12} = B V_1/RT. \quad (1.6)$$

where B is the polymer-polymer interaction energy density. Therefore equation(1.5) reduces to:

$$1/\phi_1[1/T_m - 1/T_{m0}] = - B V_2 \phi_1 / \Delta H_2 T_m \quad (1.7)$$

Recasting the data in the form of variables equal to $(1/T_m - 1/T_{m0})/\phi_1$ and ϕ_1/T_m allows B to be calculated from the slope of a plot of these variables; and the χ_{12} can be determined. This procedure allows one to average experimental data graphically. The calculation of χ_{12} from data on a single blend is possible(with T_{m0} and ΔH_2 predetermined), but not as accurate.

This analysis indicates that a melting point depression of crystalline polymer in a polymer blend implies miscibility and allow for the calculation of the interaction parameter. In using the analysis for melting point depression to predict χ_{12} , it must be recognized that a miscible polymeric diluent in a crystalline polymer can alter the spherulite dimensions. As the melting point is influenced by the

spherulite size, correction for this variable will be necessary to obtain a more accurate χ_{12} value.

If two different crystalline polymers are compatible at a high temperature they will crystallise upon cooling⁽²²⁾. The melting point of each crystalline polymer will be expressed⁽²⁶⁾ as equation(1.8) by extending equation(1.5)

$$\begin{aligned} 1/T_{m1} - 1/T_{m1}^0 &= - R V_1 / \Delta H_1 V_2 \times \chi_{12} \phi_2^2 \\ 1/T_{m2} - 1/T_{m2}^0 &= - R V_2 / \Delta H_2 V_1 \times \chi_{12} \phi_1^2 \end{aligned} \quad (1.8)$$

The melting temperature of each polymer will coincide at a certain volume fraction $\phi_{1,e}$ and the eutectic temperature $T_{m,e}$ will be observed. If $\Delta H_1 / \Delta H_2 = (V_2/V_1)^2$, then

$$\phi_{1,e} = 1/2 \{ 1 + (\Delta H_1 V_2 / R V_1 \chi_{12} [1/T_{m2}^0 - 1/T_{m1}^0]) \} \quad (1.9)$$

Fig. 1.5 shows model calculations for a crystalline-crystalline polymer mixture.

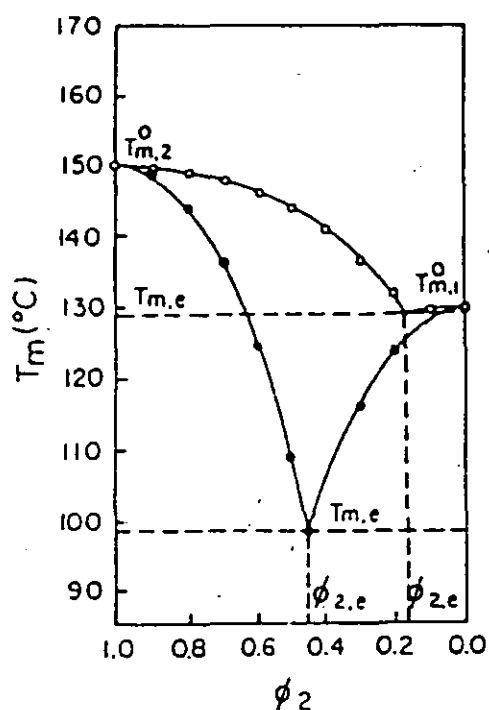


Fig. 1.5(22) Model calculation of equation(1.8) for crystalline-crystalline polymer mixture with a eutectic point $T_{m,e}$, ϕ_e : (o) $T_{C\infty}$ (critical temperature) = 200 °C, $A = 0.5$; (●) $T_{C\infty} = 500$ °C, $A = 0.5$

1.4.3 Crystallinity

In order for crystallinity to occur, the polymer chains must be capable of packing closely together in a regular, parallel array⁽²⁷⁾. Although the chains may be entirely regular in structure, polymers never crystallise completely. The main characteristic of crystalline polymers that distinguishes them from most other crystalline solid is that they are normally only partly-crystalline. This is self-evident from the fact that the density of a crystalline polymer is normally between that expected for the fully crystalline polymer and that of the amorphous polymer⁽²⁸⁾.

The crystallisation of polymers is of enormous technological importance⁽²⁸⁾. Many thermoplastic polymers will crystallise to some extent when the

molten polymer is cooled below the melting point of the crystalline phase. This is a procedure which is done repeatedly during polymer processing, and the presence of the crystals has an important effect upon polymer properties.

There are a number of factors which can affect the rate and extent to which crystallisation occurs for a particular polymer⁽²⁸⁾. They can be processing variables such as the rate of cooling, the presence of orientation in the melt and the melt temperature. Other factors include the tacticity and molar mass of the polymer, the amount of chain branching and the presence of any additives such as nucleating agents.

Many different methods have been proposed for the estimation of crystallinity⁽²⁹⁾. Although none of these methods yields an absolute crystallinity value, any single method within the domain of its validity yields essentially the same relative results as does any other method. Almost any of the methods, therefore, is satisfactory to follow changes in "crystallinity" with respect to structure and physical changes of importance.

1.4.4 Crystallisation and Crystal Growth⁽³⁰⁾

It was believed that the potential of achieving miscible polymer blends in which one or both of the components was crystalline was quite low due to the heat of fusion which would have to be overcome to achieve the necessary thermodynamic criteria for mixing. This generalisation was found to be incorrect as in miscible polymer blends, the crystalline component generally retained the ability to crystallise.

The crystallisation behaviour, for a two-phase system, including crystallisation kinetics, is expected to be equivalent to that of the unblended state. The exception to this is the heterogeneous nucleation which has been observed in several two-phase polymer mixtures (31,32). In miscible blends, where crystallisation has been studied, the crystallisable constituent displays certain characteristics similar to its unblended crystalline state (i.e., crystal lattice); however, several differences do occur. The primary change is observed with the crystallisation kinetics and a secondary change is observed with the lowering of the crystalline melting point as with polymer and low molecular weight diluent mixtures.

The spherulitic growth rate equation (1.10) can be used to study the crystallisation kinetics to predict the effect of a miscible polymer diluent on the crystallisation rate of another component. The spherulitic growth rate equation is

$$G = G_0 \exp(-\Delta F^*/RT) \exp(-4 b_0 \sigma \sigma_e T_{m0} / \Delta H_f (\Delta T) K_b T) \quad (1.10)$$

where

b_0 is monolayer thickness

σ is lateral interfacial free energy

σ_e is interfacial free energy of the chain-folded surface T_{m0} is equilibrium melting temperature

ΔH_f is heat of fusion

$\Delta T = (T - T_m)$

K = Boltzman constant

G is equal to the radial growth of the spherulite and, thus, is dr/dt .

and ΔF^* is representative of the barrier restricting polymer diffusion to the crystallising surface and has been suggested by Hoffman and Weeks⁽³³⁾ to be satisfied by the Williams, Landel, and Ferry equation:

$$\Delta F^* = 4120 T / (51.6 + T - T_g) \quad (1.11)$$

The spherulitic growth rate equation must be made to correct for concentration changes. Therefore equation(1.10) must be multiplied by $(1 - W_d)$, where W_d is the concentration of diluent in the weight fraction.

1.5 METHODS TO DETERMINE POLYMER-POLYMER MISCIBILITY

1.5.1 Definition of Polymer Miscibility

The term "Miscibility" here will be used to refer to polymer-polymer mixtures that do not exhibit gross symptoms of phase separation when blended⁽³⁴⁾. Experimentally, it is common practice⁽³⁵⁾ to look for a single main glass transition temperature or crystalline melting temperature from binary mixtures of polymers as evidence of miscibility.

1.5.2 Thermal Analysis

Thermal analysis is used as a powerful tool for analysing polymer blends. Clampitt⁽³⁶⁾ used the method to examine samples of linear and high pressure polyethylene blends. He showed that, they do not form one crystalline phase, and he resolved the Differential Thermal Analysis (DTA) curve into peaks corresponding to the fusion of the various types of crystals. Inove⁽³⁷⁾ studied the fusion crystallisation behaviour

of melt blends of high density polyethylene and polypropylene using DTA. Ke⁽³⁸⁾ investigated the effect of diluents on melting behaviour of polyethylene using the DTA technique. Sato et.al⁽³⁹⁾ demonstrated multiple peaked thermograms by studying the melting behaviour of linear and branched PE blends. The analytical application of DTA for the identification and evaluation of number of PE blends was studied by Stafford⁽⁴⁰⁾. Nakufuku⁽⁴¹⁾ studied the melting and crystallisation of PE and PP blends under high hydrostatic pressure using DTA. Gupta et.al⁽⁴²⁾ investigated the effect of addition of HDPE on the crystallisation and mechanical properties of PP and glass fibre-reinforced PP. The presence of HDPE and glass fibre in the PP matrix affects its crystallisation characteristics which were studied with the help of Differential Scanning Calorimetry (DSC). Norton et.al⁽⁴³⁾ investigated the conditions of segregated crystallisation of HDPE and LDPE blends using DSC. They found a double multipeak endotherm owing to greatly different melting behaviour of the blend components.

The Differential Scanning Calorimeter has been widely used for assessing the miscibility of small samples of polymer blends⁽⁴⁴⁻⁴⁹⁾. For this reason in the present work this technique was used to determine the miscibility of polyolefin blends by measuring the melting and crystallisation temperatures of polymers and their blends. A miscible crystalline-crystalline polymer blend exhibits a single crystalline melting temperature(T_m) endotherm intermediate between T_m 's of the unblended polymers whereas, an immiscible blend shows two separate crystalline melting temperature endotherms. Therefore a blend with single crystalline melting point is regarded as being a homogeneous system, whereas a blend with two crystalline melting

temperatures is regarded as being a heterogeneous system.

1.5.3 Mechanical Methods

Mechanical Methods for the determination of transitions in polymers and polymers blends are used frequently⁽⁵⁰⁾. The elastic and viscoelastic properties of polymers derived by subjecting polymers to small-amplitude cyclic deformation can yield important information concerning transitions occurring on the molecular scale. Data obtained over a wide temperature range can be used to ascertain the molecular response of a polymer in blends with other polymers. The transitional behaviour of the individual components will be unchanged in a highly phase-separated polymer blend, whereas, in a miscible blend, a single and unique transition corresponding to the glass transition will appear.

Dynamic mechanical analysis⁽⁵¹⁾, used to characterise polymer miscibility, (e.g, shear modulus, loss modulus etc), measures properties associated with non destructive testing. The first workers⁽⁵²⁾ to use the techniques of dynamic mechanical thermal analysis (DMTA) of polymers were Schmieder and Wolf⁽⁵³⁾, using a torsion pendulum. The advent of microprocessor control of instrumentation has led to the availability of commercial systems which are even more expensive but as simple to operate as differential thermal analysis instruments. The dynamic mechanical techniques gives quantitative measurements of modulus changes during first-order thermodynamic transitions (e.g, melting and crystallisation). Resolution of glass transitions (T_g) is rather poor by DSC/DTA, particularly in the case of minor components, and detection of secondary

transitions is almost impossible. The dynamic mechanical method detects molecular relaxation such as the α, T_g process and can frequently measure secondary (β/γ) transitions quantitatively. Theoretically the measurements are made by applying a sinusoidal stress to a perfectly elastic solid. The deformation, and hence the strain, occurs exactly in-phase with the stress. In extension or bending after allowance for the geometrical factors the dynamic Young's modulus (E^*) is given basically as (stress amplitude)/(strain amplitude). In shear deformation the dynamic rigidity modulus (G^*) is obtained. The storage component of the dynamic Young's modulus (E') is thus (amplitude of the in-phase component of stress)/(strain-amplitude), and loss component (E'') is (amplitude of the out-of-phase component of stress)/(strain amplitude). The relationships are summarised in the Argand diagram (Fig. 1.6), from which it can also be seen that the loss-tangent ($\tan \delta$) = E''/E' . This term is dimensionless and is the ratio of energy loss (dissipated as heat) per cycle to the energy stored and hence recovered per cycle.

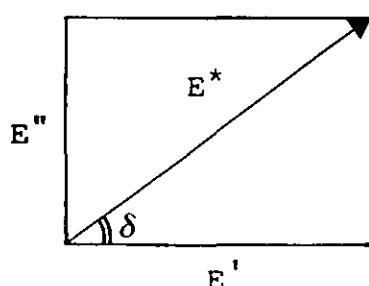


Fig. 1.6⁽⁵²⁾ Definition of dynamic Storage E' and loss E'' moduli and δ under sinusoidal loading.

1.6 RHEOLOGY OF POLYOLEFIN BLENDS

1.6.1 General

Published⁽⁵⁴⁾ information on the rheology of polymer blends began to appear shortly before 1960 and was reviewed by Plochocki⁽⁵⁵⁾. At that time, and even now, persons wanting to estimate blend viscosities have used simple interpolative rules, such as the oldest of them, the Arrhenius rule, given below:

$$\log \eta_B = w_1 \log \eta_1 + w_2 \log \eta_2 \quad (1.12)$$

or

$$\eta_B = \eta_1^{w_1} + \eta_2^{w_2}$$

where η is the viscosity w_1 and w_2 are weight fractions of the individual components, and B stands for the components and their blend (originally, a true solution of simple liquid). Heitmiller, et al.⁽⁵⁶⁾ suggested an inverse, volume-weighted rule:

$$1/\eta_B = \eta_1/\phi_1 + \phi_2/\eta_2 \quad (1.13)$$

Hayashida et al.⁽⁵⁷⁾ proposed an equation, which has been found to describe the viscosity data better in some systems. This equation is similar to equation (1.13) in its form but with the weighting factors interchanged:

$$1/\eta_B = f_2/\eta_1 + f_1/\eta_2 \quad (1.14)$$

where f_1 and f_2 represents any type of fractions, through the use of weight fractions appears to give best interpolation.

Dobrescu⁽⁵⁸⁾ suggested that a simple additivity model could also be used when the intermolecular interactions

between the two polymers are identical to interactions among molecules of each of the polymers, therefore:

$$\eta_B = \phi_1 \eta_1 + \phi_2 \eta_2 \quad (1.15)$$

where the terminology is identical to that of equation(1.13).

1.6.2 Characteristics⁽⁵⁵⁾

The main rheological characteristics of molten polyolefins consist of rate-or stress-dependent viscosity and elasticity . Little is known about the tensile melt viscosity of polyolefins in spite of the importance this characteristic has in the development of blow moulding grades of blends and in the formation of fibrillar blend texture in convergent flows.

The viscosity of molten polyolefins and the polymers blended with them have been studied extensively, including a comprehensive interlaboratory programme of investigation, using capillary or rotational viscometers and laboratory mixers. However, the form of presentation, with few exceptions, does not render them applicable for engineering use. The most appropriate form for this application seems to be the logarithmic parabola approximation for the viscosity curve:

$$\log \eta = B_0 + B_1 \log \dot{\gamma} + B_2 \log^2 \dot{\gamma} \quad (1.16)$$

where η is melt viscosity in poises and $\dot{\gamma}$ is shear rate in reciprocal seconds. The term B_0 is related to a standardized viscosity at $\dot{\gamma}^0 = 1 \text{ sec}^{-1}$, that is, $\eta^0 = 10^{B_0}$, and B_1 is a measure of the shear rate dependence of the viscosity corresponding to the power law

exponent when $B_2=0$. The approximation is usually carried out by applying the least-squares regression technique to the experimental data. One may easily extend the approximation to include the effects of temperature, hydrostatic pressure, and even composition by introduction of additional terms accounting for these effects and their interactions.

1.6.3 Predicting The Rheological Characteristics of Polyolefin Blends

The standardised⁽⁵⁵⁾ measurements of melt viscosity and elasticity are obviously convenient for predicting the rheological characteristics of a blend of selected composition from known characteristics of components. In order to perform this task some reliable blending law has to be available. The attempts undertaken in this direction were discussed in section(1.6.1).

In the case⁽⁵⁵⁾ of polyethylene and polyethylene wax blends only simple linear or logarithmic rules are available for use with polyolefins blends over the range of viscoelastic characteristics of interest to process and product engineers. The logarithmic mixing rule, introduced in the late 1950s for guidance in blending low density polyethylenes differing in Melt flow Index, is illustrated in Fig.1.7⁽⁵⁹⁾.

Bersted et al.⁽⁶⁰⁾ prefer the use of an Arrhenius type of equation(1.12) for estimating the viscosity of blends of HDPE and LDPE. Alle et al.⁽⁶¹⁾ prefer the use of volume fraction instead of weight fractions for estimating the viscosity of a PP-HDPE blend. The utility of equation (1.12) is however, limited to binary systems in which the actual mixture viscosities change monotonically with composition.

Shenoy et al.(62) demonstrated a method for estimating the rheogram of polymer blends from the melt flow index of individual components. But this method would not be effective in the case of blends produced with components whose shear-thinning behaviour changes drastically, as in the case of low density polyethylene and high density polyethylene blends where it is known that the rate of change of viscosity with shear rate of the branched and linear polyethylenes is radically different. This is also true for PP and HDPE blends as their shear thinning characterisation are also quite different.

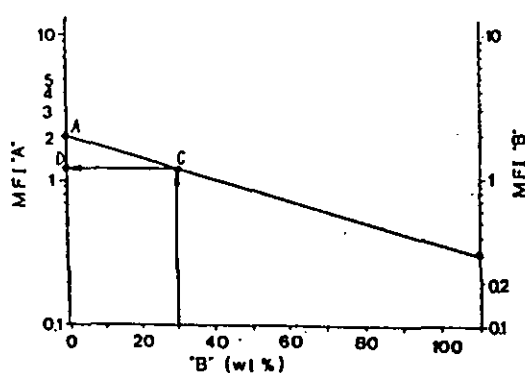


Fig. 1.7 Technical mixing rule employed in LDPE blending to obtain an A B composition of selected MFI values(59).

In the case of polyethylene blends, it has been found that none of the equations discussed above is able to give a good estimate of the blend viscosity. Thus Dobrescu(58) proposed the following equation to describe the dependence of the blend viscosity on the viscosities of the components and composition:

$$\log \eta = \phi_1 \log \eta_1 + \tau \phi_1 \phi_2 + \phi_2 \log \eta_2 \quad (1.17)$$

where η , η_1 and η_2 are viscosities of the blend and its components respectively at constant shear stress, ϕ_1 and ϕ_2 are the volume fraction of components, τ stands for "packing-coefficient" which can be evaluated from equation (1.17) using the viscosities of the components, their volume fractions and the experimental viscosity of just one blend 0.5/0.5. $\tau \simeq 0$ for HDPE/HDPE (two different molecular weights) blends and $\tau \gtrless 0$ for HDPE/LDPE blends, depending on component viscosities and their ratio.

Dobrescu⁽⁶³⁾ has proposed another improved equation in the form of:

$$\log \eta = \phi_1^2 \log \eta_1 + 2\tau \phi_1 \phi_2 (\log \eta_1 \log \eta_2)^{1/2} + \phi_2^2 \log \eta_2 \quad (1.18)$$

The equation (1.18) has advantage over equation (1.17) as the parameter τ can be positive or negative and sign change is not correlated with the nature of the blend components in equation (1.17). Equation (1.18) ensures positive values of τ for all blends investigated. For HDPE/LDPE, the parameter τ in the equation (1.18) may be correlated with component viscosities using an equation of the form:

$$\tau = 0.53613 + 0.725375 - 0.21682 S^2 \quad (1.19)$$

where

$$S = \log \eta_{\text{HDPE}} / \log \eta_{\text{LDPE}}$$

The agreement between calculated and experimental values is satisfactory. Good results have been obtained for HDPE/HDPE (two different molecular weights), HDPE/LDPE and LDPE/LDPE (two different molecular weights) blends.

CHAPTER 2

EXPERIMENTAL TECHNIQUES

2.1 INTRODUCTION

This section deals separately with the experimental techniques used in each chapter. When an experimental method is mentioned for the first time; a full description is given.

2.2 EXPERIMENTAL TECHNIQUES USED IN CHAPTER 3

2.2.1 Blend Preparation

Pellets of Ethylene-Vinyl Acetate(EVA) containing 18% VA and Low Density Polyethylene(LDPE) were mixed thoroughly in a plastic bag, and then blended in "Ridcon" single screw extruder at 200 °C to give a blend of EVA with 3.5% VA content. The extrudate was hauled-off through a water cooling bath and pelletized in a granulator. This procedure was carried out twice in order to obtain a good mixing. The same treatment was applied to EVA copolymer in order to give the same thermal and shear history as the blend.

2.2.2 Film Production

Films of EVA blend and EVA copolymer were produced on the 25 mm Betol extruder; the settings were as follows:

Temperature:

Zone 1 = 160 °C

Zone 2 = 170 °C

Zone 3 = 180 °C

Head = 190 °C

Die = 200 °C

Screw Speed = 18 RPM

Blow up ratio = 1.25

2.2.3 Melt Flow Index

This test is widely used in the plastics industry to determine the rate of extrusion of molten polymer through an extrusion plastometer at a standardised value of melt temperature, load, die length and die diameter(64).

The Davenport melt flow indexer(Model III)(65) was used. The determination of Melt Flow Index(MFI) of the samples was carried out according to the Method 720 A of BS 2782(1979)(66). The die used had a length 8 mm and an internal diameter of 2.095 mm. The test temperature was set at 190 °C, a load of 2.16 kg and extruder mixed samples were used to determine the MFI of the EVA's. The melt flow index was calculated from the following equation

$$MFI = \frac{10 W_e}{t_e} \quad (2.1)$$

where MFI = melt flow index (g/10 min)
 W_e = average cut-off weight (g)
 t_e = extrusion time per cut-off (mins)

2.2.4 Infra-red Spectrography

Most polymers absorb electromagnetic radiation in the wavelength range 1-50 μm , i.e. in the infra-red region. This is because the molecules undergo transitions between vibrational states of different energies causing both the absorption, and emission of radiation⁽⁶⁷⁾. These absorption spectra are widely used in both qualitative and quantitative analysis. They are particularly valuable in the qualitative analysis of polymers and compositions containing polymers, since the characterisation of these materials is often difficult by the more usual chemical and physical methods⁽⁶⁸⁾.

The infra-red spectra of the EVA blend and EVA copolymer films were obtained using a Pye Unicam SP3-200 infra-red instrument.

2.2.5 Thermal Analysis

Differential Scanning Calorimetry(DSC) is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature programme⁽⁶⁹⁾.

The Du Pont 910 DSC system was used, with a Du Pont 990 thermal analyser(programmer/recorder) and 990 mechanical accessory for programmed cooling. Thermograms of extruded samples were obtained by sealing them in aluminium pans. An empty aluminium pan was used as a reference. The first crystalline melting thermograms were obtained by heating the sample from 20 to 200 °C at a programmed rate of 10 deg C/min with

a sensitivity of 5 mv/cm. The samples were then cooled from 200 °C to 20 °C, at a cooling rate of 5 degree C/min, to obtain the crystallisation thermograms. The second melting thermograms were obtained using the same heating conditions as the first. All the measurements were under a nitrogen atmosphere at a flow rate of 70 ml/min. Temperature calibration of the instrument was made with indium ($T_m = 156.5$ °C) and tin ($T_m = 231.9$ °C). The crystalline melting point and crystallisation temperature were read from the thermograms obtained.

2.2.6 Crystallisation

A light microscope equipped with a heating stage was used. Extruded samples of EVA and EVA/LDPE blend (2-3 mg) were melted on a hot stage and pressed between a slide and a cover slip. These were then transferred to the microscope hot stage (120 °C) and cooled slowly at 1 degree C/min.

2.2.7 Flow Properties

The Davenport capillary extrusion rheometer was used to investigate the melt behaviour of EVA and EVA/LDPE blend. In this apparatus the polymer to be tested is heated in a barrel and then forced through a capillary die (70). From this, it is usual to assume Newtonian flow and thereby calculate the shear rate from the Newtonian flow expression

$$\dot{\gamma} = \frac{4Q}{\pi R^3} \quad (2.2)$$

where $\dot{\gamma}$ is the shear rate at the die wall (s^{-1})

Q is the volumetric flow rate (m³/s)
 R is the die radius

The shear stress (τ) can be calculated from the pressure drop (P), across the die

$$\tau = \frac{P R}{2 L} \quad (2.3)$$

where L is the die length

This leads to a definition of apparent viscosity as the ratio of shear stress to shear rate

$$\tau = \frac{\pi P R^4}{8 L Q} \quad (2.4)$$

The pressure drop, P, in the above expression is the pressure drop due to shear flow along the die. Since the pressure transducer is used to record the pressure drop, then it also picks up the pressure losses at the die entry. To overcome this problem the Bagley correction is applied using a combination of long die (length = 20 mm, and diameter = 2 mm), with an orifice die (length = 0 and diameter = 2 mm), thus

$$\tau = \frac{(P_L - P_o) R}{2 L} \quad (2.5)$$

The temperature was set at 190 °C, and number of different piston speeds used to determine shear stress, shear rate and shear viscosity at the different speeds.

2.2.8 Measurement of Spreading Coefficient

Spreading coefficient (SC) for liquid on a solid surface may be simply determined from the maximum height (h_m) of a sessile drop, as was shown by Padday⁽⁷¹⁾ by the relationship:

$$SC = - 1/2 \rho g h_m^2 \quad (2.6)$$

where

ρ is the density of liquid

g is the gravitational constant

In this experiment a travelling microscope was used to measure the maximum height of water on the surfaces of EVA films to measure their surface tension i.e. the wettability of the film surfaces.

2.2.9 Mechanical Properties

2.2.9.1 Tensile Stress-Strain

The stress-strain⁽⁷²⁾ measurement is commonly made in tension, that is by stretching the material. A tensile stress is thus applied, defined for a section of uniform cross-section area A_0 by:

$$\sigma_1 = \frac{F_1}{A_0} \quad (2.7)$$

where σ_1 is tensile stress

and F_1 is tensile force

If this tensile stress causes deformation to length l_1 , the tensile strain ϵ is defined as:

$$\epsilon = \frac{l_1 - l_0}{l_0} \quad (2.8)$$

as the material stretches so its dimensions orthogonal to the axis of applied force decrease and thus the area of cross-section decreases. However, for experimental convenience most tensile strength calculations are based on the original cross-section (A_0) since this is easily measured before the test begins.

By measuring the stress to the ultimate; i.e. measuring the force until the material breaks tensile strength(ultimate tensile stress) is conveniently defined as:

$$\sigma = F/A_0 \quad (2.9)$$

where F is force at failure
and A_0 is area of cross-section

The elongation at break can be expressed as:

$$\epsilon = \frac{l - l_0}{l_0} \times 100 \text{ percent} \quad (2.10)$$

where l is the length at failure.

2.2.9.2 Test Methods

Tensile stress at yield and break, elongation at yield and break were measured according to BS 2782, Method 326(1977) Part 3⁽⁷³⁾ on a JJ tensile testing

machine (type T 5002), at a speed of 500 mm/min. The specimens were punched out from the blown films. Test were carried out at 22 °C.

2.3 EXPERIMENTAL TECHNIQUES USED IN CHAPTER 4

2.3.1 Blend Preparation

Blends were prepared on the Baker Perkins (MPC/V30) twin-screw extruder compounder. The screws of this extruder consist of various sections that can be fitted together to give the configuration required in order to obtain a good mix.

A severe mixing screw configuration was used as follow:

F1.5/F1.5/F1/F1/FSS/9X60°P/3X90°P/OP/F1.5/F1.5/F1.5/CB

where:

- F = Feed screws
- FSS = Feed Screw Spacer
- P = Paddles
- OP = Orifice Plugs
- CB = camelback discharge screws

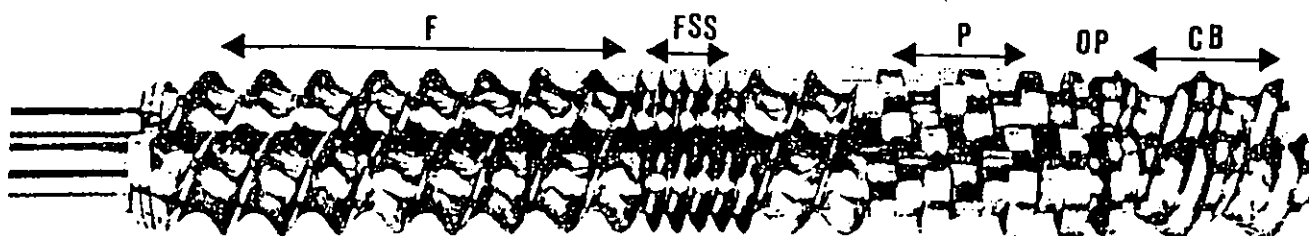


Fig. 2.1 Example of screw configuration

and the temperatures were set as:

Zone 1 = 190 °C, Zone 2 = 200 °C, Zone 3 = 210 °C, and
Zone 4 = 220 °C.

The extrudate was hauled-off through a water cooling bath and pelletized in a lace cutter(Fig. 2.2).

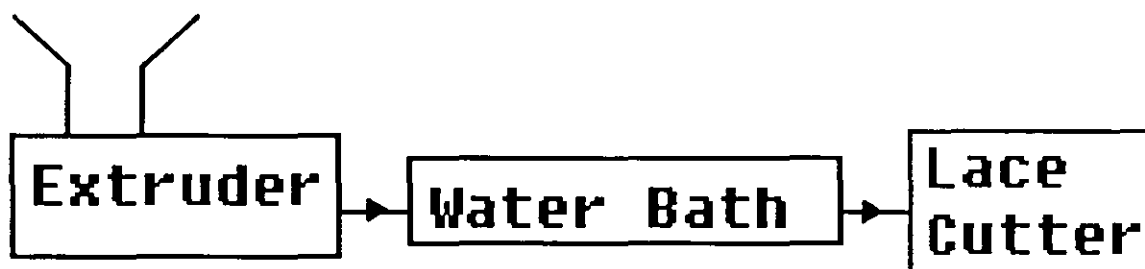


Fig. 2.2 Schematic drawing of mixing line.

2.3.2 Melt Flow Index

The melt flow indices of samples were measured according to section 2.2.3.

2.3.3 Thermal Analysis

Thermograms of blends were obtained using the Differential Scanning Calorimeter(DSC) as described in section 2.2.5. The sample weights used were 8 mg throughout.

2.3.4 Samples preparation

The Negri Bossi NB55 Injection moulding machine was used to produce dumbbell tensile test specimens of the binary blends of LLDPE/HDPE with MFI(1.0/1.0) and ternary blends of LLDPE/HDPE/LDPE with MFI(1.0/1.0/2.62).

The temperature settings were as follows:

Zone 1 = 170, Zone 2 = 200, Zone 3 = 210 and Zone 4 = 220 °C.

Mould temperature = 55 °C.

2.3.5 Mechanical Properties

Tensile strength measurements were made on the binary blends of LLDPE/HDPE with MFI(1.0/1.0) and ternary blends of LLDPE/HDPE/LDPE with MFI(1.0/1.0/2.62) according to BS 2782, Method 320 B(1976) (74) on a JJ tensile testing instrument(type T 5002) at a speed of 100 mm/min using injection moulded samples at room temperature.

2.4 EXPERIMENTAL TECHNIQUES USED IN CHAPTER 5

2.4.1 Blend Preparation

Blends were prepared in the twin-screw Baker Perkins extruder(MPC/V30) as described in section 2.3.1 with the following temperature settings:

Zone 1 =170, Zone 2 = 180, Zone 3 = 190, and Zone 4 = 200 °C.

2.4.2 Melt Flow Index

The melt flow indices of samples were measured according to the section 2.2.3.

2.4.3 Sample Preparation

2.4.3.1 Injection Moulding

The Negri Bossi NB 55 Injection moulding machine was used to produce plaque specimens. Mouldings were obtained at mould temperatures 20 °C and 50 °C. The machine temperatures were set as follow:

Zone 1 = 170, Zone 2 = 190, Zone 3 = 200, and Zone 4 = 210 °C.

2.4.3.2 Film Production

Blown films at slow and fast cooling rate were made on the 25 mm Betol extruder.

The settings were as follows:

Blow up ratio = 2.5

Screw speed = 40 rpm

Temperature:

Zone 1 = 160, Zone 2 = 170, Zone 3 = 180, Head = 190, and die = 200 °C.

2.4.4 Thermal Analysis

Thermograms of blends of extruded materials, injection moulded samples and films were obtained as described in section 2.2.5. The samples weight used were 8 mg throughout with a sensitivity of 5 mv/cm.

2.4.5 Mechanical Properties

Tensile measurements were made on the injection moulded samples and blown films according to BS 2782, Method 320 B(1976) (74) and Method 326 part 3(1977) (73) respectively. Tests were carried out on a JJ tensile testing machine (type T 5002), at speed of 100 mm/min. The specimens were punched out from the injection moulded plaques and blown films.

2.5 EXPERIMENTAL TECHNIQUES USED IN CHAPTER 6

2.5.1 Blend Preparation

Pellets of PP(Profax 6824) and LLDPE(Escorene) and MFI(0.32/2.0 respectively) were melt mixed in "Ridcon" single screw extruder at 230 °C as was described in section 2.2.1.

With the availability of the extruder compounder the pellets of PP(Profax 6824)/LLDPE(Escorene), MFI(0.32/1.0); PP(Profax 6824)/LLDPE(Dowlex), MFI(0.32/1.5); PP(Himont)/Escorene(LLDPE), MFI(1.5/2.0); and PP(Himont)/VLDPE(Norsoflex), MFI(1.5/12) were melt mixed in the Baker Perkins twin-screw extruder at 230 °C as was described in section 2.3.1.

2.5.2 Melt Flow Index

The melt flow indices of samples were measured according to the section 2.2.3 at several temperatures.

2.5.3. Density measurements

Density is defined as mass per unit volume (at defined temperature). In crystalline polymers density measurements can be used to determine the degree of crystallinity on the basis that the crystallisation of a polymer from the melt is accompanied by reduction in specimen volume due to an increase in density compared with the molten or non-crystalline polymer⁽⁷⁵⁾. The technique relies upon the difference in densities of completely crystalline polymer and that of the completely amorphous material. Making same assumption this method can yield both the volume fraction of crystals ϕ_c and the mass fraction X_c from measurement of sample density d .

If V_c is the volume of crystal and V_a the volume of amorphous material then the total specimen volume, V is given by⁽⁷⁵⁾:

$$V = V_c + V_a \quad (2.11)$$

similarly the mass of the specimen W is given by:

$$W = W_c + W_a \quad (2.12)$$

where W_c and W_a are the masses of crystalline and amorphous material in the sample respectively. Since density d is mass per volume then it follows from equation (2.12) that

$$dV = d_c V_c + d_a V_a \quad (2.13)$$

substituting for V_a from equation 2.11 into equation 2.13 and rearranging leads to

$$V_c/V = d - d_a/d_c - d_a = \phi_c \quad (2.14)$$

Since ϕ_c is equal to the volume of crystals divided by the total specimen volume. The mass fraction X_c of crystals is similarly defined as

$$X_c = W_c/W = d_c V_c/d_v \quad (2.15)$$

and combining equation (2.14) and (2.15) give

$$X_c = d_c/d(d - d_a/d_c - d_a) \quad (2.16)$$

where

- X_c = degree of crystallinity
- d_c = density of crystalline fraction
- d_a = density of amorphous fraction
- d = density of the sample.

Densities of crystalline and amorphous materials can be obtained from the literature (densities of completely amorphous and completely crystalline polyethylene are 0.853 and 1.004 g/cm³ respectively; the densities of completely amorphous and completely crystalline polypropylene are 0.853 and 0.946 g/cm³ respectively) (76) and the density of the sample can be obtained by density gradient column.

The Davenport density gradient column was used to measure the density of Escorene (LLDPE, MFI = 1.0), Profax (pp, MFI = 0.32), and their blends according to BS 2782 Method 620 D (1980) (77). A density column was

prepared in the range of 0.89-0.93 g/ml. using the mixture of isopropanol/water(density of 0.79/1.00 g/ml). The extruded melt flow index samples cooled in still air were used to determine the densities of components and their blends.

2.5.4 Infra-Red Spectroscopy

The blends Profax(PP)/Escorene(LLDPE, MFI = 1.0) (25%, 30%, 60%, and 80% LLDPE content) were dissolved in the heated mixture of toluene/xylene(50/50). The infra-red spectra of the cast film blends were obtained using a Pye Unicam SP3-200 infra-red instrument.

2.5.5 Thermal Analysis

The Du Pont 910 Differential Scanning Calorimeter(DSC) was used, as described in section 2.2.5. The following programme was used:

heating at 10 degree C/min to 200 °C;
hold at 200 degree C for 5 minutes;
cool at 5 degree C/min to 20 °C;
reheat at 10 degree C/min to 200 °C.

A range of cooling rates(10, 50, and 50 °C) were also used for the blends of Profax(PP)/Escorene(LLDPE), MFI(0.32/2.0), containing 40, 60 and 80% LLDPE.

2.5.6 Dynamic Mechanical Thermal Analysis

The dynamic mechanical properties of Profax(PP), Escorene(LLDPE, MFI = 2.0), and their blends were measured using Polymer Laboratories-Dynamic Mechanical

Thermal analyser(PL-DMTA) instrument. The bar pieces cut from tensile samples were used. Their geometry factors (K) were calculated using equation (2.17) and then fed into the PL-DMTA instrument.

$$K = - \log 2 w/100 \times (t/l)^3 \quad (2.17)$$

where t = sample thickness (m)
 w = sample width (m)
 l = sample free (unclamped) length (m)

The programmed range of -160 to 160 $^{\circ}\text{C}$ with a heating rate of 4 degree C/min and frequency of 1 Hz were applied.

2.5.7 Crystallisation

A light microscope equipped with a heating stage was used. Extruded samples of Profax(PP) and Escorene(LLDPE, MFI = 2.0) and their blends(2-3 mg) were melted on a hot stage and pressed between a slide and a cover slip. These are transferred to the microscope hot stage(135 $^{\circ}\text{C}$) and cooled slowly at 1 degree C/min .

2.5.8 Flow Properties

The Davenport capillary extrusion rheometer was used(as described in section 2.2.7) to investigate the melt behaviour of Profax(PP) and Escorene(LLDPE, MFI = 2.0) and their blends at 190 , 210 and 230 $^{\circ}\text{C}$.

2.5.9 Tensile strength

Tensile strengths of Profax(PP) and Escorene(LLDPE, MFI = 2.0) and blends were measured with JJ tensile testing instrument(type 5002) according to BS 2782, Method 320 B(1976) (74) at a speed of 100 mm/min using injection moulded samples at room temperature.

CHAPTER 3

COMPARISON OF ETHYLENE-VINYL ACETATE COPOLYMER WITH ETHYLENE VINYL ACETATE / LOW DENSITY POLYETHYLENE BLEND

3.1 INTRODUCTION

Since the beginning of the '60's when ethylene-vinyl acetate(EVA) become available, the demand for EVA copolymer has increased significantly⁽⁷⁸⁾. Small amounts of vinyl acetate introduce additional irregularity into the polyethylene structure, reducing crystallinity and crystalline melting point, polarity is increased and thereby toughness and flexibility are improved. These copolymers are used for tough films⁽⁷⁹⁾.

Physical blending is less expensive and time consuming, compared with chemical modification. In this chapter EVA made by copolymerisation was compared with EVA/LDPE blend of the same overall constitution.

EVA copolymer containing 18% VA was melt mixed with LDPE to give a blend of EVA with 3.5% VA content. This blend was compared with EVA copolymer containing 3.5% VA.

3.2 MATERIALS

The LDPE used was Shell 25-020 FJ; EVA containing 3.5% VA was Bayer V22 H864; and EVA containing 18% VA was

ATO 1020 UNS. Some of the materials characteristics are given in Table 3.1.

Table 3.1

Property	LDPE	EVA(18% VA)	EVA	EVA/LDPE (3.5 % VA)
Melt Flow Index (g/10 min), 190 °C	2.26	2.70	2.00	2.76
Density(g/cm ³) ⁺ ASTMD 1505	0.921	0.940	0.922	--

+ Data from the manufacturers

3.3 RESULTS AND DISCUSSION

3.3.1 Infra-red Spectrum

The infra-red spectra of EVA copolymer and EVA/LDPE blend from blown films are shown in Figs. 3.1 and 3.2 respectively. There was no absorption band at 16.5 μm (670 cm^{-1}) for VA as is suggested by Haslam⁽⁸⁰⁾ to calculate absolute level of VA. The ratio of vinyl acetate to ethylene was determined at 1029/729 cm^{-1} (see Table 3.2). Although it was not possible to determine the absolute level of VA in EVA/LDPE and EVA copolymer, the ratio obtained and their spectra are very similar.

Table 3.2 Ratio of Vinyl acetate/Ethylene

Polymer	VA/PE at 1029/729 cm^{-1}
EVA/LDPE blend	0.19
EVA copolymer	0.20

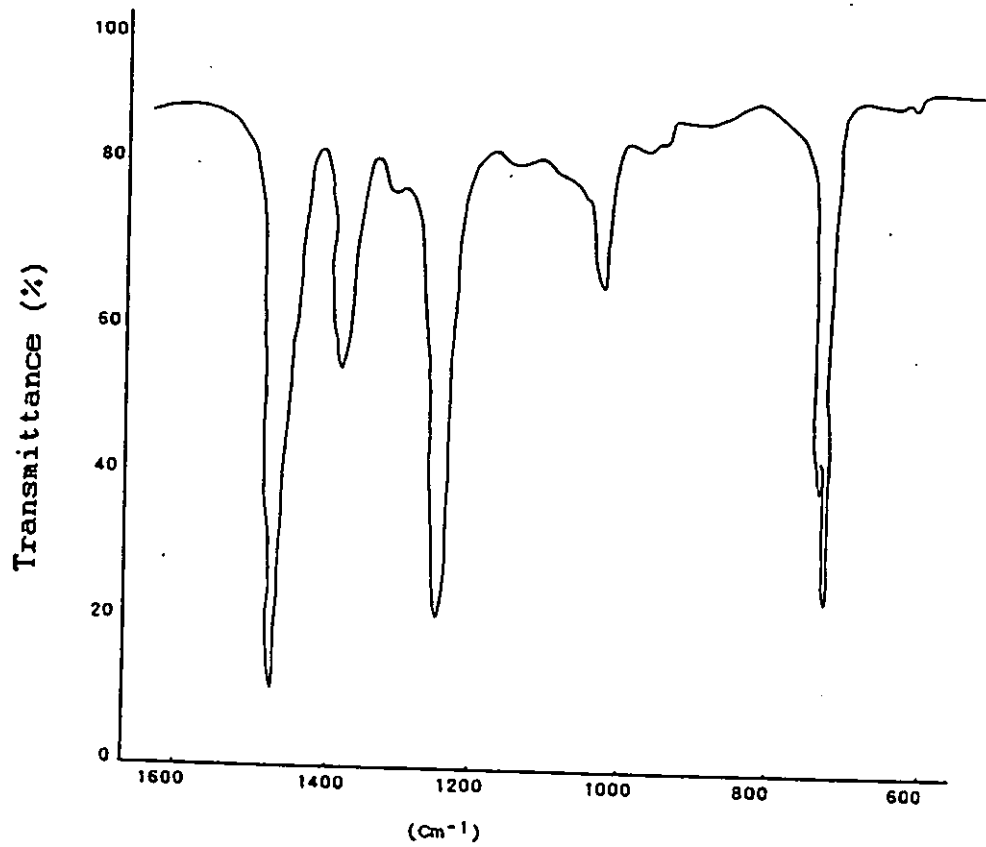


Fig. 3.1 Infra-red spectrum of EVA(3.5% VA content)

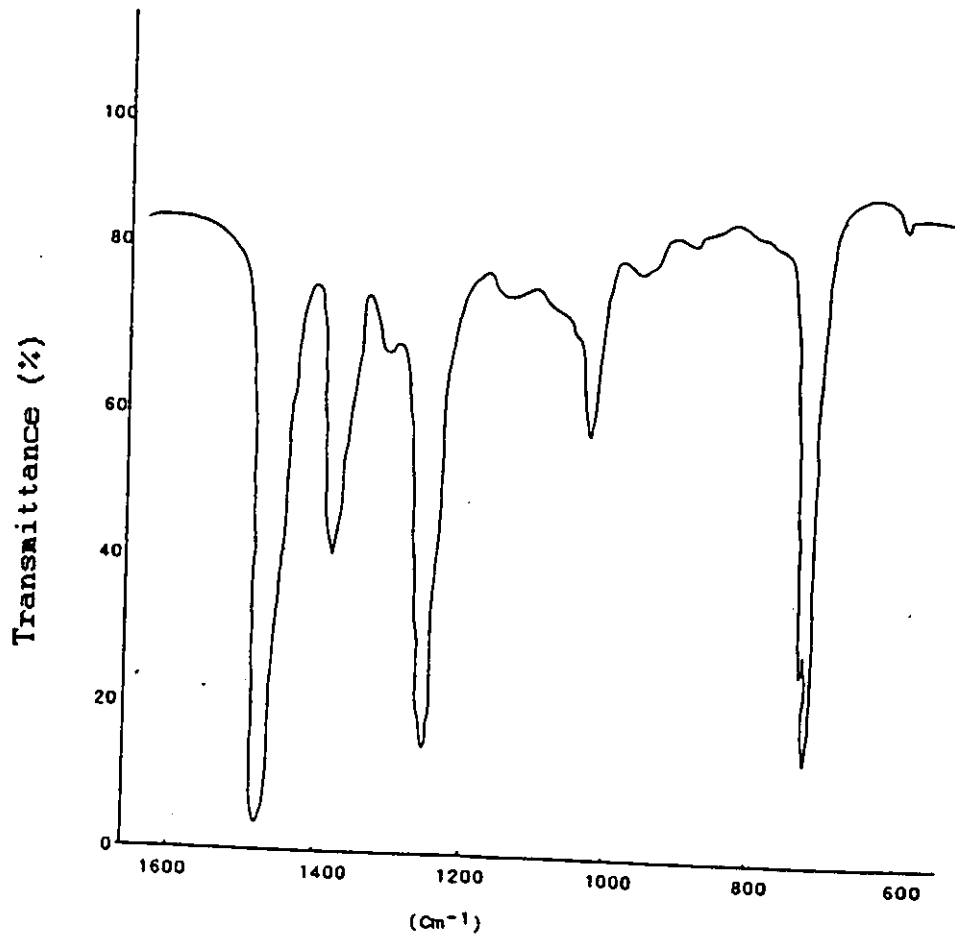


Fig. 3.2 Infra-red spectrum of EVA/LDPE Blend(3.5% VA content).

3.3.2 Thermal Analysis

Thermograms obtained by DSC of LDPE, EVA copolymer(3.5% VA content) and EVA copolymer(18% VA content), and EVA/LDPE(3.5% VA content), are shown in Figs 3.3 to 3.6. The thermogram of LDPE shows a single melting and crystallisation peak. Thermograms of both copolymers show single melting and crystallisation peaks, indicating the existence of one type of crystal species. Their melting and crystallisation temperatures are summarised in Table 3.3. The results show a shift in melting peak of EVA's copolymer, as expected, the PE melting point moving to lower temperature with VA content, and the shift is greater as the VA content increases i.e EVA(18% VA content). These results also show a shift in crystallisation temperature of EVA copolymers.

Table 3.3 Thermal Analysis of EVA and the Blend

Polymer	First melting temp. °C	Second melting temp. °C	Crystalli- sation temp. °C
LDPE	111.0	110.0	94.0
EVA(18% VA)	83.0	82.5	64.0
EVA/LDPE (3.5% VA)	113.0 85.5	108.5 85.0	82.9 64.0
EVA copolymer (3.5% VA)	106.5	104.2	91.5

The thermograms of EVA(3.5% VA content) also show a peak at 122.5 °C(The manufacturers, Bayer, was asked about this peak, but declined to make any comment). As it falls in the range of the melting point of linear

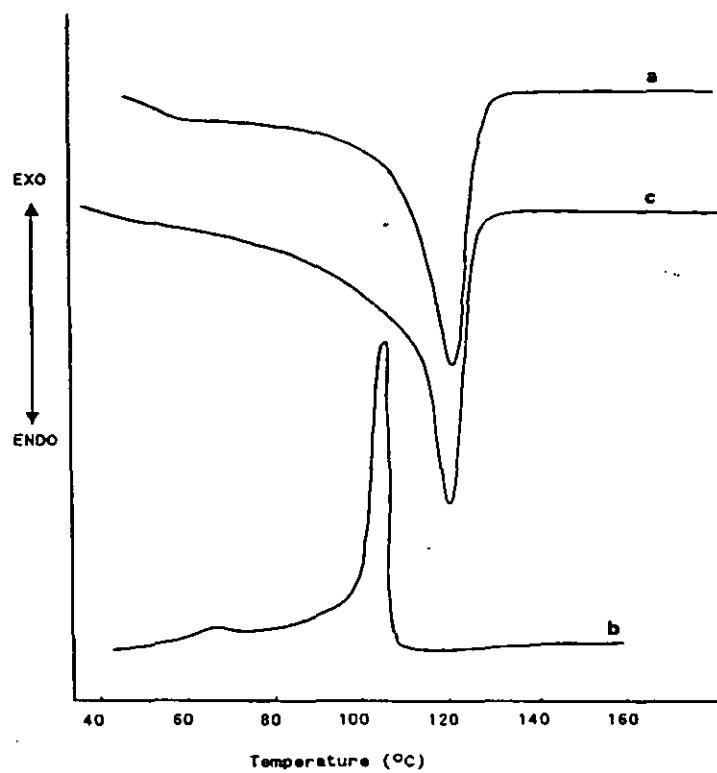


Fig. 3.3. Thermograms of LDPE. (a) first heating, (b) cooling and (c) second heating.

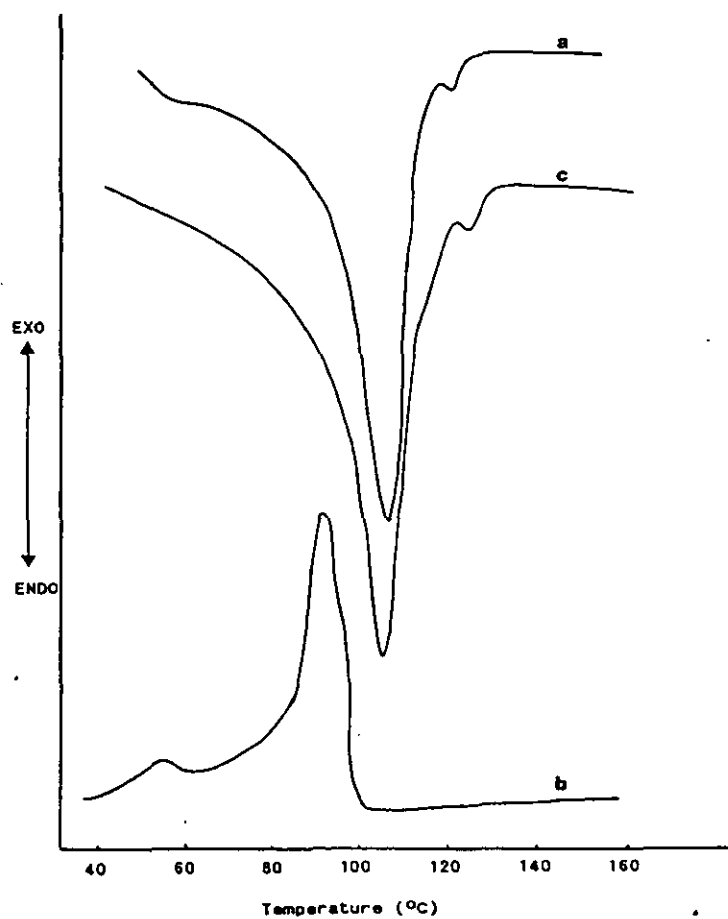


Fig. 3.4. Thermograms of EVA copolymer (3.5% VA content). (a) first heating, (b) cooling and (c) second heating.

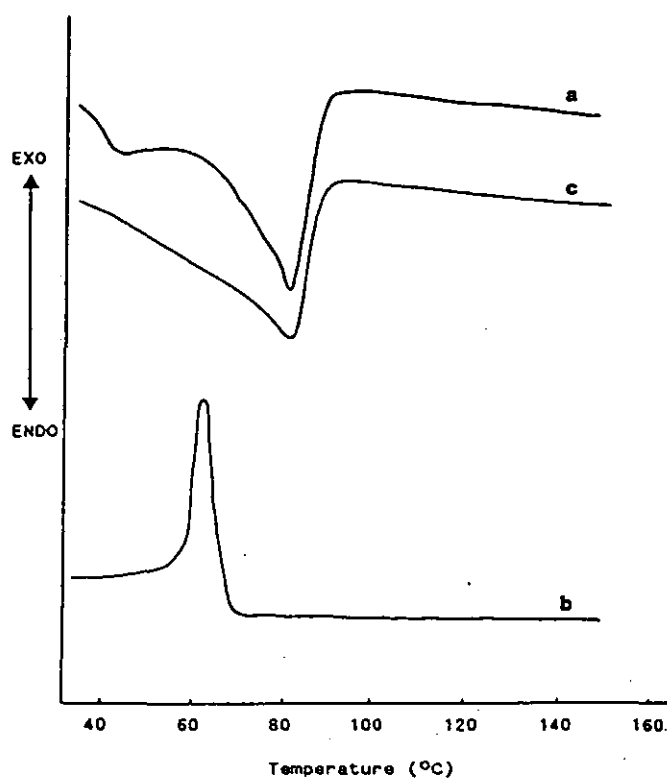


Fig. 3.5. Thermograms of EVA copolymer(18% VA content). (a) first heating, (b)cooling and (c) second heating.

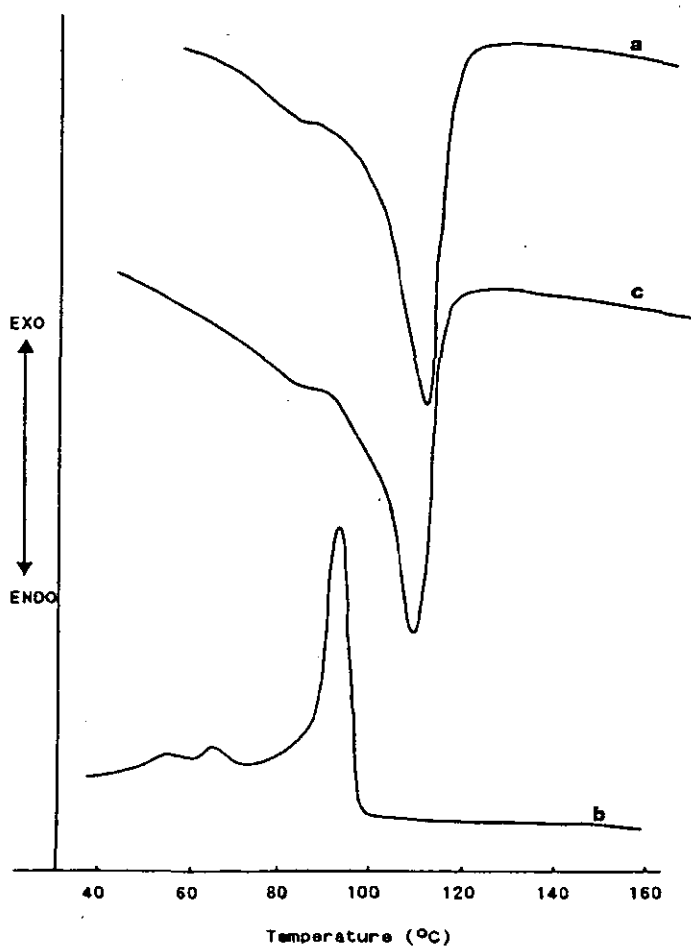


Fig. 3.6. Thermograms of EVA/LDPE(3.5% VA content). (a) first heating, (b)cooling and (c) second heating.

low density polyethylene(LLDPE), it suggests that the sample might contain a small quantity of such material.

Comparing the thermograms of EVA(3.5% VA content) and the physically blended EVA/LDPE which also contains 3.5% VA, the EVA copolymer shows a single melting and crystallisation temperature, as was mentioned earlier, whereas EVA/LDPE blend shows two distinct melting and crystallisation peaks attributed to LDPE and EVA. This indicates that EVA and LDPE have two types of crystal species, and each of them crystallises separately. There was no detectable shift in melting point of LDPE in the EVA/LDPE blend, which suggests there is no interaction between EVA and LDPE in EVA/LDPE blend. These results, therefore suggest that EVA and LDPE made by physical blending are "incompatible".

The crystallisation temperature of LDPE in EVA/LDPE blend as expected decreases, whereas there is no change in crystallisation temperature of EVA.

There is a peak at 55 °C in LDPE, EVA/LDPE blend and EVA copolymer thermograms which could not be identified. There is a shift in melting peaks for the EVA copolymer, and EVA/LDPE blend for the second time heating, which could be due to different crystallisation history between the first cooling cycle(after extruding) and the second one, obtained by DSC.

3.3.3 Crystallisation

The optical micrographs of EVA copolymer(3.5% VA content) and EVA/LDPE blend(3.5% VA content) in Figs 3.7 and 3.8 clearly show that the texture of EVA copolymer is coarser than that of the EVA/LDPE blend.

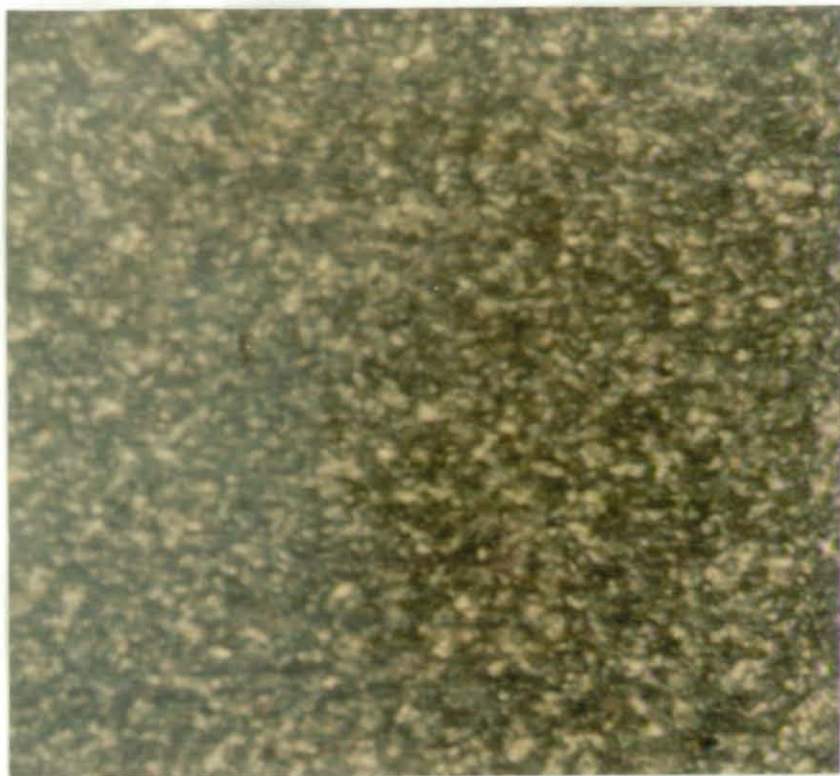


Fig. 3.7 Optical micrograph of EVA copolymer (3.5% VA) (Mag. 400X)

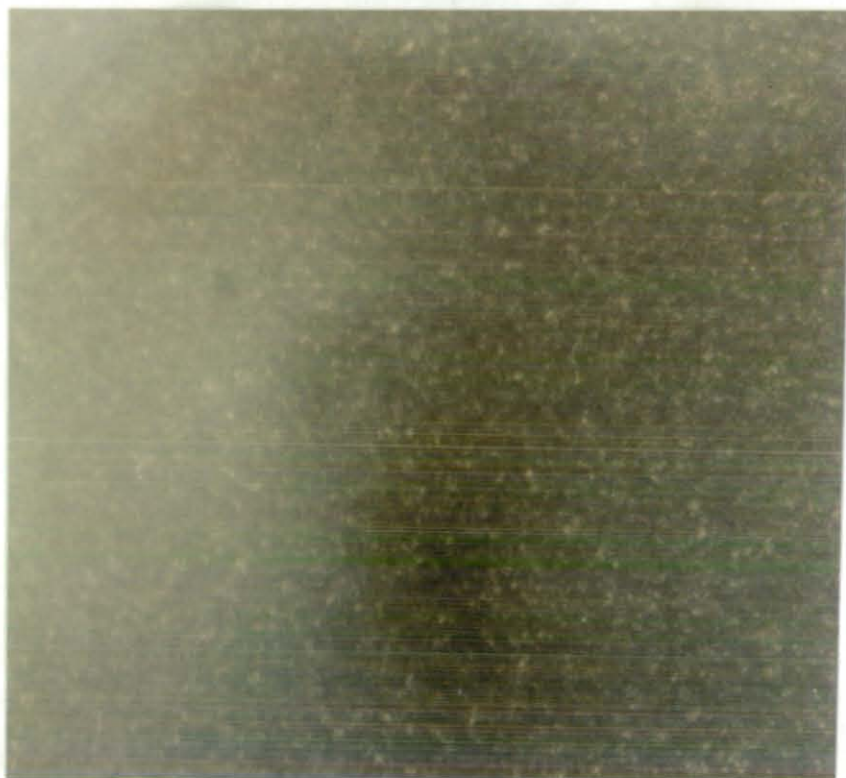


Fig. 3.8 Optical micrograph of EVA/LDPE blend (3.5% VA) (Mag. 400X)

3.3.4 Mechanical Properties

The mechanical properties of EVA copolymer and EVA/LDPE are shown in Table 3.4. Better mechanical properties were obtained for EVA copolymer than EVA/LDPE blend except the elongation at yield and break in the machine direction which were greater for EVA/LDPE blend. The better mechanical properties of EVA copolymer supports the DSC results that ethylene and VA in EVA consists of one type of crystal which leads to one melting and crystallisation peak, whereas in the EVA/LDPE blend, two distinct melting and crystallisation peaks were observed due to LDPE and EVA which suggests the incompatibility of these two polymers.

Table 3.4

Polymer		Stress (MPa)		Elongation(%)	
		Yield	Break	Yield	Break
EVA/LDPE blend	MD	21.5%	30.1%	37.5	447
	TD	10.9%	12.7%	10	159
EVA copolymer	MD	22.4%	42.2%	20	240
	TD	13.5%	17.4%	12	311

MD = Machine Direction

TD = Transverse Direction

The mechanical properties obtained in the machine direction are generally better than those in the transverse direction This is due to the orientation which is a result of polymer melt of long chain macromolecules being stretched in the flow direction. The stress/strain curves of EVA's are shown in Fig. 3.9.

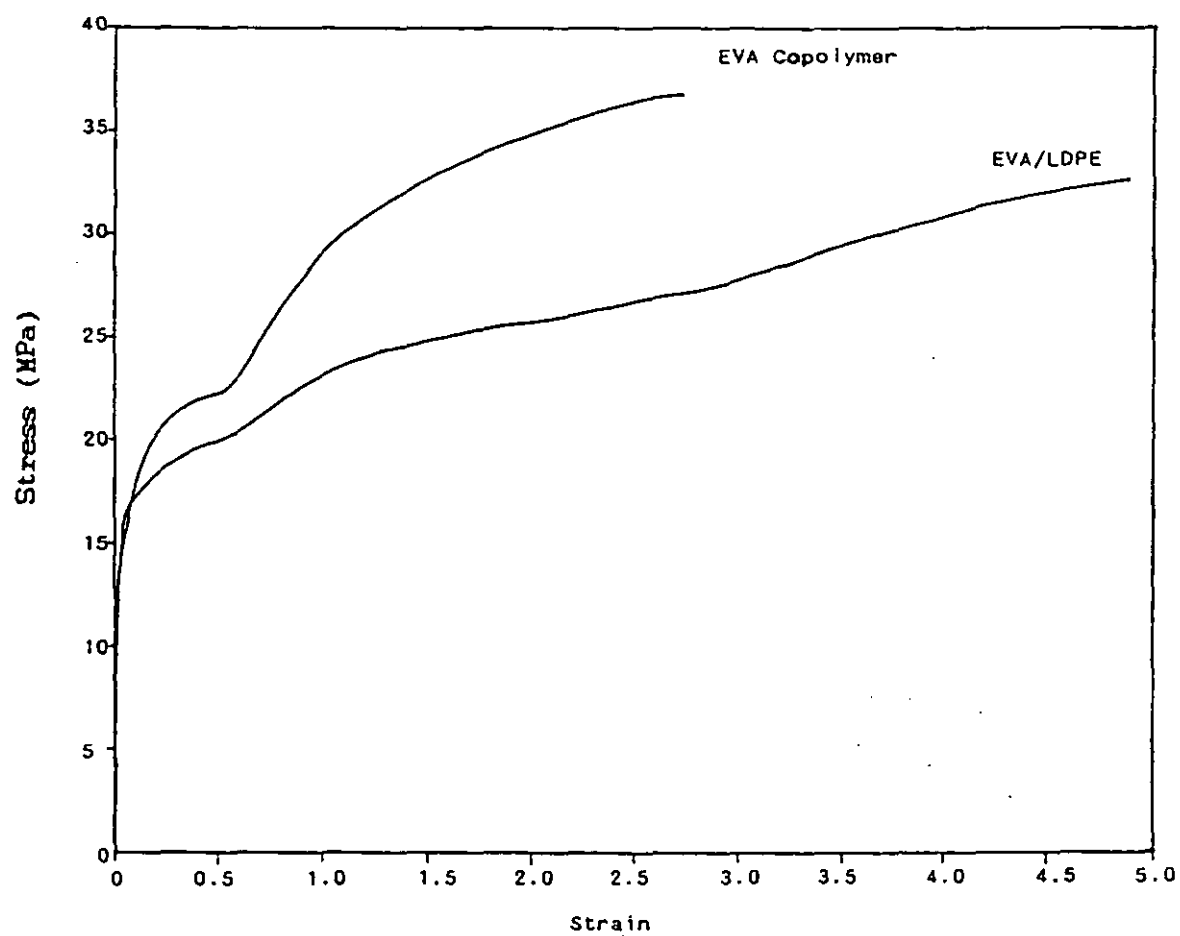


Fig. 3.9 Stress/Strain curves of EVA copolymer and EVA/LDPE blend.

3.3.5 Flow properties

The curves of shear stress versus shear rate, and shear viscosity versus shear rate are plotted in Fig. 3.10 and 3.11 respectively. The graphs show that EVA copolymer has higher viscosity than EVA/LDPE blend. This is supported by the MFI. The melt flow index of EVA/LDPE blend was found to be higher than LDPE and EVA copolymer (18% VA content). This suggests that by blending EVA and LDPE results in lowering viscosity which could be due to less entanglement between EVA and LDPE molecules, each becoming more ball-shaped.

3.3.6 Spreading Coefficient

The spreading coefficient of EVA's are shown in Table 3.5. As the spreading coefficient for EVA copolymer is more negative than EVA/LDPE blend therefore, liquids spread less on the EVA copolymer. This suggests that, it is more difficult to print or coat on the EVA copolymer surface than EVA/LDPE blend.

Table 3.5

Polymer	Sc (mN/m)
EVA copolymer (3.5% VA)	-58.9
EVA/LDPE blend (3.5% VA)	-45.3

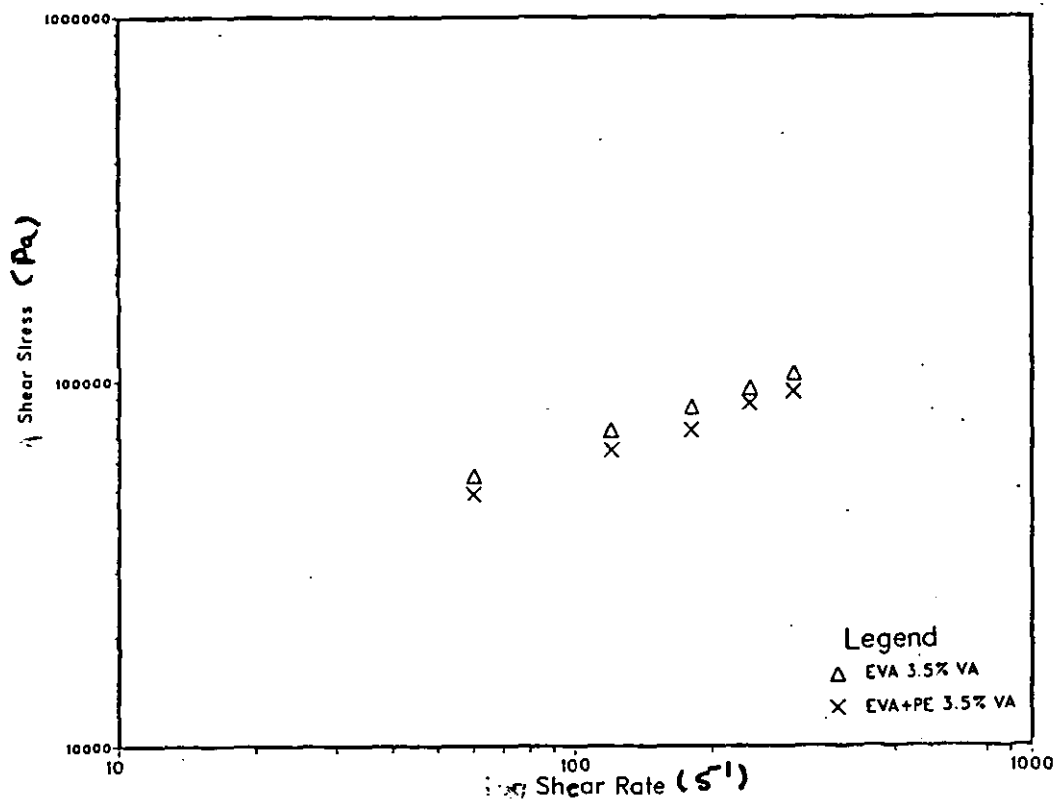


Fig. 3.10 The shear stress as a function of shear rate for EVA copolymer and EVA/LDPE blend at 190 °C.

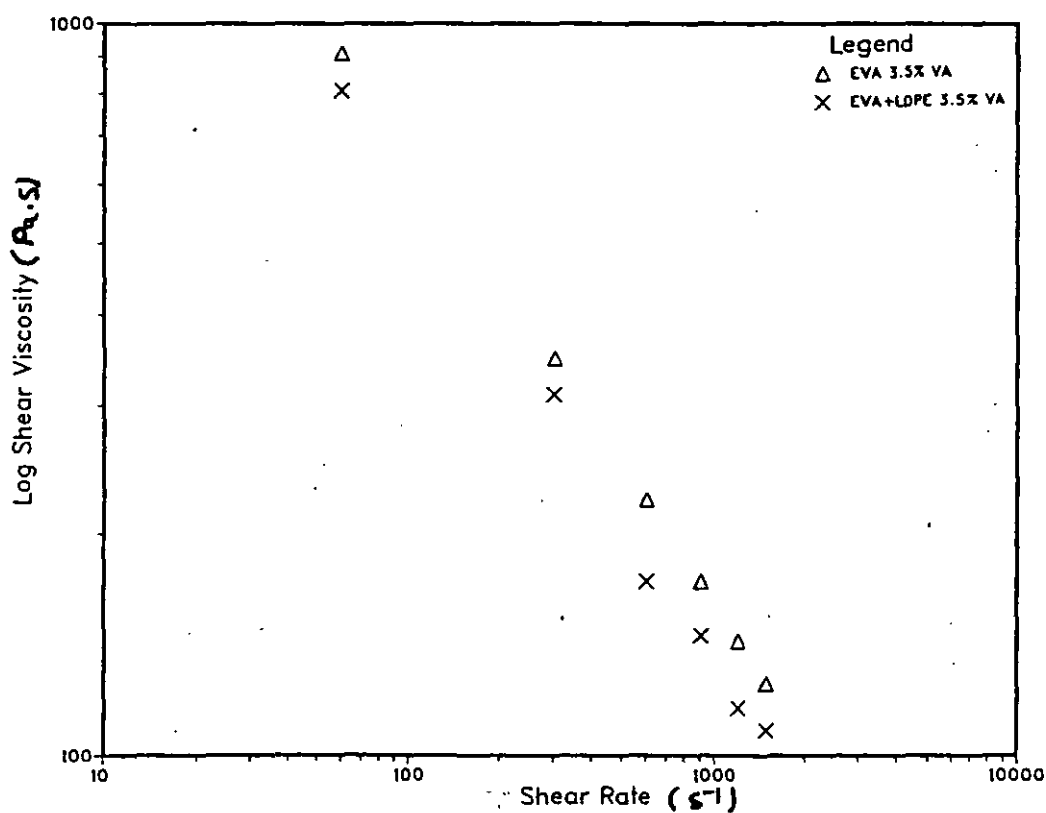


Fig. 3.11 The shear viscosity as a function of shear rate for EVA copolymer and EVA/LDPE blend at 190 °C.

3.4 CONCLUSION

Thermal analysis showed that EVA/LDPE blends made by physical blending are incompatible which results in their having poorer mechanical properties than EVA made by copolymerisation. It seems the only advantage of EVA/LDPE blends over EVA copolymers is that it is easier to print or apply a surface coating to them.

CHAPTER 4

BINARY BLENDS OF LINEAR LOW DENSITY, AND HIGH DENSITY POLYETHYLENE AND TERNARY BLENDS OF LINEAR LOW DENSITY / HIGH DENSITY/ LOW DENSITY POLYETHYLENE

4.1 INTRODUCTION

Following earlier work by Datta and Birley⁽⁴⁴⁾, on the binary blends of linear low density polyethylene and high density polyethylene, which showed that these two polymers are compatible, it seemed that interesting results might be obtained in the system of ternary blends of linear low density, high density and low density polyethylene. For this reason, several sets of binary blends of linear low density polyethylene and high density polyethylene with different melt flow indices were made. Having characterised them by Differential Scanning Calorimetry(DSC), the set of binary blends of LLDPE/HDPE with MFI(1.0/1.0 g/10 min)were blended with LDPE to obtain a set of ternary blends of LLDPE/HDPE/LDPE.

4.2 MATERIALS

The following materials were used(Table 4.1).

Table 4.1

Polymer	Producer or Trade name	Grade	MFI (g/10 min)	Density* (g/cm ³)
LLDPE	Escorene	LL1001XV	1.0	0.918
LLDPE	Escorene	LL6101XR	20.0	0.918
HDPE	ATO Chem.	2010SA60	1.0	0.960
HDPE	-	2070ML60	8.76	-
LDPE	Shell	25-020-FJ	2.62	0.921

* Data from the manufacturers.

The binary blends were prepared at the compositions shown in Table 4.2.

Table 4.2

Set no.	Polymer	MFI	Composition
1	LLDPE/HDPE	1.0/1.0	0/100, 30/70, 50/50, 70/30, 100/0
2	LLDPE/HDPE	1.0/8.76	0/100, 30/70, 50/50, 70/30, 100/0
3	LLDPE/HDPE	20/8.76	0/100, 30/70, 50/50, 70/30, 100/0

To obtain the ternary blends of LLDPE/HDPE/LDPE, the set number 1 was blended with the LDPE in the ratio of 30%, 50%, and 70% by weight for each composition to obtain the following blends as shown in Table 4.3.

Table 4.3

Set no.	Polymer	Compositions by weight percent
4	LLDPE/HDPE/LDPE	9/21/70, 15/35/50, 21/49/30
5	LLDPE/HDPE/LDPE	15/15/70, 25/25/50, 35/35/30
6	LLDPE/HDPE/LDPE	21/9/70, 35/15/50, 49/21/30

4.3 RESULTS AND DISCUSSION

4.3.1 Thermal Analysis

Thermograms of LLDPE's and HDPE's with different molecular weights are shown in Figs 4.1 to 4.4. The thermograms of both LLDPE's in their pure forms show two melting peaks after being cooled and reheated, indicating two types of crystal species. The reason for this is not clear, but there is the possibility of changes in co-monomer concentration during the polymerisation process, resulting in variations in side branch concentration along the molecular chain⁽⁴⁹⁾. This behaviour also was observed by Datta⁽⁴⁴⁾ and Edward⁽⁴⁹⁾.

Thermograms of binary blends of LLDPE/HDPE[MFI = 1.0/1.0] (Figs. 4.5-4.7) and LLDPE/HDPE[MFI = 1.0/8.76 and 20.0/8.76] (Figs. 4.8-4.13, see Appendix I) show only one melting and one crystallisation peak regardless of their molecular weights. This suggests that in all cases at all the compositions there exists one type of crystal species. Therefore, it seems, that cocrystallisation of LLDPE and HDPE has taken place, from which it can be concluded that they are compatible. These observation confirms the results obtained by Datta⁽⁴⁴⁾ and Edward⁽⁴⁹⁾, although they investigated samples at only one set of molecular weights.

The crystal melting point and crystallisation temperature of HDPE shifts to lower temperature as the content of LLDPE increases for all the molecular weights. These observations are shown more clearly in the plots of peak temperatures versus compositions in Fig. 4.14 to 4.16. Both melting and crystallisation

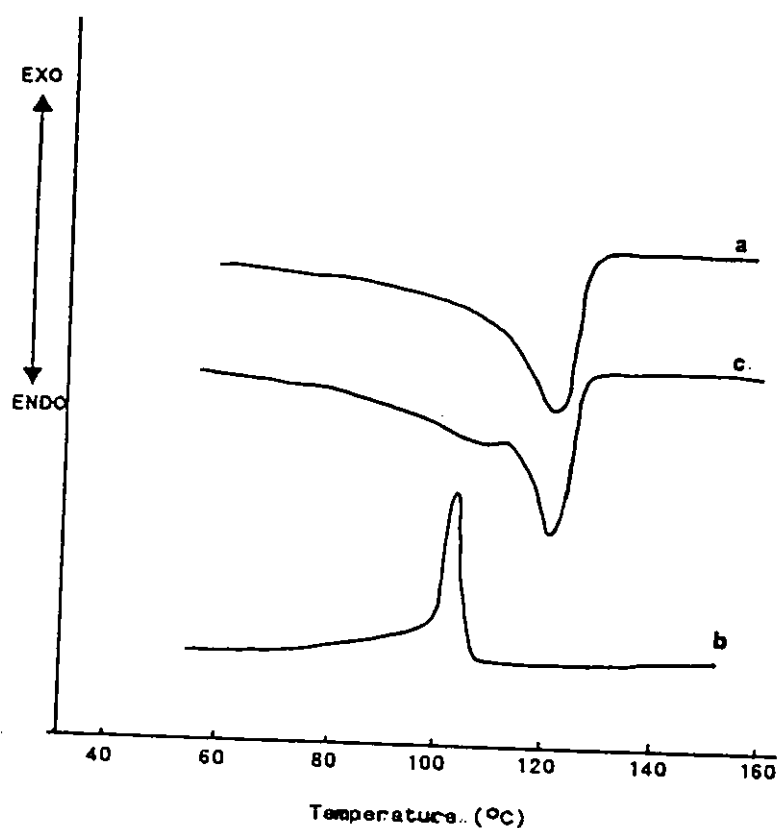


Fig. 4.1. Thermograms of LLDPE(MFI = 1.0 g/10 min) (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

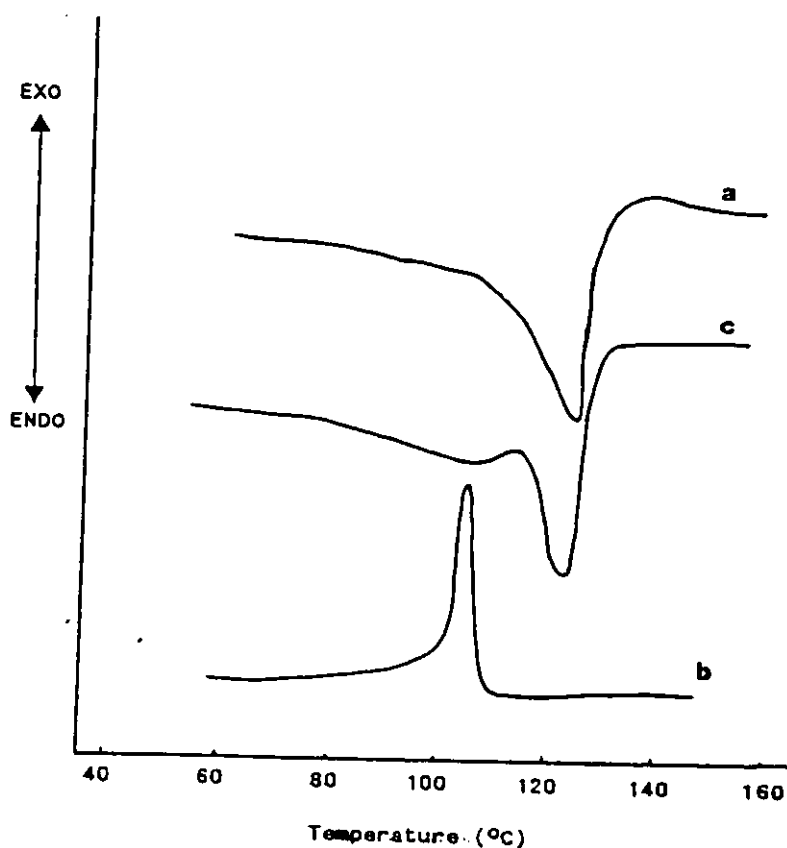


Fig. 4.2. Thermograms of LLDPE(MFI = 2.0 g/10 min) (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

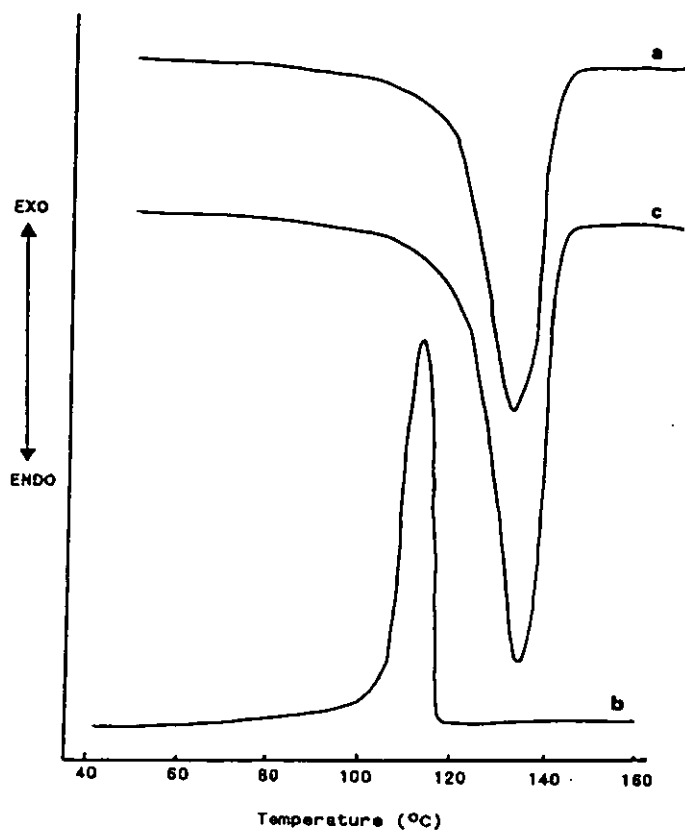


Fig. 4.3. Thermograms of HDPE(MFI = 1.0 g/10 min) (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

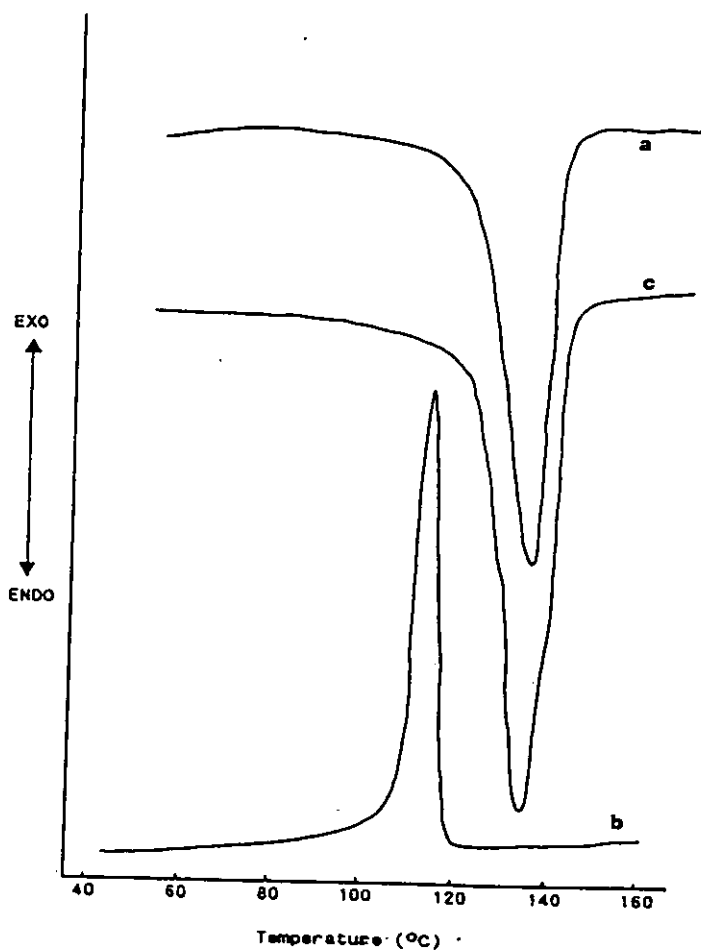


Fig. 4.4. Thermograms of HDPE(MFI = 8.76 g/10 min) (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

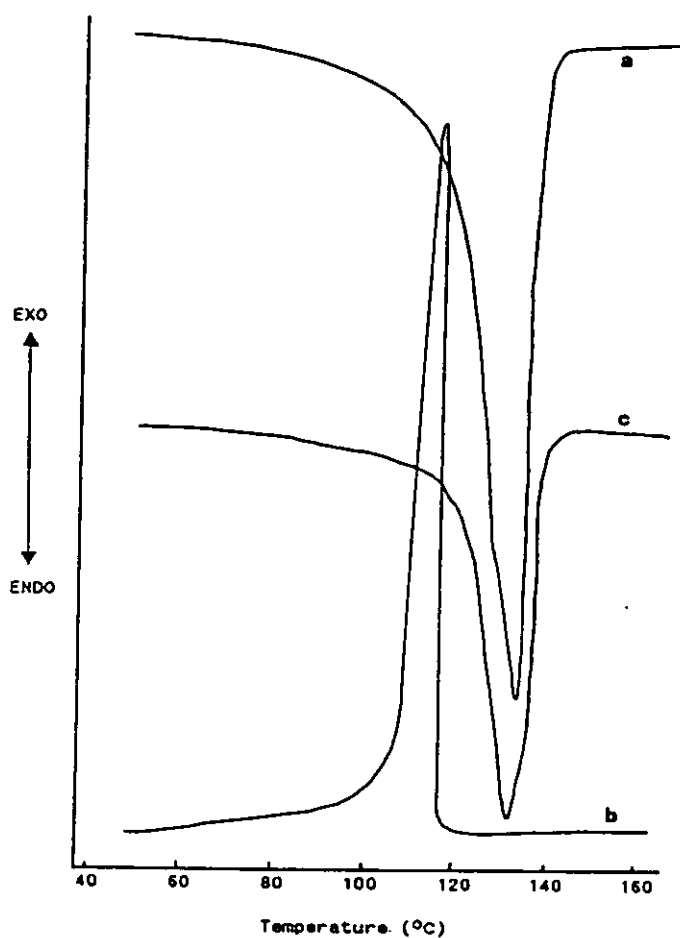


Fig. 4.5. Thermograms of Binary blend of LLDPE/HDPE-30/70 (MFI = 1.0/1.0). (a) first heating, (b) cooling and (c) second heating. Sensitivity a and b = 5, c = 10 mV/cm.

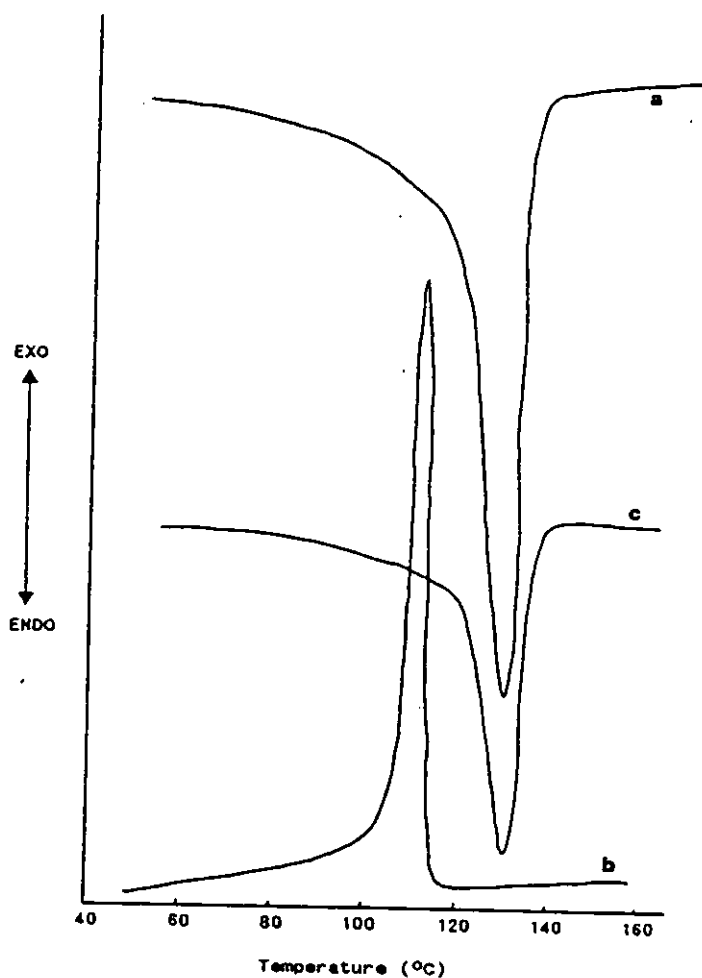


Fig. 4.6. Thermograms of Binary blend of LLDPE/HDPE-50/50 (MFI = 1.0/1.0). (a) first heating, (b) cooling and (c) second heating. Sensitivity a and b = 5, c = 10 mV/cm.

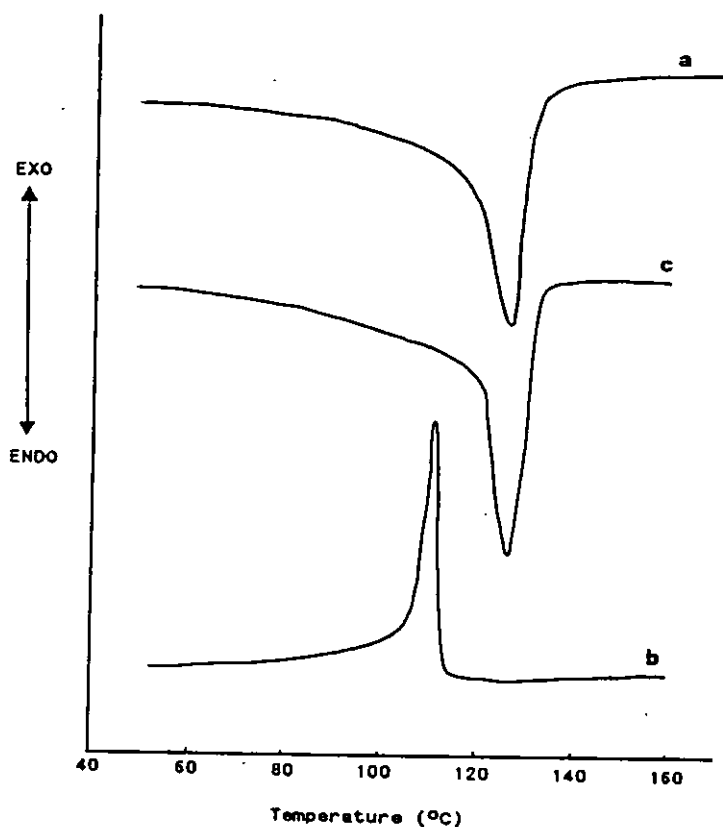
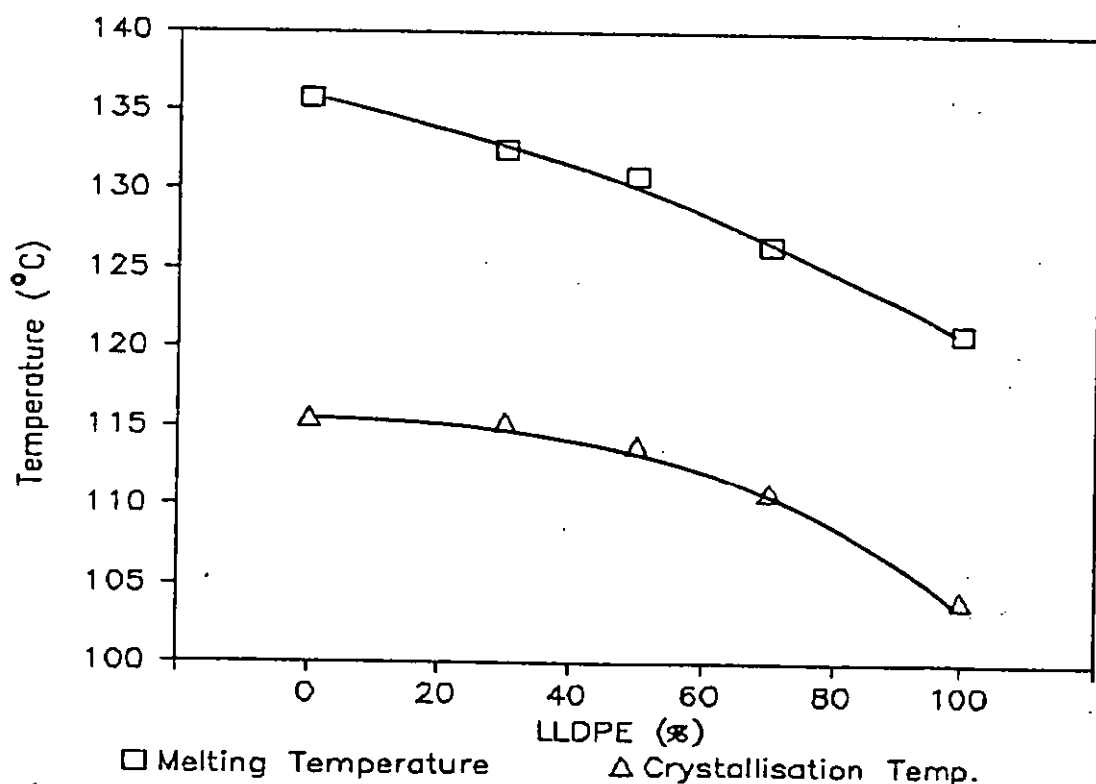
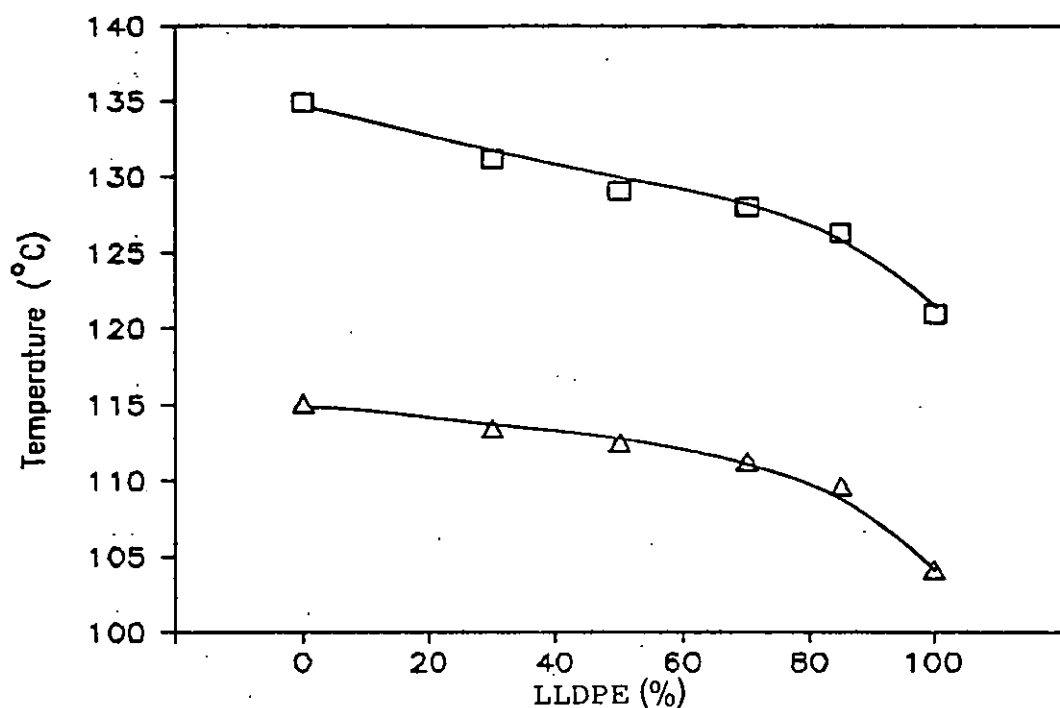


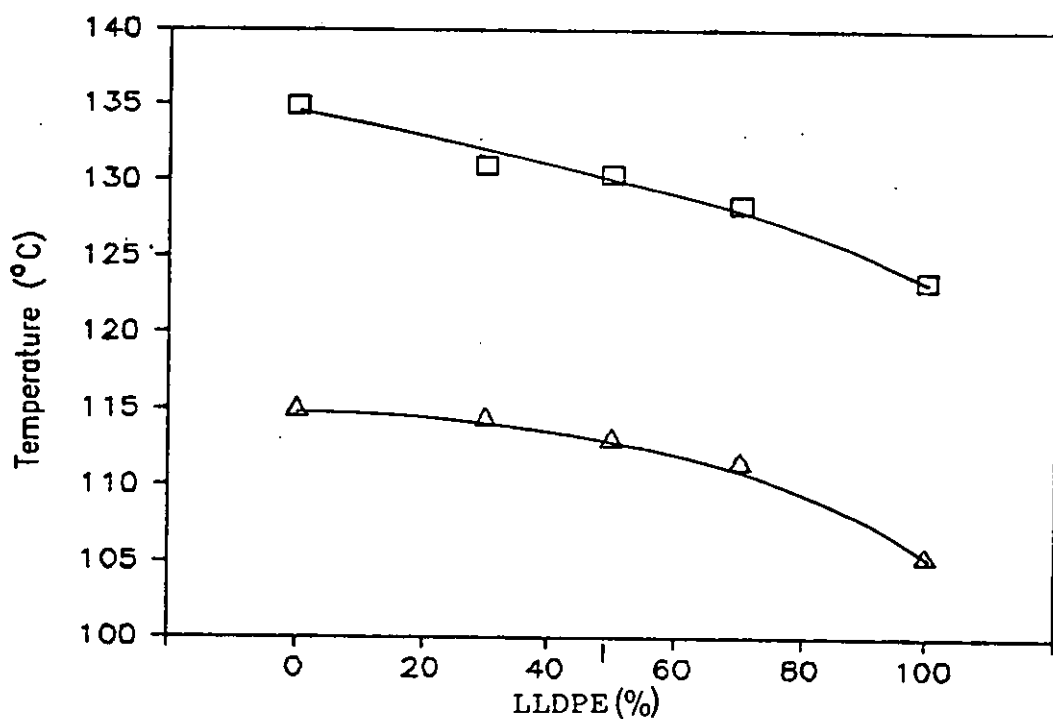
Fig. 4.7. Thermograms of Binary blend of LLDPE/HDPE-70/30 (MFI = 1.0/1.0). (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.



□ Melting Temperature Δ Crystallisation Temp.
Fig. 4.14 Melting and Crystallisation temperature versus composition of binary blends of LLDPE/HDPE, MFI = (1.0/1.0).



□ Melting Temperature △ Crystallisation Temp.
 Fig. 4.15 Melting and Crystallisation temperature versus composition of binary blends of LLDPE/HDPE, MFI=(1.0/8.76).



□ Melting Temperature △ Crystallisation Temp.
 Fig. 4.16 Melting and Crystallisation temperature versus composition of binary blends of LLDPE/HDPE, MFI=(20.0/8.76).

temperature are approximately linear with the compositions.

Thermograms of LDPE and ternary blends of LLDPE/HDPE/LDPE are shown in Figs 4.17 to 4.20 and (Figs. 4.21 to 4.26, see Appendix I). The thermograms of ternary blends show two distinct melting and crystallisation temperatures. The higher crystal melting point and crystallisation temperature attributed to the melting and crystallisation temperature of LLDPE/HDPE, whereas the lower is due to LDPE. The melting points and crystallisation temperatures associated with them are shown in Table 4.4. The melting point and crystallisation temperatures of LLDPE/HDPE shift with the contents of LLDPE and HDPE, whereas the melting point and crystallisation temperature of LDPE show little or no change.

These results show that in the case of LLDPE and HDPE, there exists one type of crystal species which is due to cocrystallisation of LLDPE and HDPE as in the case of binary blends, and there is no indication of cocrystallisation of LDPE with LLDPE/HDPE. Therefore, it can be concluded that LLDPE and HDPE act as a copolymer in ternary blends of LLDPE/HDPE/LDPE, which results in having a peak attribute to LLDPE/HDPE and another one to LDPE. This suggests that LLDPE/HDPE and LDPE are incompatible, which results in melting point depression of LDPE. The melting point depression of LDPE could be due to the following (81):

1. The kinetic effect of one solid phase which may obstruct or make irregular the growth of the lamellar crystallites of the spherulites of the other phase.
2. Thermal perturbations due to different rate of crystallisation between LLDPE/HDPE and LDPE.

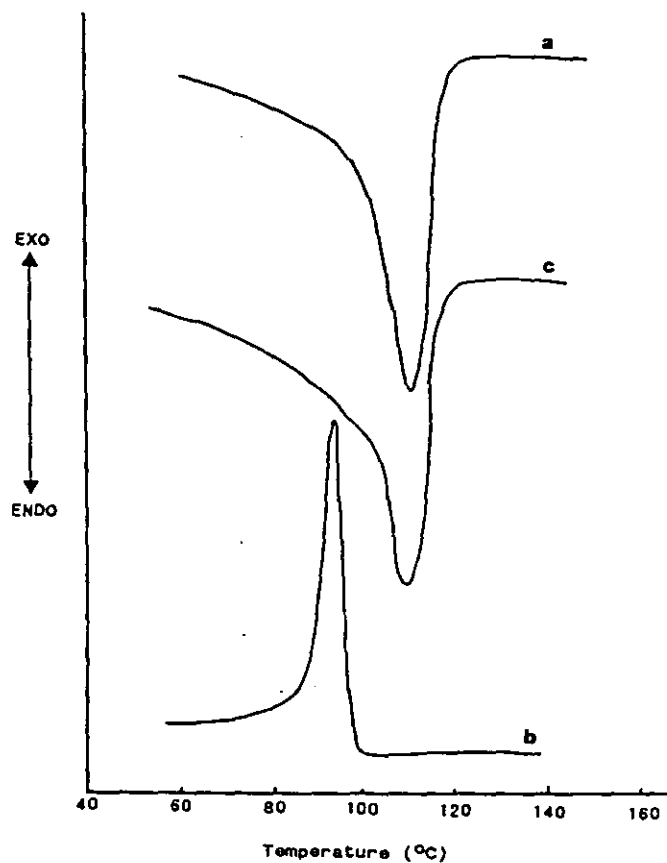


Fig. 4.17. Thermograms LDPE. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

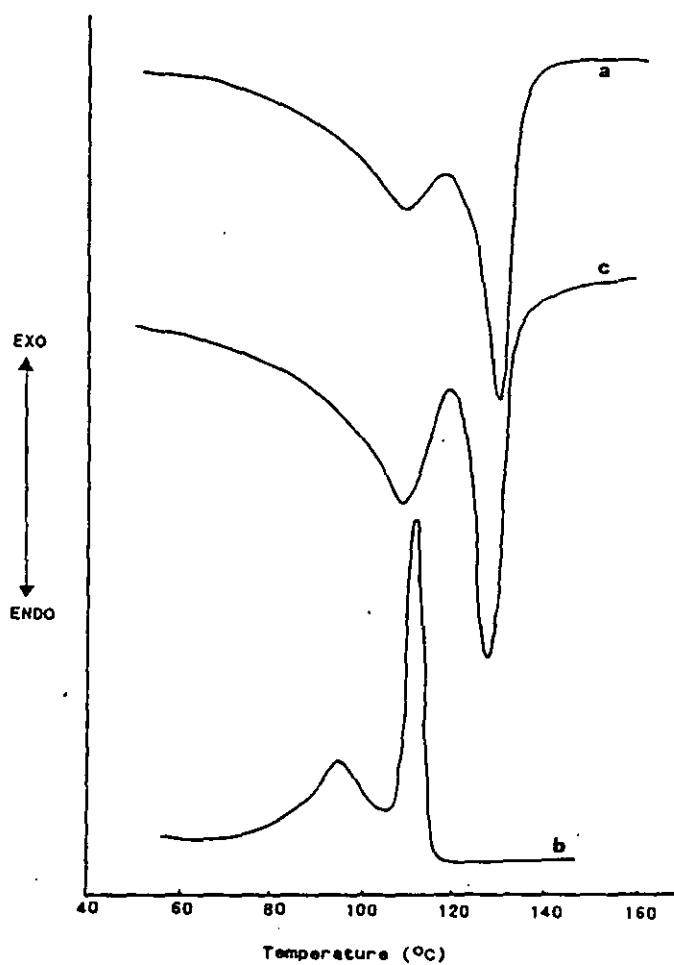


Fig. 4.18. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-9/21/70 (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

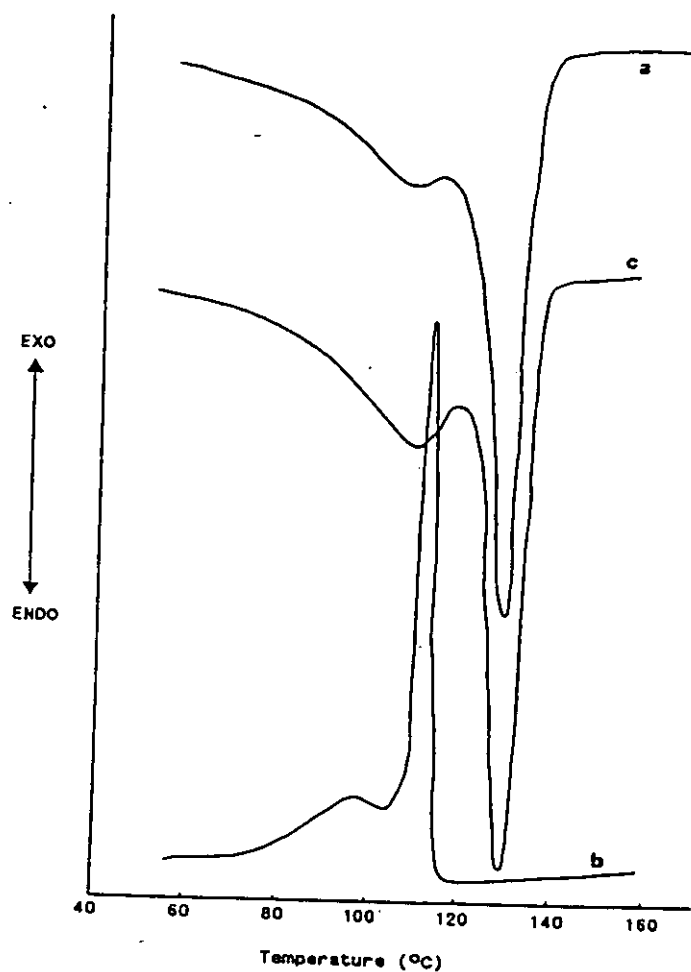


Fig. 4.19. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-15/35/50. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

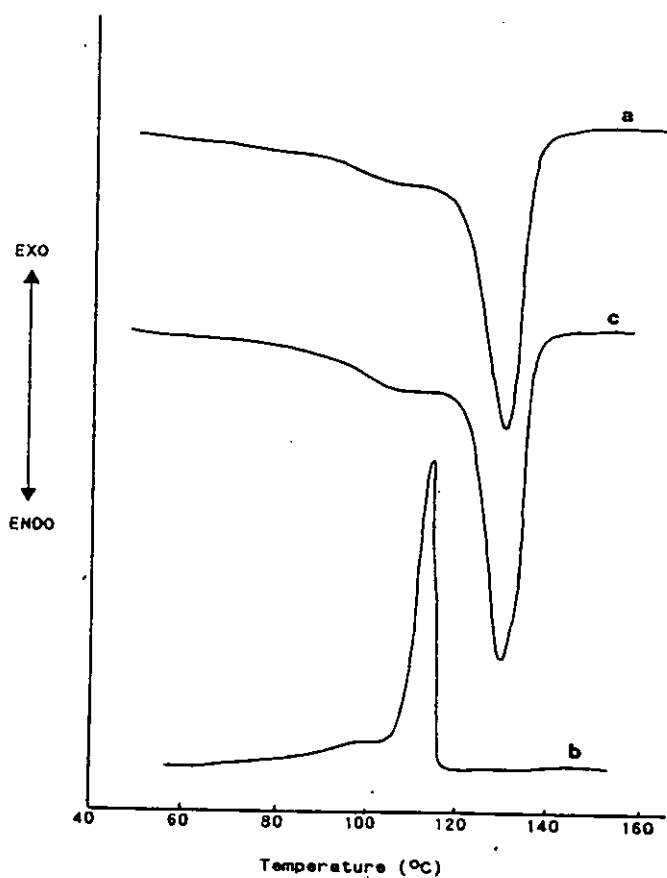


Fig. 4.20. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-21/49/30. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

Table 4.4

Polymer and composition weight percent	1st melting temp. °C	2nd melting temp. °C	crystallisation temp. °C
HDPE	133.6	135.2	115.0
LLDPE	-	107.5	-
LDPE	122.1	121.0	104.1
LL/HD/LD-9/21/70	111.3	110.5	94.5
LL/HD/LD-15/35/50	109.5	109.0	95.0
LL/HD/LD-21/49/30	130.0	127.6	111.6
LL/HD/LD-30/70/0	107.5	108.8	97.0
LL/HD/LD-35/35/30	129.6	129.5	113.4
LL/HD/LD-49/21/30	106.5	108.0	97.0
LL/HD/LD-50/50/0	130.4	130.0	114.0
LL/HD/LD-15/15/70	134.9	132.5	115.3
LL/HD/LD-25/25/50	108.5	108.5	94.5
LL/HD/LD-35/15/50	126.5	125.5	110.0
LL/HD/LD-70/30/0	107.5	107.5	96.5
LL/HD/LD-21/9/70	128.3	127.9	112.7
LL/HD/LD-35/15/50	105.0	107.0	96.5
LL/HD/LD-49/21/30	131.0	130.0	112.5
LL/HD/LD-70/30/0	131.9	130.9	113.8
LL/HD/LD-21/9/70	111.5	109.5	95.5
LL/HD/LD-35/15/50	126.9	125.2	108.3
LL/HD/LD-49/21/30	108.0	108.0	95.0
LL/HD/LD-70/30/0	126.0	125.4	110.5
LL/HD/LD-21/9/70	110.0	108.9	95.0
LL/HD/LD-35/15/50	131.5	127.6	111.2
LL/HD/LD-70/30/0	127.4	126.5	110.9

4.3.2 Mechanical Properties

The tensile strength at yield and break for LLDPE, HDPE, and their blends are plotted against the composition in Fig. 4.27. The tensile strength at yield for pure HDPE is much higher than pure LLDPE, due to the high degree of crystallinity of HDPE. As the content of LLDPE increases the yield strength decreases; the relationship is approximately linear. The tensile strength at break for HDPE is lower than that of LLDPE. This is because HDPE is more crystalline than LLDPE, which results in failure at a lower strain. This observation can be seen more clearly in the stress-strain curves of HDPE, LLDPE, and their blends in Fig. 4.28. The HDPE sample breaks just beyond the yield point which is characteristic of highly crystalline polymers, whereas for LLDPE and the blends tend to be cold drawn for a period of time before failure occurs. The tensile strength at break for LLDPE/HDPE blends are much higher than pure HDPE and slightly higher than pure LLDPE. This supports the DSC results that LLDPE and HDPE are compatible.

Elongation at yield and break for HDPE, LLDPE and their blends are shown in Fig. 4.29. The elongation at yield and break for LLDPE is much higher than that of HDPE. This is because, the higher the degree of crystallinity the lower the capability of the system to elongate. There is little or no change in the elongation at yield for the blends as the content of LLDPE increases, but there is a great improvement in elongation at break with increasing the content of LLDPE.

The tensile strengths at yield and break for LDPE and ternary blends of LLDPE/HDPE/LDPE are shown in Figs. 4.30 to 4.33. The tensile strength at yield and break for LDPE is lower than HDPE and LLDPE. This is due to

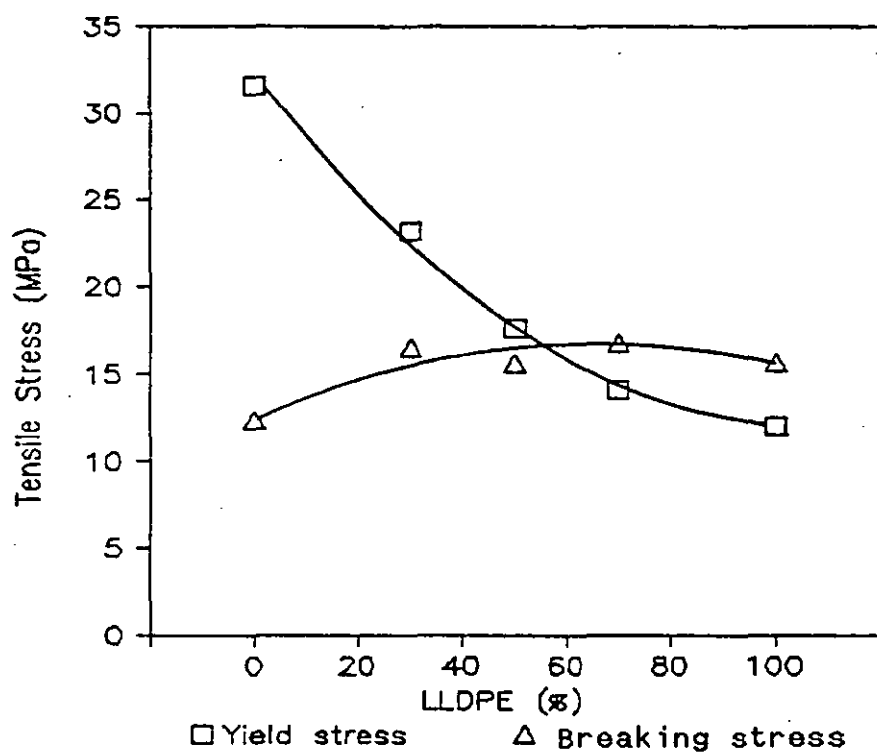


Fig. 4.27 Tensile Strength of LLDPE, HDPE, and their blends.

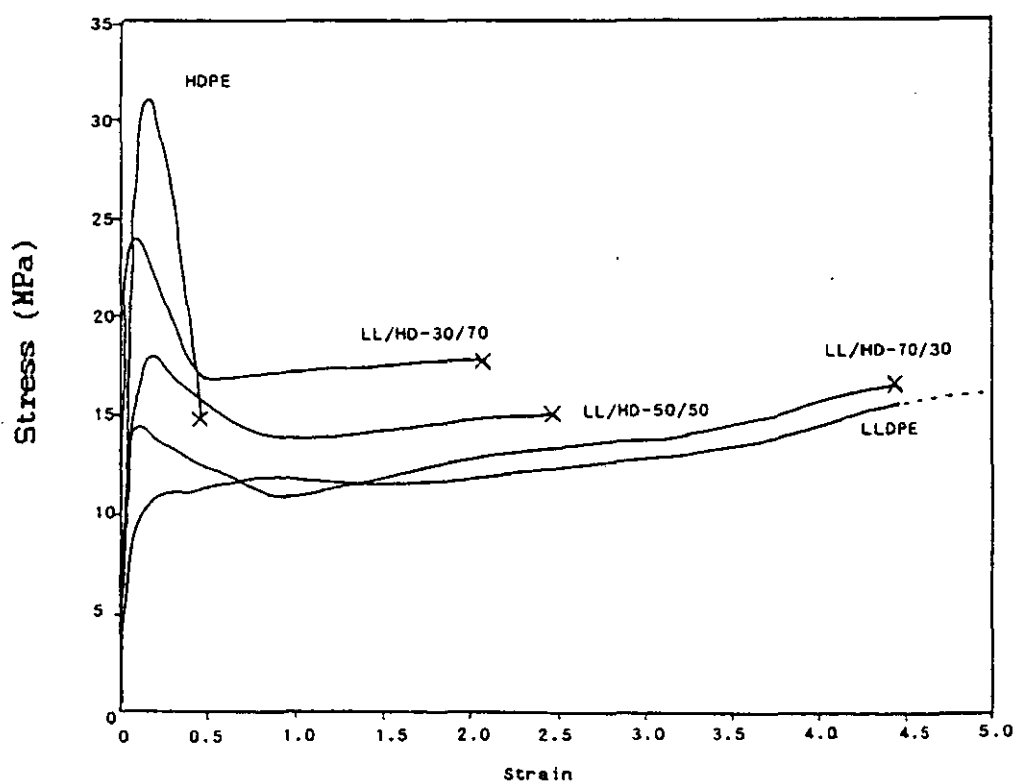


Fig. 4.28 Stress/Strain curves of LLDPE, HDPE and their blends.

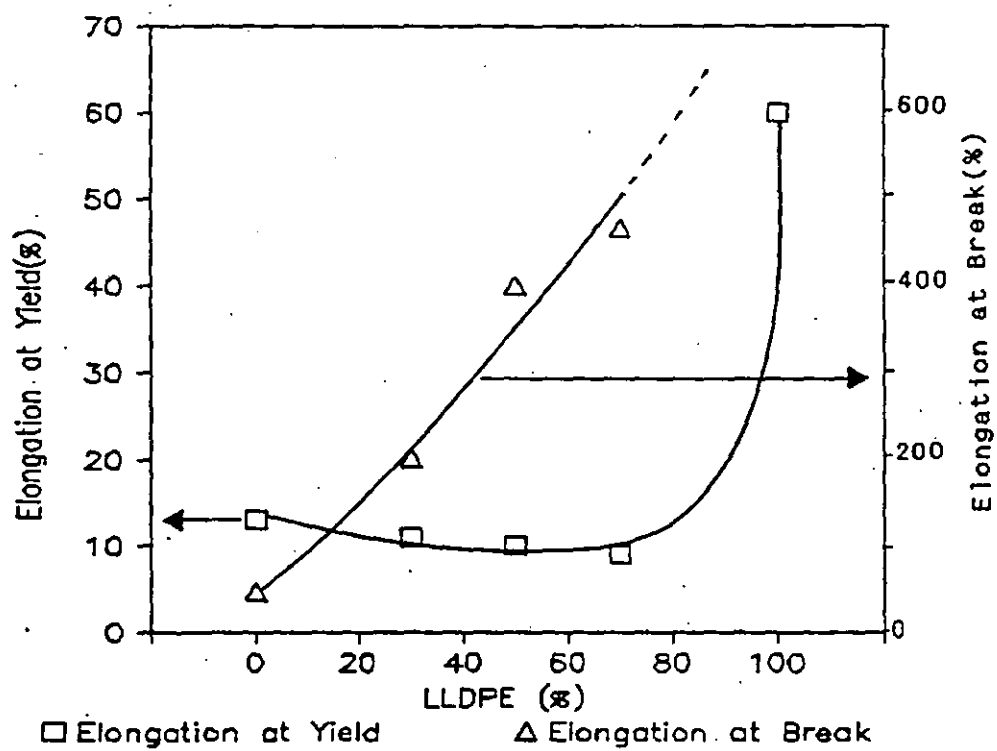


Fig. 4.29 Elongation of LLDPE, HDPE, and their blends.
The LLDPE sample did not break.

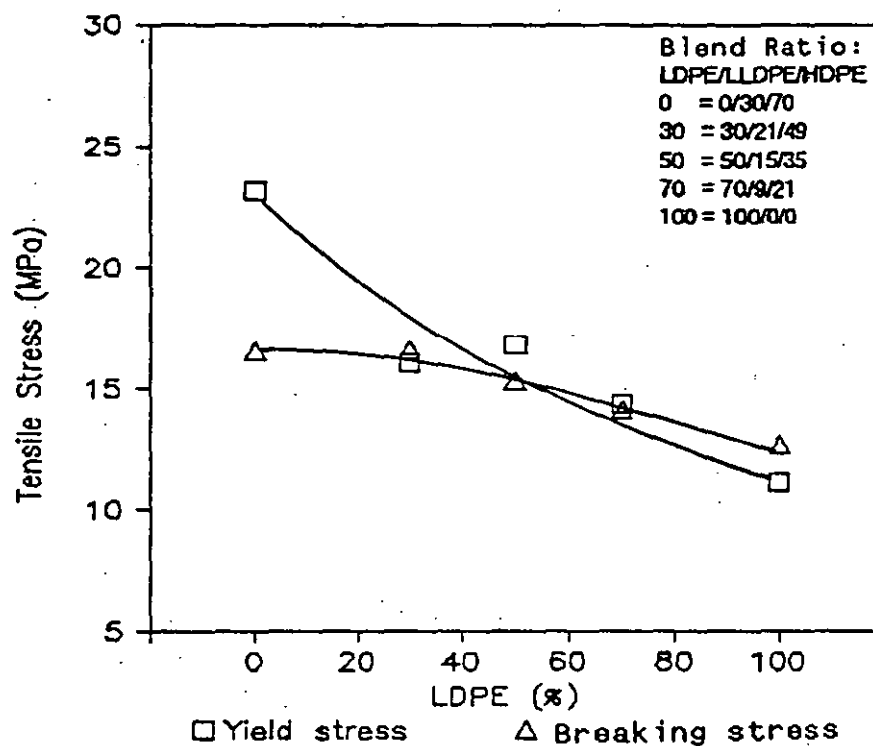


Fig. 4.30 Tensile Strength of Ternary blends of LLDPE/HDPE/LDPE.

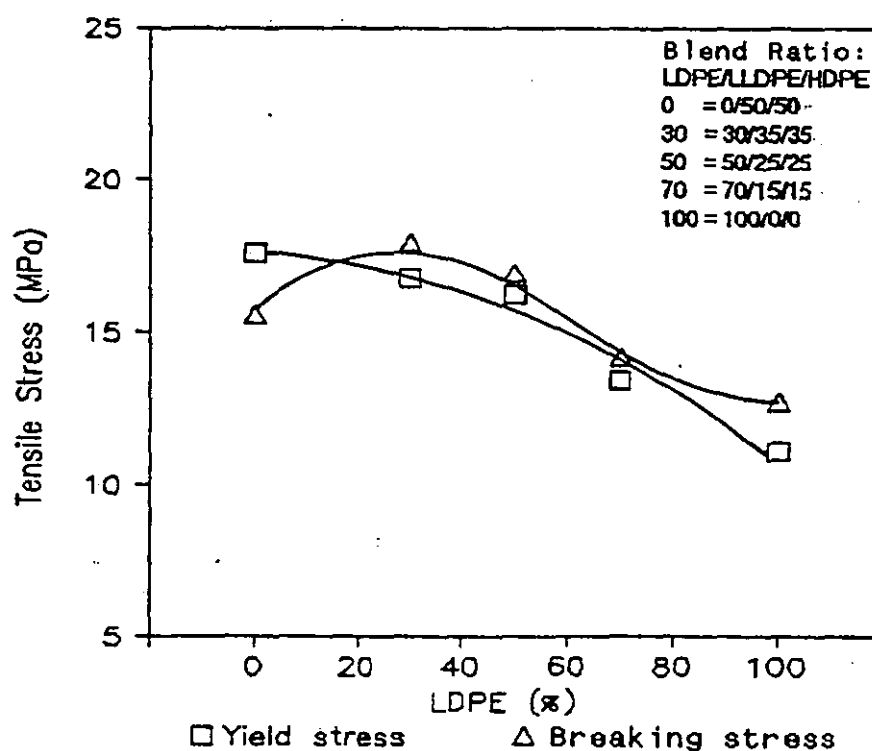


Fig. 4.31 Tensile Strength of Ternary blends of LLDPE/HDPE/LDPE.

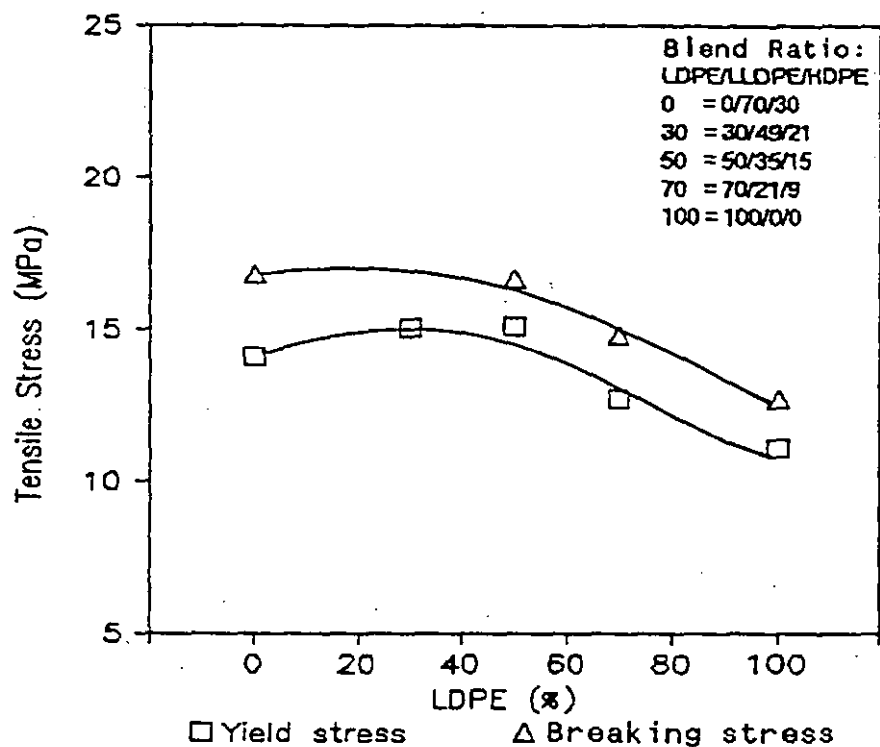


Fig. 4.32 Tensile Strength of Ternary blends of LLDPE/HDPE/LDPE.

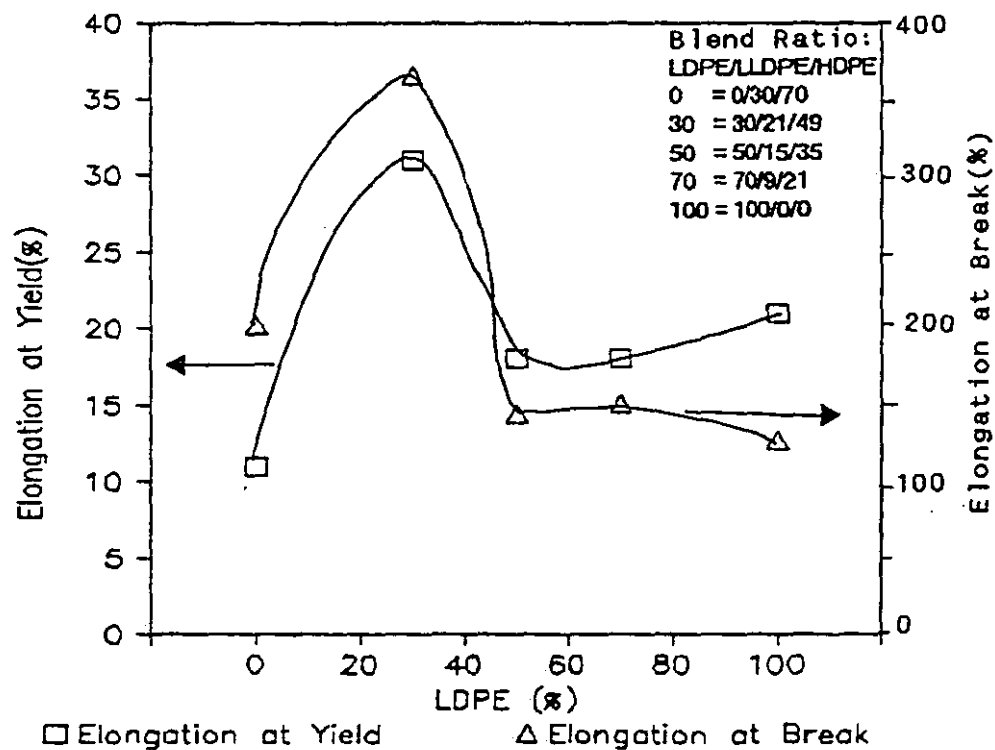


Fig. 4.33 Elongation of Ternary blends of LLDPE/HDPE/LDPE.

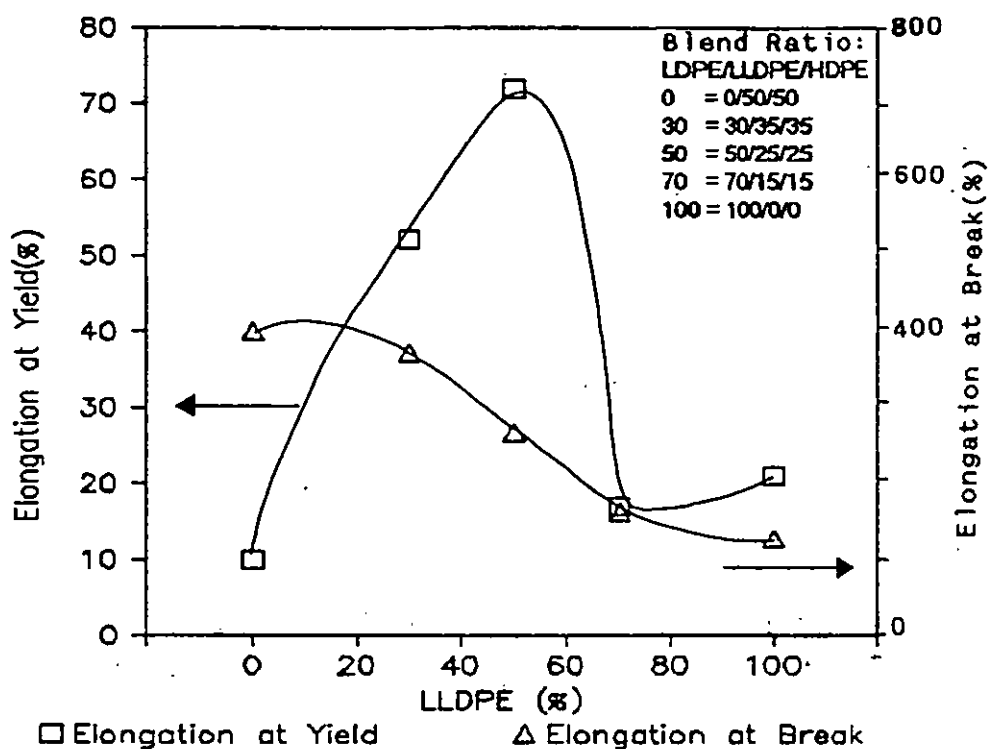


Fig. 4.34 Elongation of Ternary blends of LLDPE/HDPE/LDPE.

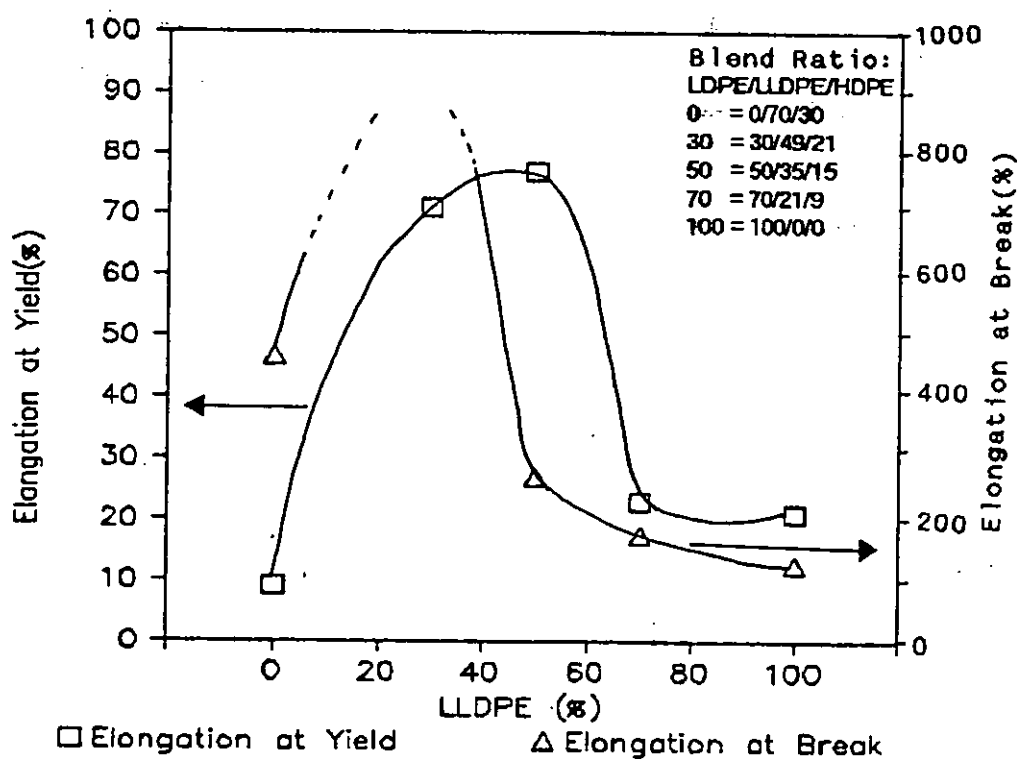


Fig. 4.35 Elongation of Ternary blends of LLDPE/HDPE/LDPE. The blend of LD/LL/HD-30/49/21 did not break.

having lower degree of crystallinity than HDPE, and having shorter chain length than LLDPE, due to long chain branching. In all the compositions used ternary blends show lower tensile strength at yield and break than the binary blends of LLDPE/HDPE. As the content of LDPE increases, the tensile strength decreases. This is attributed to the two-phase character of LLDPE/HDPE and LDPE, as was seen earlier by DSC.

Elongation at yield and break for LDPE and ternary blends are shown in Figs. 4.33 to 4.35. The graphs show that by adding LDPE to binary blends of LLDPE/HDPE, results in an improving elongation at yield for all the compositions, and even higher than each component. The elongation at break for the compositions of LLDPE/HDPE/LDPE-21/49/30, 35/35/30 and 49/21/30 are more or less in the same range as in the binary blends.

4.4 CONCLUSION

Blends of linear low density polyethylene and high density polyethylene have been found to be compatible regardless of their molecular weights. There is some deterioration in tensile stress at break with increasing HDPE content.

Ternary blends of linear low density polyethylene/high density polyethylene/low density polyethylene showed two distinct phases; one was attributed to LLDPE/HDPE, which behaved as a copolymer and the other one was associated with LDPE. The only advantage of ternary blends over binary blends seems to be the improvement in elongation at yield.

CHAPTER 5

BLENDS OF LINEAR LOW DENSITY AND LOW DENSITY POLYETHYLENE

5.1 INTRODUCTION

Following the introduction of linear low density polyethylene(LLDPE) in 1977, by Union Carbide, and later by Dow Chemical Co. and others from 1978 onwards, interest become focussed on the modification of low density polyethylene(LDPE). Blending of LLDPE with LDPE, can result in improving the film draw-down of conventional polymer and obtaining physical properties advantages of LLDPE without having to undertake the equipment modification required for optimum LLDPE extrusion(3).

Studies of LLDPE and LDPE blends have been reported widely in the literature(3,45,48,49,82-84). The present chapter extends this by investigating the effect of cooling rate.

5.2 MATERIALS

The linear low density polyethylene was Escorene(LL1001XV) with density of $0.918 \text{ (g/cm}^3\text{)}$ and MFI(190 °C; 2.16 Kg) of 1.0 (g/10 min) . The low density

polyethylene was Shell(25-010F) with density of $0.921(\text{g/cm}^3)$ and MFI of $2.62(\text{g/10 min})$.

5.3 RESULTS AND DISCUSSION

5.3.1 Thermal Analysis of Quenched Extruded Samples

Thermograms of samples for LDPE, LLDPE and their blends from the Baker Perkins twin screw extruder are shown in (Fig. 5.1 to 5.5). The thermogram of LLDPE shows two melting peaks after being cooled and reheated, indicating two types of crystal species, as was explained earlier in chapter 4. The thermograms of the blends for the first heating show only one melting peak, whereas for the second heating, they show two distinct melting peaks. The lower peak is attributed to melting of LDPE, and the higher endotherm is associated with melting of LLDPE. This observation conflicts with the results of Datta⁽⁸⁵⁾ who found two melting endotherms in the first heating. This suggests that the characteristics of LLDPE and LDPE blends strongly depend on their thermal history and/or shear history, as for the first heating the blends were quenched in water after being thoroughly mixed in a twin-screw extruder.

The above observations indicate that different crystallisation conditions can lead to very different results. If the samples are quenched as for the first heating thermograms, they exhibit only a single endotherm, which suggests that cocrystallisation has taken place, as a result of LDPE being trapped in the crystal domain of LLDPE. On the other hand if the sample is prepared by slow cooling, each component has

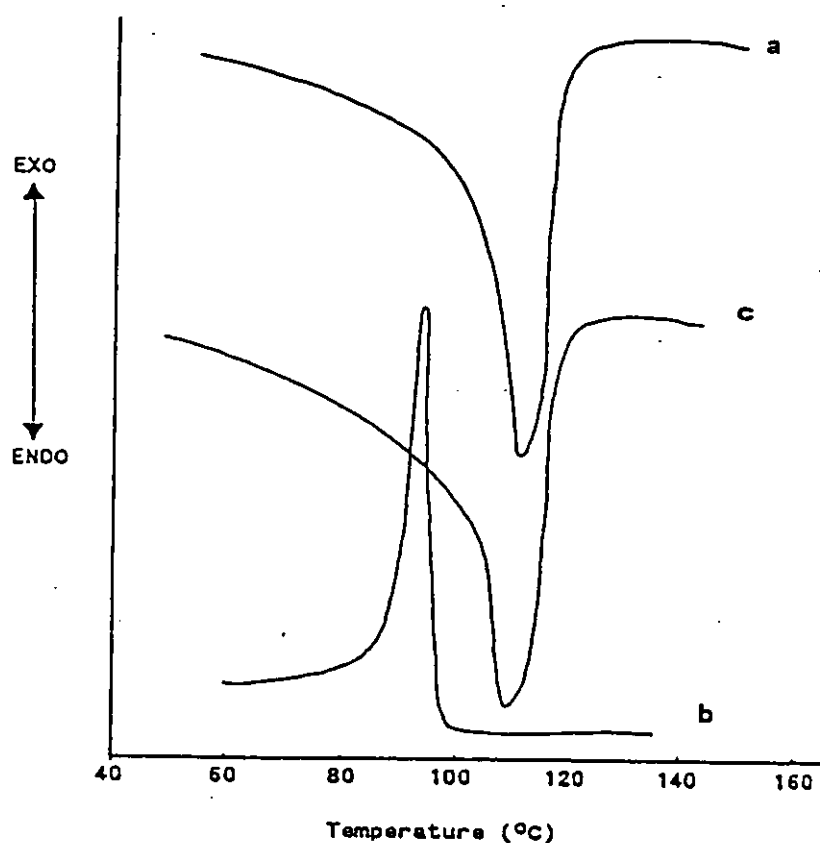


Fig. 5.1 Thermograms of LDPE. (a) first heating, (b) cooling and (c) second heating.

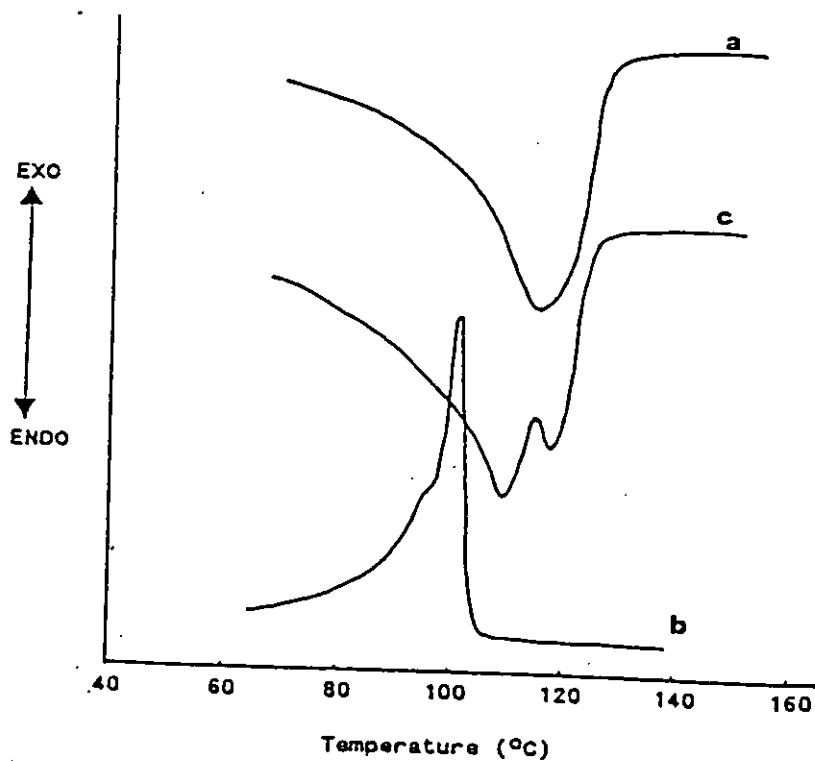


Fig. 5.2 Thermograms of LLDPE/LDPE-30/70. (a) first heating, (b) cooling and (c) second heating.

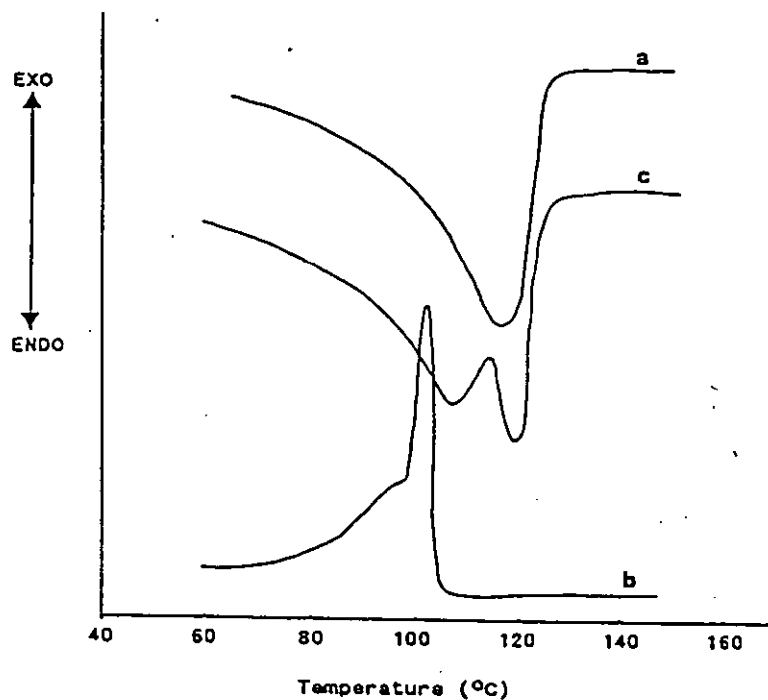


Fig. 5.3 Thermograms of LLDPE/LDPE-50/50. (a) first heating, (b) cooling and (c) second heating.

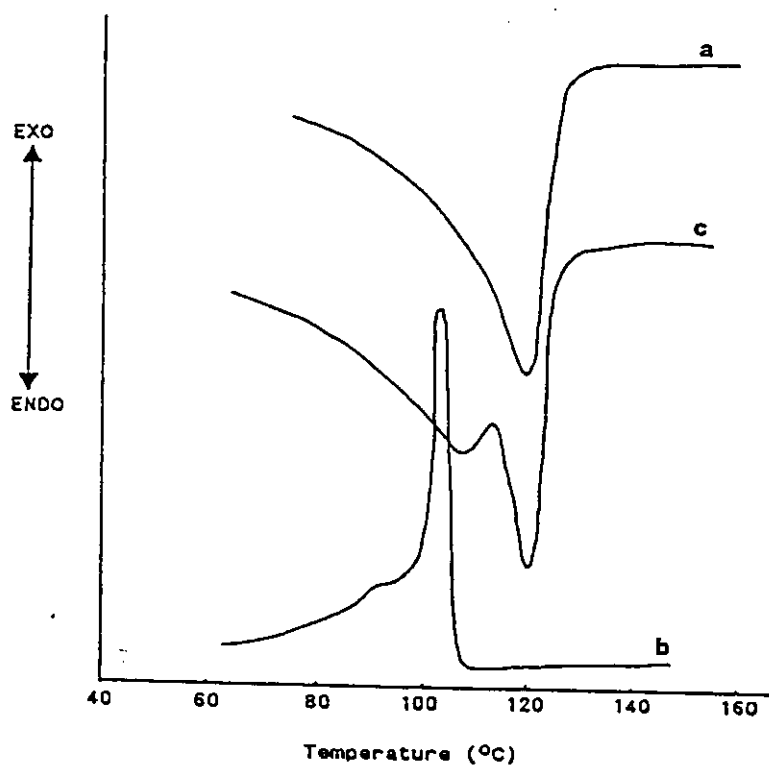


Fig. 5.4 Thermograms of LLDPE/LDPE-70/30. (a) first heating, (b) cooling and (c) second heating.

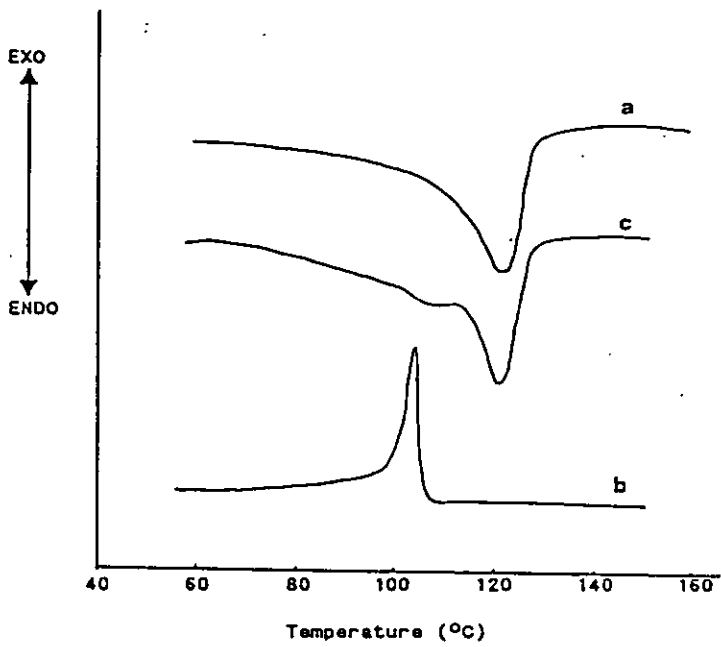


Fig. 5.5 Thermograms of LLDPE. (a) first heating, (b) cooling and (c) second heating.

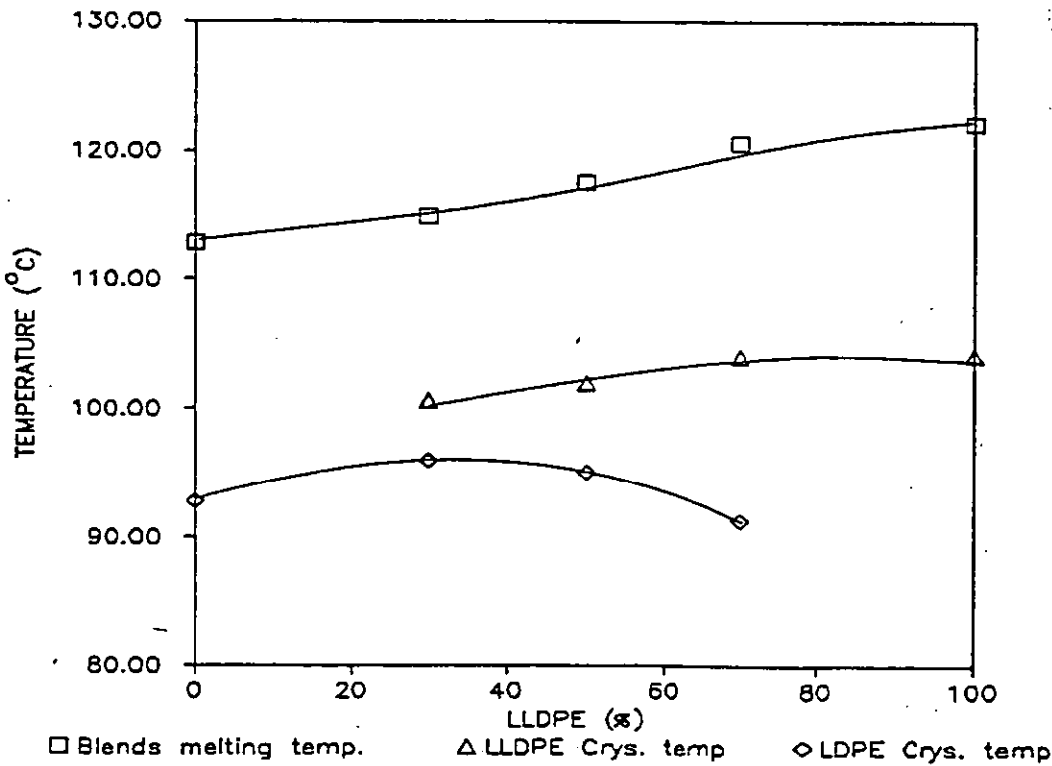


Fig. 5.6 Fusion on first heating and crystallisation temperatures as a function of composition for LLDPE/LDPE blends.

time to segregate and grow into separate types of crystal, as for the second heating thermograms.

The thermal analysis shows that the first crystalline melting peak of LDPE shifts to higher temperature as the content of LLDPE increases, being linear with the composition. This is shown more clearly in the plots of peak temperature versus composition in (Fig. 5.6).

The melting points of both LLDPE and LDPE for the second heating were depressed by the other component, possibly due to the factors which were mentioned previously in chapter 4.

During crystallisation the thermograms show a sharp peak at higher temperature which is attributed to LLDPE and a less distinct peak at lower temperature due to LDPE. As the content of LLDPE increases the crystallisation temperature of LLDPE increases too. The crystallisation temperature of LDPE at first increases and then from the 50/50-LLDPE/LDPE blend it decreases. This is shown more clearly in the plot of crystallisation temperature versus composition in (Fig. 5.6).

The conclusion from thermal analysis is that blends of LLDPE and LDPE are compatible in the melt. Depending on the rate of cooling the two types of crystal may stay mixed to show a one phase system. To investigate this, and to determine the effect on mechanical properties for the blends, injection moulded samples were obtained at two different mould temperatures. The blends were injected into 1 mm plaques at a mould temperature of 20 °C to obtain mouldings without segregation of the two types of crystal, and at a mould temperature of 50 °C to allow these two types of crystal to segregate.

The blends were also used to make blown films, at fast and slow cooling rates to achieve the same objective.

The effect of low shear rate was investigated by passing the blends through a Melt Flow Indexer.

5.3.2 Thermal Analysis of MFI Samples

To investigate whether crystals of LLDPE and LDPE blends would segregate at low shear rate the extruded blend of LLDPE/LDPE-30/70, was passed through a Melt Flow Indexer at 190 °C. Two sets of extrudates were obtained, one being quenched in water and the other one cooled in the air. The thermograms obtained are shown in (Figs.5.7 and 5.8). The thermograms of first heating for the quenched sample show only one melting peak, attributed to the LLDPE/LDPE blend, whereas the sample cooled in the air shows two distinct melting peaks due to LDPE and LLDPE. This shows that even at low shear rate, LLDPE and LDPE blends will not segregate to form two phases, providing the cooling rate is high.

5.3.3 Thermal Analysis of Injection Moulded Samples

5.3.3.1 Mould temperature of 20 °C

The thermograms obtained are shown in Figs. 5.9 to 5.11. As was expected the thermograms of first heating show only one melting peak attributed to LLDPE/LDPE blends.

During re-crystallisation, as for extruded samples , two peaks appeared of which the lower crystallisation

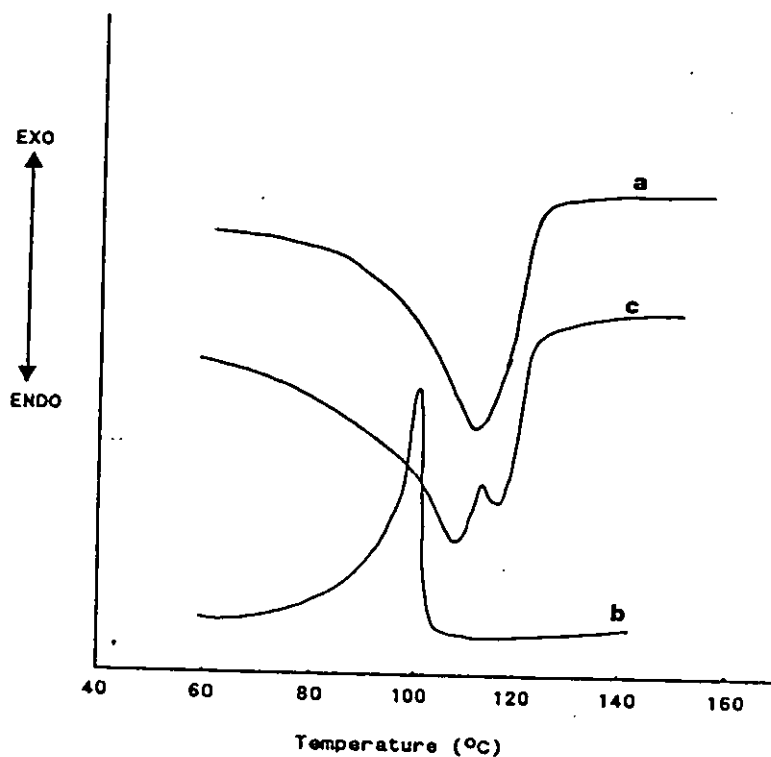


Fig. 5.7 Thermograms of blend of LLDPE/LDPE-30/70, passed at 190 °C through Melt Flow Indexer and quenched in cold water. (a) first heating, (b) cooling and (c) second heating.

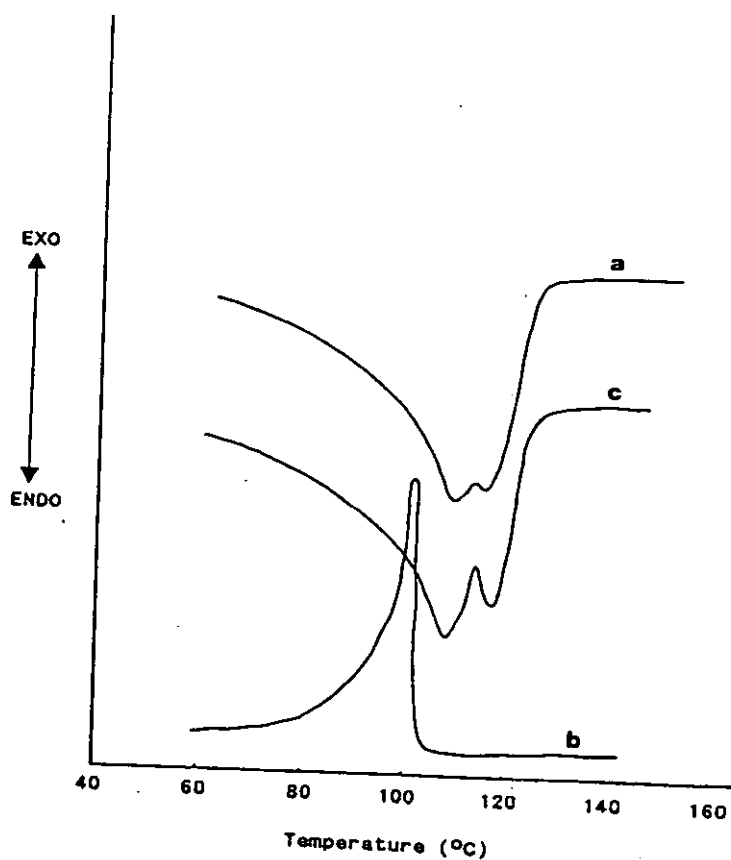


Fig. 5.8 Thermograms of blend of LLDPE/LDPE-30/70, passed at 190 °C through Melt Flow Indexer and cooled slowly in air. (a) first heating, (b) cooling and (c) second heating.

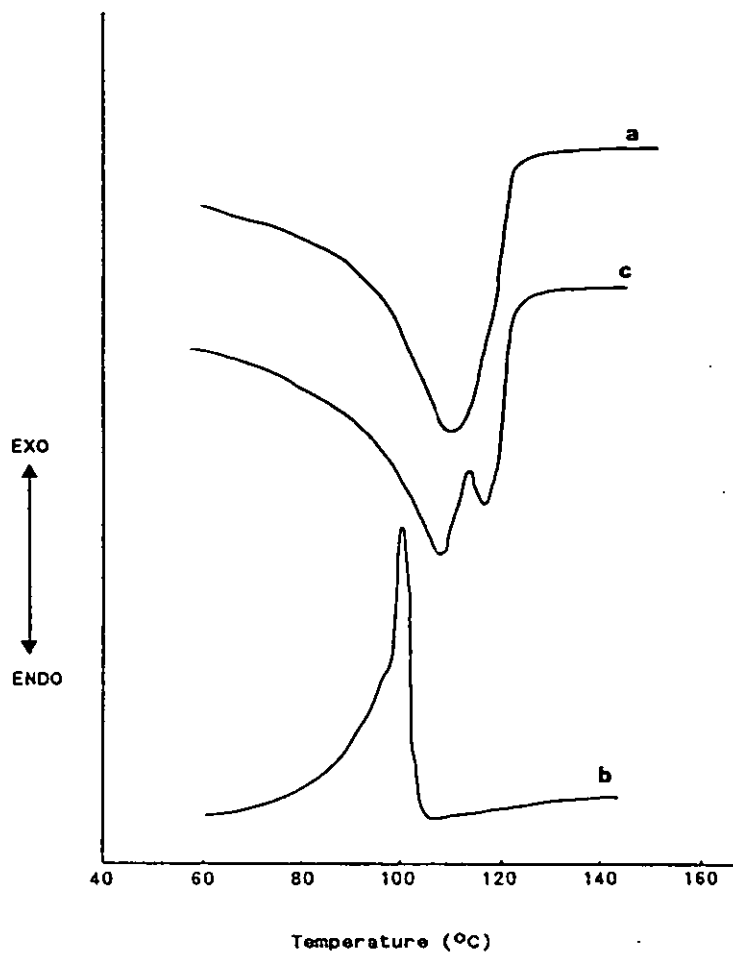


Fig. 5.9 Thermograms of blend of LLDPE/LDPE-30/70, injection moulded sample, mould temperature of 20 °C. (a) first heating, (b) cooling, and (c) second heating.

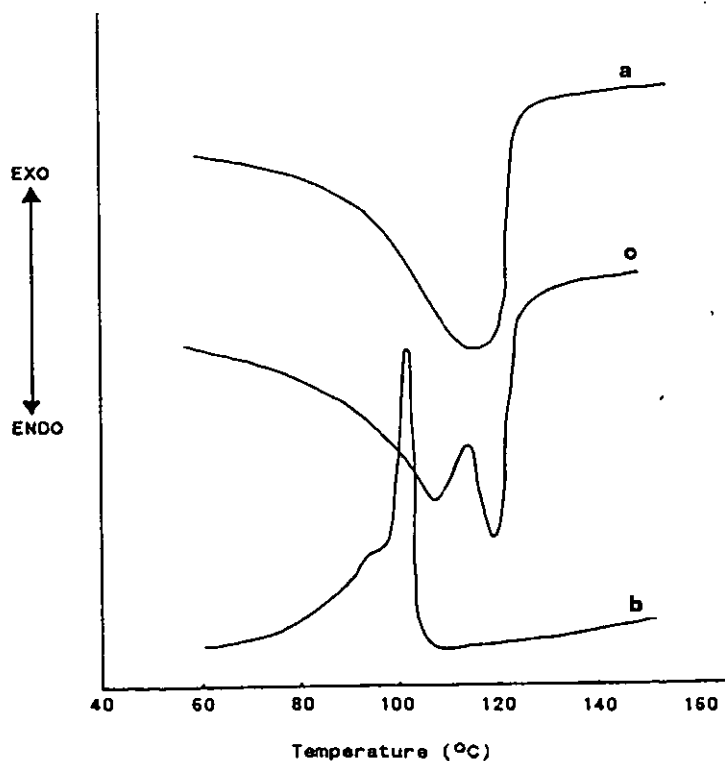


Fig. 5.10 Thermograms of blend of LLDPE/LDPE-50/50, injection moulded sample, mould temperature of 20 °C. (a) first heating, (b) cooling and (c) second heating.

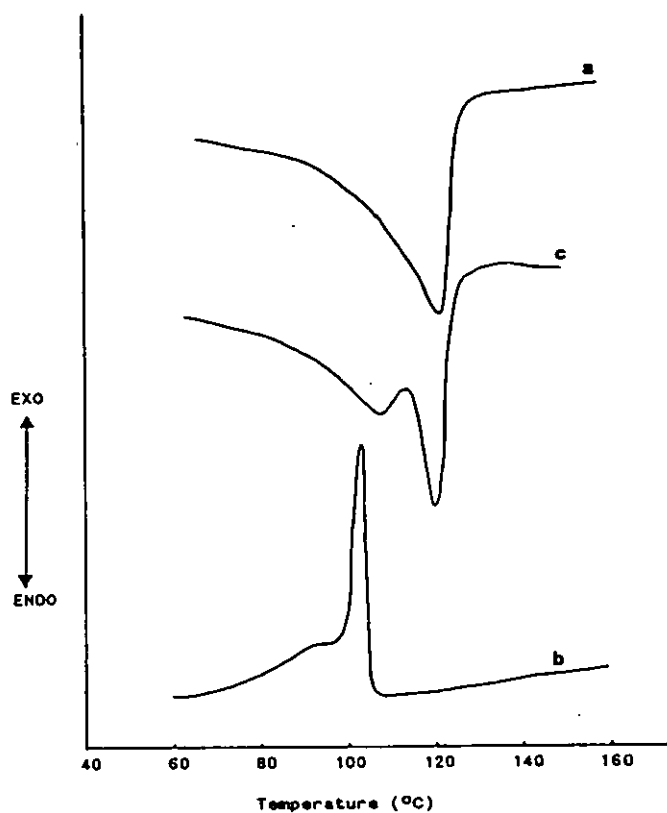


Fig. 5.11 Thermograms of blend of LLDPE/LDPE-70/30, injection moulded sample, mould temperature of 20 °C. (a) first heating, (b) cooling, and (c) second heating.

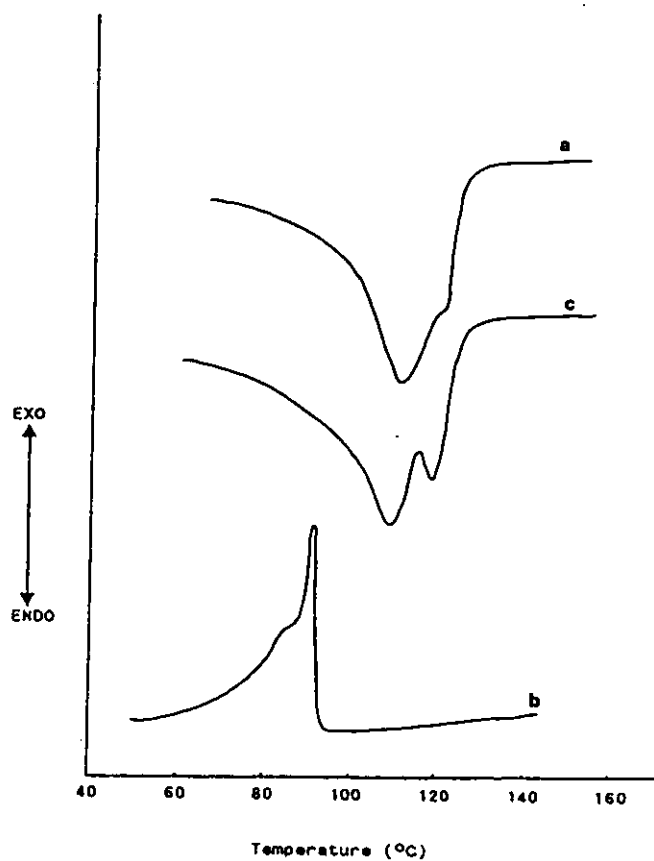


Fig. 5.12 Thermograms of blend of LLDPE/LDPE-30/70, injection moulded sample, mould temperature of 50 °C. (a) first heating, (b) cooling, and (c) second heating.

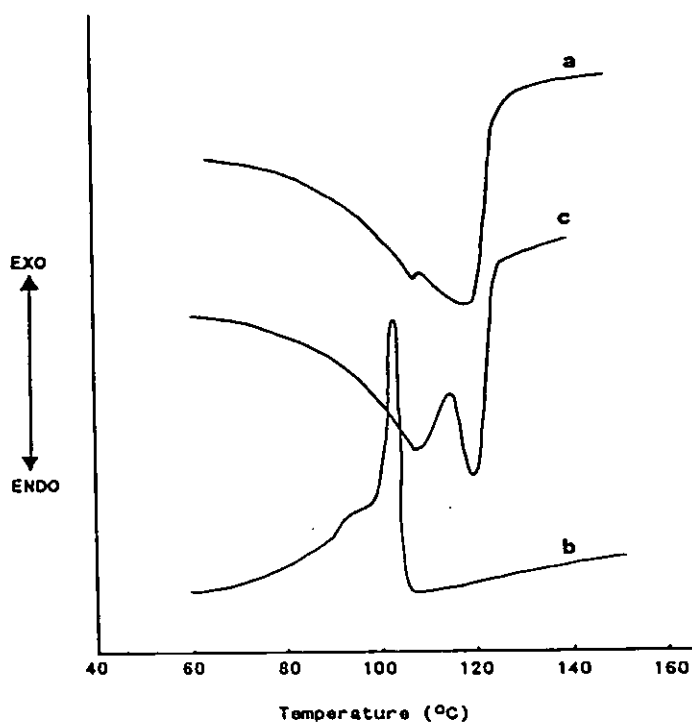


Fig. 5.13 Thermograms of blend of LLDPE/LDPE-50/50, injection moulded sample, mould temperature of 50 °C. (a) first heating, (b) cooling and (c) second heating.

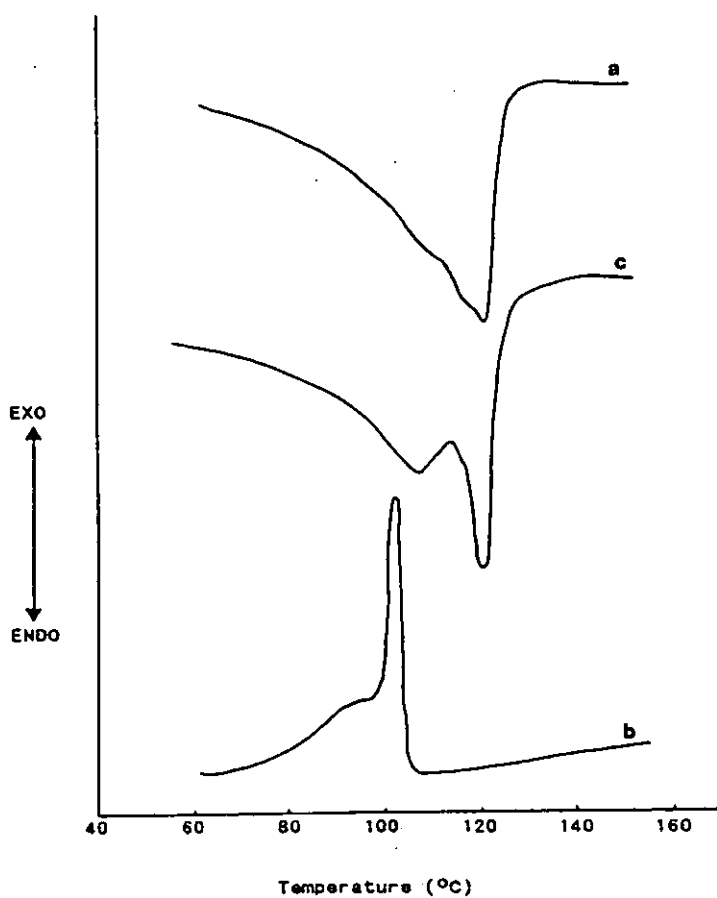


Fig. 5.14 Thermograms of blend of LLDPE/LDPE-70/30, injection moulded sample, mould temperature of 50 °C. (a) first heating, (b) cooling, and (c) second heating.

temperature is attributed to LDPE and the higher is due to LLDPE.

The above results show as before that by quenching the samples, it is possible to keep the two components compatible in the melt and on cooling, to show only a single crystalline phase.

5.3.3.2 Mould temperature of 50 °C

The thermograms obtained (Figs. 5.12-5.14) show two melting, and two crystallisation peaks for the first heating. The lower is attributed to LDPE and the higher is associated with LLDPE. This indicates the importance of cooling rate, as high mould temperature allows the segregation and growth of the two types of crystal.

5.3.4 Thermal Analysis of Blown Film

5.3.4.1 Fast Cooling Rate

The thermograms obtained for the first heating (Figs. 5.15-5.17, see Appendix II) show one melting peak associated with LLDPE/LDPE blends except for the 50/50 blend (Fig. 5.16, see Appendix II) which shows segregation of the peaks. Generally these thermograms compared with those of injection moulded products (mould temperature of 20 °C) show signs of broadening of the first melting peak. This can be explained by the cooling rate of blown film which is much slower than injection moulding, resulting in the tendency of the two types of crystal to segregate.

5.3.4.2 Slow Cooling Rate

The thermograms obtained (Figs. 5.17-5.20, see Appendix II) for the first heating show two distinct melting peaks for LDPE and LLDPE as in the case of injection moulded specimens (50 °C). These observations confirm the results obtained by injection moulding which show the importance of cooling rate.

5.3.5 MECHANICAL PROPERTIES

5.3.5.1 Injection Mouldings

The tensile stresses at yield and break for LLDPE, LDPE, and their blends for injection moulded samples are shown in Figs. 5.21 and 5.22.

The tensile stresses at yield for LDPE and LLDPE are similar, as they have similar degrees of crystallinity.

There is little or no change in tensile stress at yield for the transverse direction (TD), as the content of LLDPE increases. The mould temperature was found to have little effect in the transverse direction. In the machine direction (MD) the samples did not reach yield.

The tensile strengths at break for TD show that as the content of LLDPE increases, the breaking strength increases. The mould temperature has little effect on the breaking strength, and similarly with yield stress, the breaking strength for hot mould products (50 °C), as expected, is higher than for the cold mould products (20 °C). This could be explained as at low mould temperature the polymer melt cools rapidly, results in having fine crystal structure with low degree of crystallinity which results in lower strength. On the other hand high mould temperature means slower cooling of the melt which results in large crystal structure

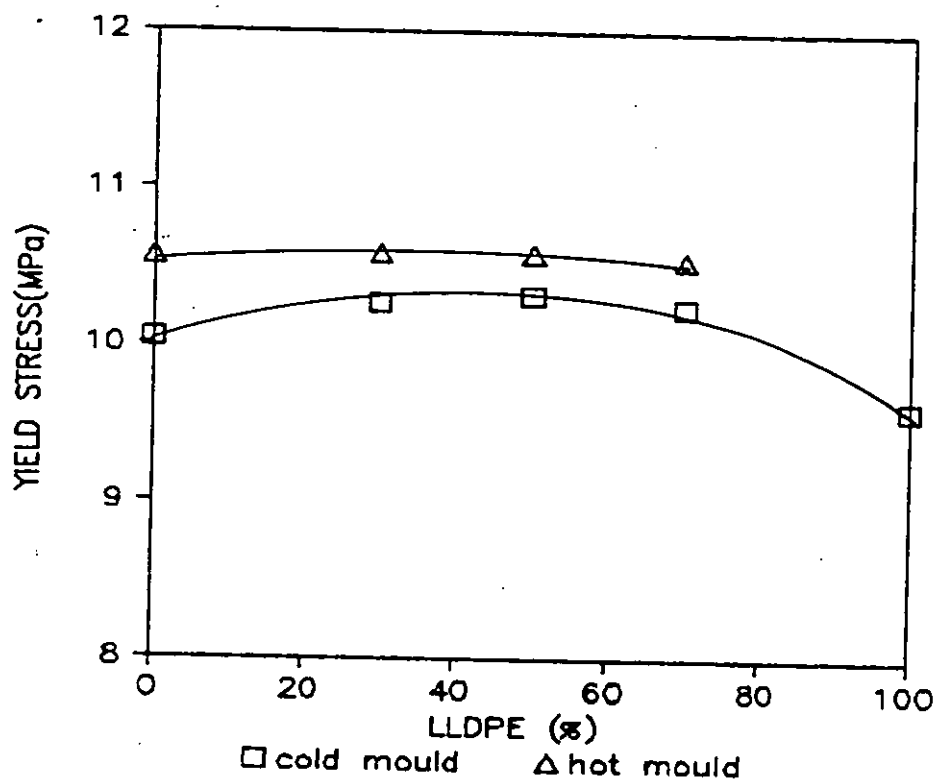


Fig. 5.21 Tensile Stress at yield for injection moulded samples(transverse direction).

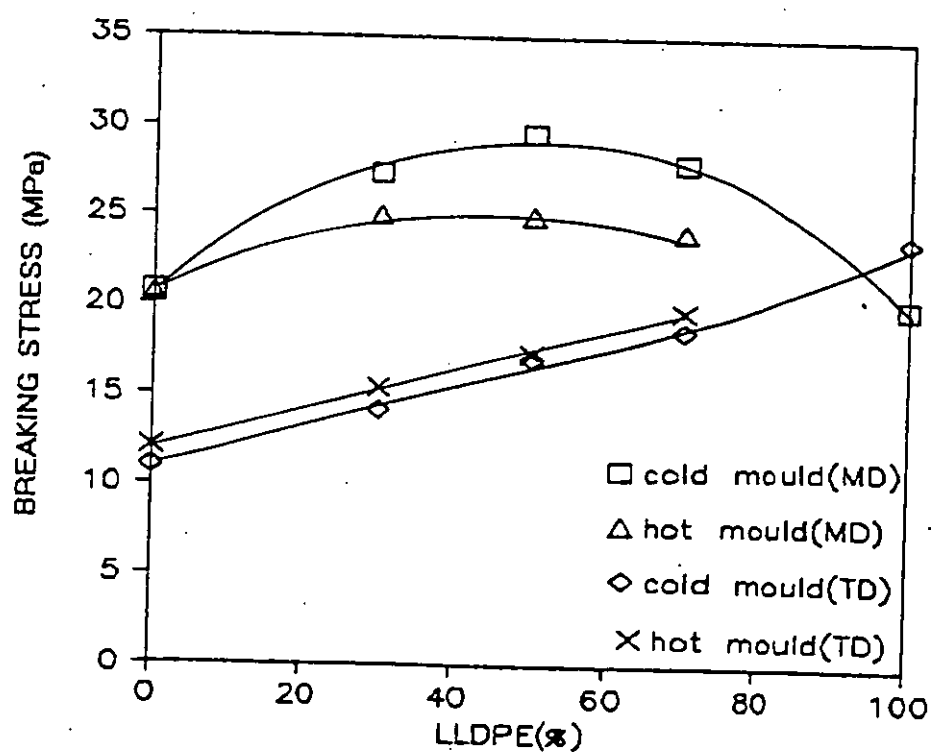


Fig. 5.22 Tensile Strength at break for injection moulded samples.

and encourages crystallisation, hence increases the strength.

However very different and interesting results were obtained in the machine direction. The effect of mould temperature can be seen very clearly, as for quenched samples considerably higher tensile strengths were obtained. As the content of LLDPE increases the breaking strength increases too and reaches its optimum for LLDPE/LDPE-50/50 blend, and then starts to decrease. This clearly shows the effect of fast cooling rate which was detected on the DSC by showing only one melting peak for the first heating. In this case compatibility i.e. a one phase system, dominates the texture of the solid, as was explained earlier. The other factor which may have influenced this characteristic could be orientation. Because in general anything that increases the mobility of the molecules decreases orientation⁽⁸⁶⁾. Therefore lower mould temperature and hence faster cooling rate increases orientation.

The elongation at break for LDPE, LLDPE, and their blends is shown in Figs. 5.23 and 5.24. The elongation in TD seems to be little affected by the mould temperature. Higher elongation was obtained for hot mould samples as in the case of strength. The elongation at break for MD shows generally higher elongation for quenched samples, except for 70/30-LL/LD which was lower.

The above observations show that mould temperature i.e. rate of cooling only affects the machine direction. Therefore one might suggest that this is due to orientation. This is not true as in the next section the effect of cooling rate can be seen in the MD and TD

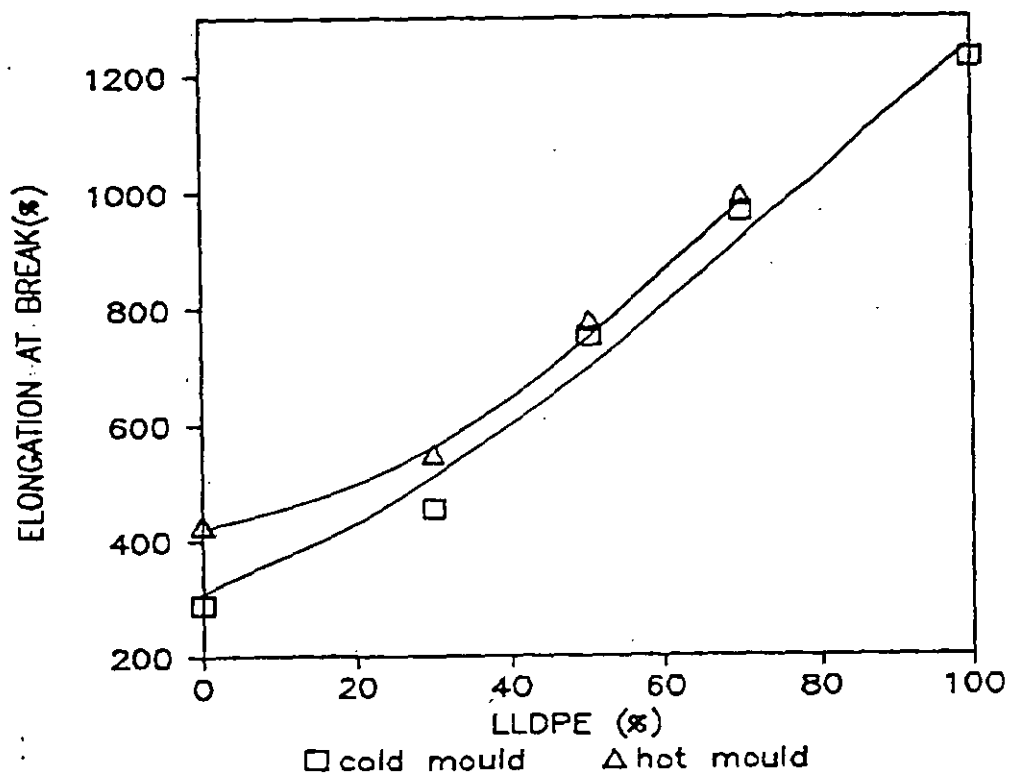


Fig. 5.23 Elongation at Break for injection moulded samples(transverse direction).

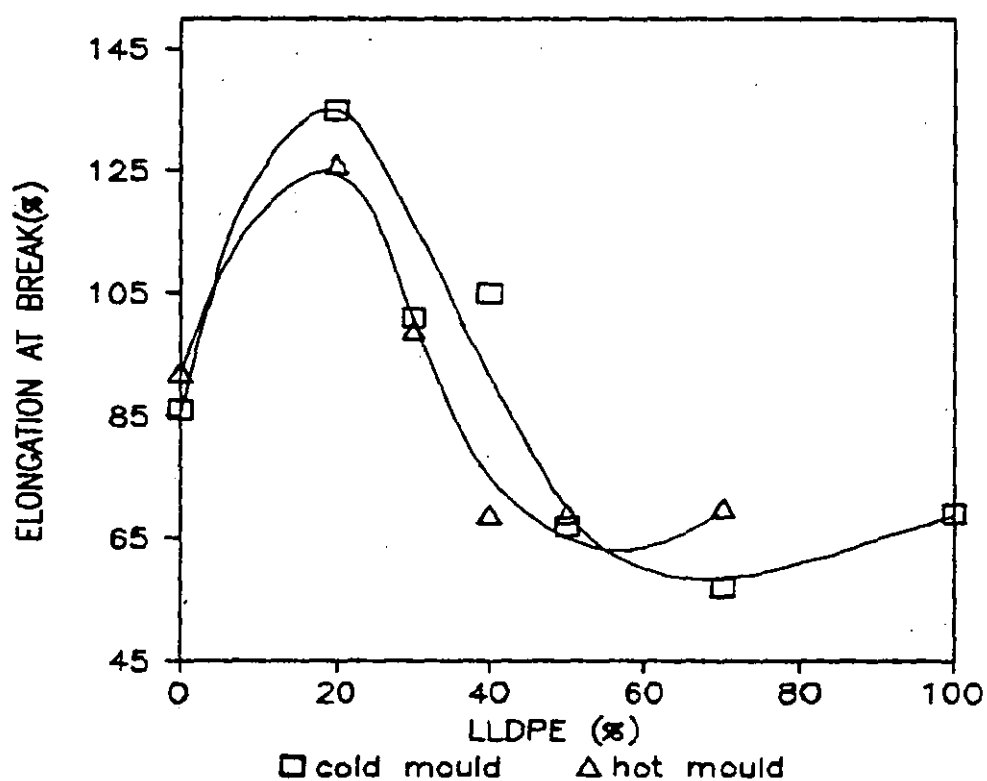


Fig. 5.24 Elongation at Break for injection moulded samples(machine direction).

for the blown film. Orientation might play a role but the main factor is the cooling rate.

5.3.5.2 Blown Film

The tensile strengths at yield and break for LDPE, LLDPE films and their blends are shown in Figs. 5.25 to 5.28. the yield data in the transverse direction are scattered. To explain this phenomenon, we have to go back to the thermograms of the films. It seems when the first heating gives a sharp peak(e.g Fig. 5.15, rapidly cooled, see appendix II), this results in higher yield stress than for the slow cooled sample(e.g Fig. 5.18, see Appendix II). Similarly the lowering of the yield stress seems to be associated with the broadening (or segregation) of the fusion peak(e.g Fig. 5.16, see Appendix II).

The tensile stress at yield in the machine direction for the quenched samples is higher than for slow cooled samples, and reaches its optimum for the 50/50 blend. This is the opposite to expectation as normally we would expect rapid cooling to give lower values, especially of yield stress. This behaviour is ascribed to the miscibility of LLDPE and LDPE in the melt, quenching of which prevents segregation of the two crystal species as was found for injection moulded samples. The blend of LLDPE/LDPE-30/70 did not reach yield in the machine direction, this suggests that this is indicative of this blend ratio being the least miscible of the series. It is surprising, therefore that this is one of the most frequently used blend ratios exploited commercially.

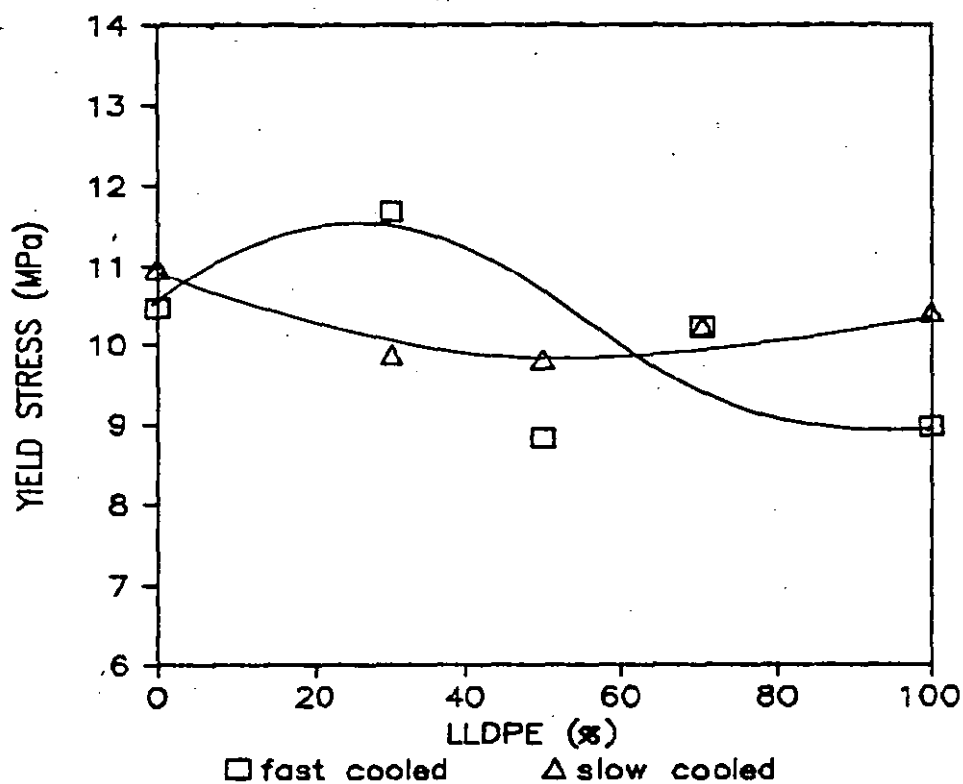


Fig. 5.25 Tensile Stress at yield for blown film(transverse direction).

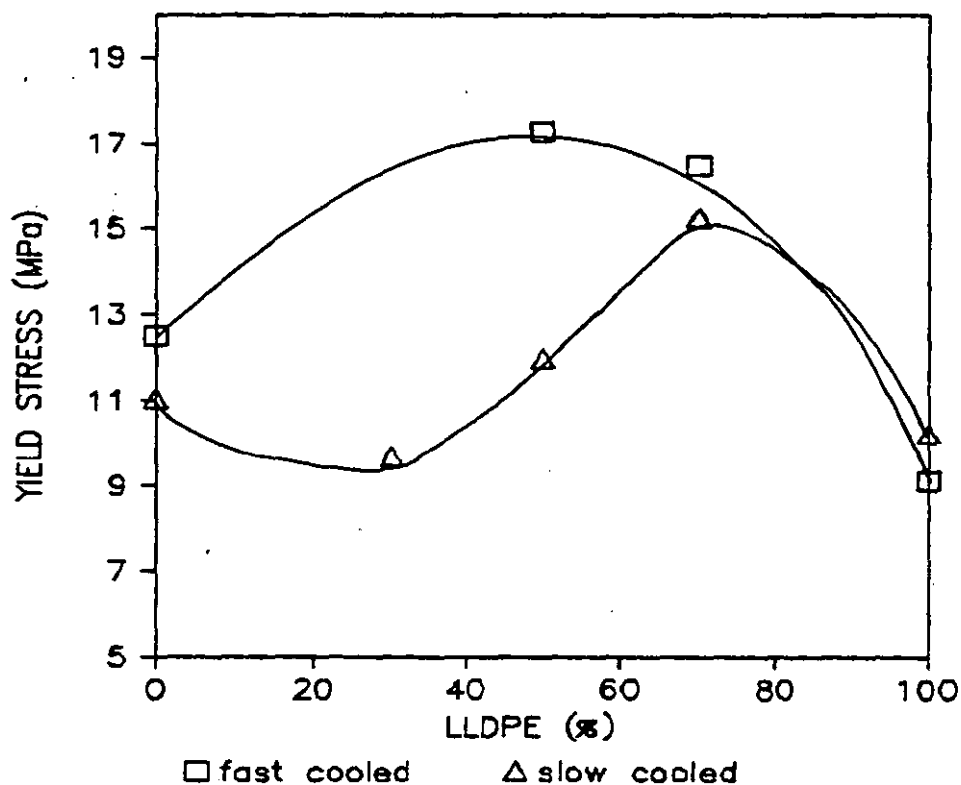


Fig. 5.26 Tensile Stress at yield for blown film(machine direction).

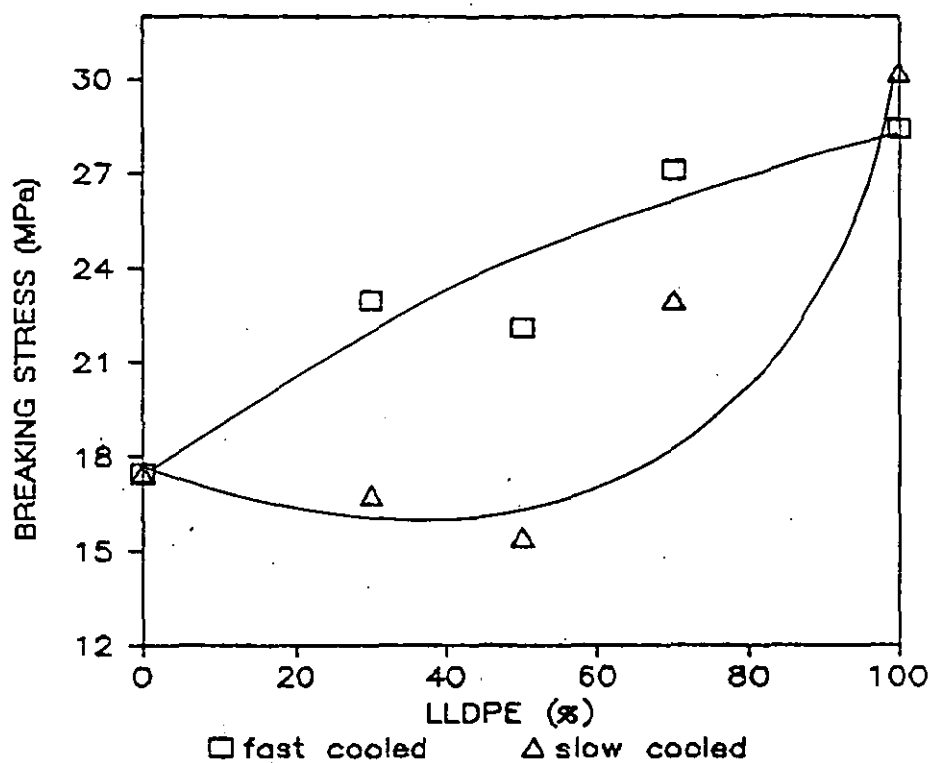


Fig. 5.27 Tensile Strength at break for blown film(transverse direction).

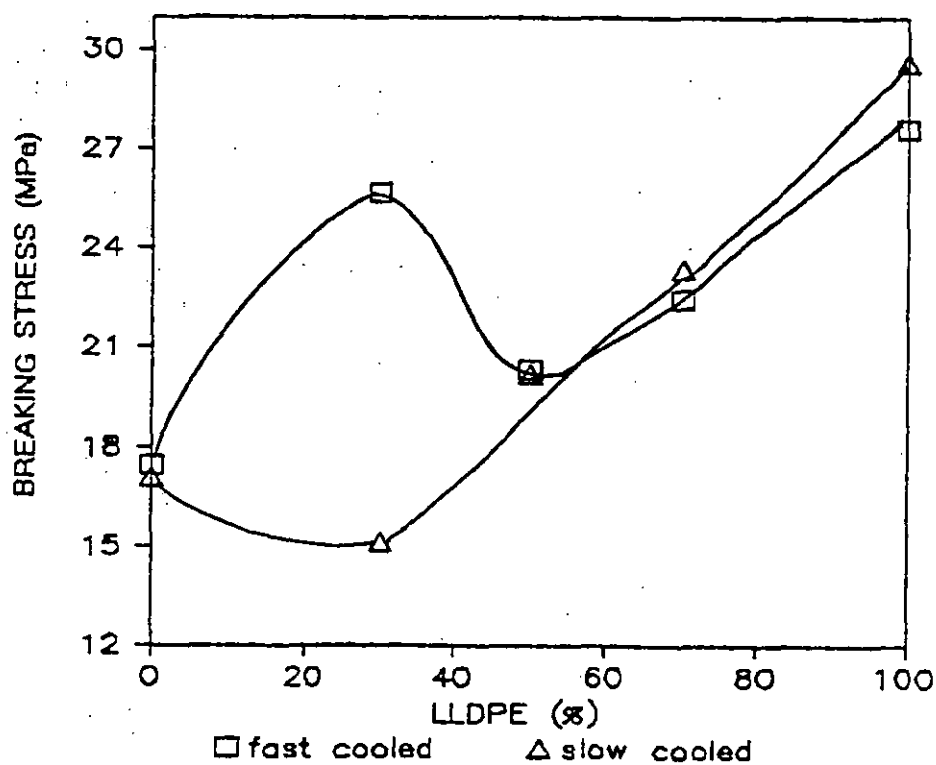


Fig. 5.28 Tensile Strength at break for blown film(machine direction).

The tensile strengths at break in TD and MD are generally higher for quenched samples than slow cooled samples.

The mechanical properties of blown films show the effects of cooling rates in TD and MD and confirm the results obtained by the injection moulded samples.

5.4 CONCLUSION

LLDPE and LDPE blends which have been mixed intensively show, on thermal analysis only a single fusion peak. Although they are not thermodynamically stable, the blends do not segregate even at low shear rate provided the cooling is rapid. This suggests that the blends of LLDPE and LDPE are miscible in the melt, which can result in having a superior product provided the cooling rate is reasonably fast.

CHAPTER 6

BINARY BLENDS OF POLYPROPYLENE AND LINEAR LOW DENSITY POLYETHYLENE

6.1 INTRODUCTION

In recent years there has been a great deal of commercial interests in melt blending of isotactic polypropylene (iPP) with polyethylene and/or ethylene-propylene rubber (EP(D)M). This is a common method of improving the impact resistance of polypropylene (PP) (87).

Polypropylene is a semi-crystalline polymer with glass transition temperature in the $-20 - 0^{\circ}\text{C}$ range. The polyethylene (PE) in view of its lower glass transition temperature will be expected to have higher impact resistance than PP, particularly at low temperatures. There have been a number of studies on the behaviour and on the possible improvement in the impact resistance of PP by melt blending with high density polyethylene or EP(D)M, resulting in a number of publications and patents (42,43,61,81,88-101), but there are few studies on the melt blending of PP with LLDPE. This omission is rectified in the present work.

In this chapter several different blends of PP/LLDPE were investigated. An unusual and interesting result was detected by DSC when small amounts of LLDPE were added to PP. In the last part of this chapter several

processing techniques were used to find an application for this unusual behaviour.

6.2 MATERIALS

The following materials as shown in Table 6.1 were used.

Table 6.1

	Producer or trade name	Grade	MFI (g/10 min)	Density (g/ml)
LLDPE	Escorene	LL1001XV	1.0 ⁺	0.918
LLDPE	Escorene	LL1001XV	2.0 ⁺	0.918
LLDPE	Dowlex	2045	1.5 ⁺	0.9185
pp	Profax	6824	0.32 [*]	0.9064
pp	Himont		1.5 [*]	
VLDPE	Norsoflex	1960	12.0 ⁺	0.895

⁺ tested at 190 °C.

^{*} tested at 230 °C.

The blends were prepared by melt mixing on a single or twin screw extruder. The compositions are shown in Table 6.2.

Table 6.2

Blends	MFI (190/230 °C)	Compositions
Escorene/Profax	1.0/.32	0/100, 20/80, 30/70, 60/40, 80/20, 100,0
Escorene/Profax	2.0/.32	0/100, 5/95, 10/90, 15/85, 20/80, 30/70, 40/60, 70/30

Table 6.2 Cont.

Blends	MFI (190/230 °C)	Compositions
Dowlex/Profax	1.5/.32	0/100, 5/95, 10/90, 15/85, 20/80, 0/100
Escorene/Himont	2.0/1.5	0/100, 5/95, 10/90, 15/85, 20/80, 0/100
VLDPE/Himont	12/1.5	0/100, 10/90, 20/80

6.3 RESULTS AND DISCUSSION

6.3.1 Density Measurements

The densities of LLDPE, PP and their blends (Fig. 6.1) were determined by density gradient columns and also calculated by the use of general mixture law⁽⁴⁰⁾:

$$100/D = (C_1/D_1) + (C_2/D_2)$$

where C_1 and C_2 are weight per cent of the components, and D_1 , D_2 are the corresponding densities. The experimentally determined and calculated densities of these blends agree well and they follow the additivity rule as was found by Stafford⁽⁴⁰⁾ for blends of high and low density polyethylene.

The degree of crystallinity of LLDPE, PP and their blends using equation 2.16 and also calculated by the use of general mixture law is shown in Fig. 6.2. The degree of crystallinity of PP, as expected, was found to be greater than the LLDPE due to having less irregularity structure.

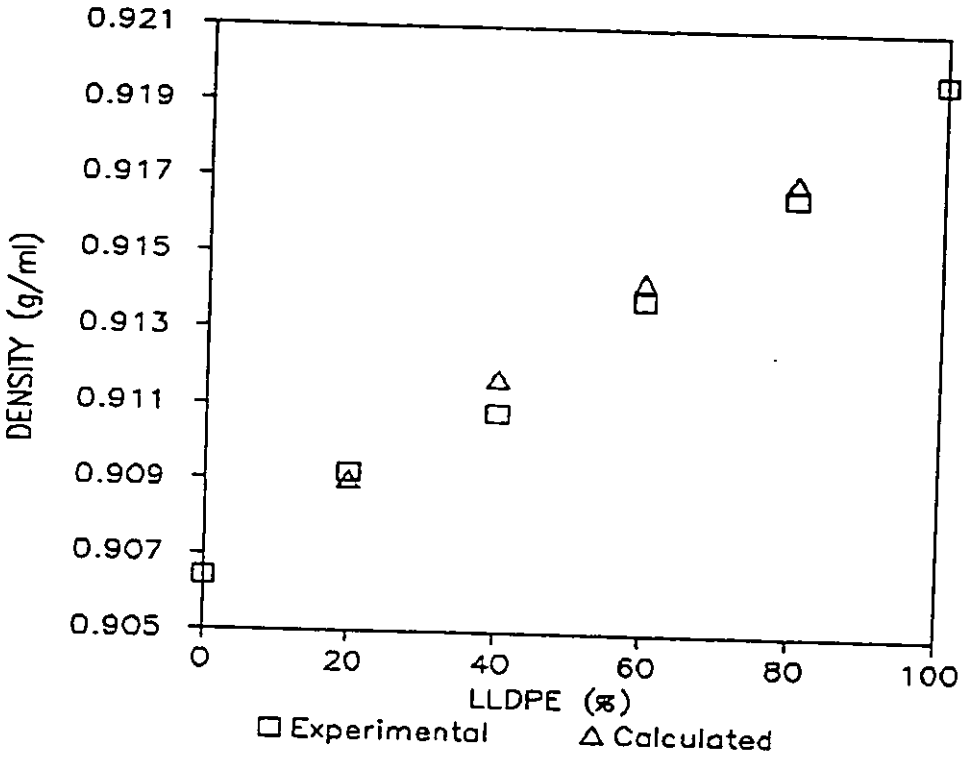


Fig. 6.1 The densities of LLDPE, PP, and their blends.

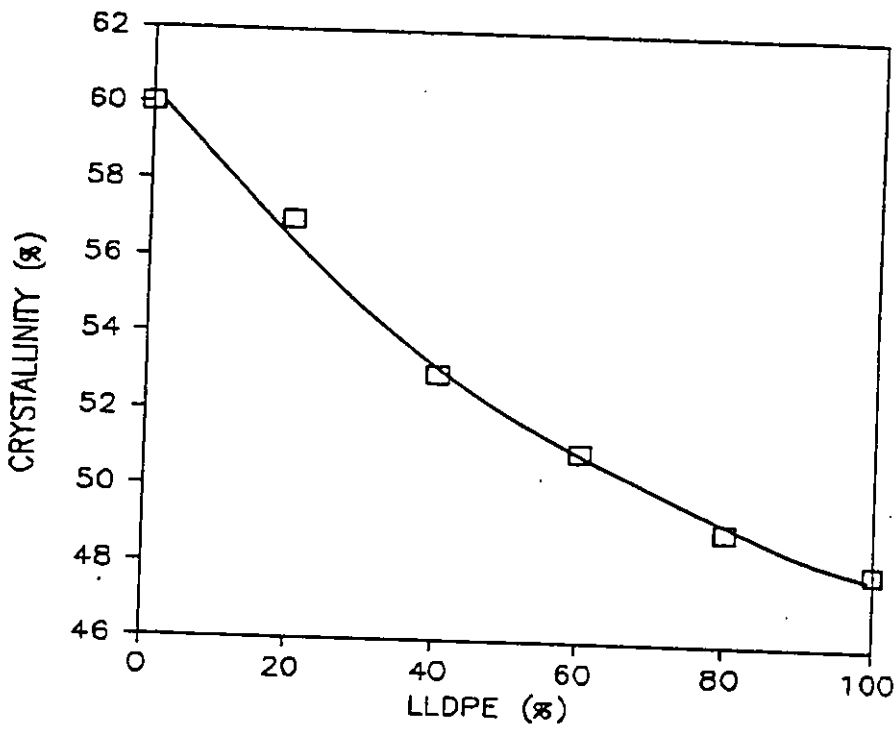


Fig. 6.2 The crystallinity of LLDPE, PP, and their blends.

The crystallinity of LLDPE/PP blends show a gradual decrease with increase in LLDPE contents. These show an almost linear relationship between crystallinity and composition as in the case of density.

6.3.2 Determination of the proportions of LLDPE/PP blends using infra-red spectroscopy

The spectra of LLDPE/PP blends at room temperature are shown in Figs. 6.3 to 6.6. The absorbance band of LLDPE at 720 and PP at 1165 cm^{-1} were measured and the plot of the ratio of these bands versus the blend compositions is shown in Fig. 6.7. This shows a linear relationship of the absorbance band with composition which shows that the blends made on the extruder contain accurate proportion of LLDPE/PP in each composition set. Although Pek Choo Ng et. al(102) suggested a method to overcome the problem associated with the sensitivity of ethylene absorbance to crystallinity level by making the measurements above the melting point of crystalline polyethylene(145-150 °C), theses results do not show any interference as was demonstrated by Po-Len Yeh(103) in Table 6.3 for the sequential propylene-ethylene copolymer at different temperatures. The E/P absorbance ratio shows little decrease as temperature increases and reaches an equilibrium value of 0.12 at high temperature. The reduction being in the melting region for linear polyethylene(103).

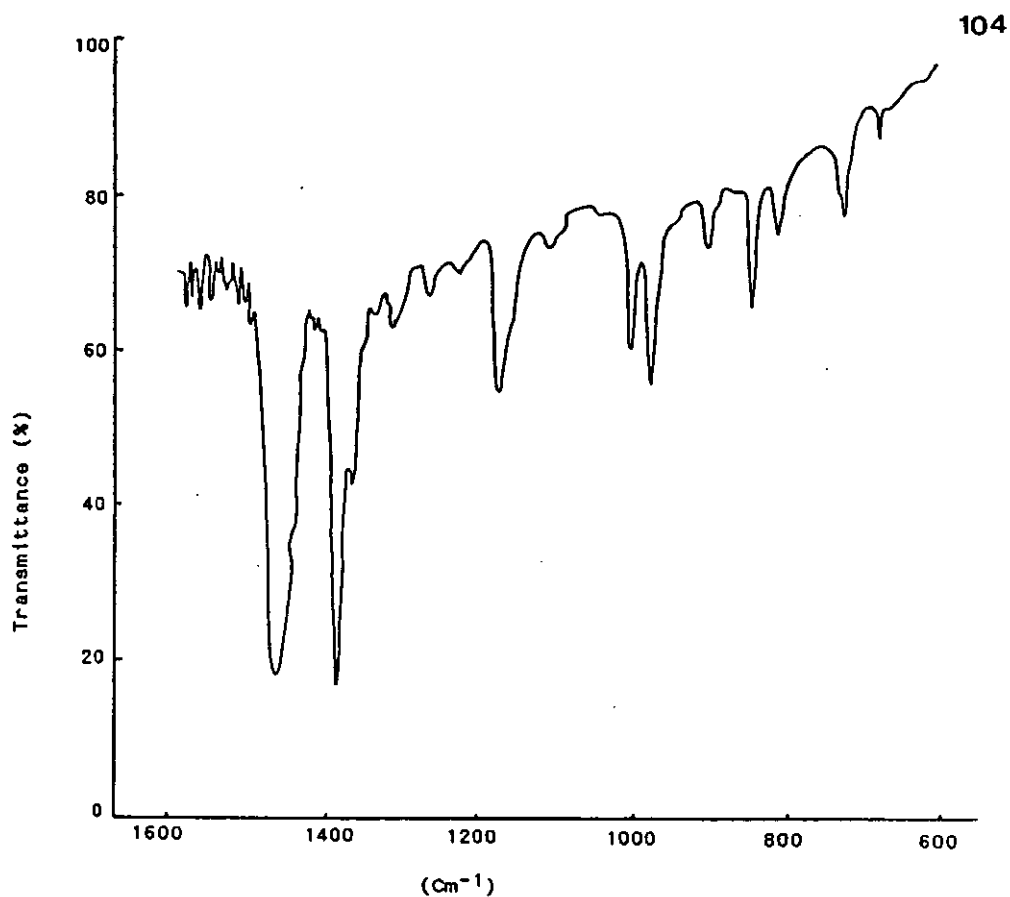


Fig. 6.3. Infra-red spectrum of LLDPE/PP-20/80 blend.

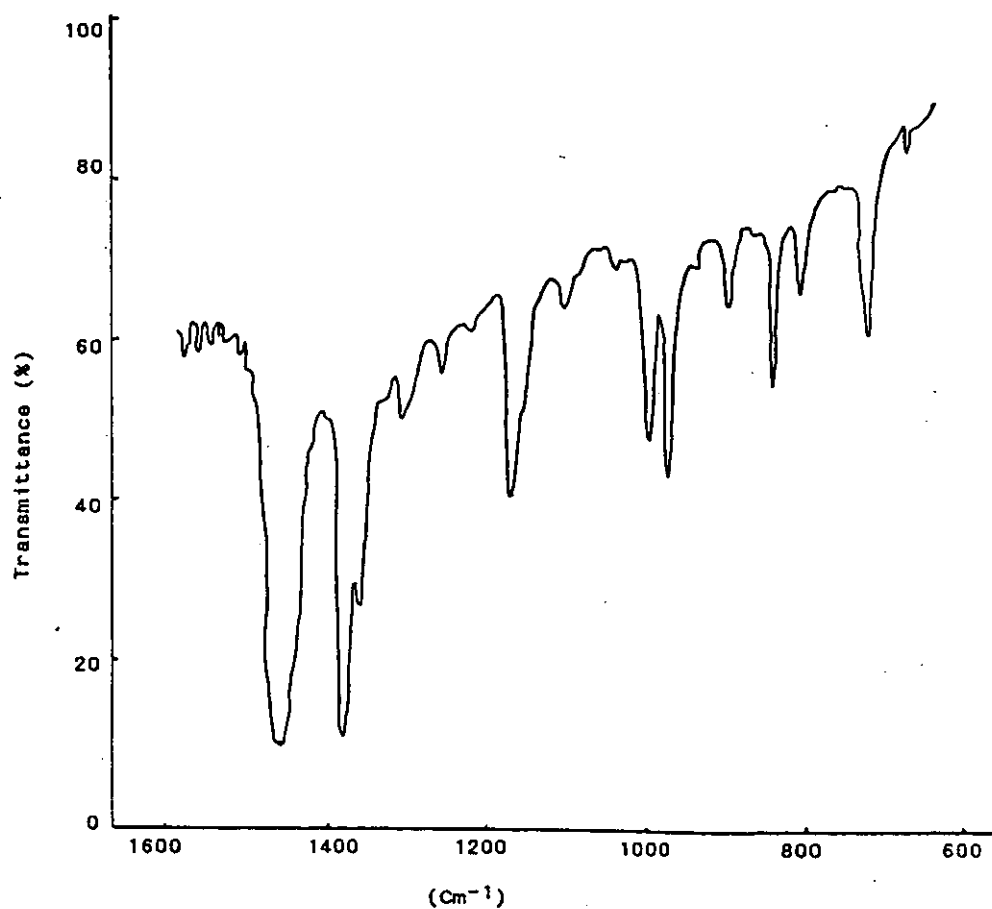


Fig. 6.4. Infra-red spectrum of LLDPE/PP-30/70 blend.

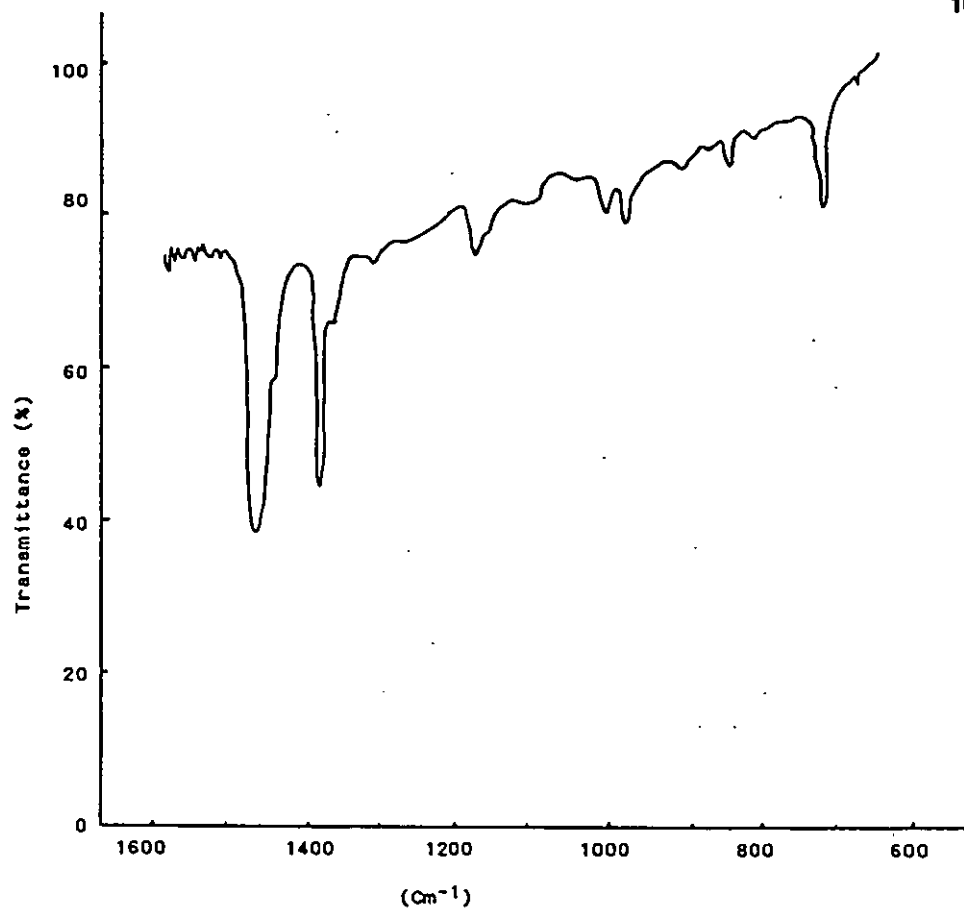


Fig. 6.5. Infra-red spectrum of LLDPE/PP-60/40 blend.

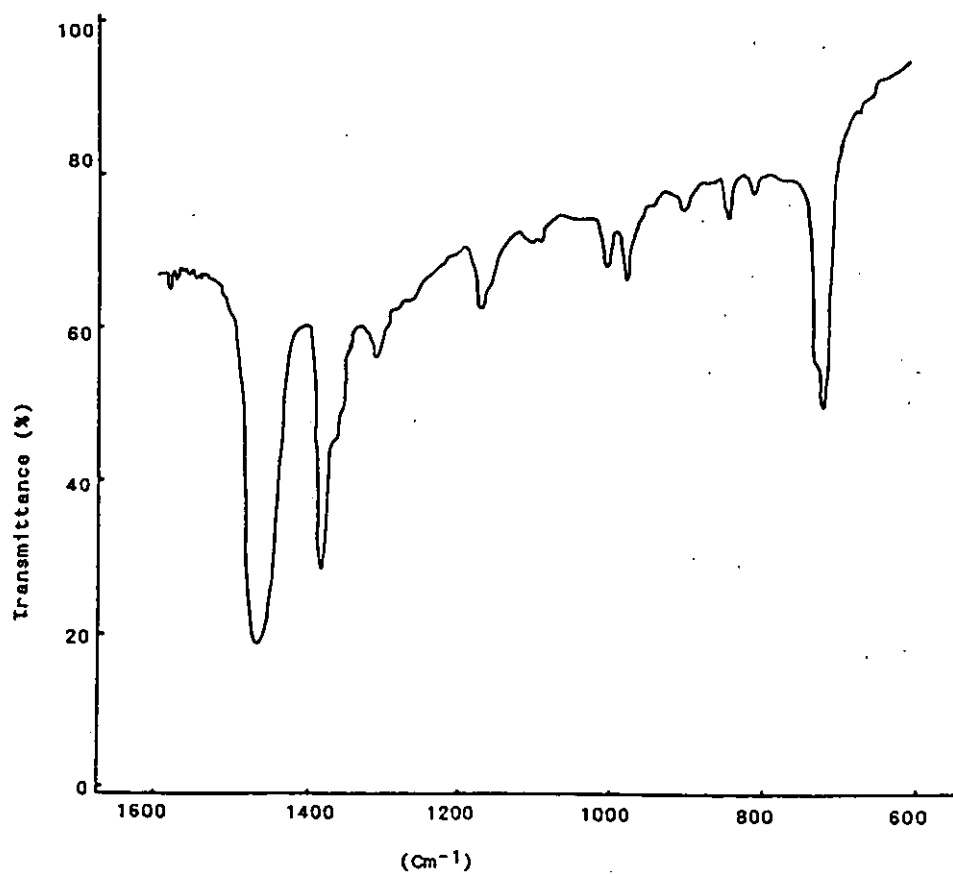


Fig. 6.6. Infra-red spectrum of LLDPE/PP-80/20 blend.

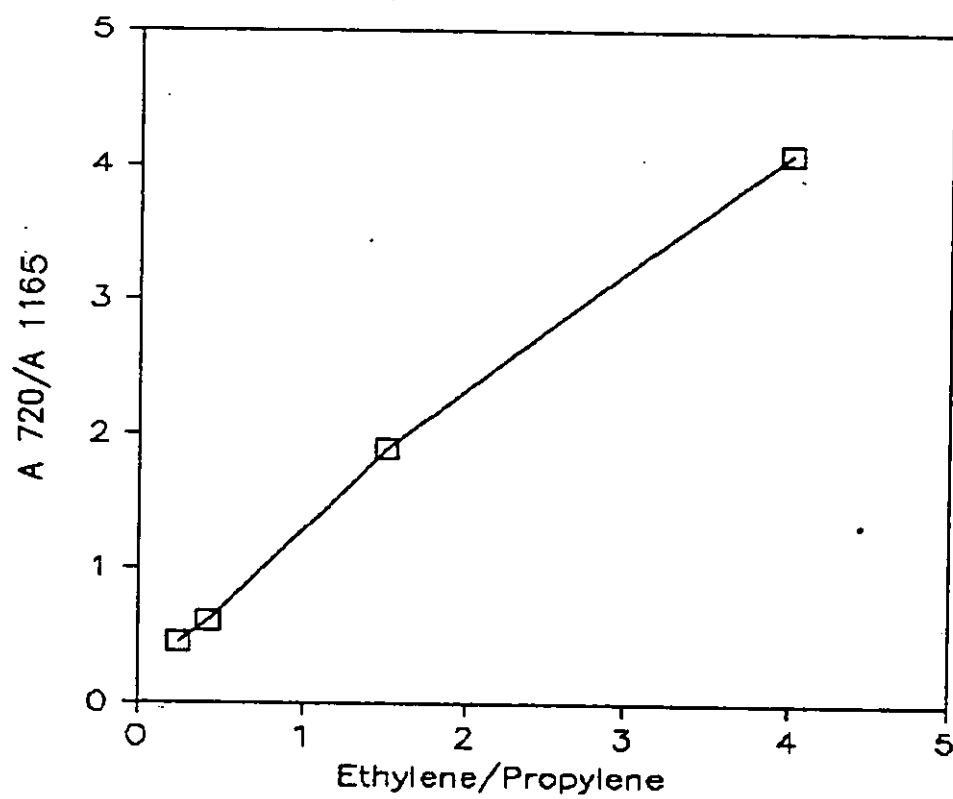


Fig. 6.7 The absorption band ratio of ethylene/propylene.

Table 6.3(103)

The effect of temperature on the sequential copolymer

Temperature measured (°C)	Absorbance at 1165 cm^{-1} (P) *	Absorbance at 720 cm^{-1} (E) *	Absorbance ratio (E/P)
45	1.274	0.1746	0.137
68	1.128	0.1619	0.143
84	1.019	0.1416	0.139
107	0.894	0.1183	0.132
121	0.797	0.1034	0.130
134	0.743	0.0891	0.120
149	0.672	0.0809	0.120

* Absorbance of the major part of the doublet

6.3.3 Thermal Analysis

Thermograms of LLDPE(Escorene), PP(Profax 6824), and their blends are shown in Figs. 6.8 to 6.17 and (6.18 to 6.22, see Appendix III). The melting and crystallisation temperatures are summarised in Table 6.4 and 6.5. The thermograms of blends show two distinct melting peaks. The lower peak is attributed to melting of LLDPE, and the higher endotherm is associated with melting of PP. The melting temperatures of PP in the mixture indicate slightly lower melting points than observed with pure PP, while that of LLDPE hardly shifts in going from mixture to pure component. It was found that generally, only the melting point of the higher melting polymer is lowered in blends of two crystalline polymers. This shift may be explained by the Flory theory of melting temperature depression of polymer-diluent mixture. This was also observed by Inoue⁽³⁷⁾ in the case of nylon 6 and nylon 11 blends.

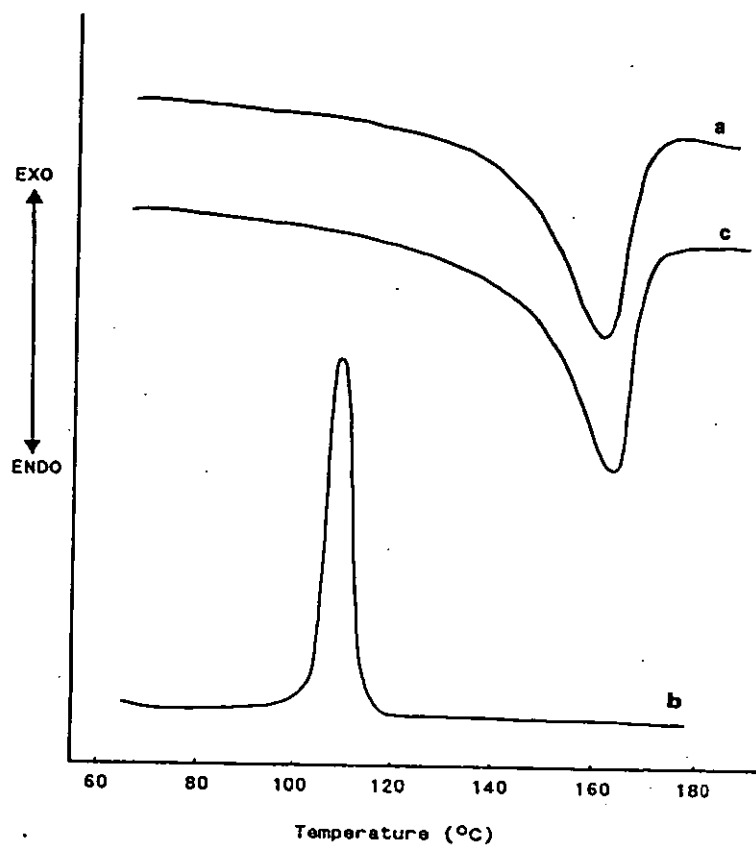


Fig. 6.8 Thermograms of PP(Profax 6824). (a) first heating, (b) cooling, and (c) second heating.

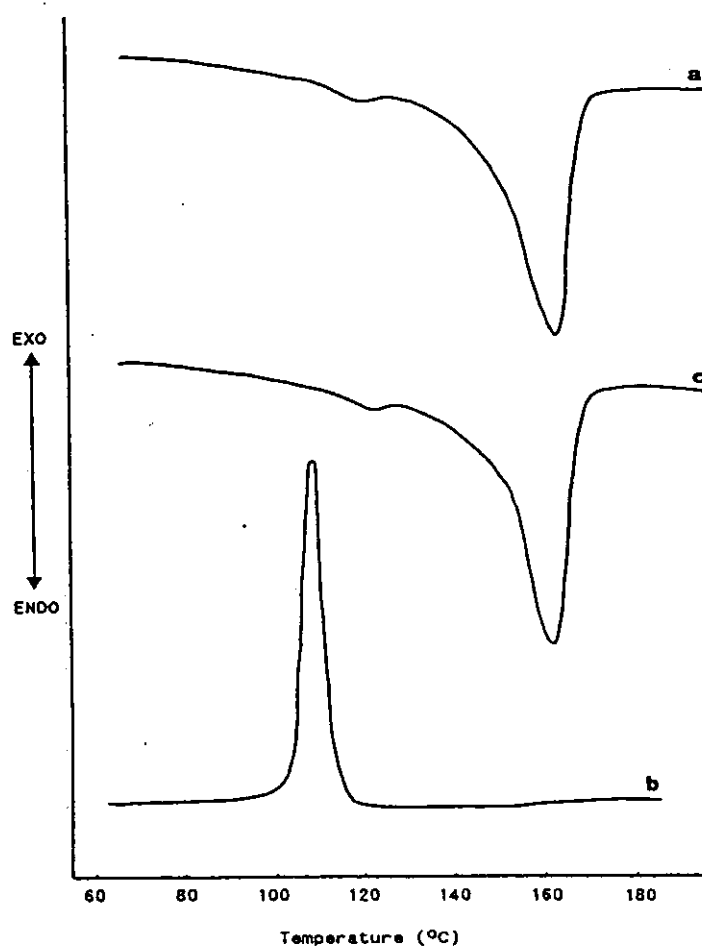


Fig. 6.9 Thermograms of LLDPE(MFI=2)/PP-5/95 blend. (a) first heating, (b) cooling, and (c) second heating.

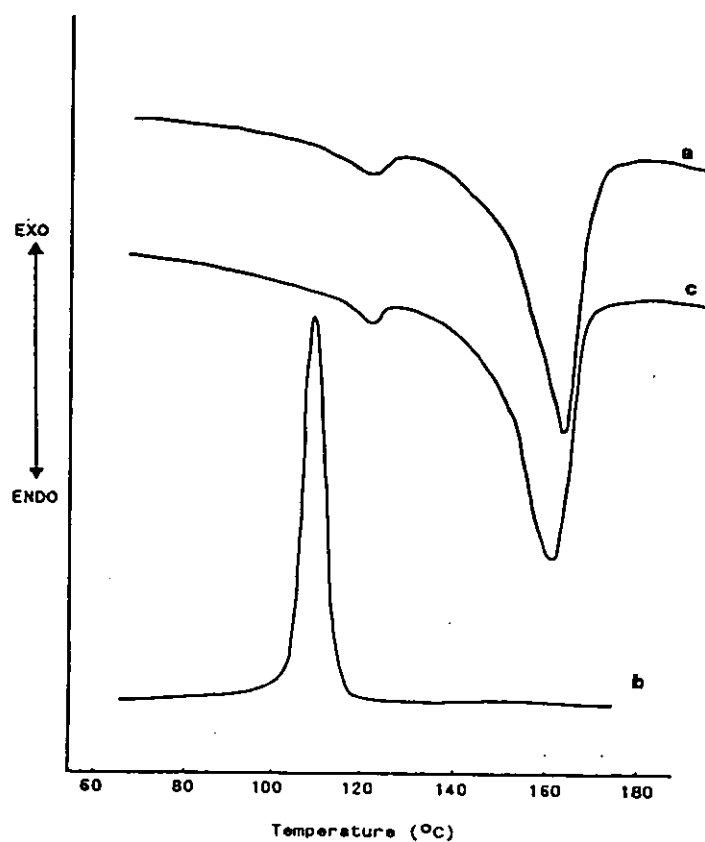


Fig. 6.10 Thermograms of LLDPE(MFI=2)/PP-10/90 blend. (a) first heating, (b) cooling, and (c) second heating.

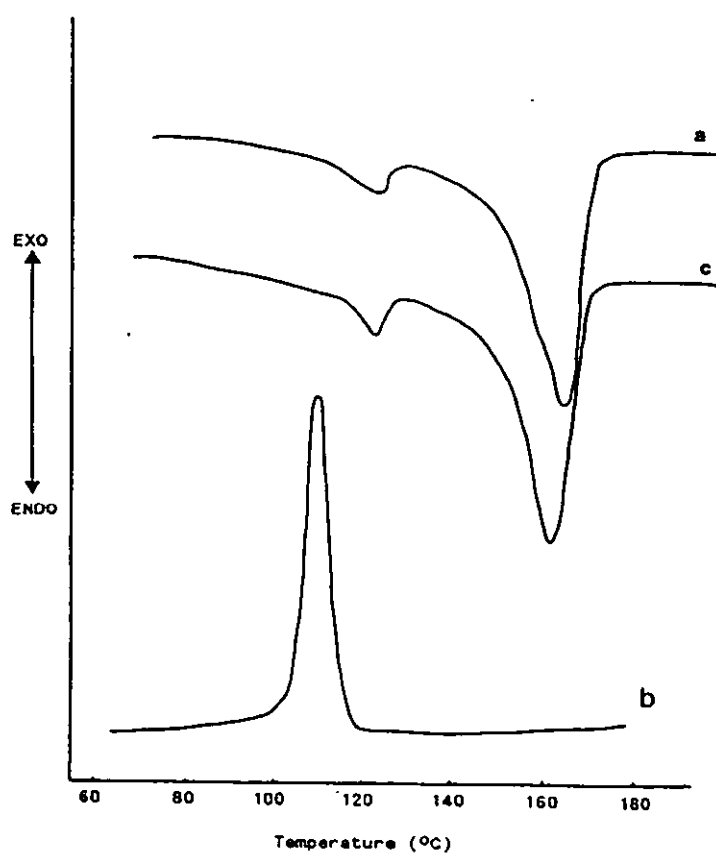


Fig. 6.11 Thermograms of LLDPE(MFI=2)/PP-15/85 blend. (a) first heating, (b) cooling, and (c) second heating.

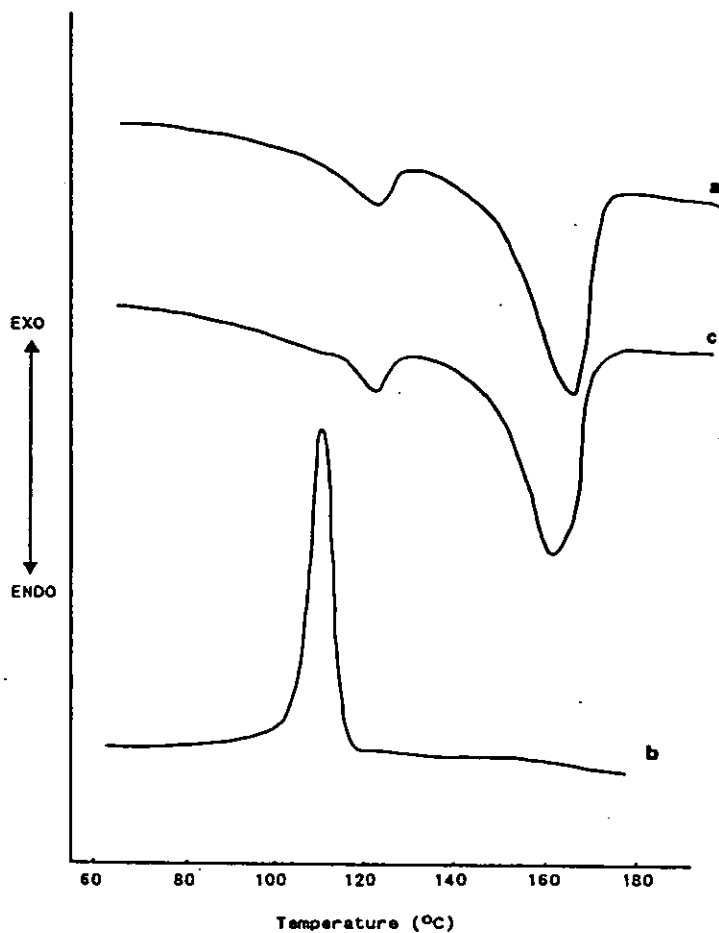


Fig. 6.12 Thermograms of LLDPE(MFI=2)/PP-20/80 blend. (a) first heating, (b) cooling, and (c) second heating.

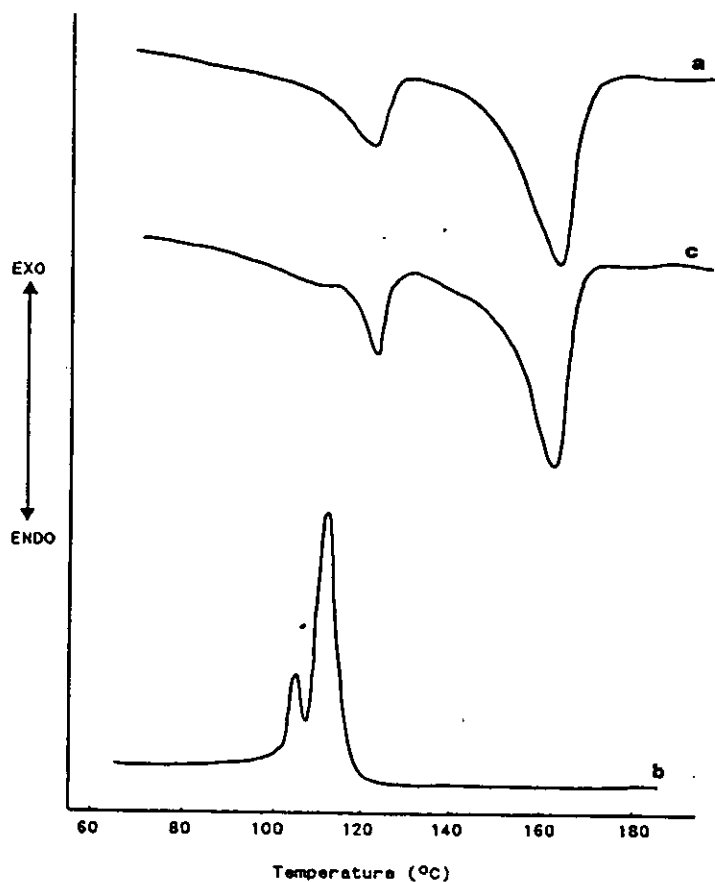


Fig. 6.13 Thermograms of LLDPE(MFI=2)/PP-30/70 blend. (a) first heating, (b) cooling, and (c) second heating.

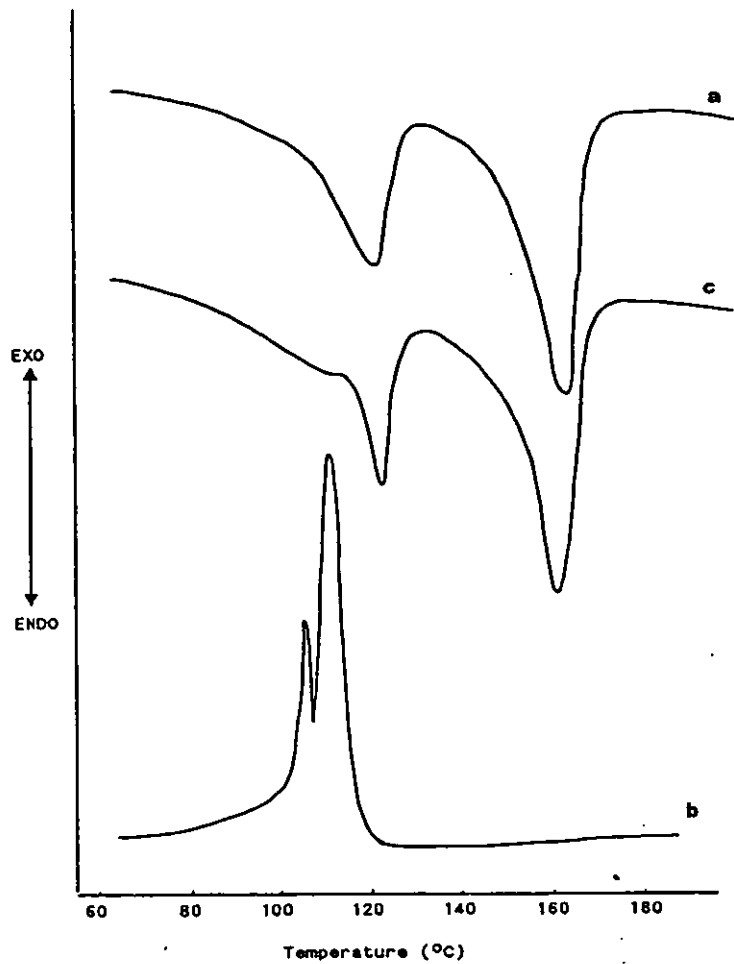


Fig. 6.14 Thermograms of LLDPE(MFI=2)/PP-40/60 blend. (a) first heating, (b) cooling, and (c) second heating.

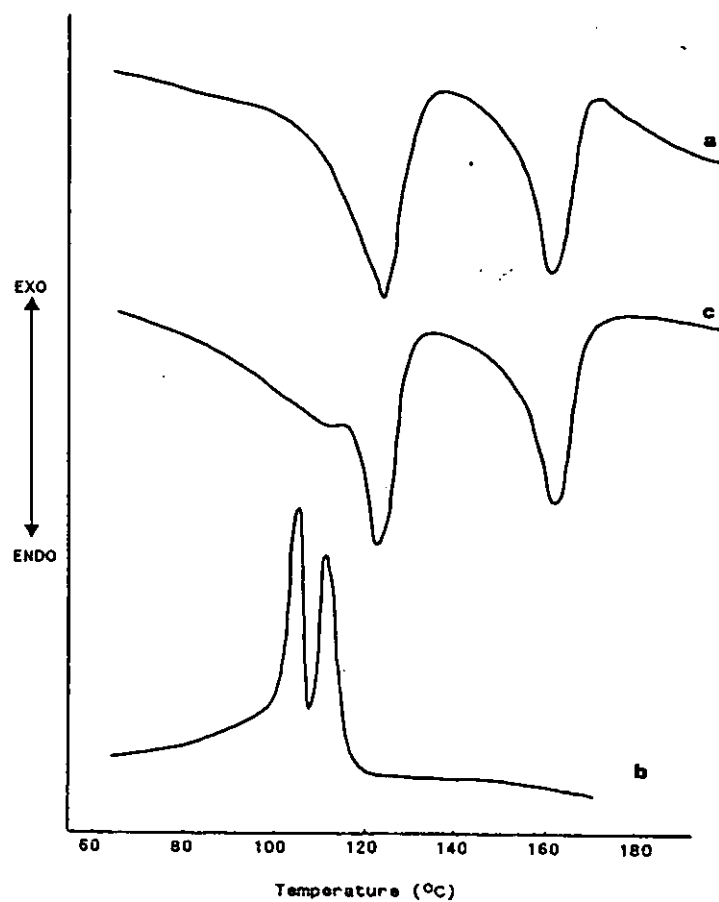


Fig. 6.15 Thermograms of LLDPE(MFI=2)/PP-60/40 blend. (a) first heating, (b) cooling, and (c) second heating.

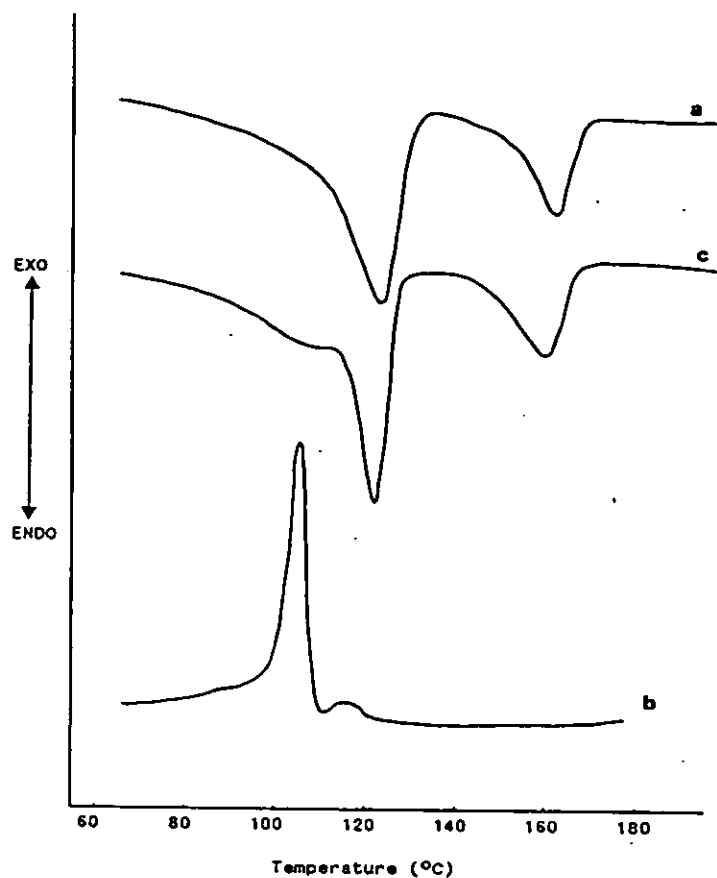


Fig. 6.16 Thermograms of LLDPE(MFI=2)/PP-70/30 blend. (a) first heating, (b) cooling, and (c) second heating.

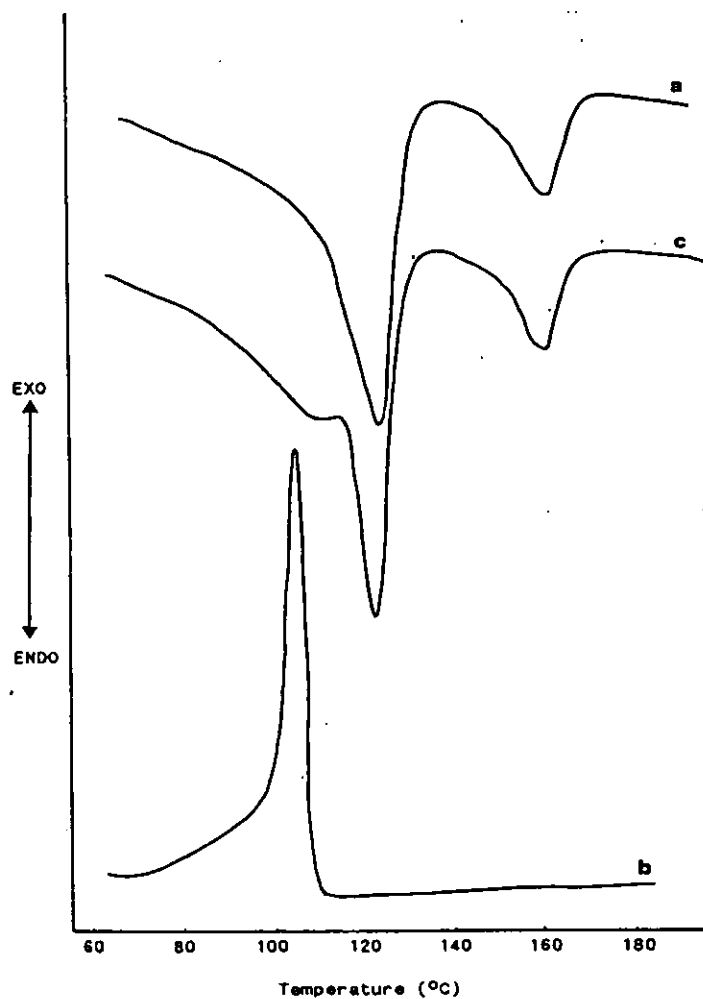


Fig. 6.17 Thermograms of LLDPE(MFI=2)/PP-80/20 blend. (a) first heating, (b) cooling, and (c) second heating.

Table 6.4

The melting and crystallisation temperature of LLDPE/PP blends and their components (MFI 2/0.32 g/10 min) .

Samples	First melting temp (°C)	Second melting temp (°C)	Crystallisation temp (°C)
PP	163.5	165	110
5% LLDPE	122	122	109
	164	162	
10% LLDPE	122.5	122.5	109.5
	164	161.5	
15% LLDPE	123	123	110
	165	162	
20% LLDPE	122.5	122.5	110
	165	162	
30% LLDPE	122.5	122.5	105.5
	163.5	161.5	112
40% LLDPE	122.5	122.5	105.5
	161	163.5	111.5
60% LLDPE	124.5	122.5	105.5
	161.5	160.5	112
70% LLDPE	122.5	122	104.5
	160.5	159.5	114.5
80% LLDPE	123	122	105
	161	160	
LLDPE	125.5	122.5	105

Upon cooling two distinct crystallisation peaks appeared between 20 and 80 per cent of LLDPE. The lower crystallisation temperature is attributed to the crystallisation of LLDPE whereas the higher one is due to PP. It is not possible to detect any crystallisation peak at very low concentration of either component.

Table 6.5

The melting and crystallisation temperature of LLDPE/PP blends and their components (MFI 1/0.32 g/10 min) .

Samples	First melting temp (°C)	Second melting temp (°C)	Crystallisation temp (°C)
PP	163.5	165	110
20% LLDPE	120	121.5	107.8
	162.8	160.6	
30% LLDPE	120	120.7	108.8
	161	159.5	
60% LLDPE	120.5	121.2	105
	161	158.5	108.6
80% LLDPE	121.7	120.8	103.89
	160	159.9	
LLDPE	122.1	121	104.1

The thermograms of LLDPE/PP (Escorene/Profax-MFI 2/0.32), with a range of cooling rates are shown in Figs. 6.23 to 6.25. The results show a shift to a lower temperature in melting and crystallisation temperature of LLDPE and PP, as the cooling rate increases. This can be explained, as the crystallisation take place the polymer is a viscous liquid and a sufficient time must be allowed for the chains to assemble into the three-

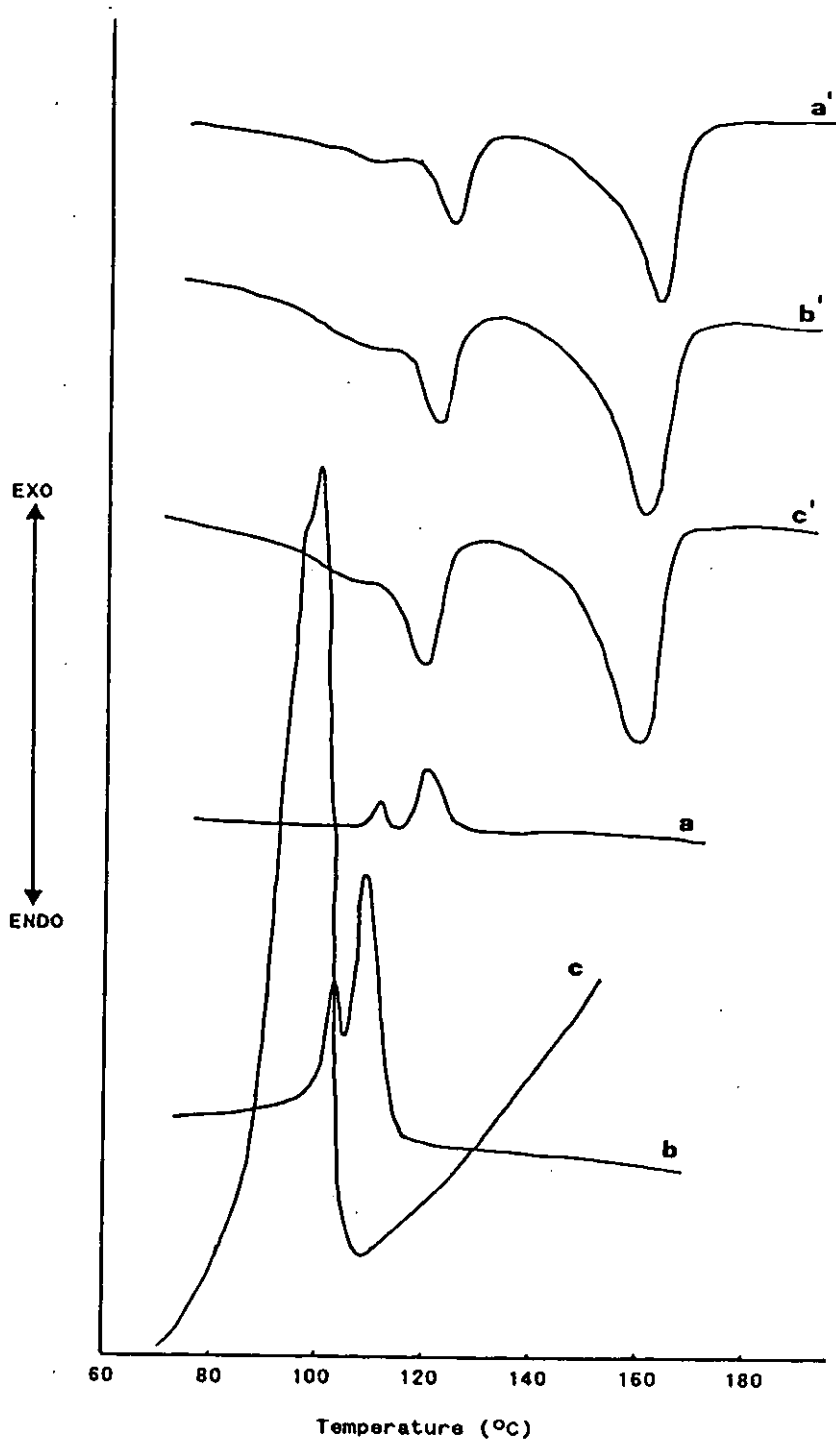


Fig. 6.23 Thermograms of LLDPE(MFI=2)/PP-40/60 blend; with a range of cooling rates. (a) cooling at 1 degree C/min, (a') heating at 10 degree C/min[after being cooled at 1 degree C/min]; (b) cooling at 5 degree C/min, (b') heating at 10 degree C/min[after being cooled at 5 degree C/min]; (c) cooling at 50 degree C/min, (c') heating at 10 degree C/min[after being cooled at 50 degree C/min].

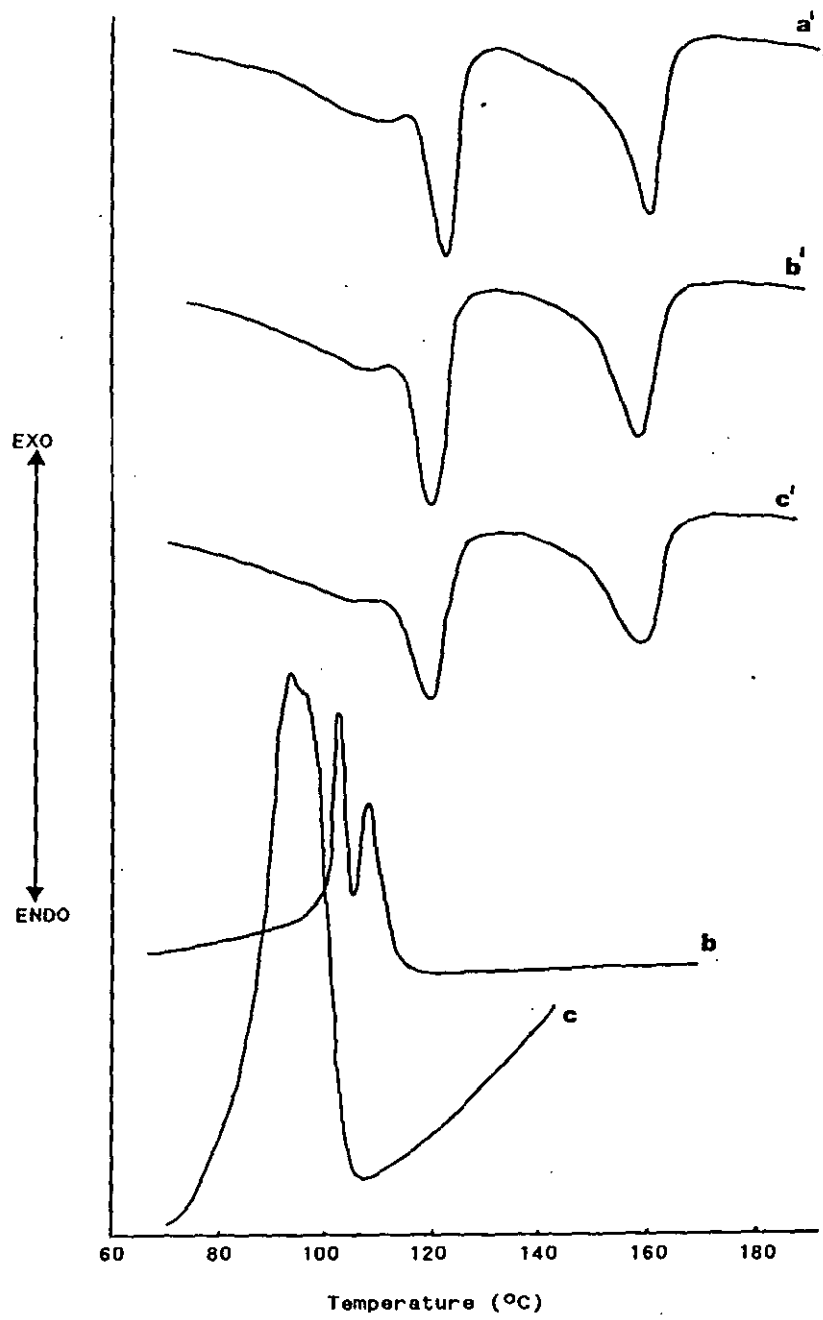


Fig. 6.24 Thermograms of LLDPE(MFI=2)/PP-60/40 blend; with a range of cooling rates. (a') heating at 10 degree C/min[after being cooled at 1 degree C/min]; (b) cooling at 5 degree C/min, (b') heating at 10 degree C/min[after being cooled at 5 degree C/min]; (c) cooling at 50 degree C/min, (c') heating at 10 degree C/min[after being cooled at 50 degree C/min].

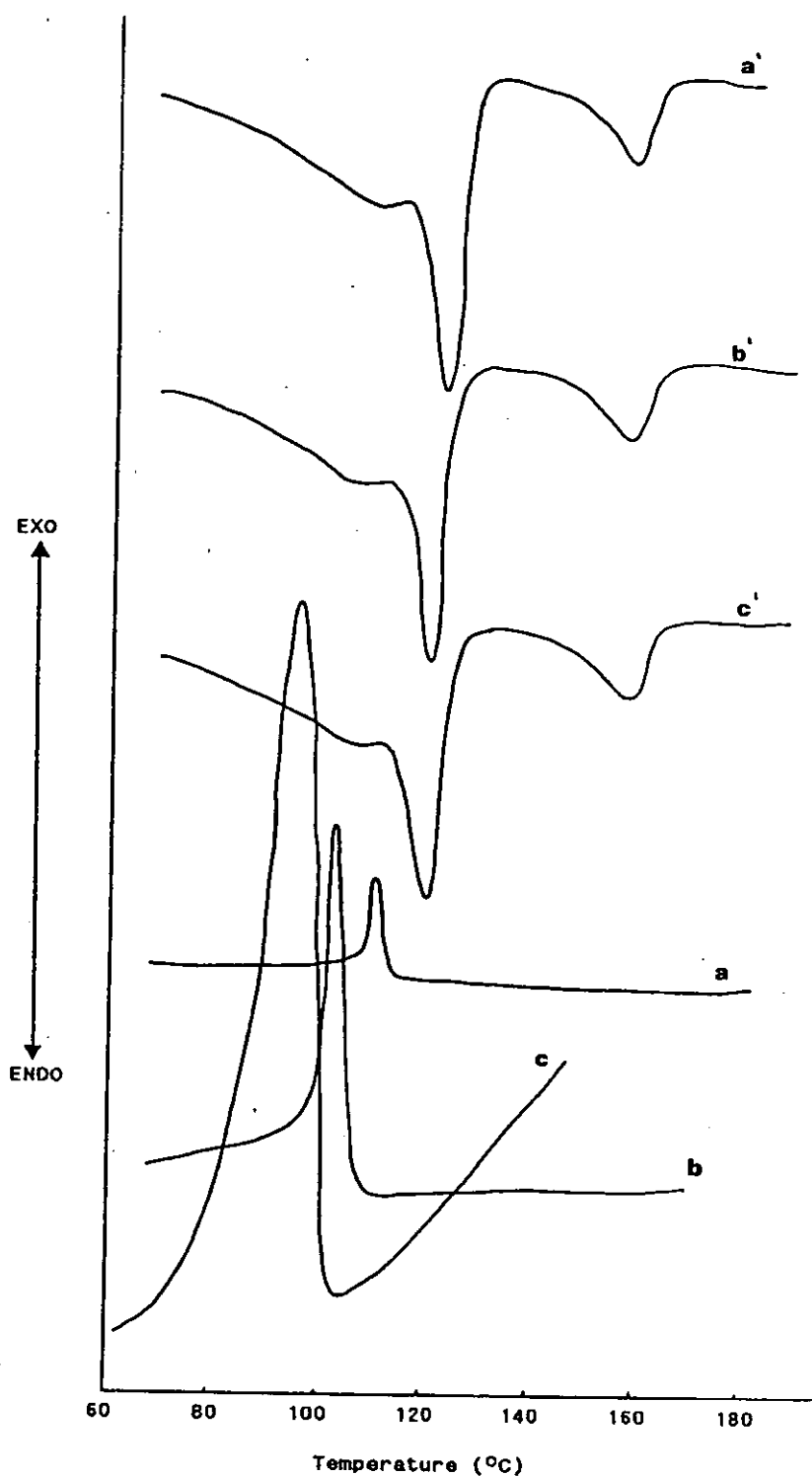


Fig. 6.25 Thermograms of LLDPE(MFI=2)/PP-80/20 blend; with a range of cooling rates. (a) cooling at 1 degree C/min, (a') heating at 10 degree C/min[after being cooled at 1 degree C/min]; (b) cooling at 5 degree C/min, (b') heating at 10 degree C/min[after being cooled at 5 degree C/min]; (c) cooling at 50 degree C/min, (c') heating at 10 degree C/min[after being cooled at 50 degree C/min].

dimensional order for crystallite formation. Thus rapid cooling from the melt prevents the development of significant crystallinity, which results in having smaller size of crystals and lower crystallisation temperature. This also leads to having lower melting temperature due to contribution from the interfacial energy in the smaller crystallites, i.e. there is an excess of free energy associated with the disordered chains emerging from the ends of ordered crystallites and this is relatively greater for the smaller crystallites, resulting in lower melting temperature⁽¹⁰⁴⁾. This can be seen more clearly in Figs. 6.26 to 6.29. The results also show the melting temperature of PP decreases as the content of LLDPE increases for each cooling rate, whereas there is little change in melting temperature of LLDPE when is cooled at 1° and 5 °C and hardly any changes at 50 °C. This is due to melting depression of PP as was explained earlier.

The thermograms also show an increase in the height of crystallisation peaks as the cooling rate increases. This is again due to lack of sufficient time for crystallite formation or the higher rates. This is more clear when 50 °C/min. is used. In this case the crystallisation peaks no longer produce two sharp peaks but rather a crystallisation peak with a shoulder. For the blend of LLDPE/PP-40/60 the shoulder is attributed to LLDPE and for blend of LLDPE/PP-60/40, the shoulder is associated with PP.

Further investigations of thermograms were carried out by measuring the height of endotherm and exotherm peaks at a cooling rate of 5 °C/min. Figs. 6.30 and 6.31 show the height of melting and crystallisation peaks plotted versus the composition. The plot shows that the height of melting and crystallisation peaks of PP increases as

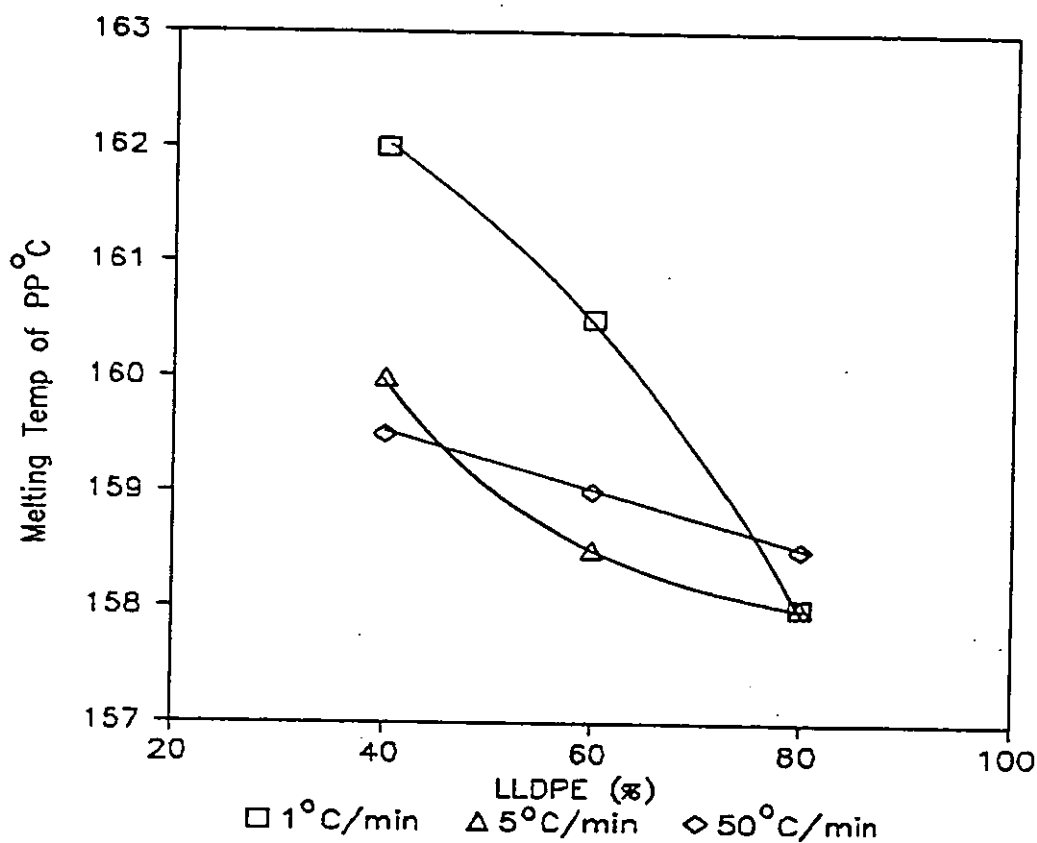


Fig. 6.26 Melting temperatures of polypropylene at various cooling rate.

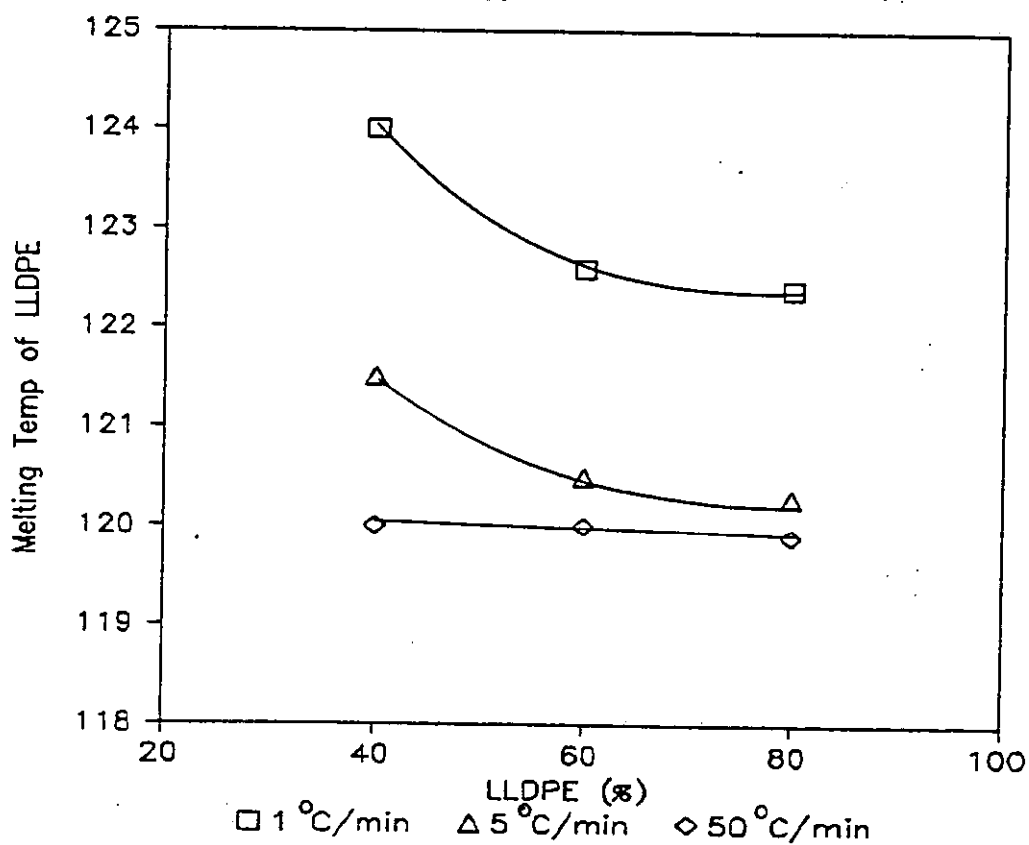


Fig. 6.27 Melting temperature of linear low density polyethylene at various cooling rate.

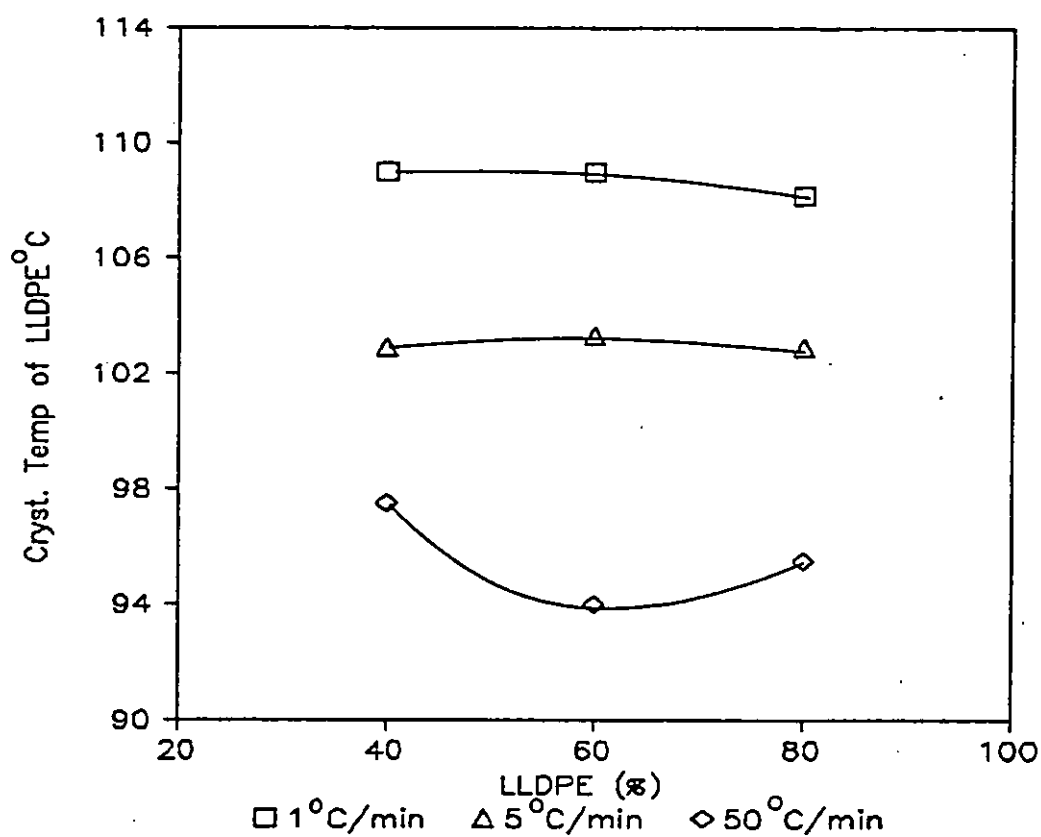


Fig. 6.28 Crystallisation temperatures of LLDPE at various cooling rate.

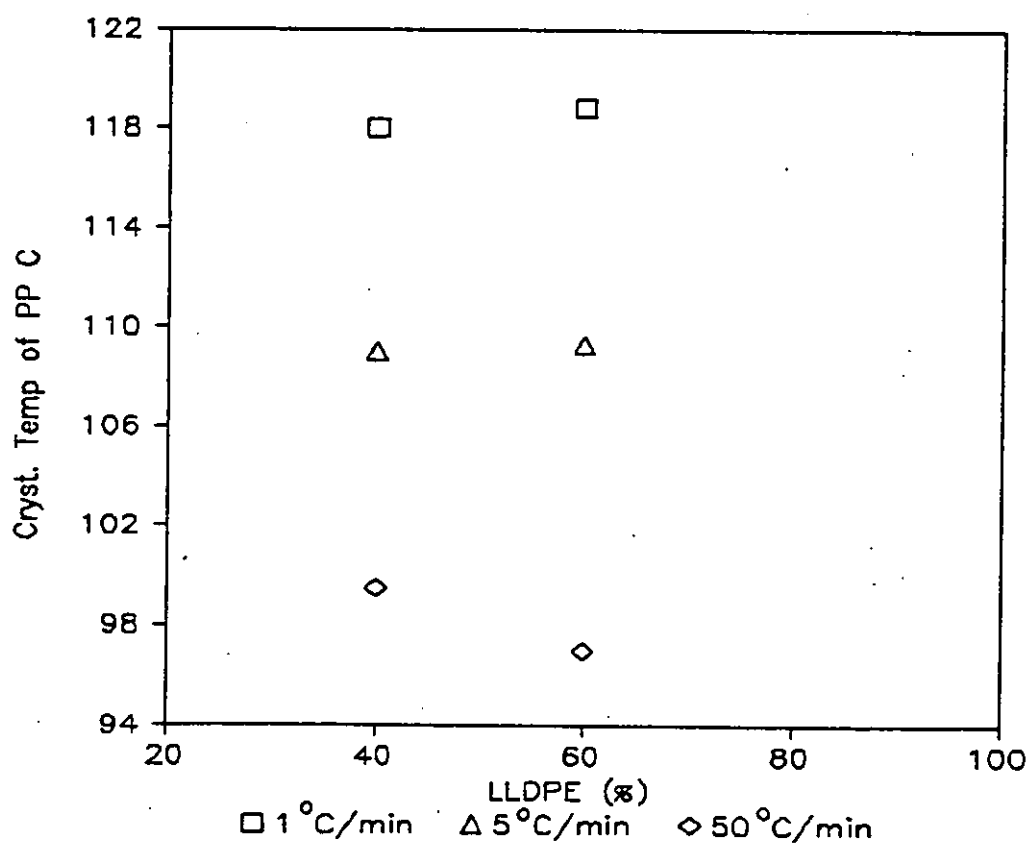


Fig. 6.29 Crystallisation temperatures of polypropylene at various cooling rate.

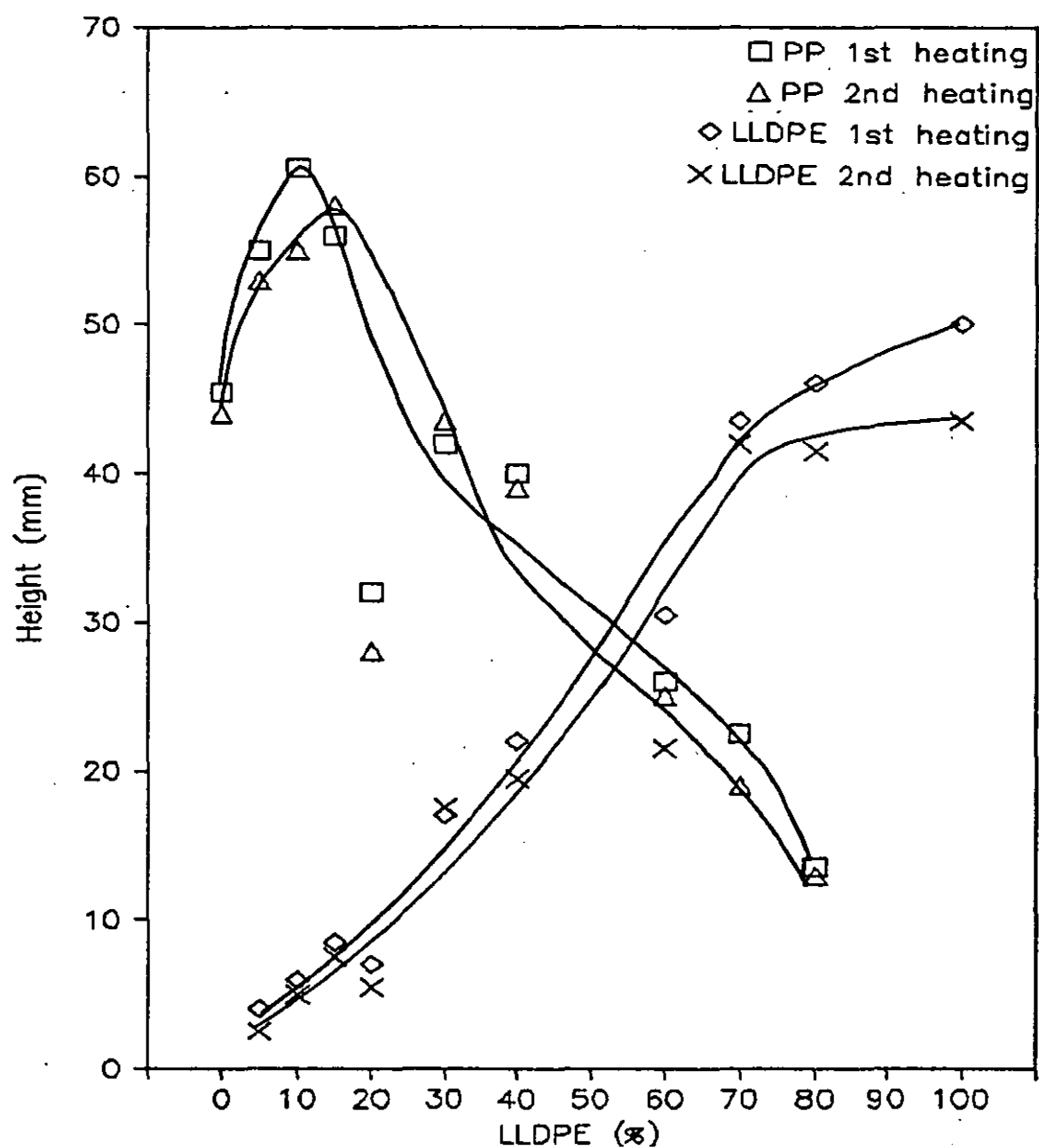


Fig. 6.30 The height of melting peaks of LLDPE, PP, and their blends.

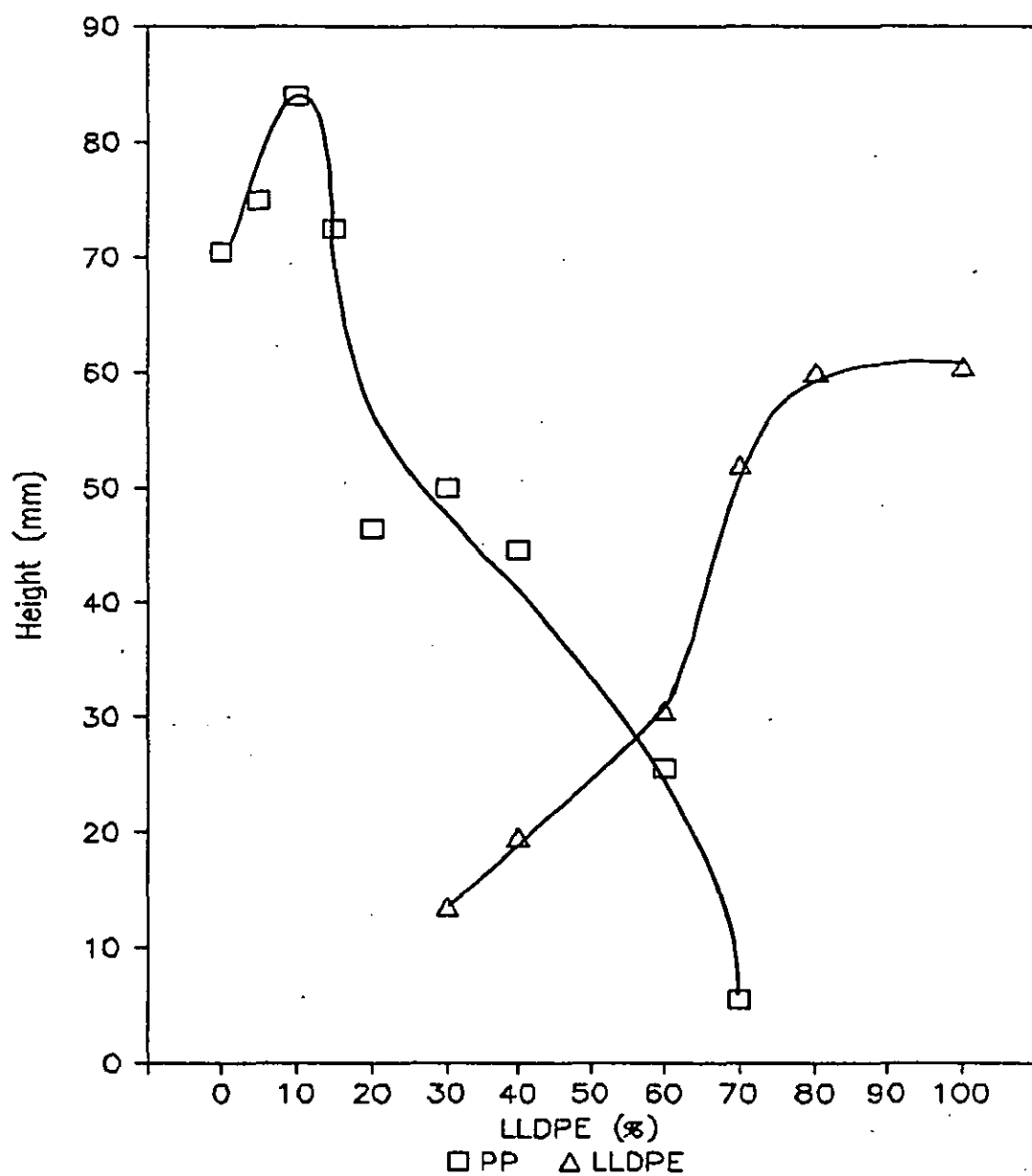


Fig. 6.31 The height of crystallisation peaks of LLDPE, PP, and their blends.

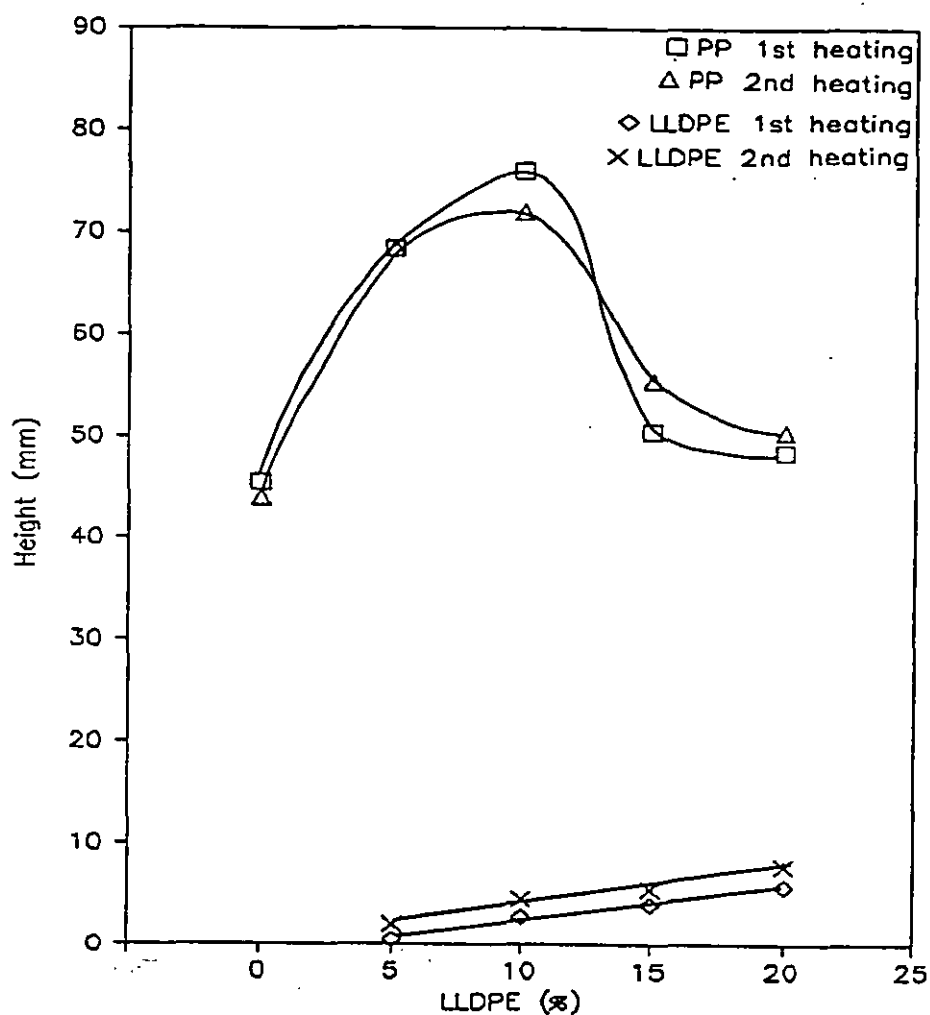


Fig. 6.37 The height of melting peaks of PP(Profax), and PP/LLDPE(Dowlex) blends.

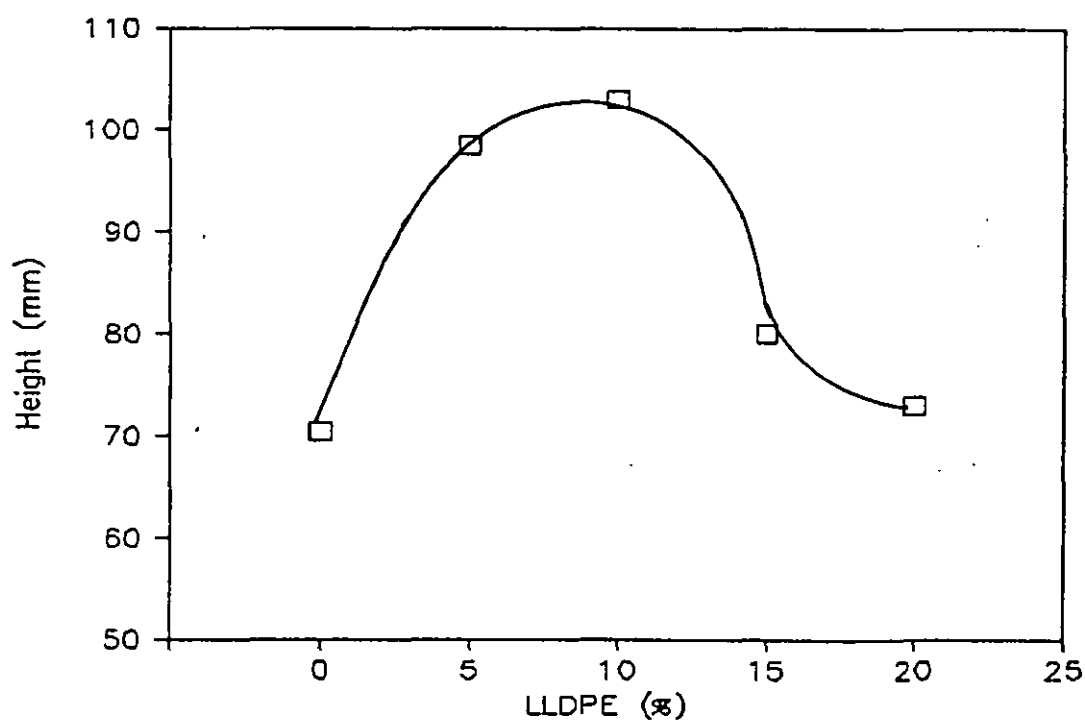


Fig. 6.38 The height of crystallisation peaks of PP(Profax), and PP/LLDPE(Dowlex) blends.

the contents of LLDPE increases, and reaches its maximum at 10 percent of LLDPE and then starts to decrease, whereas, for LLDPE they show almost a linear relationship with the content of LLDPE. This unexpected behaviour in increase of melting and crystallisation peaks of PP upon adding small amounts of LLDPE could suggest the nucleation of PP by LLDPE. The same observation was found for LLDPE(Dowlex) and PP(Profax 6824). Their thermograms are shown in (Figs. 6.32-6.36, see Appendix III) and the plot of the height of melting and crystallisation peaks versus the compositions are shown in Figs. 6.37 and 6.38. Three processing techniques were used to utilize this behaviour for possible exploitation commercially; this is to be discussed in section 6.4.

6.3.4 Dynamic Mechanical Thermal Analysis

The dynamic mechanical thermal analysis(DMTA) data for LLDPE, PP, and their blends are shown in Fig. 6.39 , where modulus and loss tangent $\tan\delta$, are plotted as a function of temperature(-160° to 140°C). While modulus decreases with increasing temperature, $\tan\delta$ shows three peaks in descending order of temperature.

The peaks at 20°C are associated with amorphous PP(it was not possible to detect a peak for LLDPE/PP-80/20 blend i.e. at low concentration of PP). The peak at -10°C is attributed to β transition in LLDPE. This peak can only be detected for LLDPE and the blend of LLDPE/PP-80/20. The depression of the β peak with increasing content of PP could be due to reduction of interfacial zone of crystal and amorphous region of ethylene-based copolymer as was demonstrated by McCrum et al(105). They suggested that an interfacial content

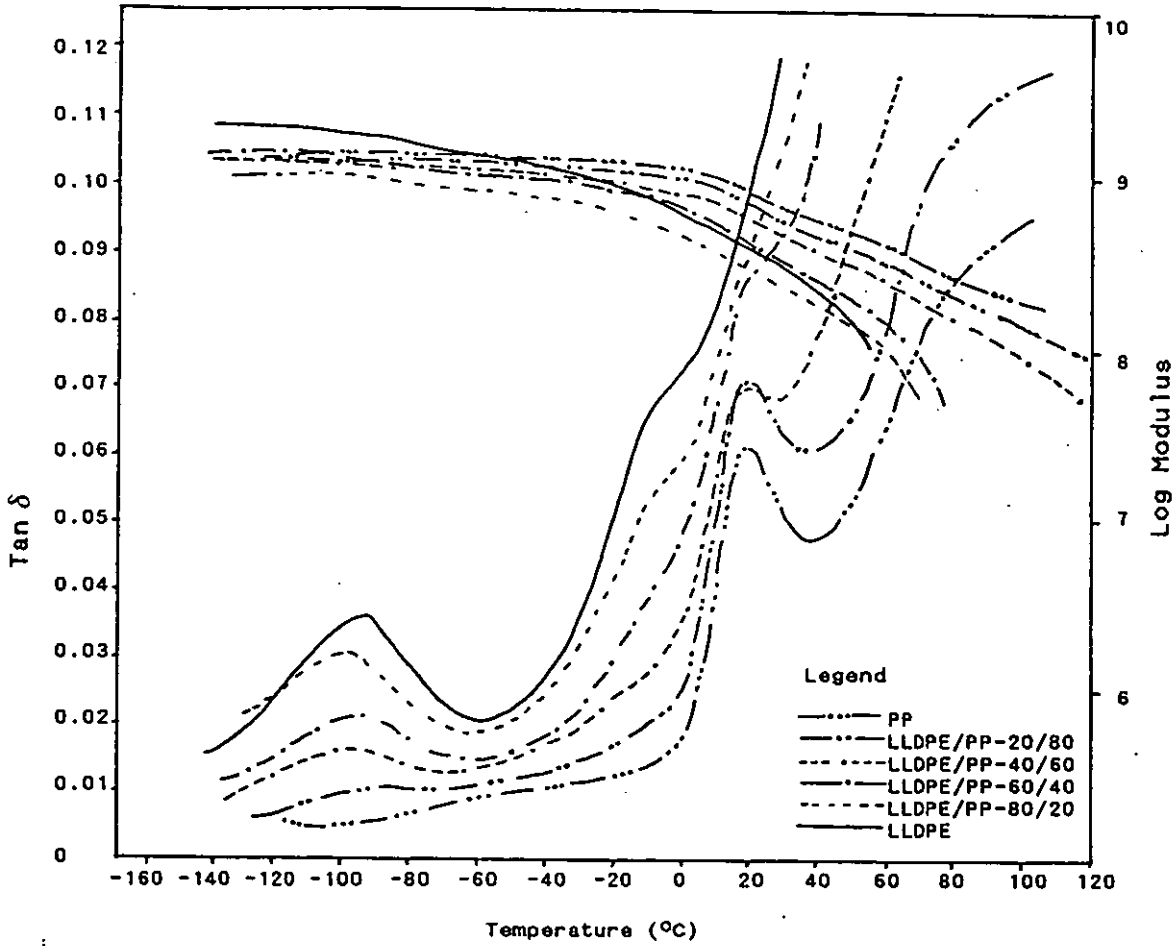


Fig. 6.39 Dynamic mechanical measurement of LLDPE, PP, and their blends.

of at least 10-15% is necessary for this transition to be observed. The peaks between -87.5 and -95 °C for LLDPE and the blends are attributed to amorphous LLDPE. Generally these peaks shift to lower temperature as the content of LLDPE increases. This could be due to the reduction of crystallinity of the blend as was seen earlier in Fig. 6.2.

The mechanical loss $\tan \delta$ shows that, the blend manifests relaxation behaviour intermediate between that of the two components, except for the blend of LLDPE/PP-40/60 at the glass transition temperature of PP. The LLDPE displays the highest magnitude, whereas the PP shows the lowest. This characteristic is very interesting as these blends are immiscible which was seen earlier by DSC.

The PP sample has higher or equal modulus compared to the blends in the low temperature region about -100 °C except for pure LLDPE which is higher. At higher temperature i.e from about -40 °C the modulus for PP becomes higher than all the blends.

The loss peak attributed to the glass transition of PP occurs for all the samples at 20 °C, indicating that the matrix of PP is essentially unaffected by addition of the LLDPE.

6.3.5 Morphology

Optical micrographs of LLDPE, PP and their blends are shown in Figs. 6.40 to 6.45. The micrographs show that the size of spherulites of pure PP is much larger than that of spherulites of pure LLDPE. As these blends are immiscible two phase systems were observed, and

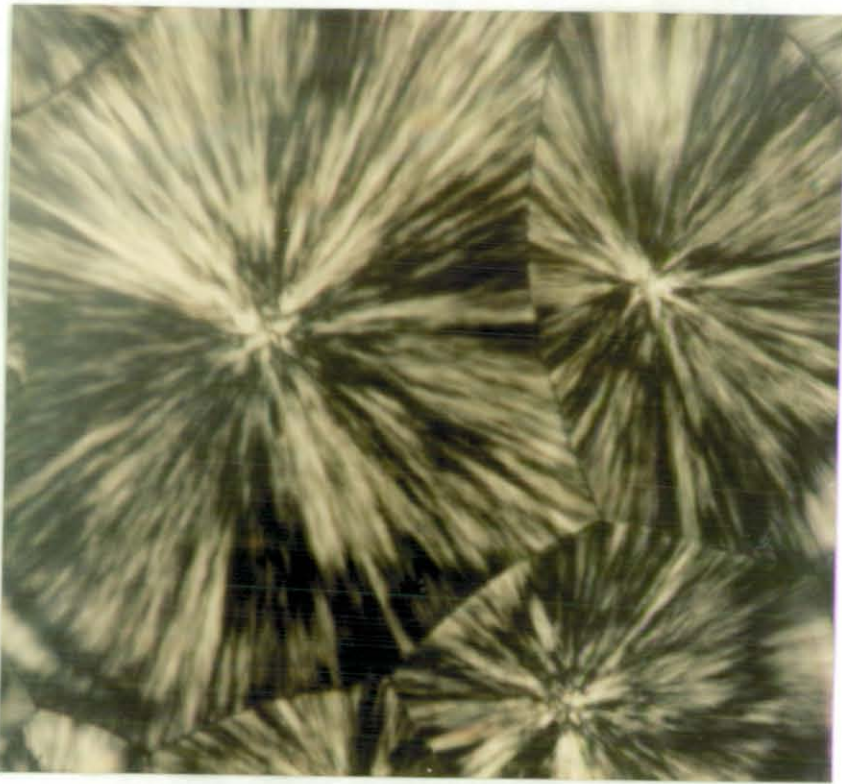


Fig. 6.40 Optical micrograph of PP (Profax) (Mag. 400X)

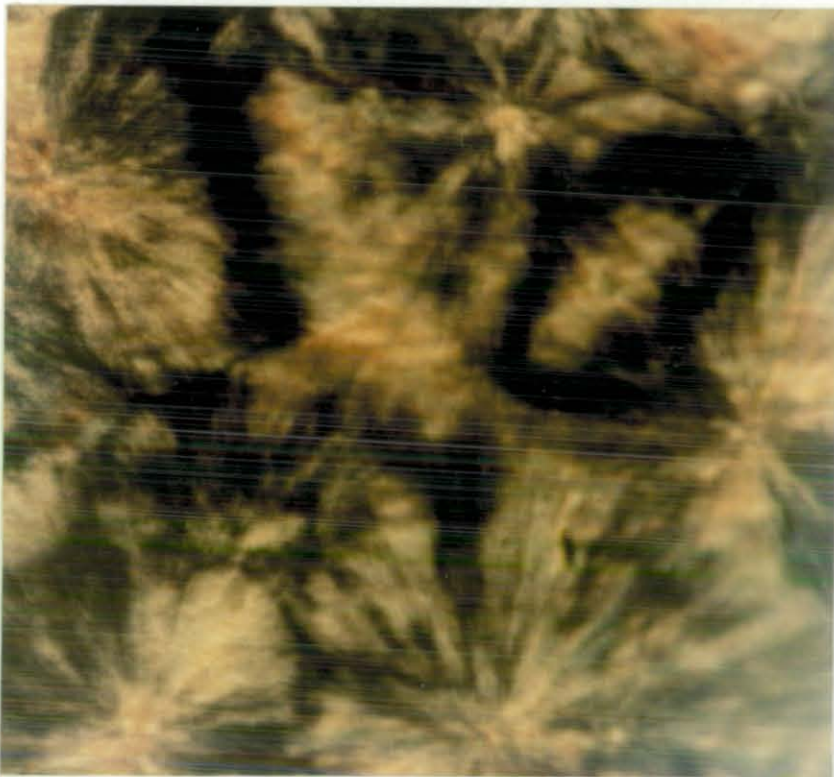


Fig. 6.41 Optical micrograph of LLDPE/PP-20/80 (Mag. 400X)

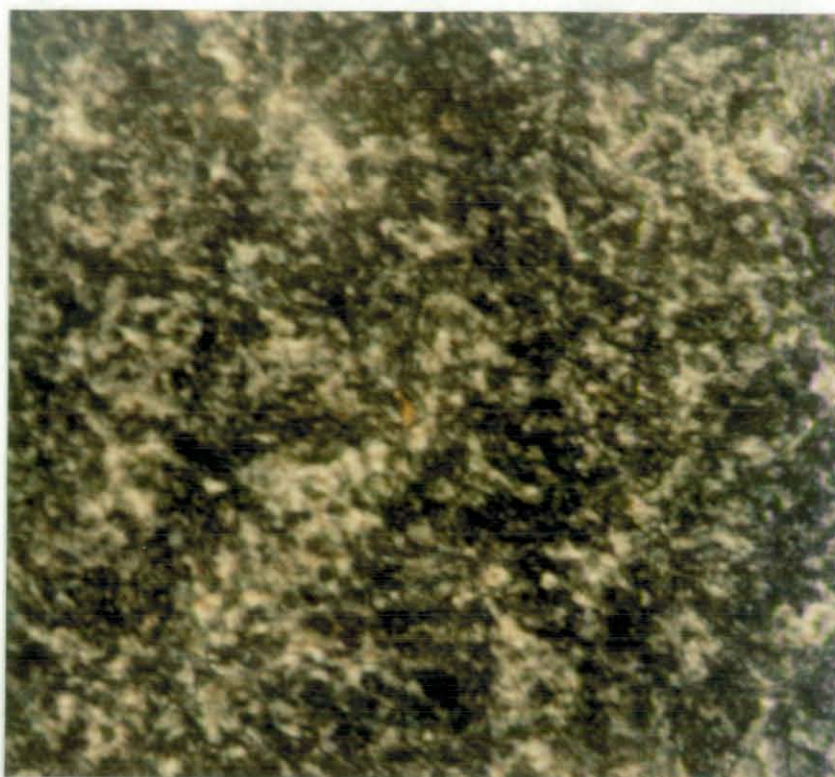


Fig. 6.42 Optical micrograph of LLDPE/PP-40/60 (Mag. 400X)

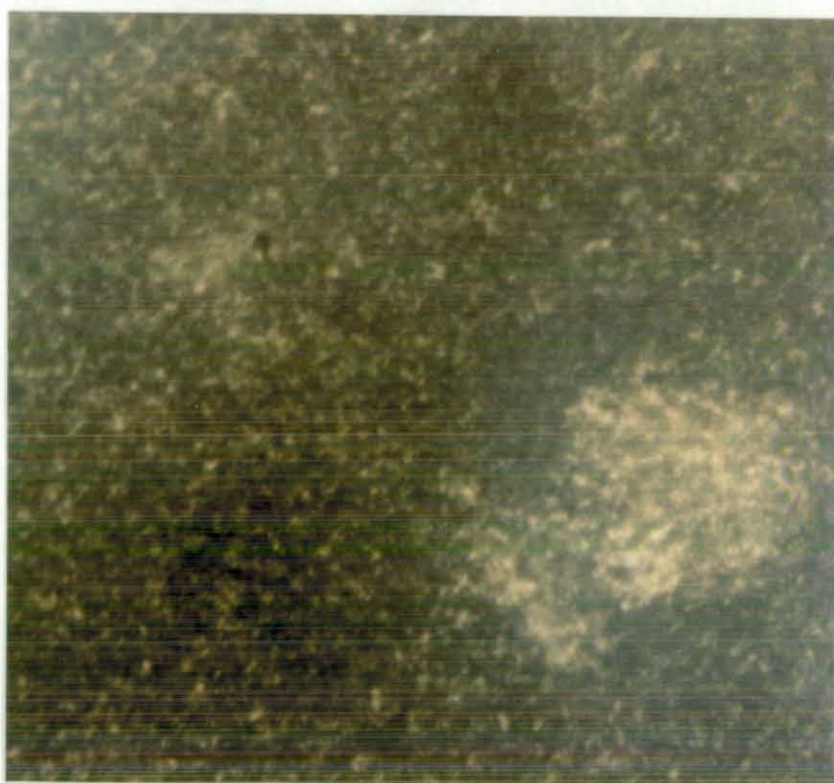


Fig. 6.43 Optical micrograph of LLDPE/PP-60/40 (Mag. 400X)

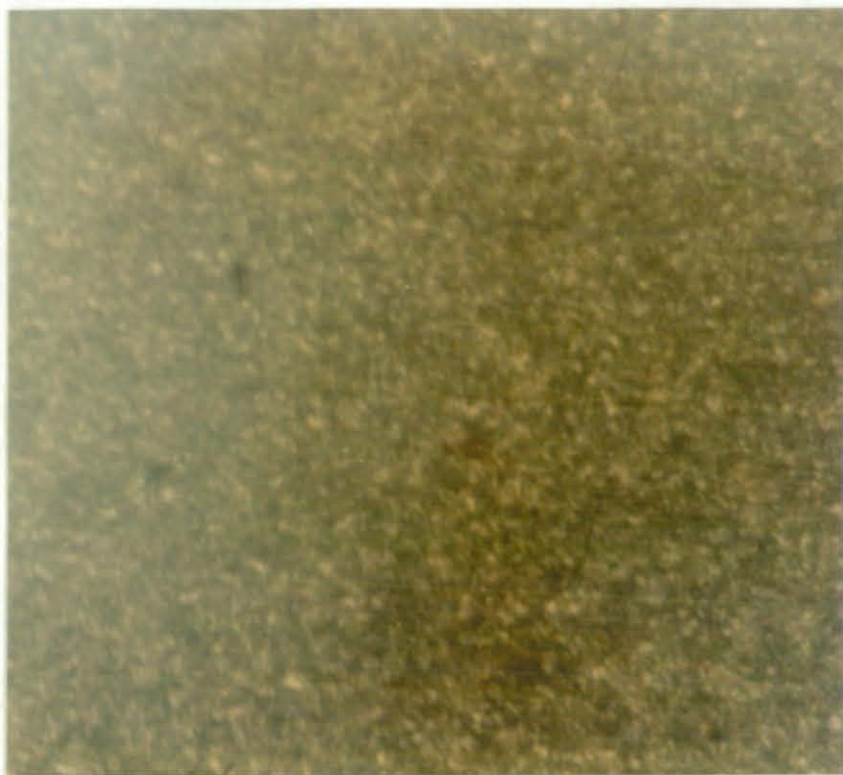


Fig. 6.44 Optical micrograph of LLDPE/PP-80/20 (Mag. 400X)

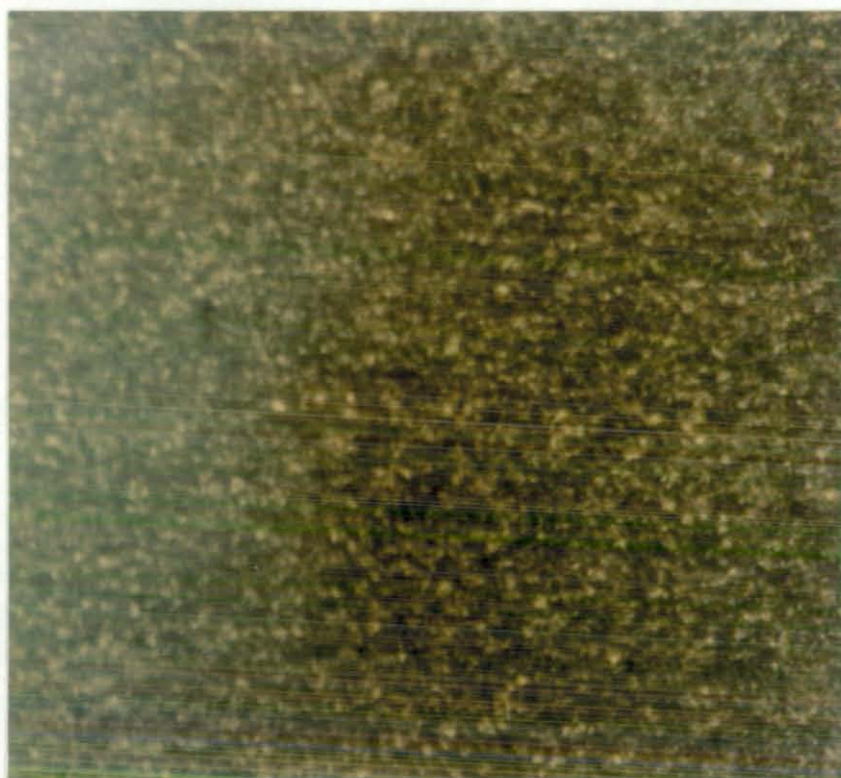


Fig. 6.45 Optical micrograph of LLDPE (Escorene) (Mag. 400X)

components crystallised separately into discrete phases. The addition of LLDPE causes a reduction in the average dimensions of PP spherulites and results in them becoming irregular and coarse with increasing LLDPE content.

6.3.6 Melt Flow Index

The results of Melt Flow Index (MFI) of LLDPE, PP, and their blends at various temperatures (190°, 210°, and 230 °C) are shown in Fig. 6.46. The MFI of PP is lower than that of LLDPE, and since their structures are not too dissimilar, suggests that PP has higher molecular weight than that of LLDPE. The graph shows as the melt temperature increases the MFI increases due to easier flow of materials. The MFI data of the blends are almost linear with the compositions and their values are intermediate between those of the parent polymers.

Shenoy et.al (62,106-108) have proposed a method to estimate the rheograms of polymer melts at various melt temperatures from melt flow index, using the inverse of MFI data, which is a direct function of melt viscosity, as a shift factor i.e ($a_T = 1/\text{MFI}$). In this way the MFI of the materials can be easily measured using a relatively inexpensive apparatus compared to the cost of a rheometer. The main difference from a capillary rheometer is that it operates at constant shear stress. To investigate the possibility of melt transition in the blends, the melt flow indices of LLDPE/PP blends and their parent polymers at various temperatures were treated according to both an Arrhenius model in a plot of $\log(1/\text{MFI})$ as function of the reciprocal absolute temperature $T^{-1}(\text{K})$, and of the reciprocal temperature

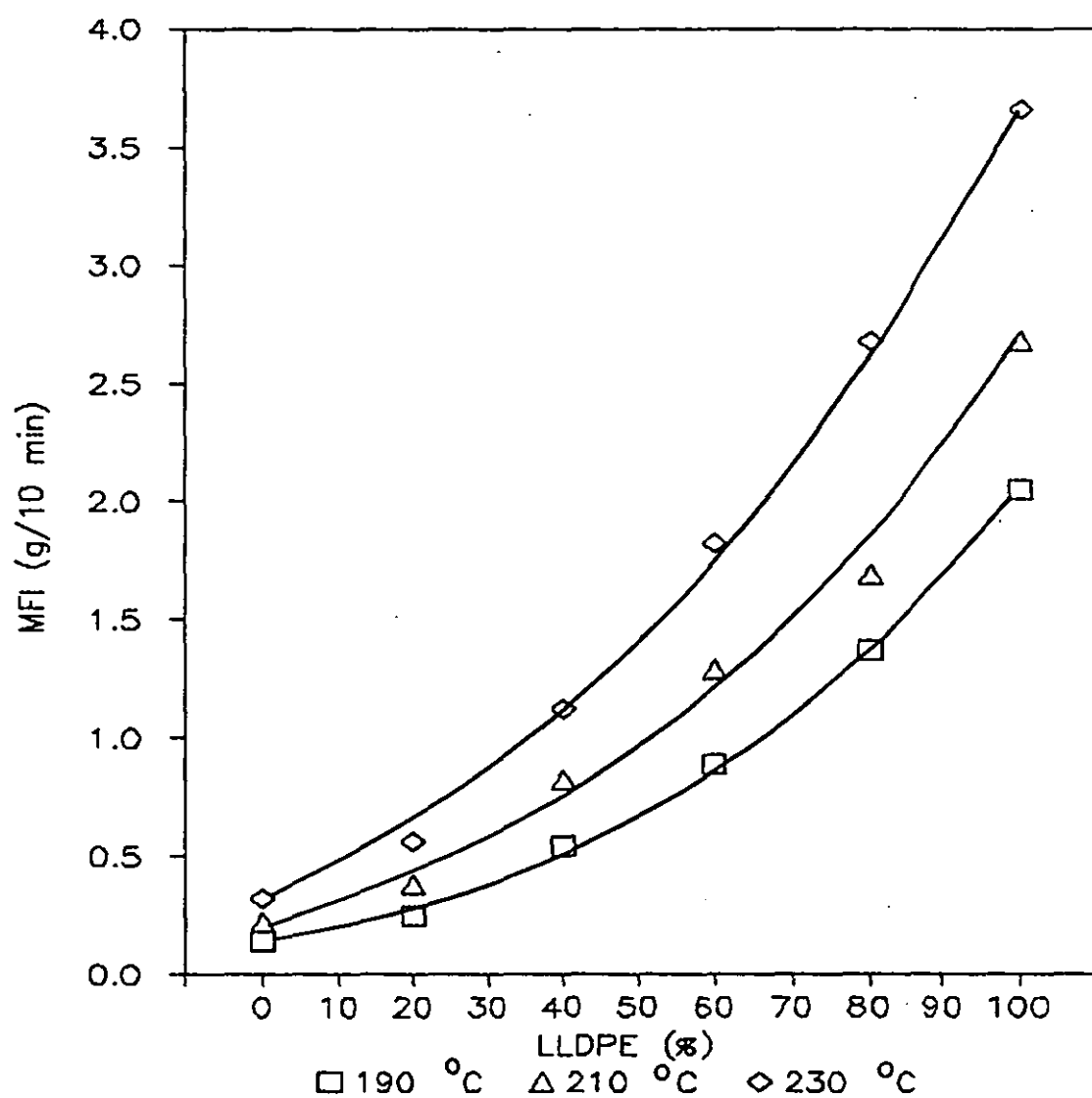


Fig. 6.46 Melt Flow Index of LLDPE, PP, and their blends at various temperatures.

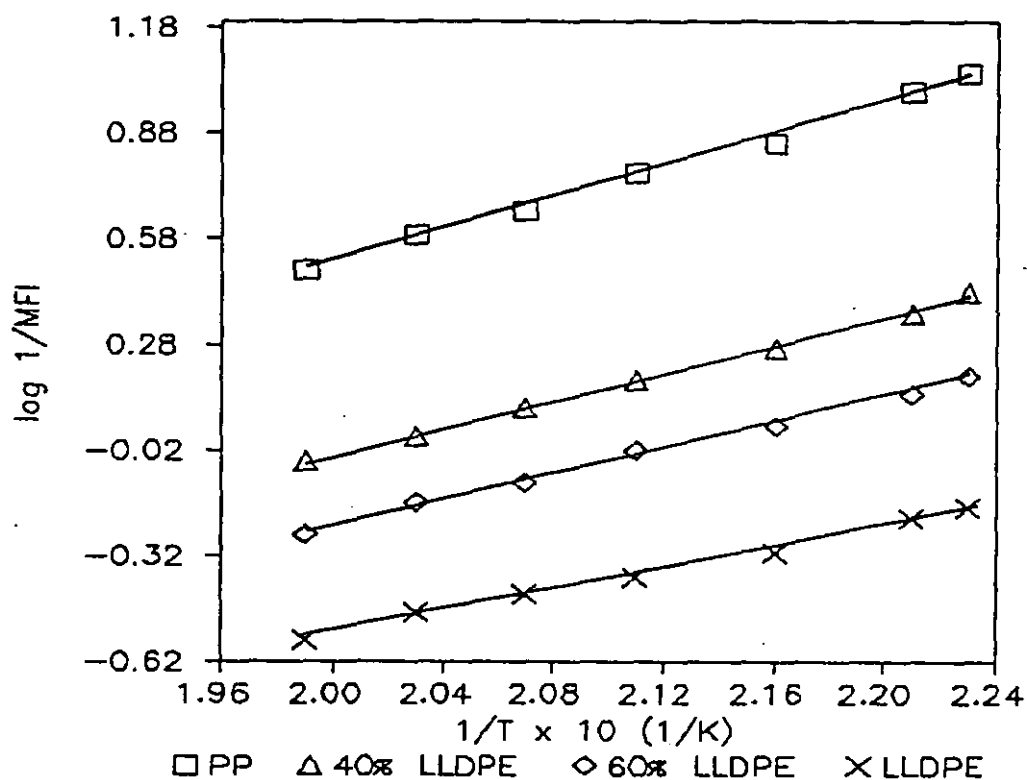


Fig. 6.47 Inverse of MFI(1/MFI) as a function of temperature according to Arrhenius equation(1/T).

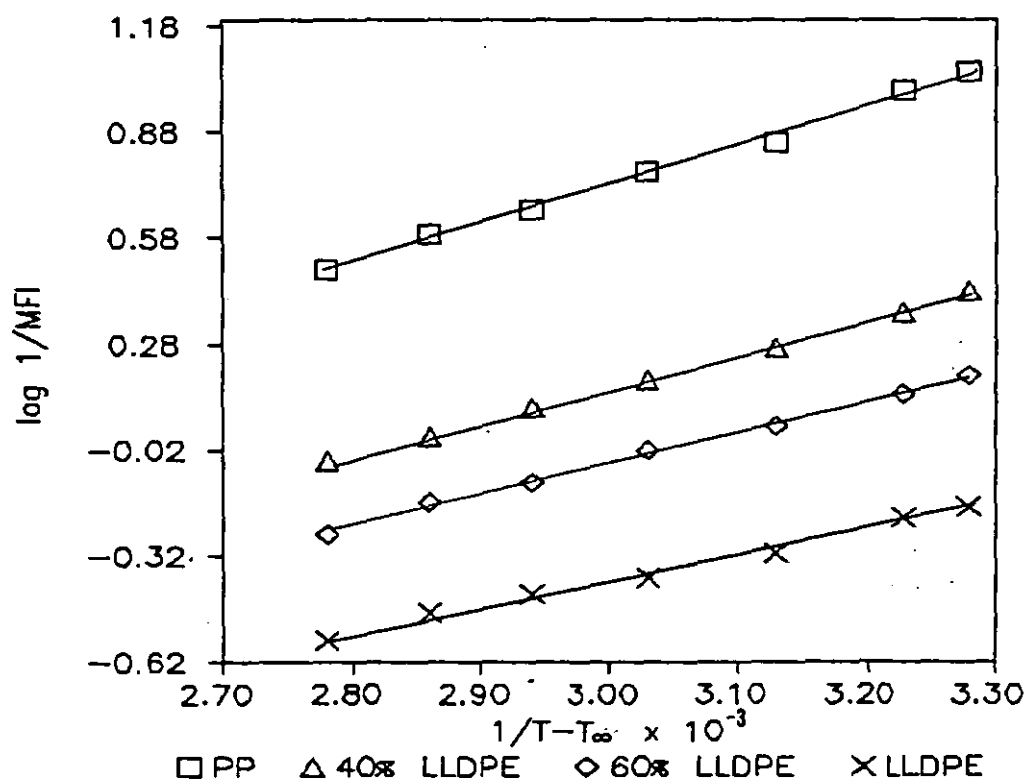


Fig. 6.48 Inverse of MFI(1/MFI) as a function of temperature according to VFTH equation(1/T-T_∞).

difference $(T - T_{\infty})^{-1}$ according to the Vogel(109), Fulcher(110), and Tamman-Hesse(111) (VFTH) equation,

$$y = Ae^{B/(T - T_{\infty})}$$

where y can stand for inverse of the MFI, A and B are characterising constants. T_{∞} is chosen at a value which gives the best straight line, and usually is about 50 °C below the glass transition temperature(112). The value was found to be ($T_{\infty} = 143$ K). Both the Arrhenius and VFTH models Figs. 6.47 and 6.48 respectively show straight lines with no indication of melt transitions which is equivalent to the finding for homopolymer melts.

6.3.7 Flow Properties

The flow curves for LLDPE, PP, and their blends for different temperatures are shown in Figs. 6.49 to 6.51, in terms of shear stress against shear rate. The curves show that the blends and their components follow non-Newtonian behaviour with increase in shear rates for all the temperatures. The curves also show that as the melt temperature increases the shear stress decreases due to easier flow of materials. At low shear rate and low temperature i.e 190 °C the PP and blends show peculiar behaviour. The stress values of the blends are not intermediate and as the shear rate increases the curve for PP crosses that for the blends(except the LLDPE/PP-80/20 blend) due to the greater non-Newtonian behaviour. However at high shear rate and high temperature i.e 230 °C the stress values for the blends fall mostly between those of the pure polymers.

The viscosity data for LLDPE, PP and their blends are presented in Fig. 6.52 to 6.54, as a function of shear

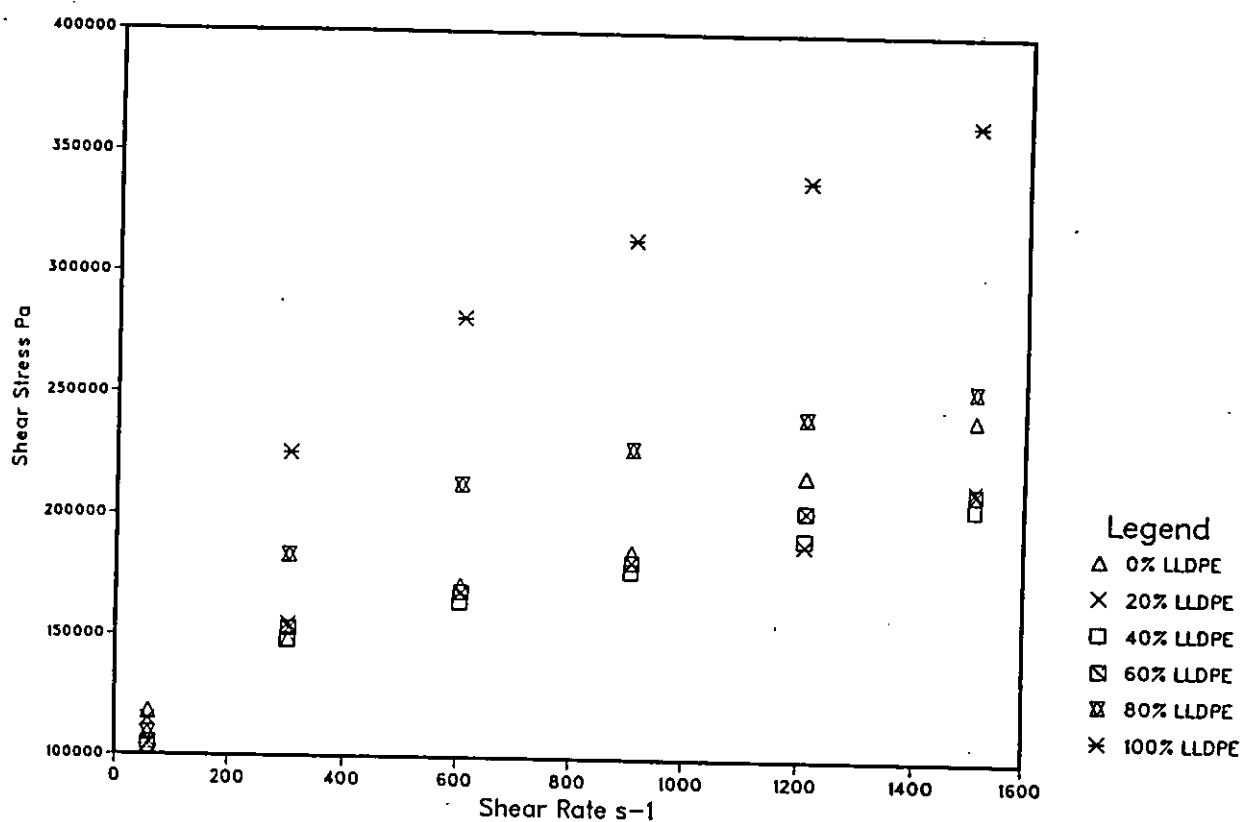


Fig. 6.49 The shear stress as a function of shear rate for LLDPE, PP, and their blends at 190 °C.

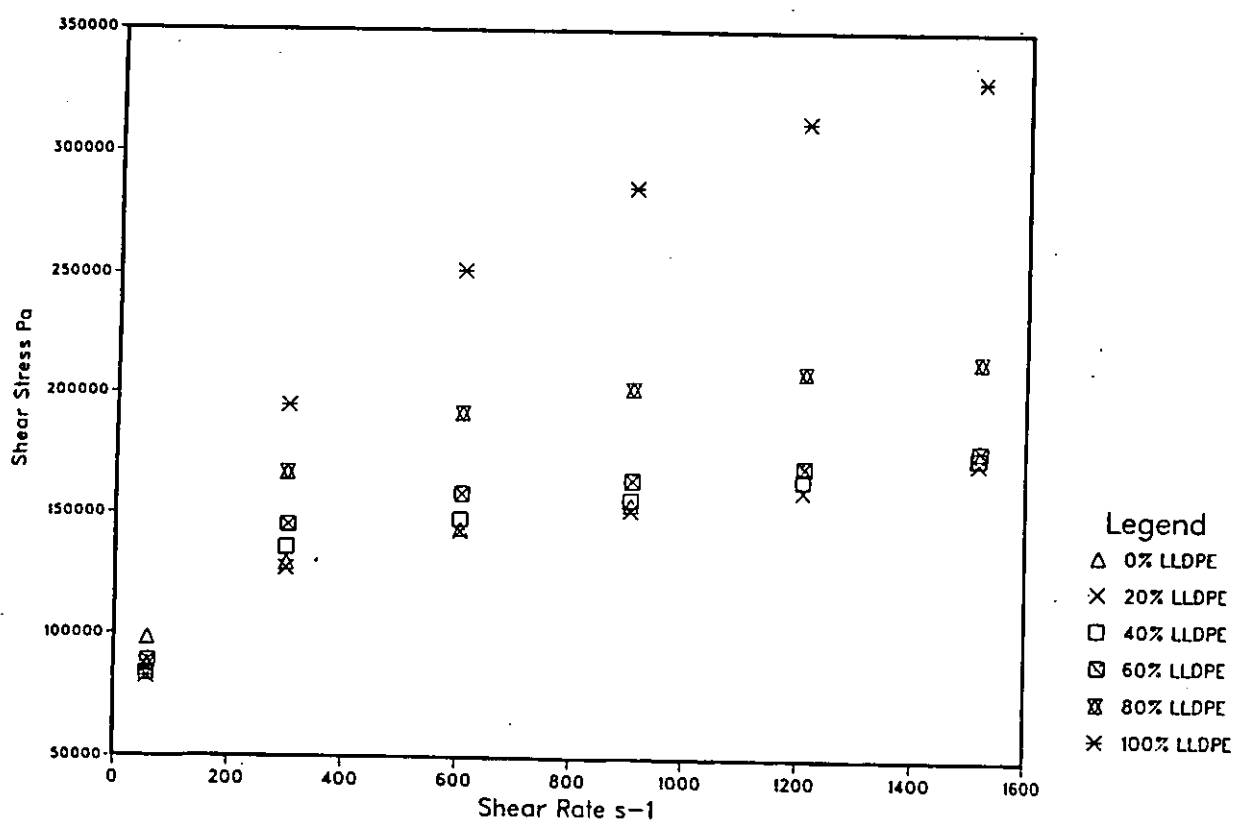


Fig. 6.50 The shear stress as a function of shear rate for LLDPE, PP, and their blends at 210 °C.

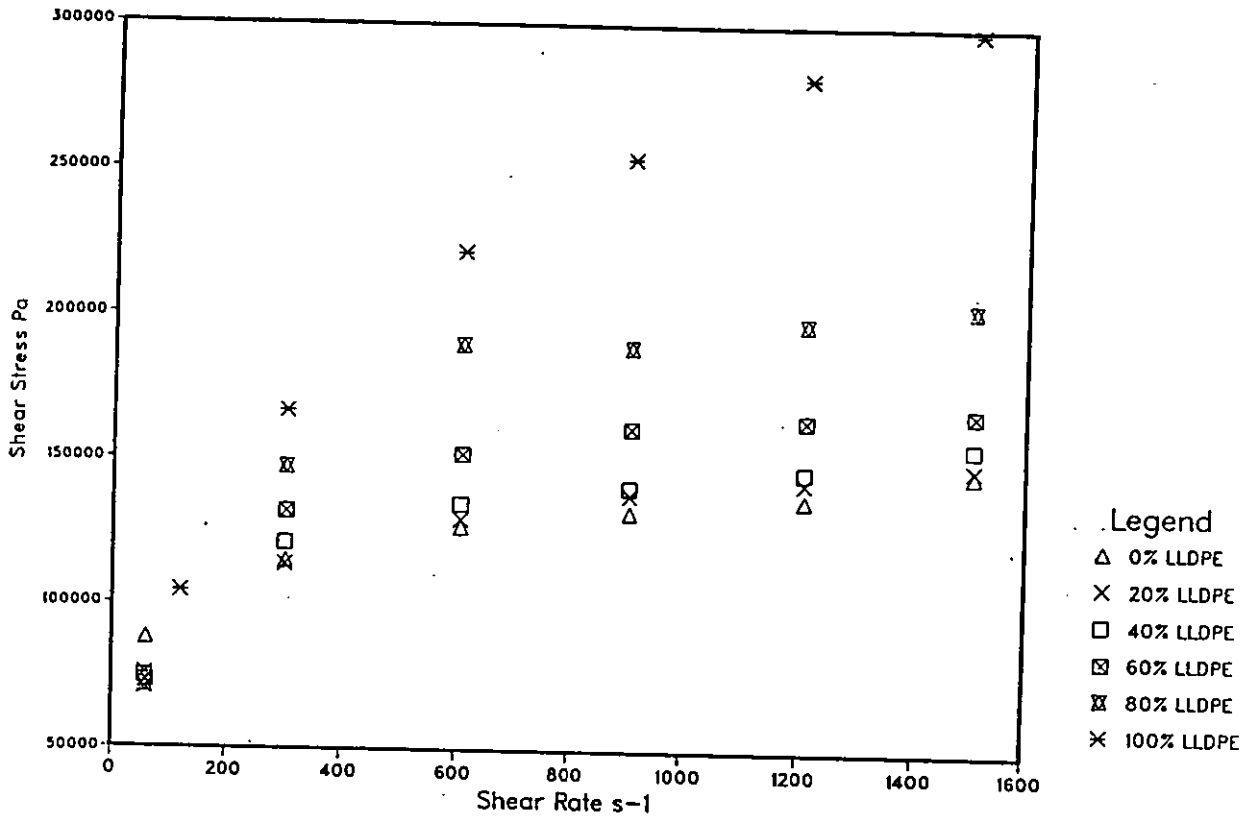


Fig. 6.51 The shear stress as a function of shear rate for LLDPE, PP, and their blends at 230 °C.

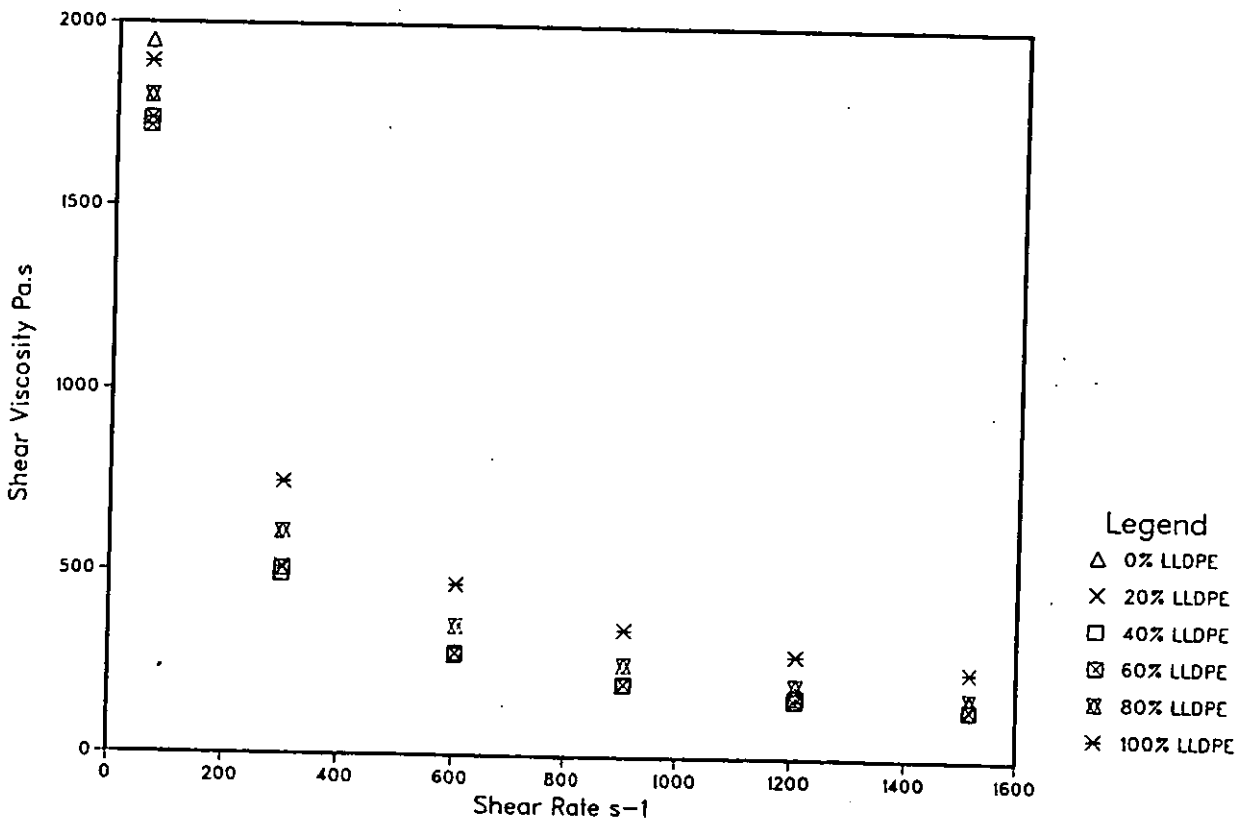


Fig. 6.52 The shear viscosity as a function of shear rate for LLDPE, PP, and their blends at 190 °C.

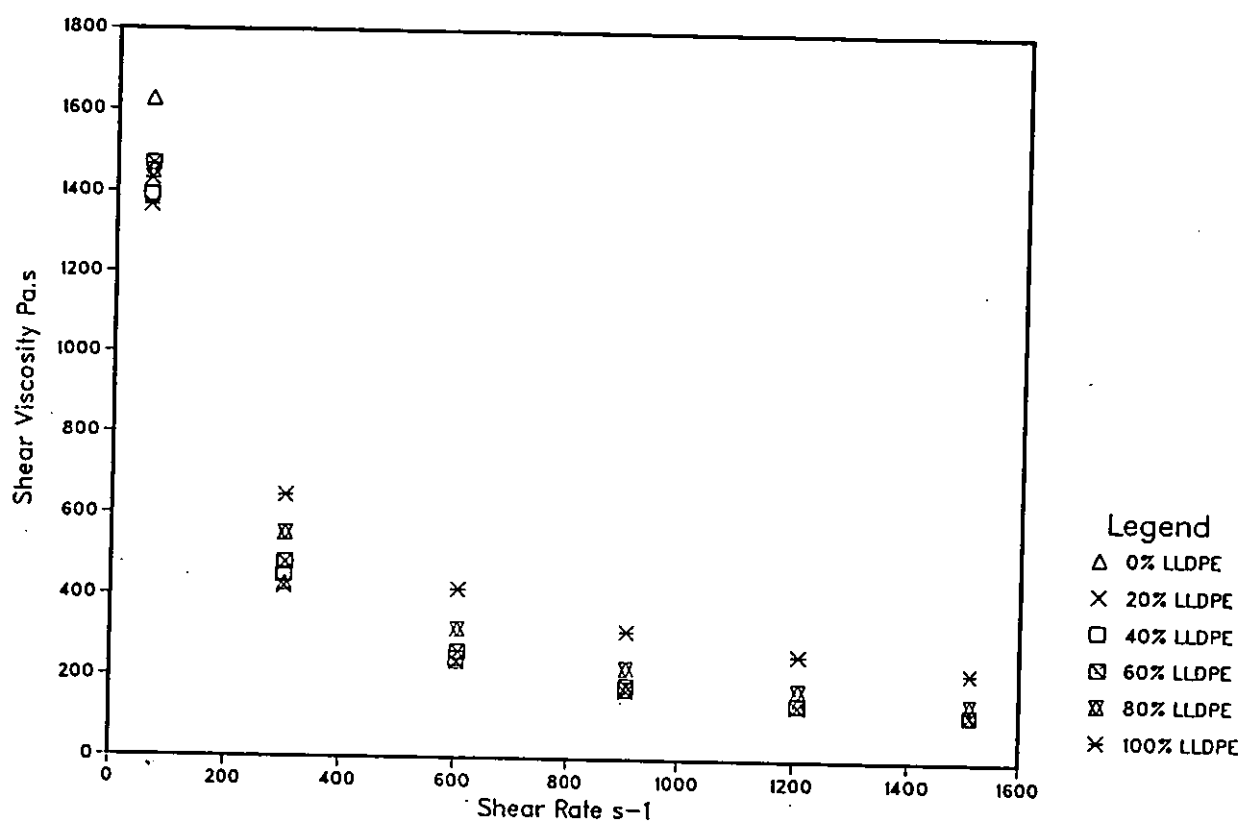


Fig. 6.53 The shear viscosity as a function of shear rate for LLDPE, PP, and their blends at 210 °C.

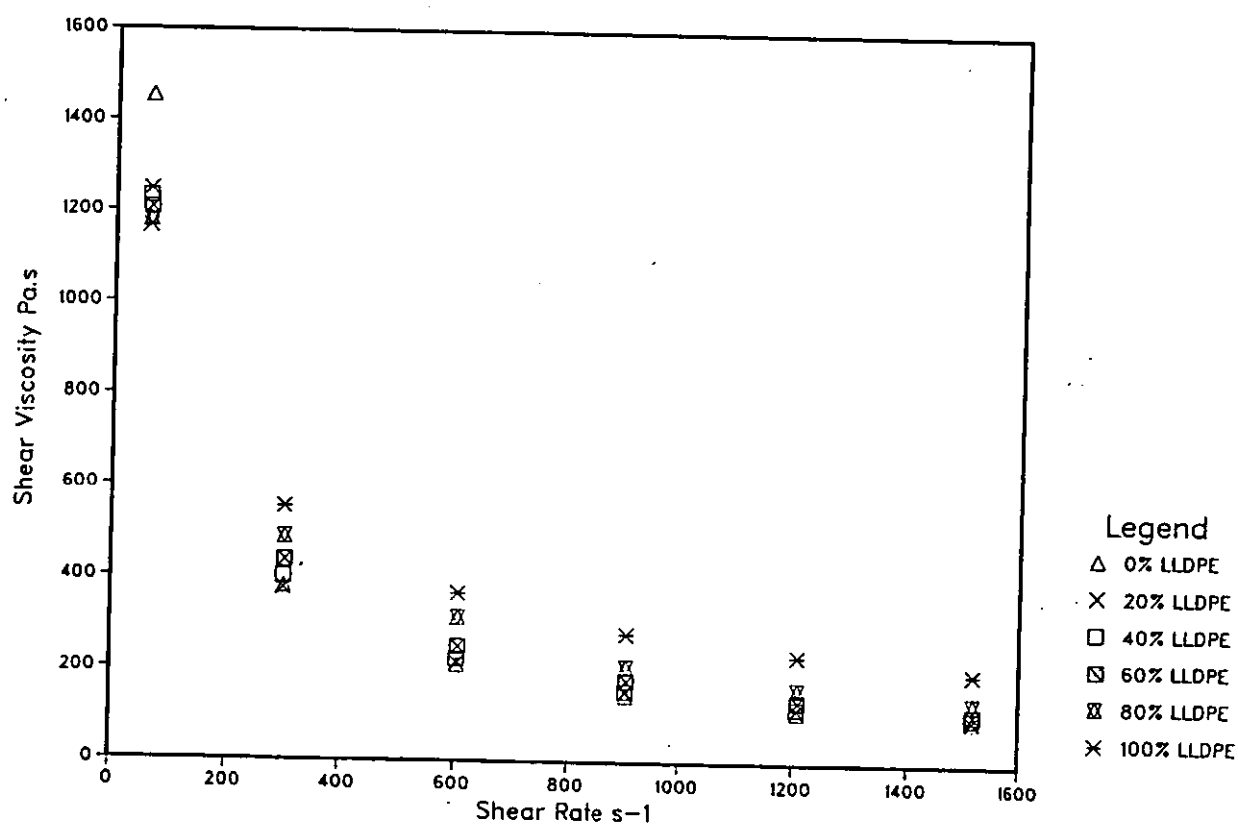


Fig. 6.54 The shear viscosity as a function of shear rate for LLDPE, PP, and their blends at 230 °C.

rate at various temperatures. In the low shear rate region i.e. 60 s^{-1} , the PP value is higher than that of LLDPE and the blends, for all melt temperatures. This supports the MFI results which showed that PP has lower MFI and therefore higher molecular weight than that of LLDPE for all the three measurements at 190, 210, and 230 °C. As the shear rate increases the viscosity decreases markedly due to the shear thinning of the melt i.e. pseudoplastic affect⁽¹¹³⁾. This also causes the viscosity of PP to become lower than that of LLDPE as a result of being more pseudoplastic. This was also observed by Romanini⁽¹¹⁴⁾ in the case of HDPE and LLDPE. The viscosities of the blends and their components also decrease with increase in temperature due to easier flow of materials, as a result more adjacent molecules can readily disentangle and slip past each other⁽¹¹³⁾. The blends show almost the same viscosity at higher shear rate for all the melt temperatures.

6.3.8 Tensile Properties

Tensile stresses at yield and break for LLDPE/PP blends and their components against composition are shown in Fig. 6.55. The tensile strength at yield for PP is higher than that of LLDPE due to its greater stiffening of the chain. The graph shows that the tensile strength at yield increases monotonically as the content of PP increases despite incompatibility in the blends as was detected by DSC and DMTA. This behaviour is also true for tensile stress at break except for the blend of LLDPE/PP-20/80 which drops sharply.

Elongations at yield and break plotted against composition in Fig. 6.56 show that the elongation at yield for PP is lower than that of LLDPE as a result of

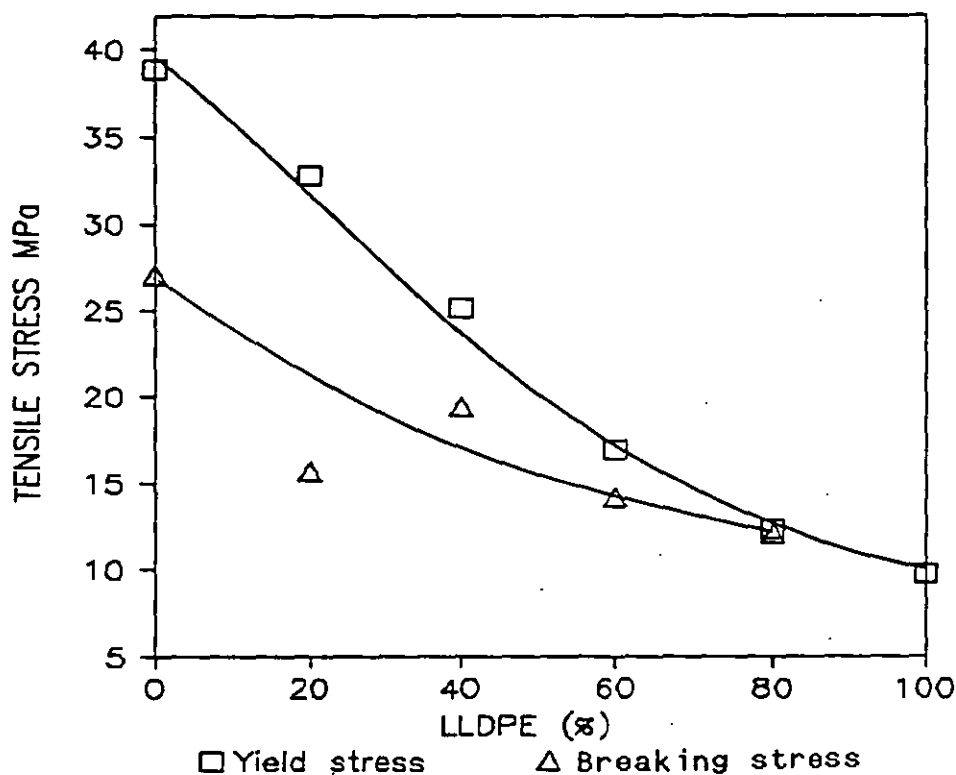


Fig. 6.55 Tensile Stresses at yield and break for LLDPE, PP, and their blends.

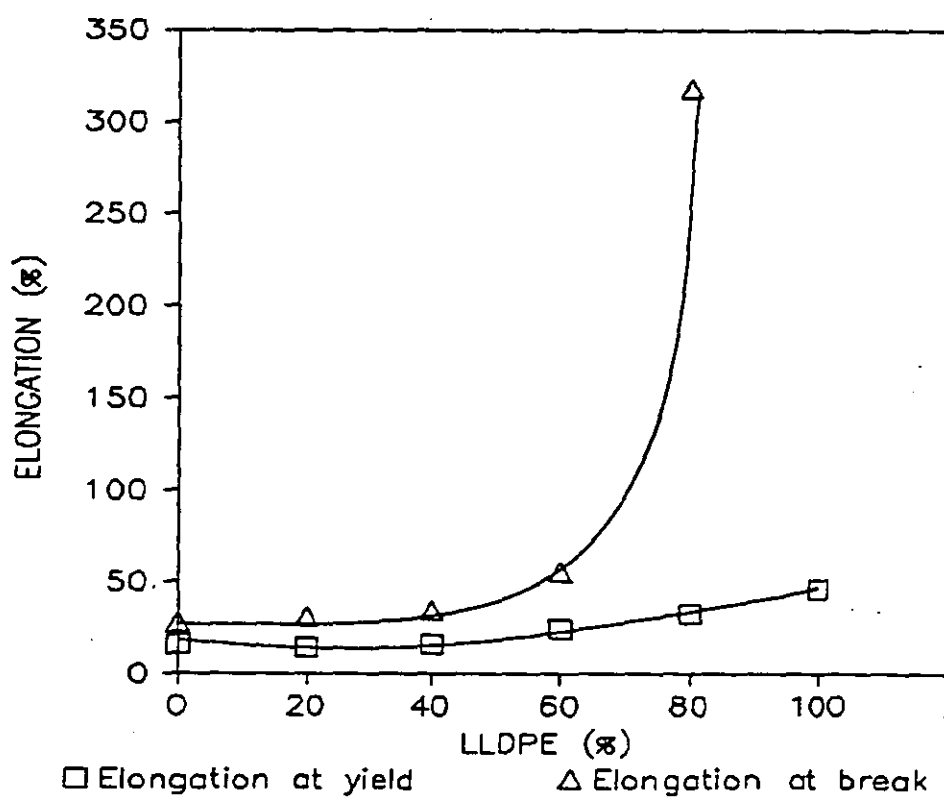


Fig. 6.56 Elongation at yield and break for LLDPE, PP, and their blends.

its higher degree of crystallinity. In general, the higher the crystallinity the lower the elongation at yield and break. The graph also shows that the elongation too, increases monotonically as the content of LLDPE increases. The increase in elongation at yield is little as the content of LLDPE increases but this is more obvious for the elongation at break. There is a sudden jump for the LLDPE/PP-80/20. The LLDPE sample did not break. The test was carried out up to 720% strain.

Typical stress-strain curves for LLDPE/PP blends and their components are shown in Fig. 6.57. The yield stress tends to decrease as the content of LLDPE increases. The secant modulus was taken from the stress-strain curves at 2 percent elongation. The modulus of the blends in Fig. 6.58 shows true positive synergism. A distinct maximum is seen at 20% LLDPE content. This supports the results of Noel et al(97), Lovinger et al(88) and Deanin et al(115) who found maxima of modulus at 10, 20 and 25% HDPE, respectively in the blend of HDPE and PP.

The strength of crystalline polymers depends on their degree of crystallinity. To examine this if we look at the micrographs of LLDPE, PP, and their blends(Figs. 6.40-6.45) show that the spherulites sizes in LLDPE are very small as a result of high nucleation and growth rates, whereas the opposite is true for PP. These micrographs show that LLDPE has strong influence in the reduction of the spherulitic size in the blends, which could increase overall crystallinity, and lead to promotion of intercrystalline links. The increasing of the overall crystallinity, results in enhancement of modulus and strength(88,117). But in this case although the micrographs show the reduction in spherulite size, there is no indication of increasing the crystallinity

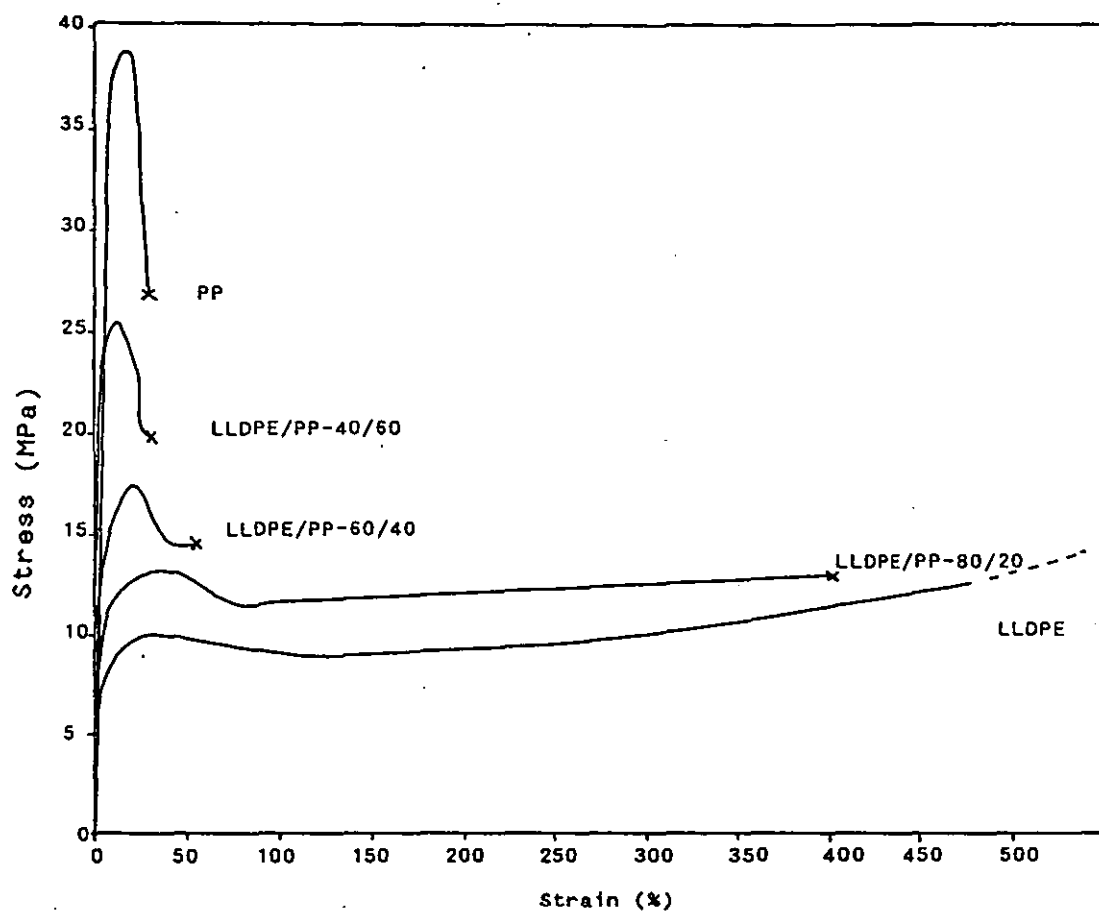


Fig. 6.57 Stress/Strain curves for LLDPE, PP, and their blends.

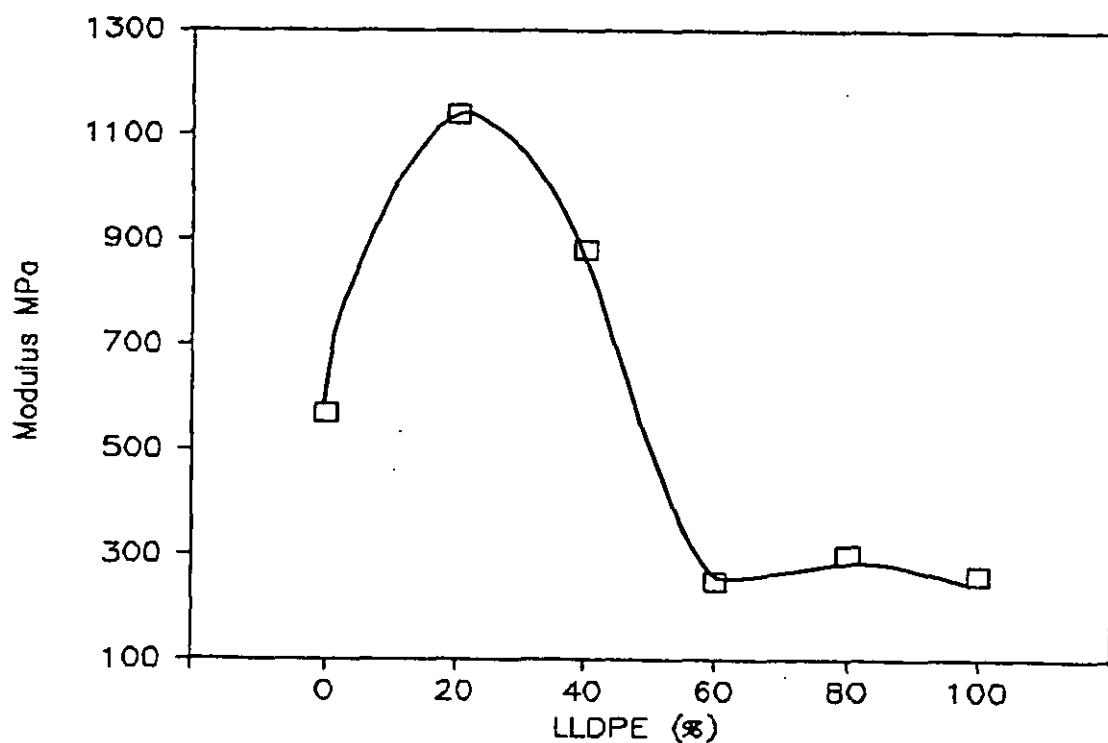


Fig. 6.58 Tensile modulus(at 2% elongation) for LLDPE, PP, and their blends.

of the blends as was demonstrated earlier by measuring the densities of the blends and the plot of crystallinity versus composition in Fig. 6.2. This could be due to difference in the cooling rates of the specimen for micrographs and density measurements.

The peaks in modulus at 20 and 40% LLDPE is not fully understood. However, at small strain involved in modulus determination (2%), incompatibility is expected to have little influence, whereas the effect of tie chains and intercrystallinity links should be significant (88). Padden et al (116), in the case of HDPE and PP, have shown that in comparison to PP which has only a few intercrystalline links because of its slow growth of spherulites, HDPE has high density of intercrystalline links. In this way, and because of its role in reducing spherulites size, HDPE could be functioning as a stiffener for PP matrix. This could also be true in the case of LLDPE, for the blends of LLDPE/PP-20/80 and 40/80.

6.4 Conclusion

Thermal analysis of linear low density polyethylene and polypropylene have shown two distinct melting and crystallisation temperatures attributed to LLDPE and PP, which suggests that these polymers are immiscible. This is also supported by DMTA results.

The addition of small amounts of LLDPE to PP seems to cause mild nucleation of PP. This was detected by DSC which showed an increase in melting and crystallisation peaks heights.

6.5 EVALUATION OF BLENDS IN PROCESSING PLASTICS

6.5.1 Introduction

Following the interesting behaviour of PP by adding small amounts of LLDPE which was detected earlier by DSC; three processing techniques were used on these blends (0-20% LLDPE contents) to investigate the significance of the interaction of PP and LLDPE on the process and end products. It is suggested that LLDPE causes the mild nucleation of PP which could result in having a superior product in these blend ratios. These developments have been brought to the attention of relevant local companies who are considering the implications.

6.5.2 Injection moulding

Injection moulding is widely used in the plastics industries therefore, it seemed reasonable to investigate the blends in this process first.

The Negri Bossi NB 55 injection moulding machine was used to produce plaques of the PP/LLDPE (Himont/Escorene, MFI=1.0 g/10 min.) and PP/VLDPE (Himont/Norsoflex) blends at 230 °C. Mouldings were obtained at mould temperature of 19 °C. The impact strength of these plaques was measured at room temperature and also at -20 °C using the Rosand Falling Weight Instrumented Impact Tester.

6.5.3 Extrusion blow moulding

An application of these blends could be in the making of bottles; as in this method of processing nucleation is helped by orientation which is applied by inflating the soft plastic parison.

The Hayssen Europa extrusion blow moulder was used to make bottles at 180 °C for PP(Himont) and the blends at a mould temperature of 8 °C. The LLDPE(Escorene MFI=1.0 g/10 min.) bottles were made at 170 °C with the same mould temperature. Tensile strength of specimens cut from the bottles was measured using the JJ tensile testing machine at a speed of 50 mm/min.

6.5.4 Tape Production

Further consideration for the application of these blends could be in the production of strapping tapes. In this process the LLDPE firstly could act as a mild nucleating agent and secondly, above 120 °C could act as softener/processing aid.

The blend of LLDPE/PP-10/90(Escorene/Himont) and PP(Himont) were passed through a single screw extruder(Betol) at 200 °C using a slit die. The tape was hauled-off through a water bath by a conveyer with a variable speed nip roller and then fed through an oven at 125 °C. The tape was then finally passed through a calender at 140 °C to give further orientation and a good surface finish with a uniform thickness. The drawing was carried out below the melting point of PP to reduce the level of molecular slippage among neighbouring molecules which results in having extended chain crystals and fewer chain folds and defects. Because of the high ultimate strength of

the carbon-carbon bond, a fully aligned polymer has a very high strength and modulus⁽¹¹⁸⁾. Tensile and Tear tests were measured on the tapes using the JJ Tensile Testing Instrument at a speed of 50 mm/min.

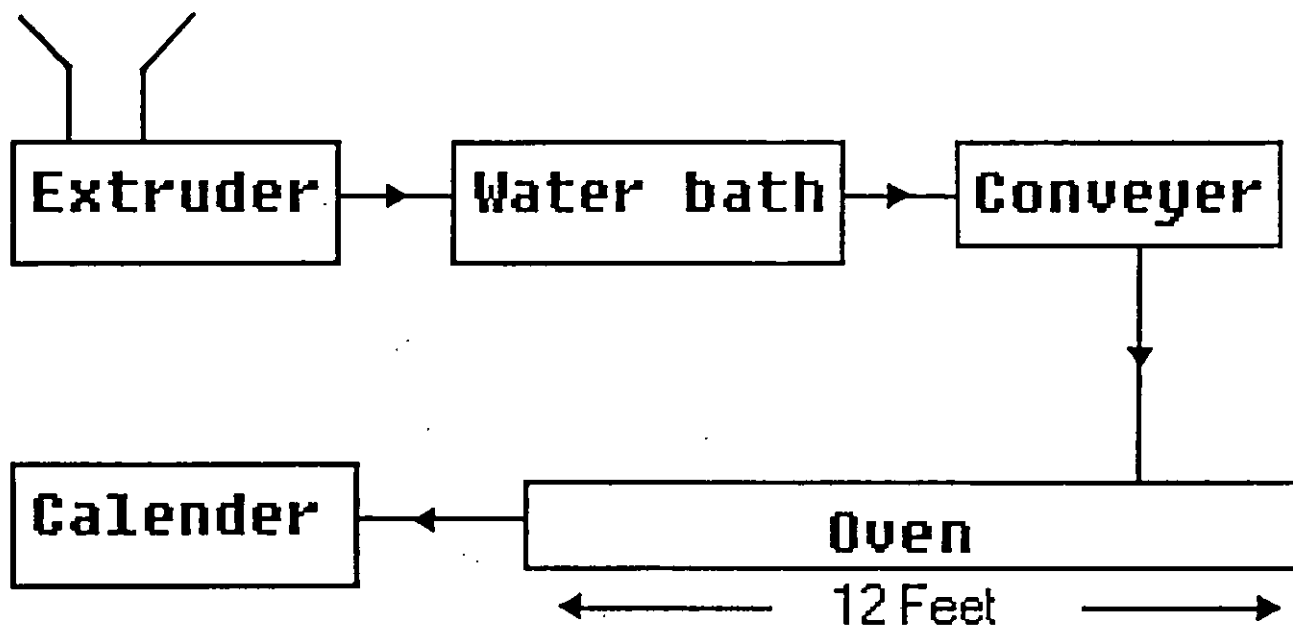


Fig 6.59 Schematic drawing of process used for the production of the strapping tapes.

6.5.5 Mechanical Properties

6.5.5.1 Impact strength of injection moulded samples

The impact strengths of PP/LLDPE, PP/VLDPE blends and their components in Fig. 6.60 show that the impact strength of the blend increases as the content of either LLDPE or VLDPE increases. The impact strength reaches its maximum for the 10% LLDPE or VLDPE content and then decreases. This is in line with the results obtained by DSC (Figs. 6.30 and 6.31) which showed the optimum increase in the height of thermograms of melting and crystallisation temperature for the blend of LLDPE/PP-10/90. The interesting point is that

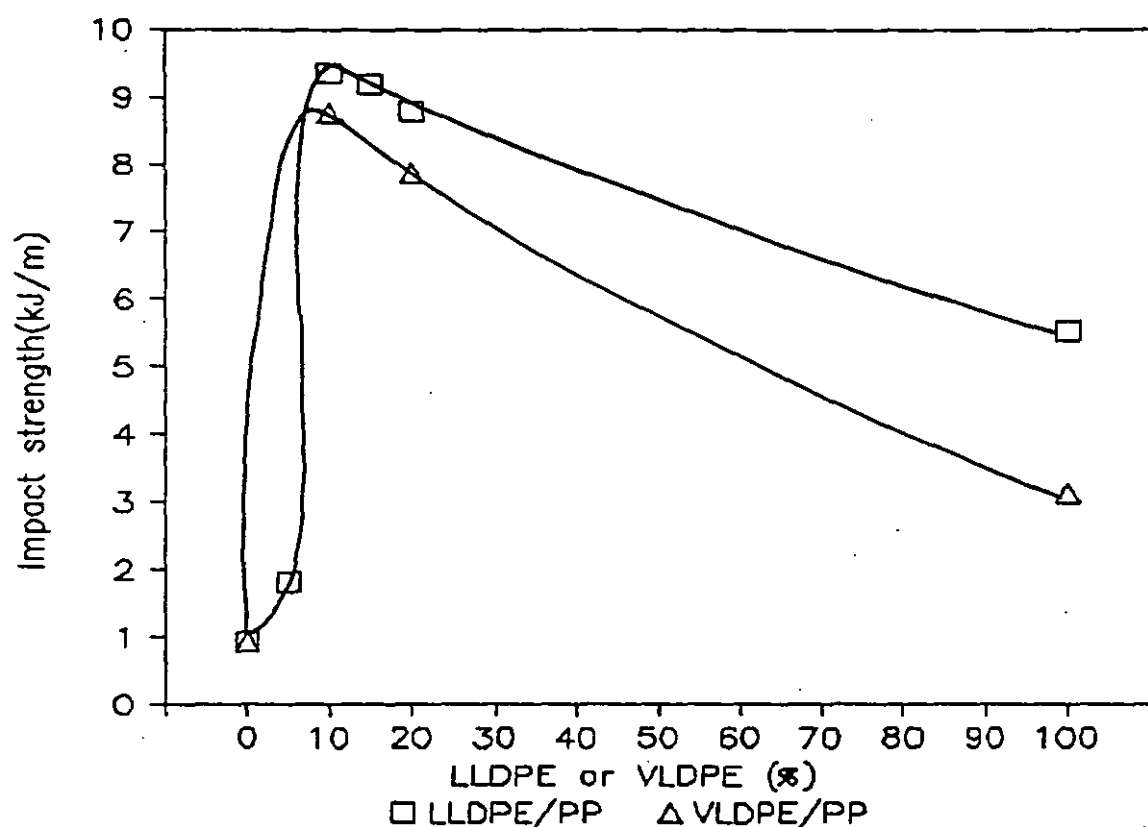


Fig. 6.60 The impact strength of LLDPE, VLDPE, PP, and their blends at room temperature.

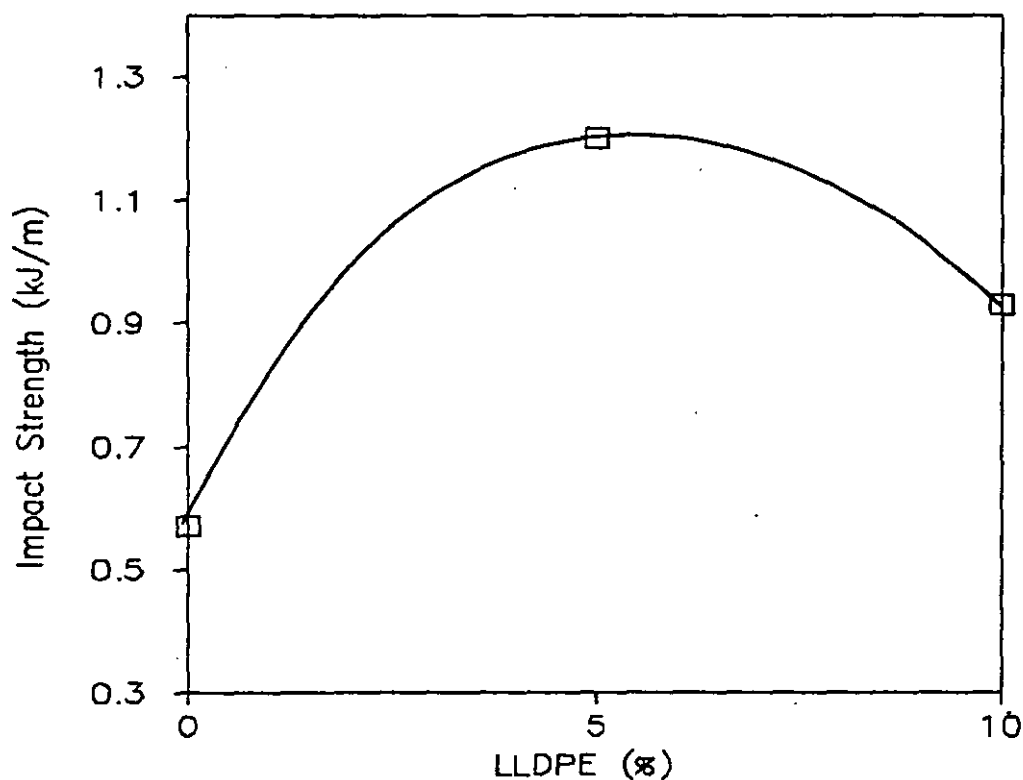


Fig. 6.61 The impact strength of PP and PP/LLDPE blends at -20 °C.

although DSC shows an increase in crystallinity, but this has no effect on the reduction of toughness possibly due to the other positive factor which can not be explained. The impact strength of PP was found to be lower than LLDPE or VLDPE. The LLDPE shows better impact strength than VLDPE in the virgin form or in the blend.

The impact strength of PP/LLDPE blends and PP at -20°C in Fig. 6.61 shows an enhancement. A distinct maximum is seen at 5% LLDPE content. It seems that LLDPE shows drastic deterioration in impact strength at low temperature. This could be the reason for showing higher strength at 5% instead of 10% LLDPE content. Although the blend with 10% LLDPE content shows poor impact strength nevertheless its value is much greater than PP alone.

6.5.5.2 Tensile strength of bottles

The tensile stresses at yield and break are given in Figs. 6.62 and 6.63 respectively; both show a positive effect. A distinct maximum is seen at 5% LLDPE content. This, again supports the DSC results and injection moulded samples which showed an optimum strength at 5 or 10% LLDPE content.

The elongation at break in Fig. 6.64 shows an initial increase at 5% LLDPE content, followed by a decrease for the 10% LLDPE content but maintaining the elongation higher than that of PP. The rest of the blends, as expected, show an increase in elongation as the content of LLDPE increases.

The elongation at yield in Fig. 6.65 shows a sharp increase in elongation for the 5% LLDPE content and

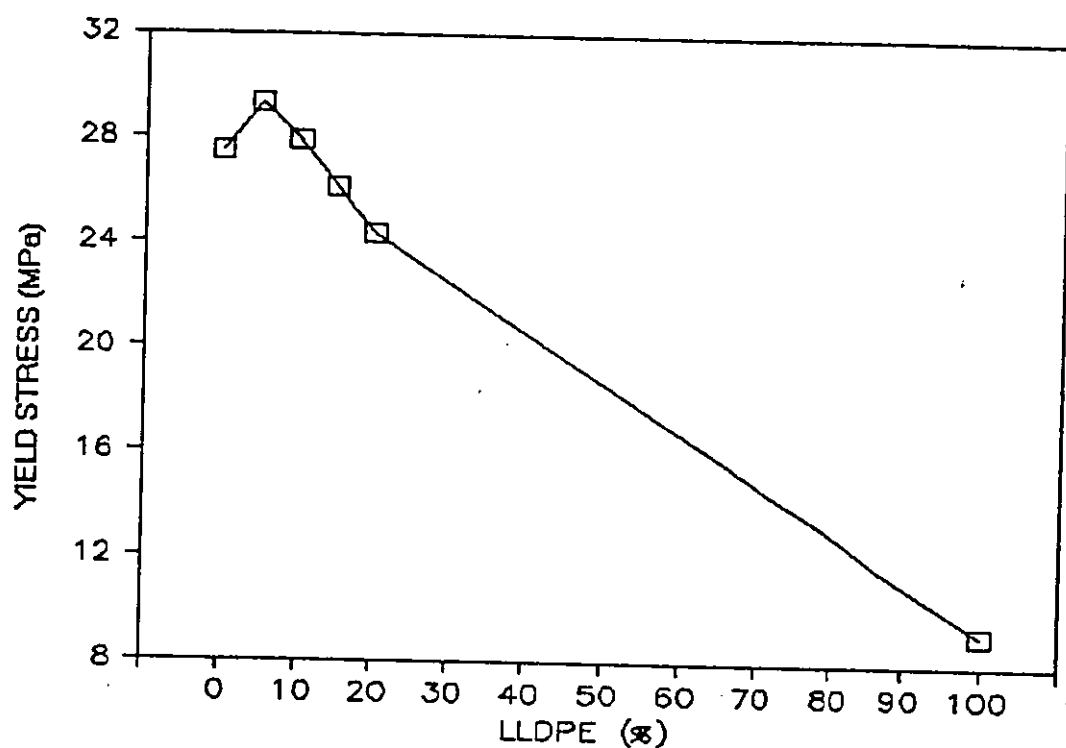


Fig. 6.62 Tensile strength at yield for LLDPE, PP, and LLDPE/PP bottles.

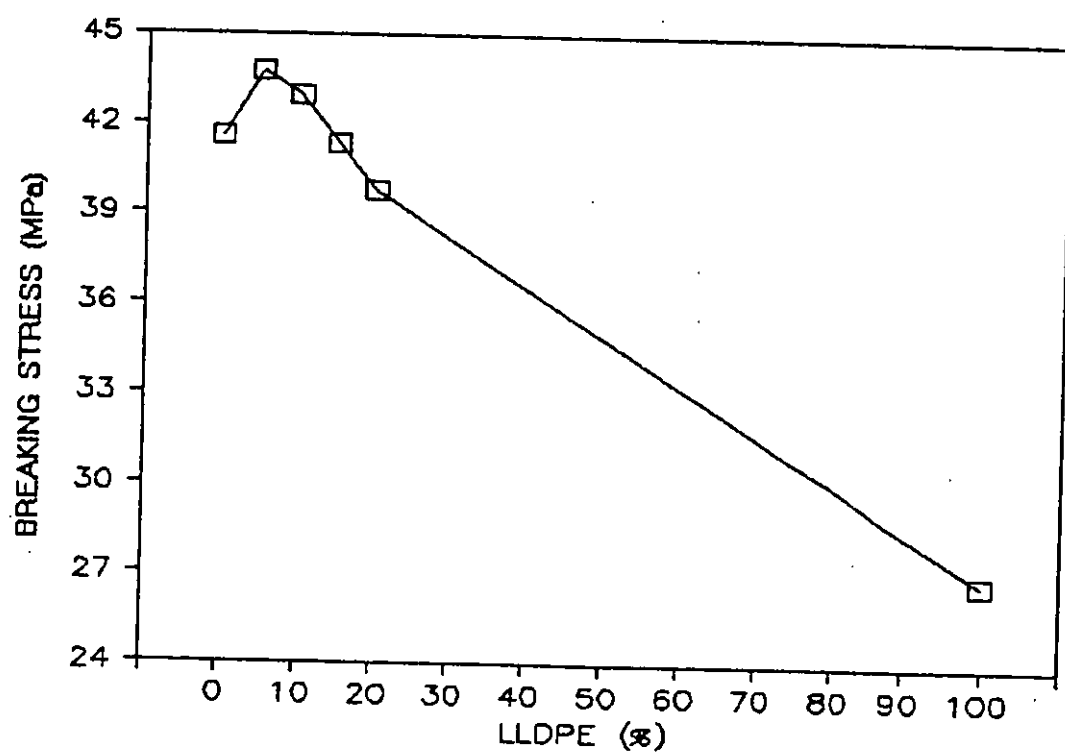


Fig. 6.63 Tensile stress at break for LLDPE, PP, and LLDPE/PP bottles.

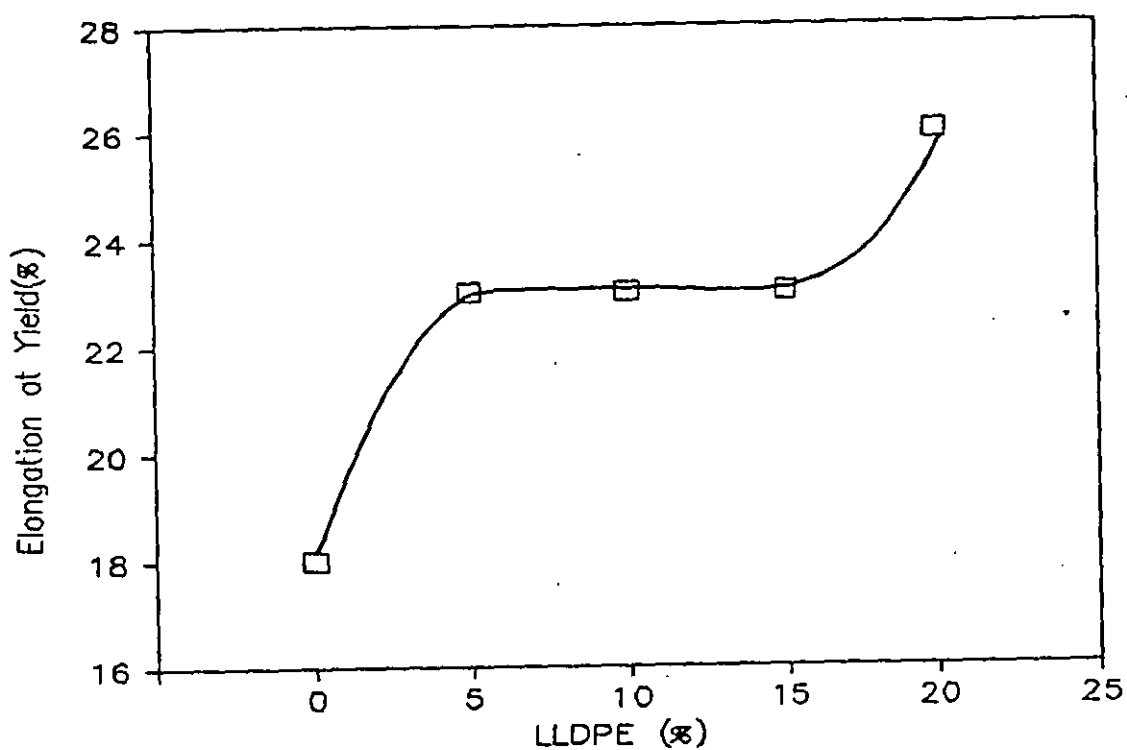


Fig. 6.64 Elongation at yield for PP and PP/LLDPE bottles.

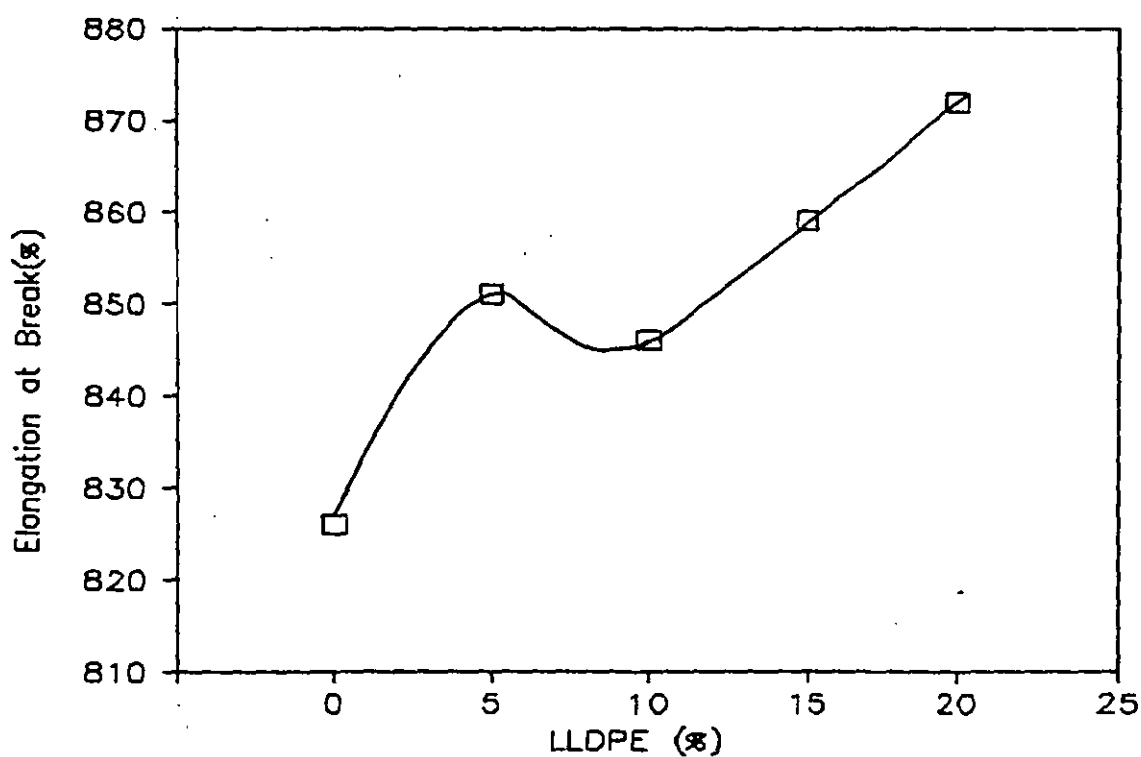


Fig. 6.65 Elongation at break for PP and PP/LLDPE bottles.

then as expected, increases after a steady period from 15% LLDPE content.

6.5.5.3 Tensile and Tear Strengths of Tapes

The tensile stresses at yield and break of tapes are shown in Figs. 6.66 and 6.67 respectively, with thickness as an important function. It can be seen that the thickness of tapes is a major factor in higher strength due to higher orientation(as was explained earlier). These results do not show the expected benefit of addition of LLDPE to improve the strength of PP(as was seen for injection mouldings and bottles) when similar orientation applied. However, the tape made from the blend can be drawn more easily; and to a lower thickness which results in higher yield strength. There is no improvement in breaking stress with the blend, even at lower thickness as in the case of yield strength.

The elongation at yield in Fig. 6.68 shows some benefit of addition of LLDPE to PP at low thickness for the blend tapes. The elongation at break in Fig. 6.69 shows that as the orientation increases the elongation decreases, and as was seen with breaking stress there is no improvement in elongation with the blend.

Further tensile tests were made after choosing three sets of the above tapes(PP with a thickness of 0.74 mm; blend 1 with a thickness of 0.71 mm; and blend 2 with a thickness of 0.62 mm), and drawing them with a ratio of 2:1 at 115 °C and 125 °C in the JJ tensile testing chamber. The breaking stresses obtained, summarised in Table 6.6 and in Fig.6.70 show that the breaking stress as expected increases with increase in draw ratio, and

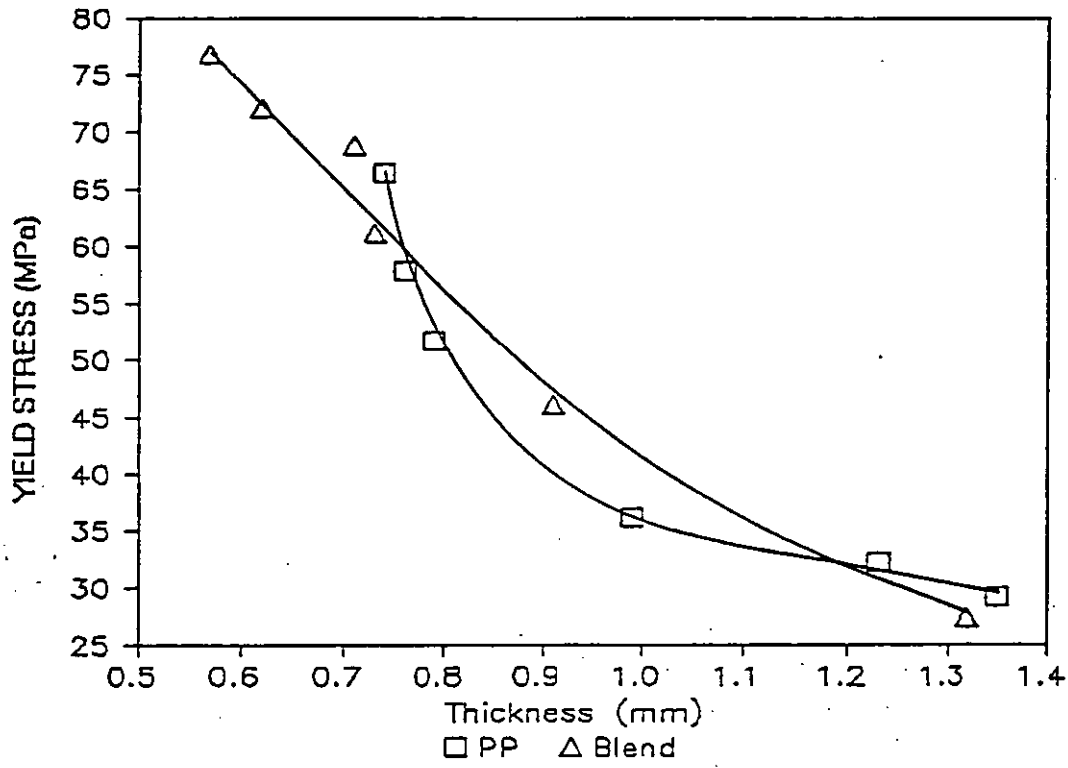


Fig. 6.66 Tensile stress at yield for PP and PP/LLDPE blend tapes according to their thicknesses. 1.38 and 1.35 mm are the thicknesses of undrawn PP and blend tapes respectively.

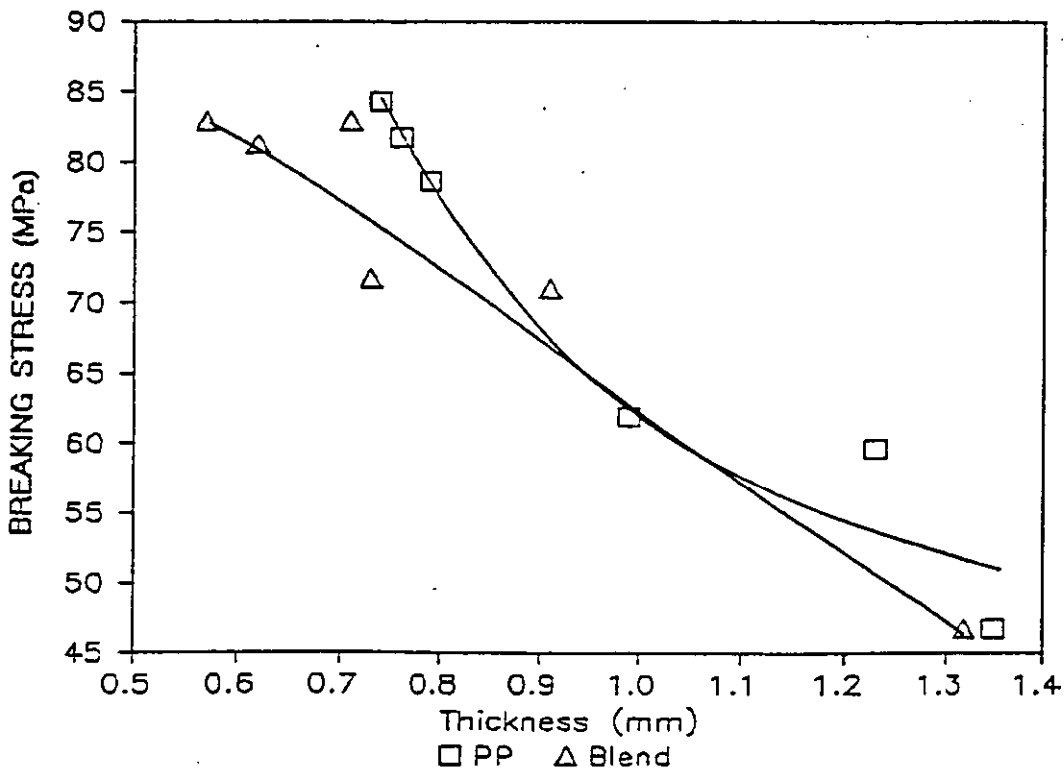


Fig. 6.67 Tensile stress at break for PP and PP/LLDPE blend tapes according to their thicknesses. 1.38 and 1.35 mm are the thicknesses of undrawn PP and blend tapes respectively.

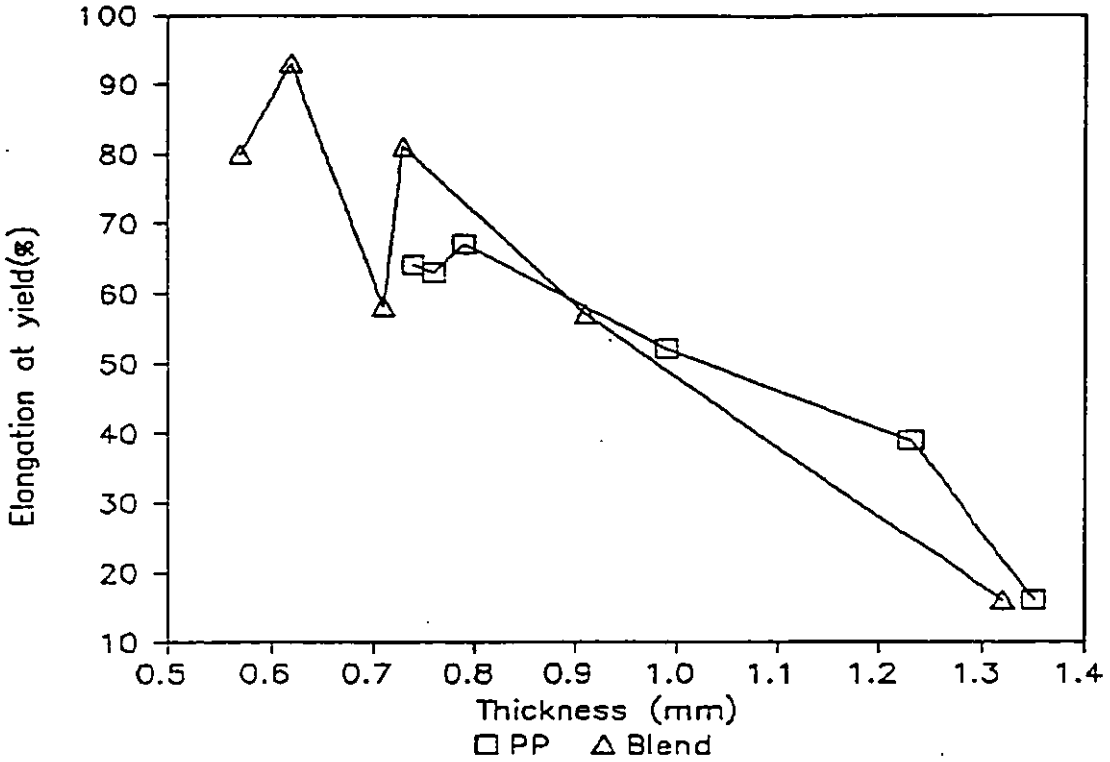


Fig. 6.68 Elongation at yield for PP and PP/LLDPE blend tapes according to their thicknesses. 1.38 and 1.35 mm are the thicknesses of undrawn PP and blend tapes respectively.

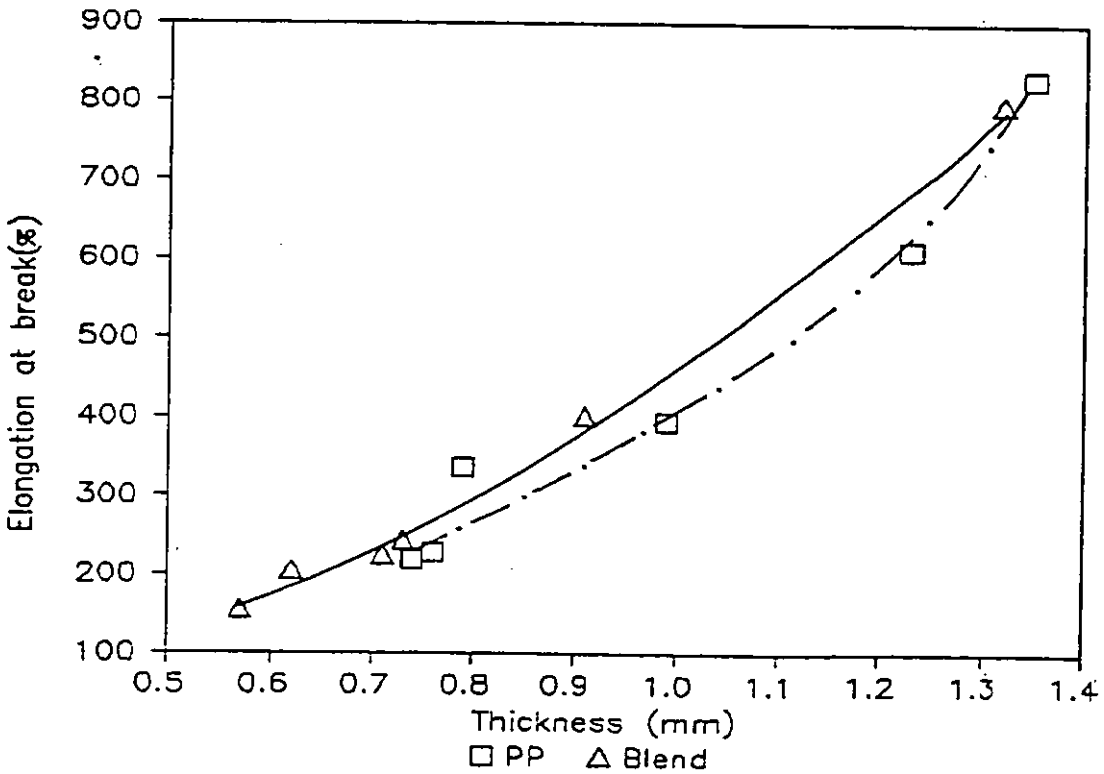


Fig. 6.69 Elongation at break for PP and PP/LLDPE blend tapes according to their thicknesses. 1.38 and 1.35 mm are the thicknesses of undrawn PP and blend tapes respectively.

blends show higher breaking stresses than that of PP due to their lower original thicknesses and further reduction in their thicknesses than that of PP. The data also show that with PP higher strength is obtained at 125 °C whereas for the blends is 115 °C. This can be explained as in the case of the blends when drawn at 125 °C is just above the melting temperature of LLDPE, and as was explained earlier the orientation process is more effective below the melting point of PP and LLDPE. These tapes did not show a yield point.

Table 6.6

Breaking Stress (MPa)				
	Thickness (mm)		Draw ratio 2:1 at	
			115 °C	125 °C
PP	0.74	84.30	237.16	259.97
Blend 1	0.62	81.29	277.38	259.80
Blend 2	0.71	82.83	318.20	268.36

The elongations at break obtained, are summarised in Table 6.7 and in Fig. 6.71 show that the elongation decreases sharply as the draw ratio increases for PP and the blends which is in line with the previous results, due to loss of extensibility. There is not much difference in elongation when drawn at 115 and 125 °C, and LLDPE seems to have no effect in improving the elongation of PP.

Keys to the Figs 6.70 and 6.71:

	Thickness (mm)	Draw Ratio 2:1
1. PP	0.74	-----
2. PP	0.74	Drawn to 0.47 mm at 115 °C.
3. PP	0.74	Drawn to 0.47 mm at 125 °C.
4. Blend 1	0.62	-----
5. Blend 1	0.62	Drawn to 0.37 mm at 115 °C.
6. Blend 1	0.62	Drawn to 0.39 mm at 125 °C.
7. Blend 2	0.71	-----
8. Blend 2	0.71	Drawn to 0.38 mm at 115 °C.
9. Blend 2	0.71	Drawn to 0.42 mm at 125 °C.

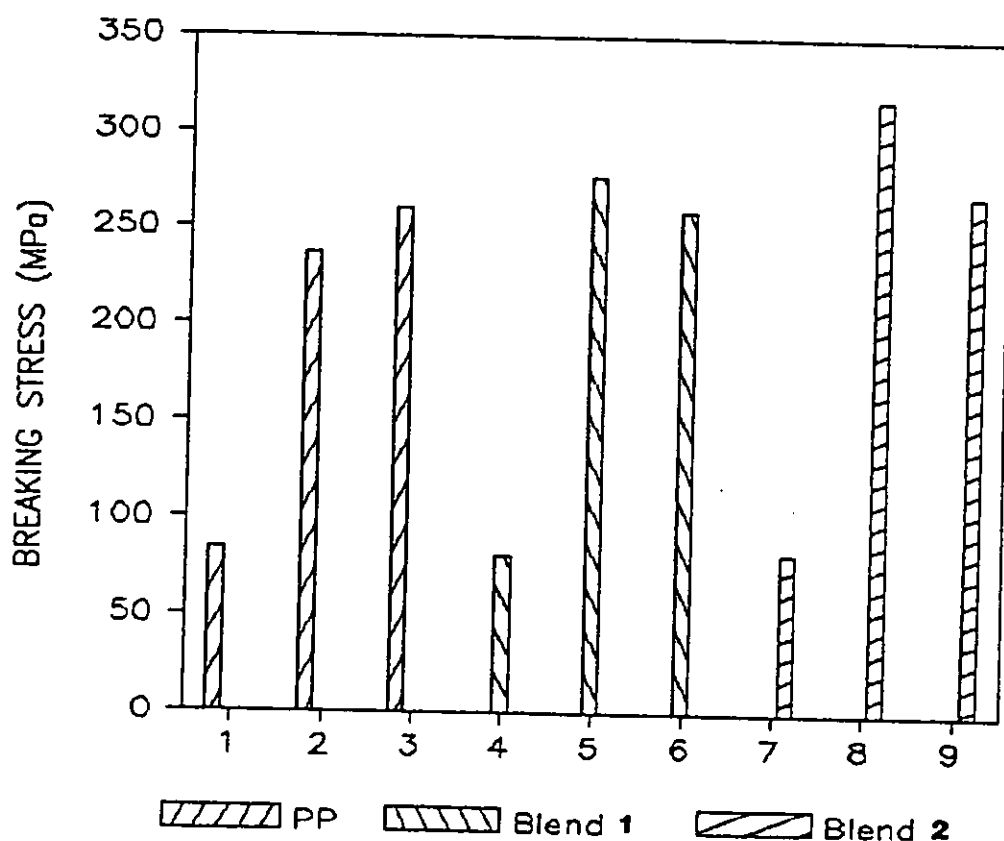


Fig. 6.70 Tensile stresses at break for PP and PP/LLDPE tapes.

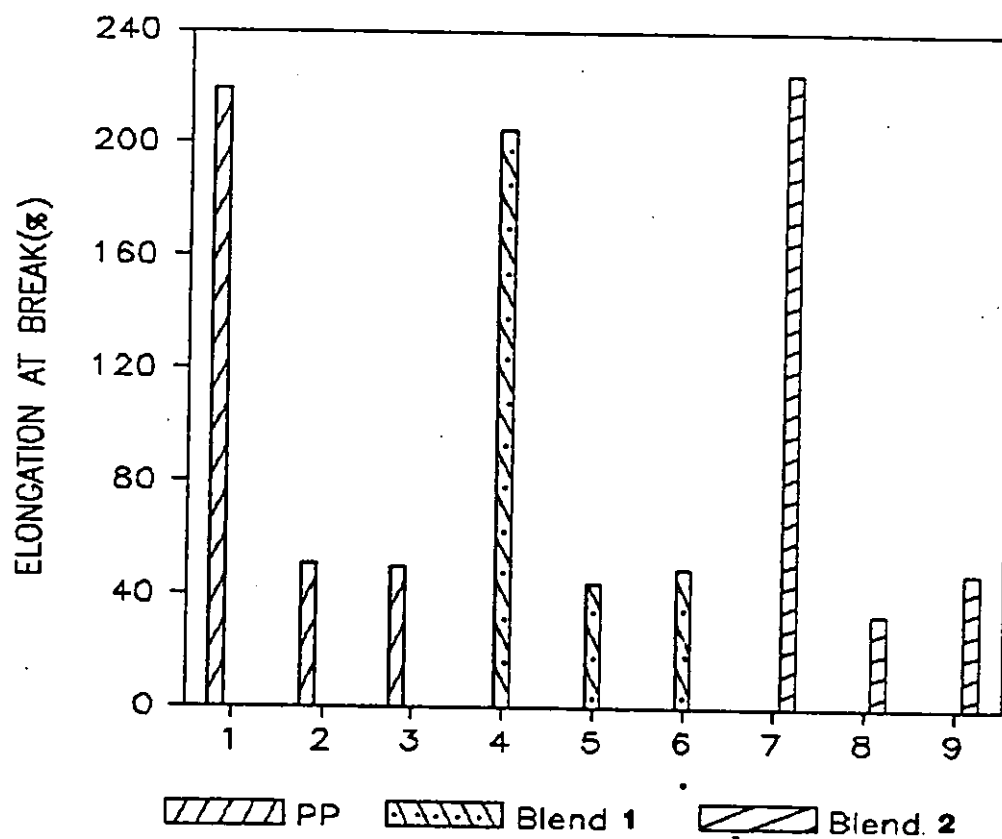


Fig. 6.71 Elongations at break for PP and PP/LLDPE tapes.

Keys to the Fig. 6.72:

	Thickness (mm)	Draw Ratio 2:1
1. PP	0.77	-----
2. PP	0.77	Drawn to 0.45 mm at 115 °C.
3. PP	0.77	Drawn to 0.45 mm at 125 °C.
4. Blend 1	0.63	-----
5. Blend 1	0.63	Drawn to 0.39 mm at 115 °C.
6. Blend 1	0.63	Drawn to 0.39 mm at 125 °C.
7. Blend 2	0.70	-----
8. Blend 2	0.70	Drawn to 0.40 mm at 115 °C.
9. Blend 2	0.70	Drawn to 0.42 mm at 125 °C.

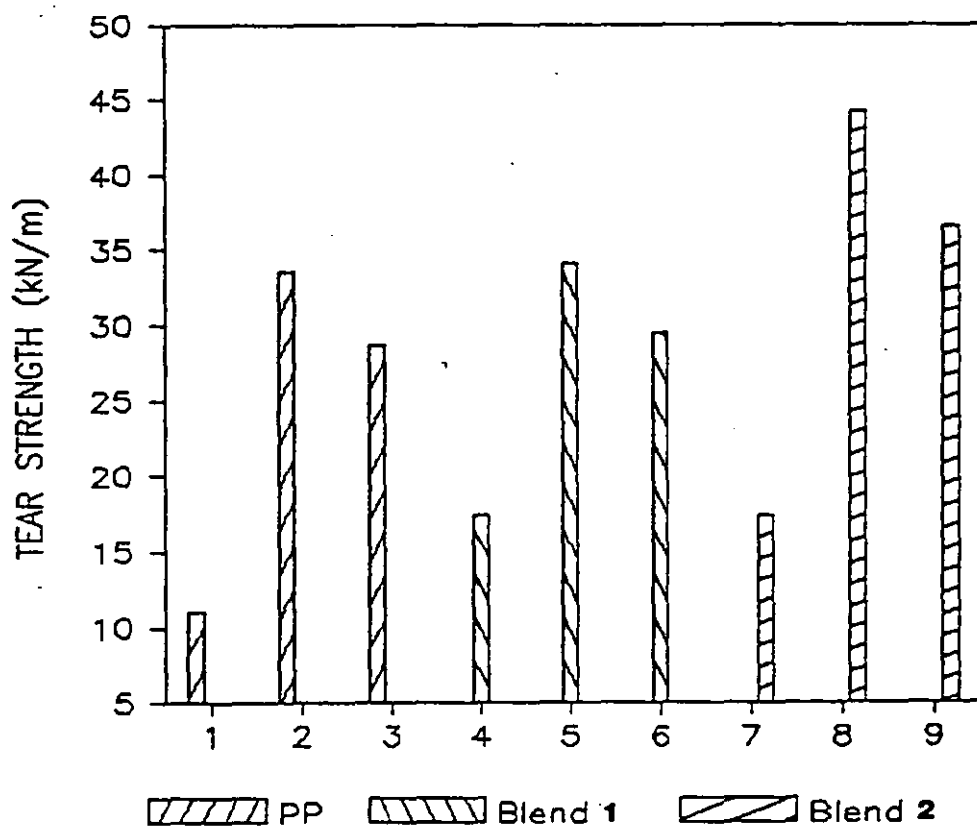


Fig. 6.72 Tear strengths of PP and PP/LLDPE tapes.

Table 6.7

Elongation at Break (%)				
	Thickness (mm)		Draw ratio 2:1 at 115 °C	125 °C
PP	0.74	219	51	50
Blend 1	0.62	205	44	49
Blend 2	0.71	225	33	48

The tear strengths of PP and the blends are summarised in Table 6.8 and in Fig. 6.72 follow the breaking stress trends, with the blend with higher orientation showing the higher tear strength. In this case PP as well as the blends show better tear strength after drawing at 115 °C rather than at 125 °C.

Table 6.8

Tear Strength (kN/m)				
	Thickness (mm)		Draw ratio 2:1 at 115 °C	125 °C
PP	0.77	11.05	33.50	28.61
Blend 1	0.63	17.34	34.07	29.43
Blend 2	0.70	17.30	44.18	36.53

6.5.6 Discussion and Conclusions

The addition of LLDPE(5-15%) to PP was found by DSC to increase the total PP crystallinity with respect to both the melting and crystallisation peaks heights. The mechanical properties measured for injection moulded samples and bottles showed an improvement in mechanical

properties within these ratios. The impact strength of injection moulded samples tested at room temperature showed an optimum strength at 10% LLDPE content, whereas when tested at -20 °C, an optimum strength was found at 5% LLDPE content. This could be due to the poor behaviour of LLDPE at low temperature as was seen earlier. The bottles also showed the optimum yield and breaking stresses at 5% LLDPE content instead of 10 percent. This could be due to lower mould temperature of the blow moulder compared to the injection moulding machines.

To interpret these improvements in mechanical properties of injection moulded samples and bottles; it is suggested that LLDPE acts as a nucleating agent (which was detected by DSC). This could effect a reduction of the spherulitic size in the blends, could increase overall crystallinity, and promote intercrystalline links as was explained earlier. It has been shown that yield stress and breaking stress are improved with decreasing spherulite size, as a result of yielding and failure which are usually initiated at inter-spherulitic boundaries^(88,117). Therefore, at low concentration of LLDPE the above characteristics account for the improvement in mechanical properties whereas at high concentration of LLDPE incompatibility causes failure to occur early at interphase boundaries, thus reducing the strengths.

Light Scattering of bottles when measured in the melt showed no meaningful data due to similarity in density of PP(760 Kg/m³ at 220 °C) and PE(746 Kg/m³ at 210 °C)⁽¹¹⁹⁾, but when the bottles examined by naked eye in the solid state, the blend of LLDPE/PP-5/95 showed better clarity, which confirms the mild nucleation of PP.

The addition of LLDPE to PP in the production of tapes seems to have no improvement in mechanical properties of the blends with similar orientation, except the elongation at yield which is improved. However, the blend tapes could be drawn further than that of PP tapes, which results in greater orientation and hence higher strengths. The other significances of blend tapes are easier processability, softer feel and more resistance to splitting.

The blend tapes also show better break and tear strengths when drawn at lower temperature. It seems; it is important that processing, i.e orientation, should be applied below the melting points of LLDPE and PP, although only 10 percent of LLDPE was added.

The above investigation suggests that LLDPE acts as a mild nucleating agent and also as a plasticising additive. This behaviour in the blend of LLDPE and PP (5 or 10% LLDPE content) can be used to advantage in mechanical properties in the production of injection moulding components, bottles and also to some extent in the production of tapes.

CHAPTER 7

SUMMARY OF CONCLUSIONS AND COMMERCIAL EXPLOITATION

7.1 General Conclusions

The present work has dealt with a variety of polyolefin blends, and shown the advantages of polymer miscibility in chapter 3, 4, and 5. It also examined the case of immiscible polymer blends in chapter 6.

In chapter three the blends of EVA/LDPE were compared to EVA copolymer; these blends were found to be incompatible and had poorer mechanical properties than the copolymer, although they have the advantage of being easier to print.

In chapter four binary blends of LLDPE and HDPE proved to be miscible, with some improvement in properties. The ternary blends of LLDPE/HDPE/LDPE behaved as two phase systems; LLDPE/HDPE behaved as a copolymer and constituted one phase with LDPE as the other.

In chapter five the blends of LLDPE and LDPE showed interesting results. Although these blends had been reported in the literature to be immiscible, it was found that if these blends were mixed thoroughly, they were miscible in the melt and did not segregate on cooling to the solid state provided they were cooled quickly. The miscible systems gave improved mechanical properties.

In chapter six, blends of LLDPE and PP are shown to be immiscible, but the addition of small amounts of LLDPE to PP causes mild nucleation of PP. The benefit of this behaviour in the production of bottles, injection moulded samples and to in the production of strapping tapes has been discussed.

The present work also showed that the two polymers under investigation need not be miscible to give the benefits on blending as was seen for the blend of LLDPE and PP and also to some extent for the blend of LLDPE and LDPE.

7.2 COMMERCIAL APPLICATIONS

Polyolefins are among the most used polymers in industry due to their low cost and the wide range of applications. Their consumption (HDPE, PP, LD & LLDPE) in Western Europe for the year 1989 is shown in Fig. 7.1(120), in which packaging has the largest share of the market in the form of films or sheets. These are produced mostly either by blending or coextrusion techniques of two or three polymers to achieve the specific combinations of properties.

Packaging applications include flexible packaging, industrial uses, envelope windows, and wraps; flexible packaging is further divided into food, nonfood, and tobacco markets(121).

Bags are among the fastest growing applications for HDPE film, replacing bleached and unbleached kraft paper(121). Both HDPE and LLDPE films have made significant inroads into the grocery-sack market. More than 60 percent of LLDPE is blended with other polymers. Grocery sacks made by blending have the

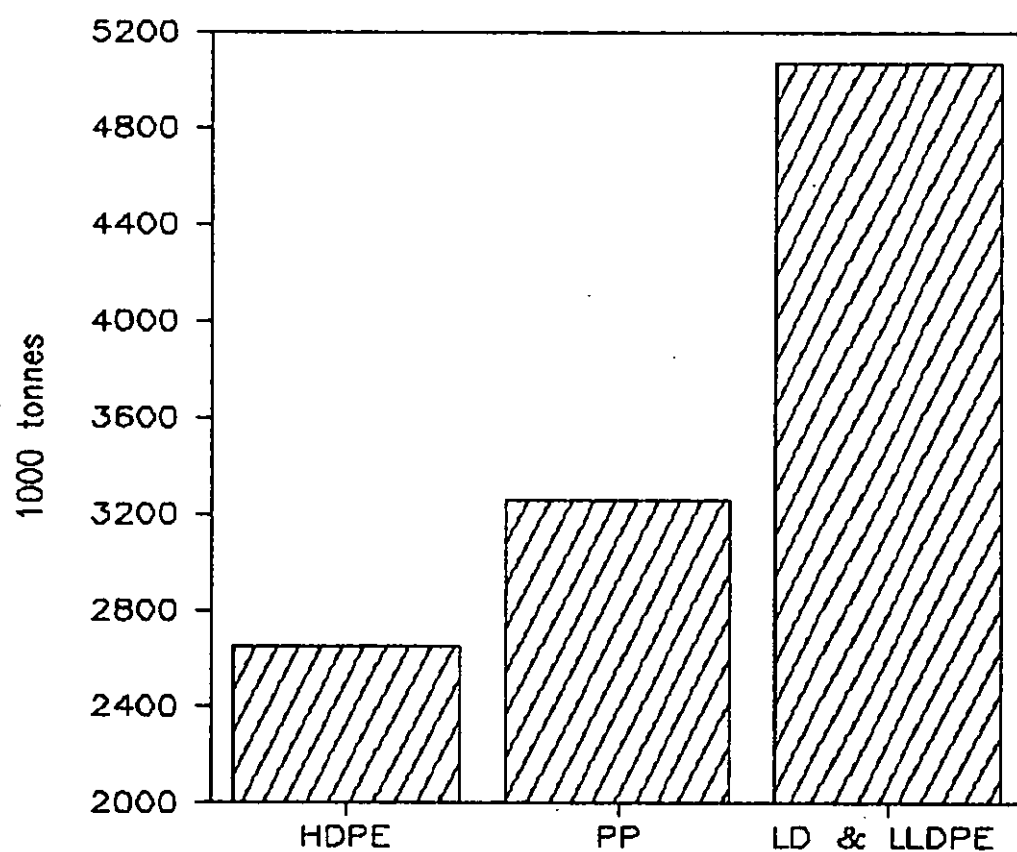


Fig. 7.1 Consumption of selected polyolefins in Western Europe for the year 1989(120).

composition of 30% LLDPE/70% LDPE, or a blend of LLDPE with a low level of HDPE. The advantage of these blends over the original LDPE sacks is the ability to produce a thinner gauge sack while retaining acceptable properties. Polypropylene is also added to LLDPE for increased stiffness compared to pure LLDPE. Applications include garment bags, grocery sacks, merchandise bags and refuse bags⁽³⁾. In coextruded products, LLDPE is used for strength and LDPE for transparency and seal range or to increase thickness. LLDPE also used most often in conjugation with LDPE to improve performance at the lowest possible cost, for example for refuse bags, and large-volume articles⁽¹²¹⁾.

Films serving the industrial packaging market, e.g, pallet overwrap, shipping sacks, and explosive bags are HDPE, EVA, and LDPE. Stretch films(LLDPE and EVA), in which the film is stretched around the article to be wrapped and is then heat sealed, gained considerable market share as the trend moved towards stretch wrapping and away from the energy intensive shrink-wrap system⁽¹²¹⁾.

7.3 SUGGESTION APPLICATIONS

The blend of LLDPE/EVA can be used in the production of films where there is a need of printing on them with moderate loss in mechanical properties compare to EVA copolymer.

The blends of LLDPE and HDPE also can be used in the production of films for packaging materials with improvement in their properties for such applications as were discussed above.



(a) Commercial extrudate blend (100 μm)



(b) IPTME blend of HDPE and LLDPE (100 μm)

Fig. 7.2 Comparison of commercial blend(a), and IPTME blend(b).

Polymer industries have to take advantage of advanced mixing techniques which are available for making blends to achieve the required properties. The micrographs in Fig. 7.2 compare the commercial blend with the blend made at IPTME. The commercial blend shows the uneven mixing whereas the IPTME blend shows a good mixing as a result of being mixed in the Baker Perkins twin screw extruder with special screw configuration for such an operation.

The ternary blends of LLDPE/HDPE/LDPE showed that even three polymers can be blended together with balanced properties which opens the area for the blending of scrap materials as a means of cost saving. The applications would be in the packaging industries.

The blend of LLDPE and LDPE showed that if these two polymers are mixed thoroughly (as was explained above), and cooled quickly, it is possible to get superior products due to miscibility of these two polymers in the melt and solid state. Their applications would be in injection moulding components and film production with improved properties.

The polymer industry should recognize the benefit of addition of small amounts of LLDPE to PP which showed an improvement in properties of injection mouldings components and also bottle production. They should also recognize the benefit in the production of tapes, the ability to apply high orientation, and produce tapes with softer feel and more resistance to splitting.

The blend of LLDPE and PP could also have application in the production of biaxially oriented films as in this process the interaction of LLDPE and PP could be more significant.

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APPENDIX I

THERMOGRAMS OF CHAPTER 4

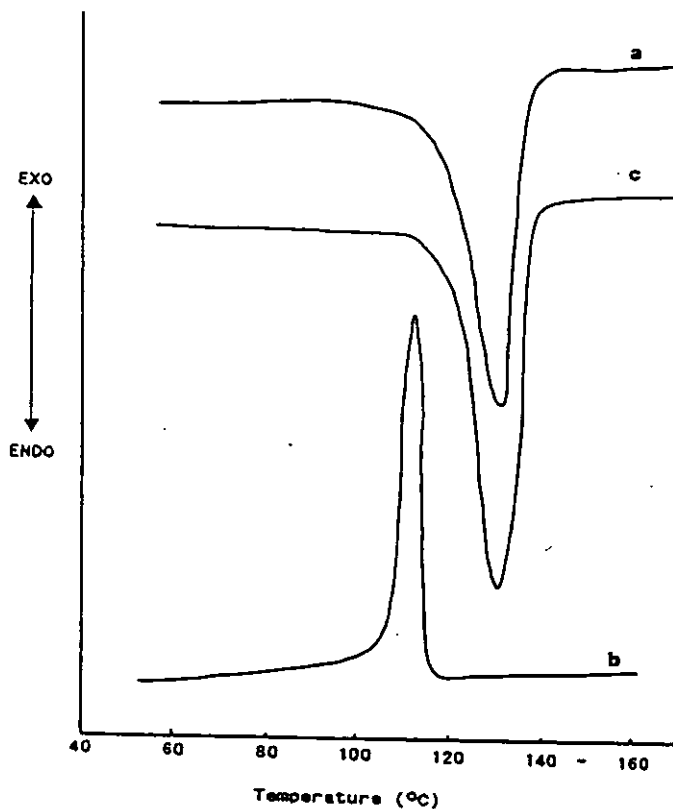


Fig. 4.8. Thermograms of Binary blend of LLDPE/MDPE-30/70(MFI = 1.0/8.75). (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

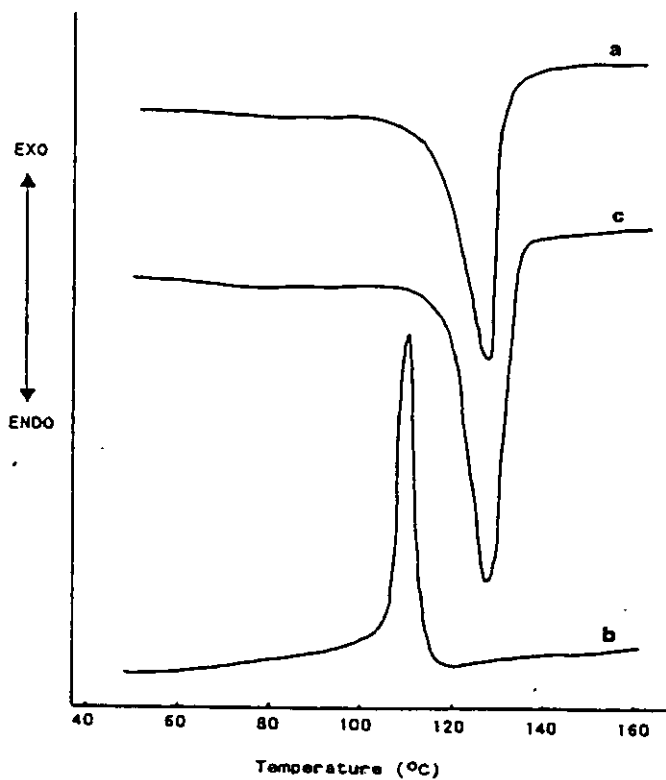


Fig. 4.9. Thermograms of Binary blend of LLDPE/MDPE-50/50(MFI = 1.0/8.75). (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

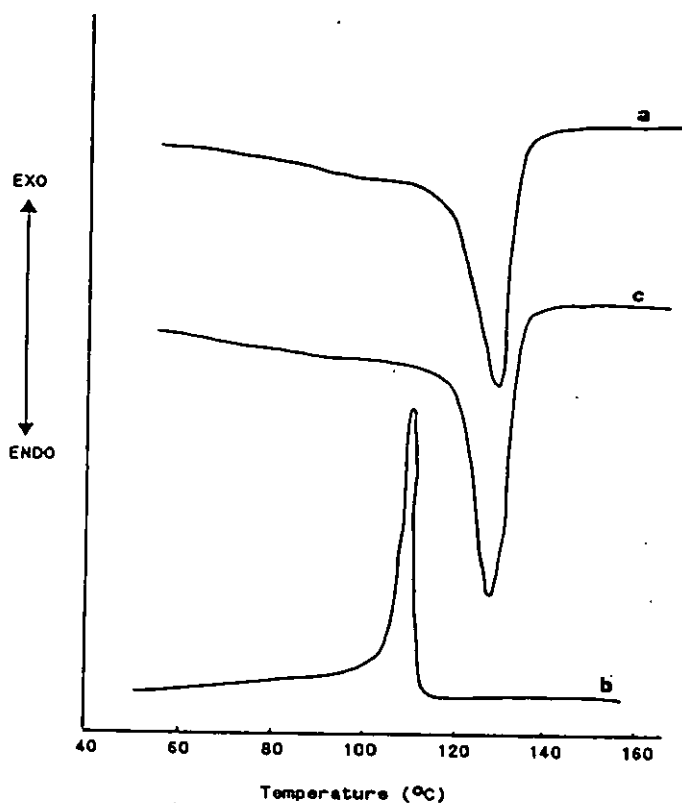


Fig. 4.10. Thermograms of Binary blend of LLDPE/HDPE-70/30(MFI = 1.0/8.76). (a) first heating, (b) cooling, and (c) second heating. Sensitivity = 10 mV/cm.

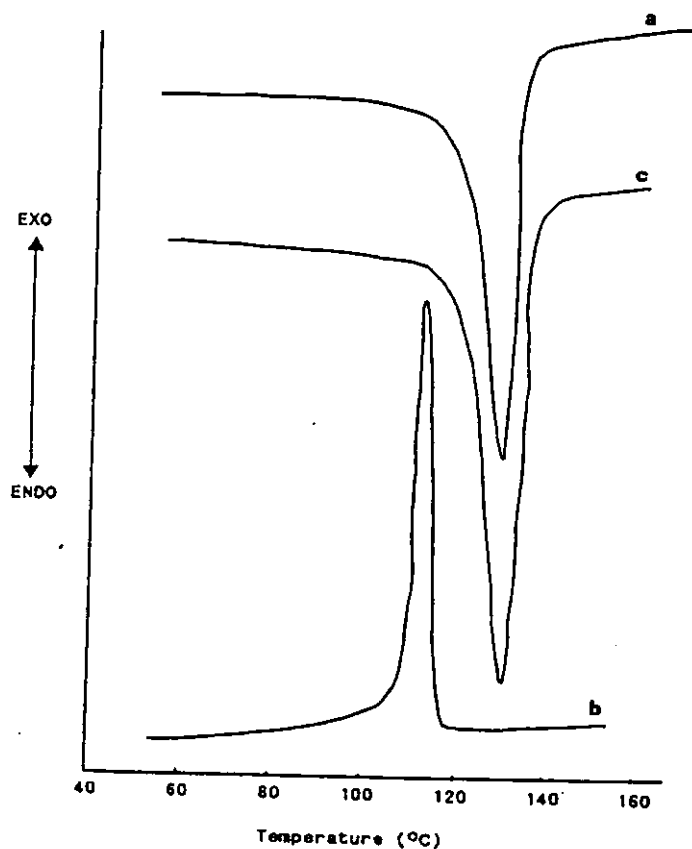


Fig. 4.11. Thermograms of Binary blend of LLDPE/HDPE-30/70(MFI = 20.0/8.76). (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

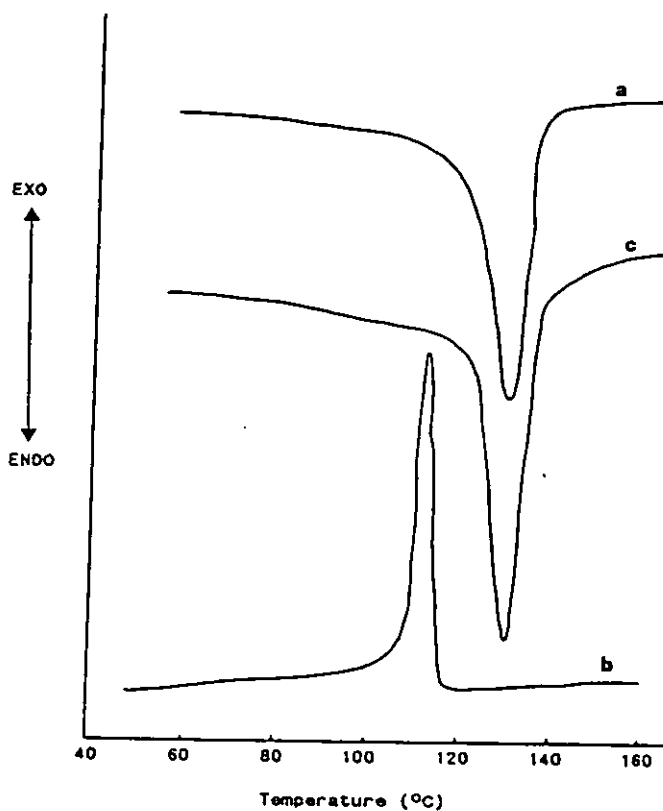


Fig. 4.12. Thermograms of Binary blend of LLDPE/HDPE-50/50(MFI = 20.0/8.76). (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

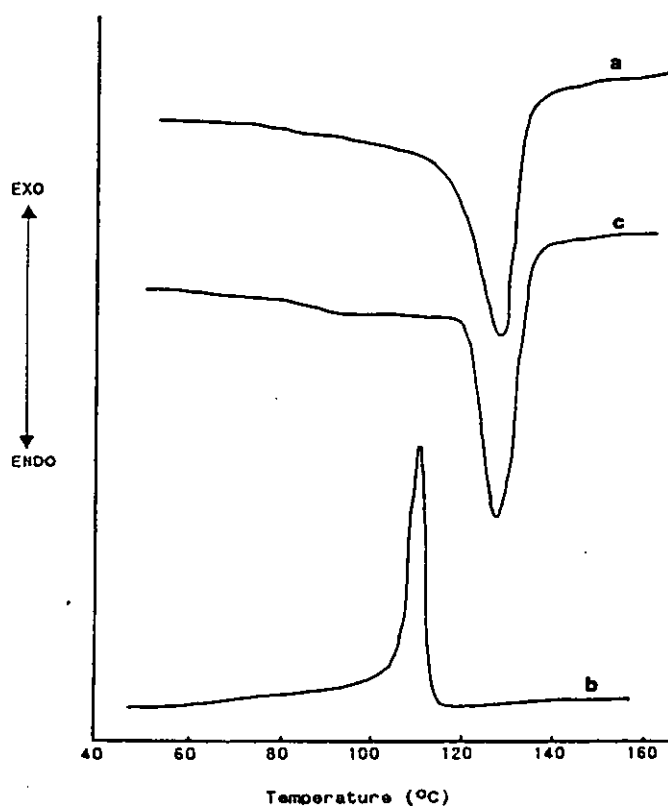


Fig. 4.13. Thermograms of Binary blend of LLDPE/HDPE-70/30(MFI = 20.0/8.76). (a) first heating, (b) cooling and (c) second heating. Sensitivity = 10 mV/cm.

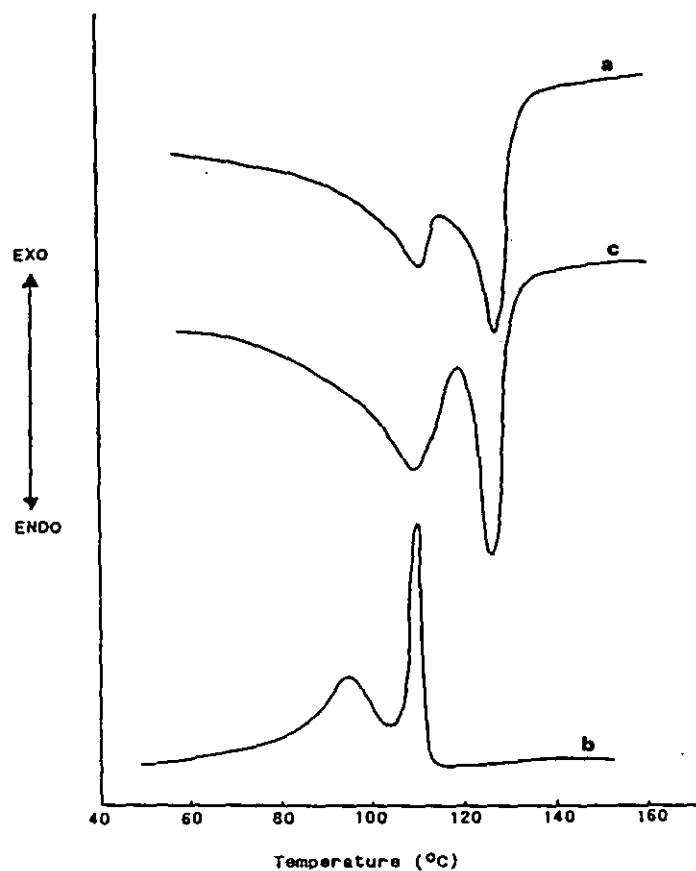


Fig. 4.21. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-15/15/70. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

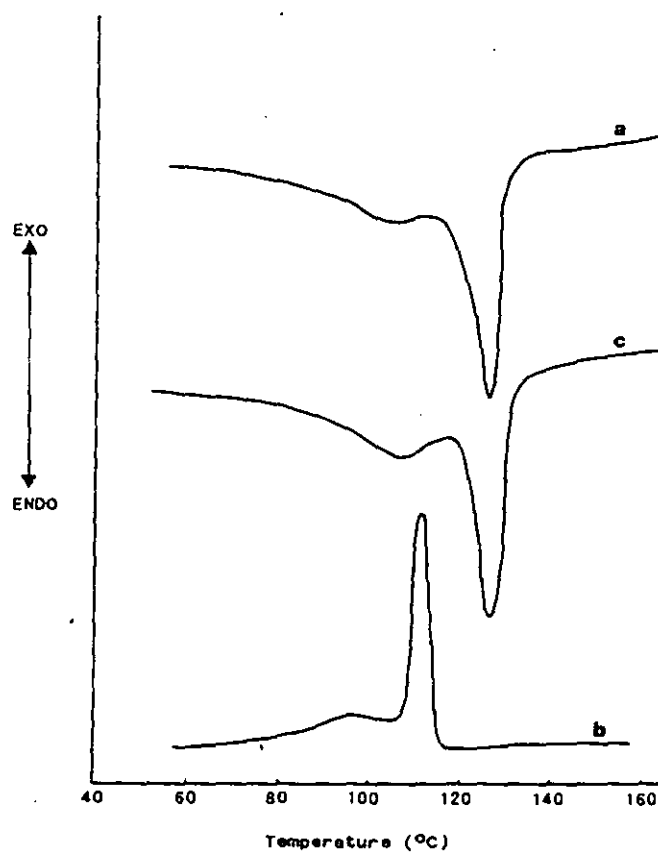


Fig. 4.22. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-25/25/50. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

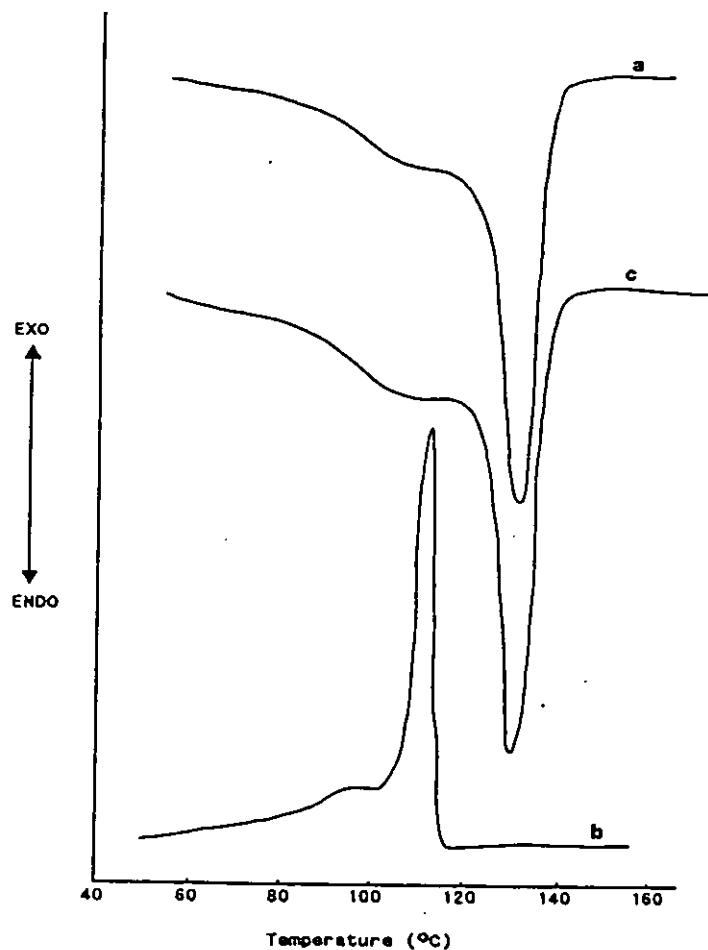


Fig. 4.23. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-35/35/30. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

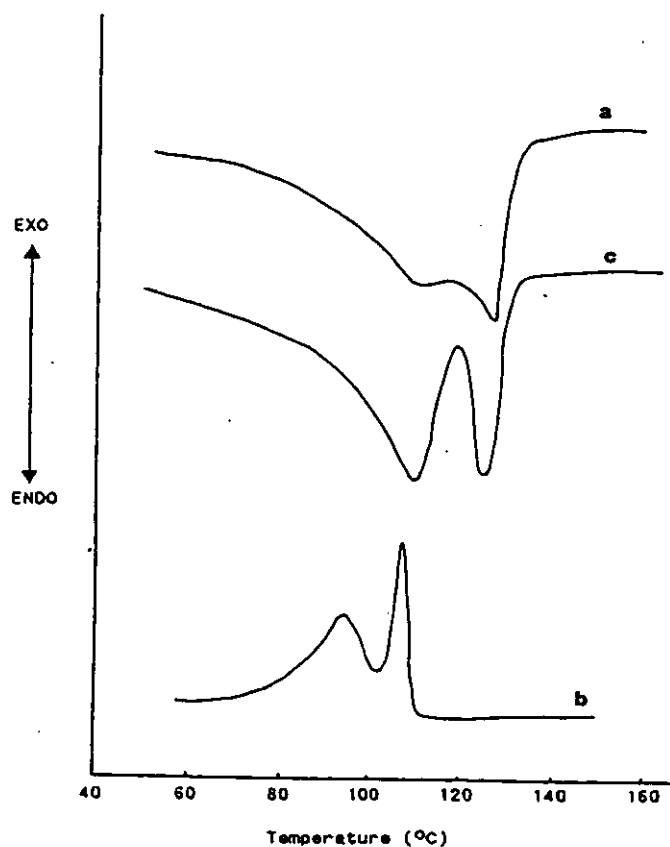


Fig. 4.24. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-21/9/70. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

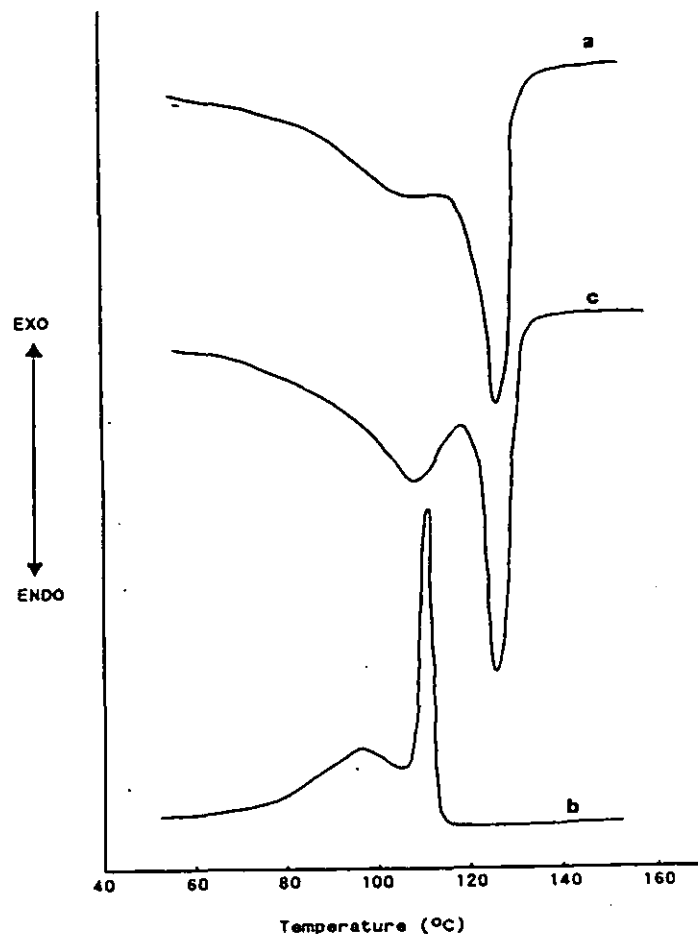


Fig. 4.25. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-35/15/50. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

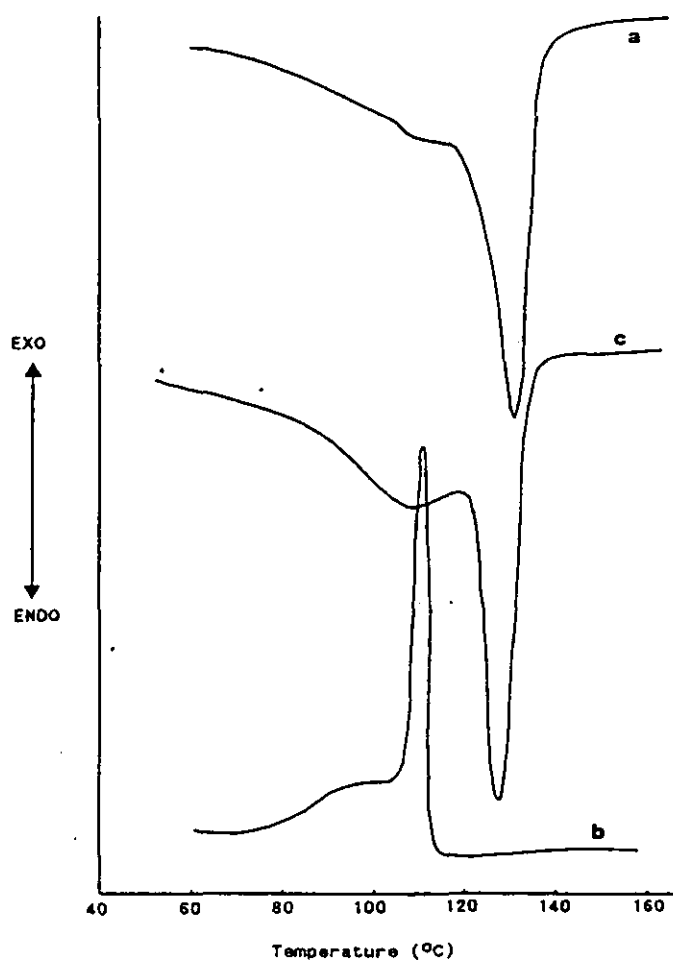


Fig. 4.26. Thermograms of Ternary blends of LLDPE/HDPE/LDPE-49/21/30. (a) first heating, (b) cooling and (c) second heating. Sensitivity = 5 mV/cm.

APPENDIX II

THERMOGRAMS OF CHAPTER 5

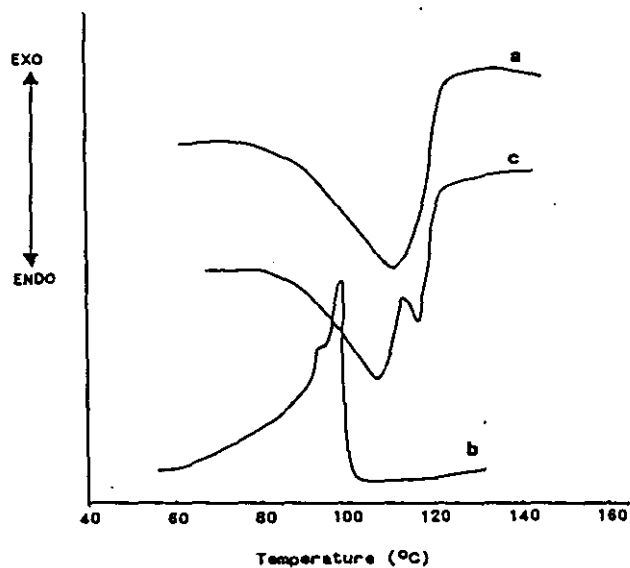


Fig. 5.15 Thermograms of blend of LLDPE/LDPE-30/70, blown film, fast cooling rate. (a) first heating, (b) cooling and (c) second heating.

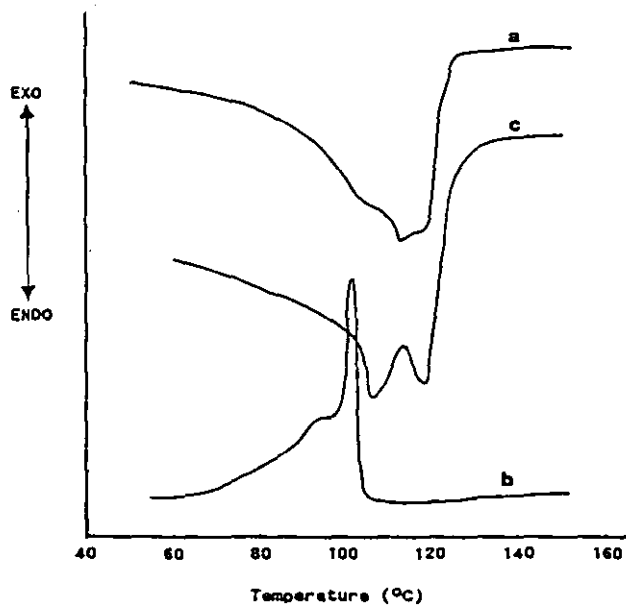


Fig. 5.16 Thermograms of blend of LLDPE/LDPE-50/50, blown film, fast cooling rate. (a) first heating, (b) cooling and (c) second heating.

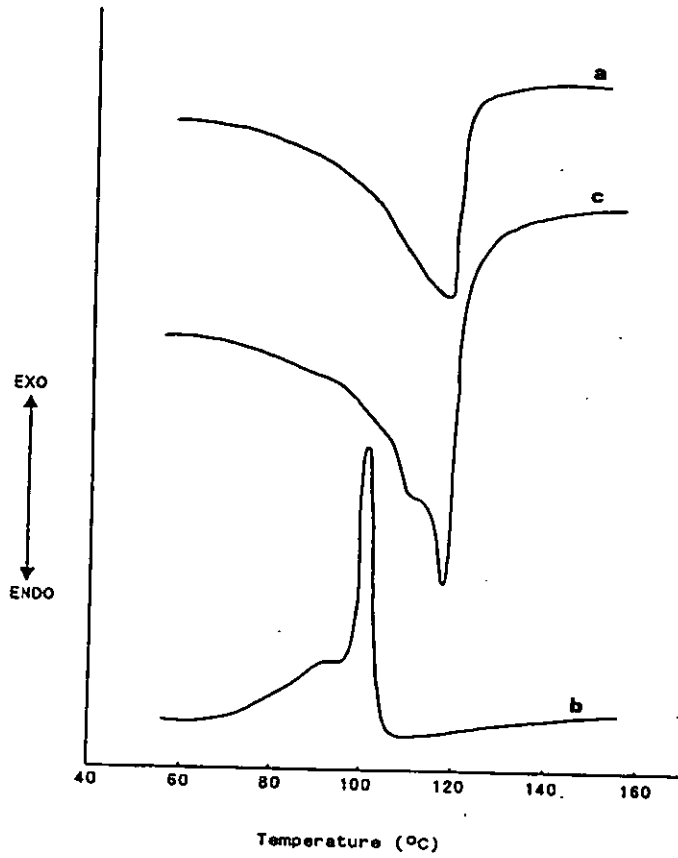


Fig. 5.17 Thermograms of blend of LLDPE/LDPE-70/30, blown film, fast cooling rate. (a) first heating, (b) cooling, and (c) second heating.

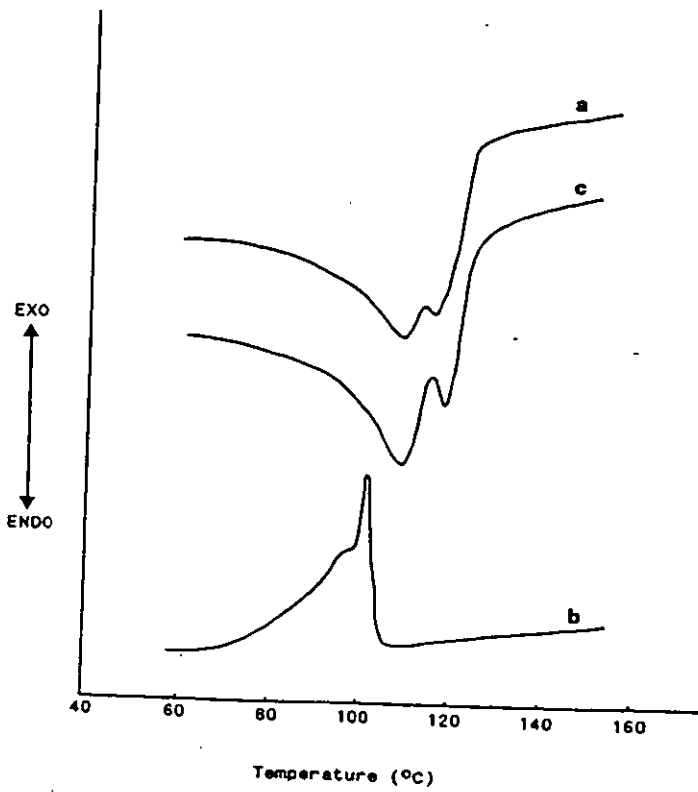


Fig. 5.18 Thermograms of blend of LLDPE/LDPE-30/70, blown film, slow cooling rate. (a) first heating, (b) cooling, and (c) second heating.

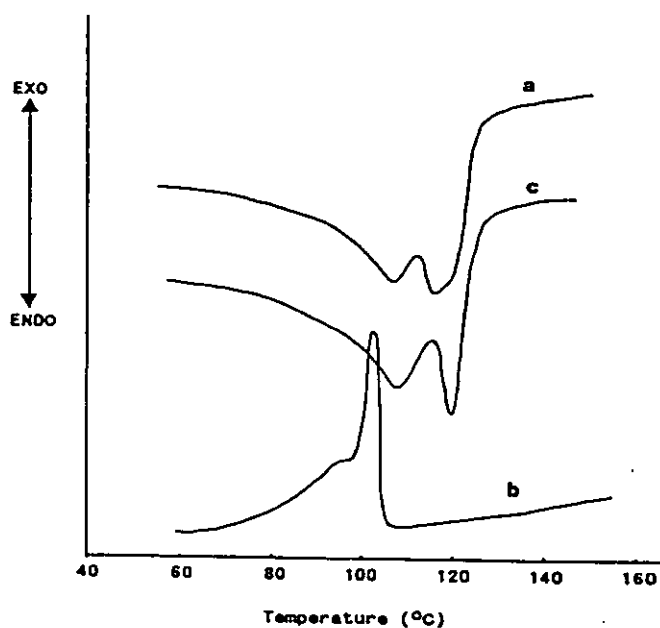


Fig. 5.19 Thermograms of blend of LLDPE/LDPE-50/50, blown film, slow cooling rate. (a) first heating, (b) cooling and (c) second heating.

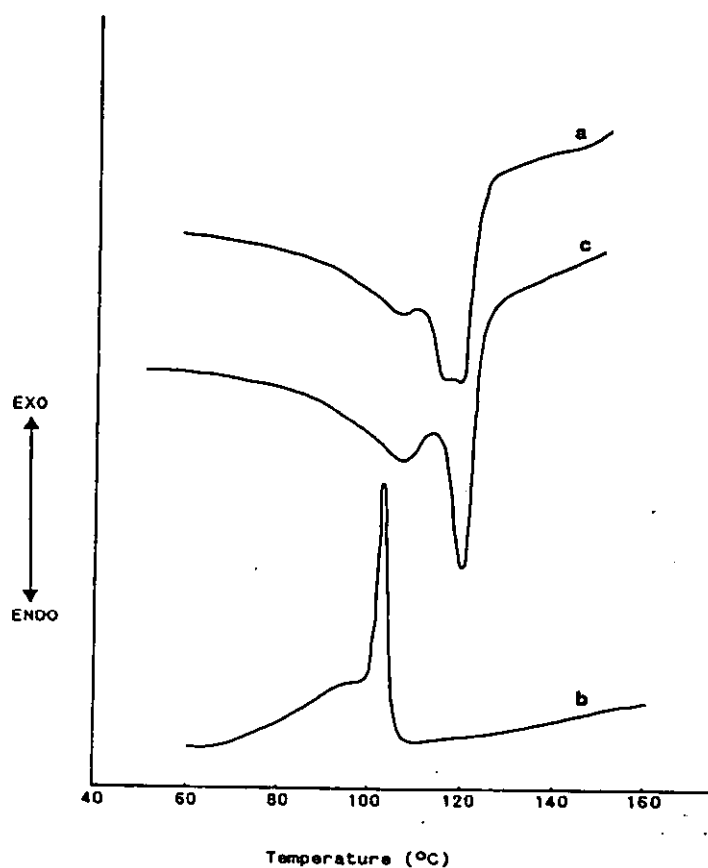


Fig. 5.20 Thermograms of blend of LLDPE/LDPE-70/30, blown film, slow cooling rate. (a) first heating, (b) cooling, and (c) second heating.

APPENDIX III

THERMOGRAMS OF CHAPTER 6

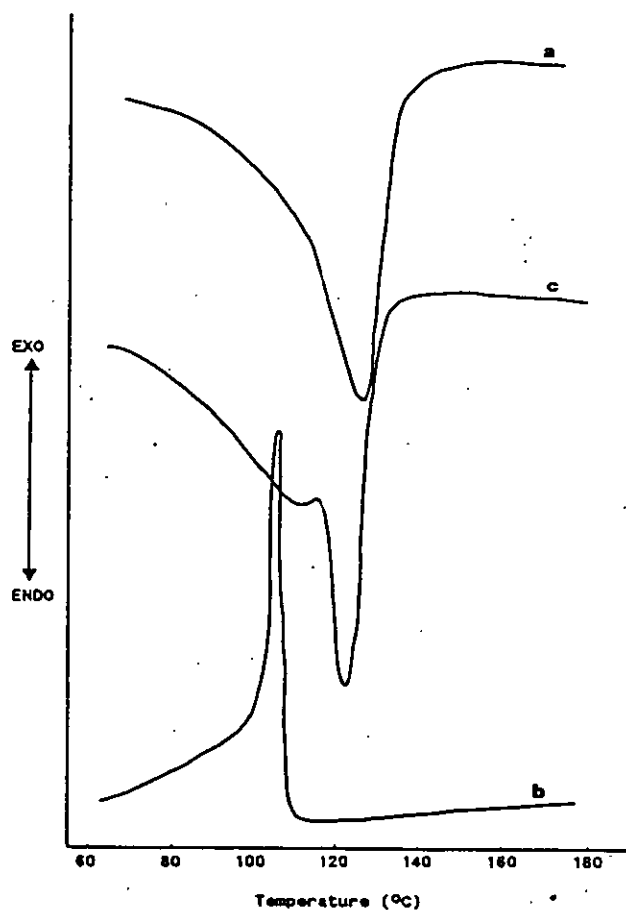


Fig. 6.18 Thermograms of LLDPE(MFI=2 g/10 min). (a) first heating, (b) cooling, and (c) second heating.

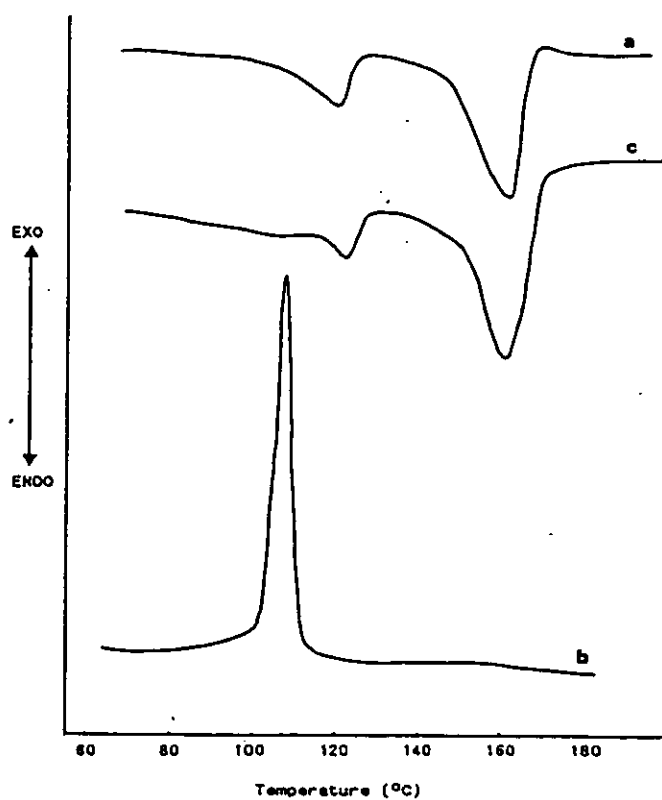


Fig. 6.19 Thermograms of LLDPE(MFI=1)/PP-20/80 blend. (a) first heating, (b) cooling, and (c) second heating.

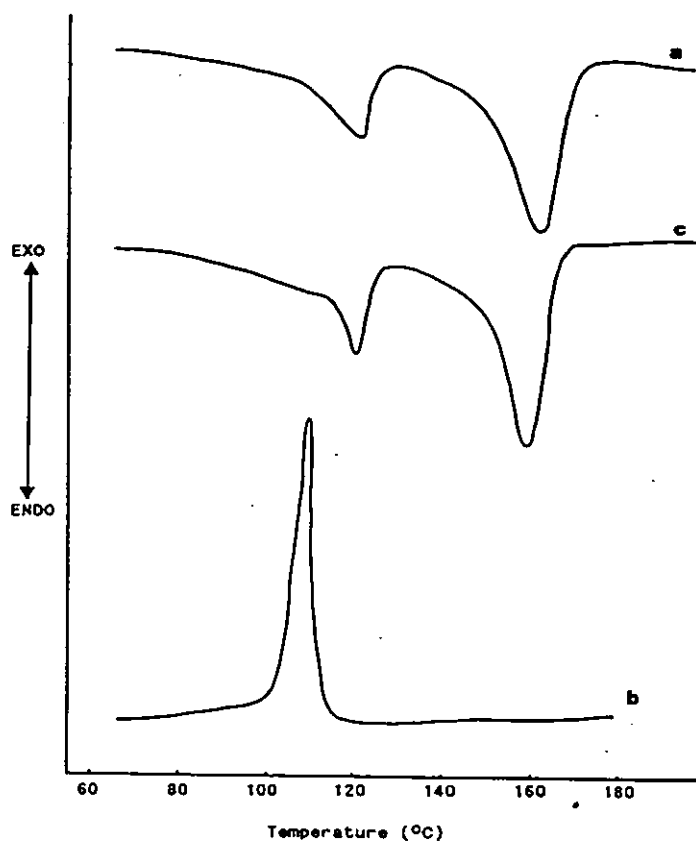


Fig. 6.20 Thermograms of LLDP(MFI=1)/PP-30/70 blend. (a) first heating, (b) cooling, and (c) second heating.

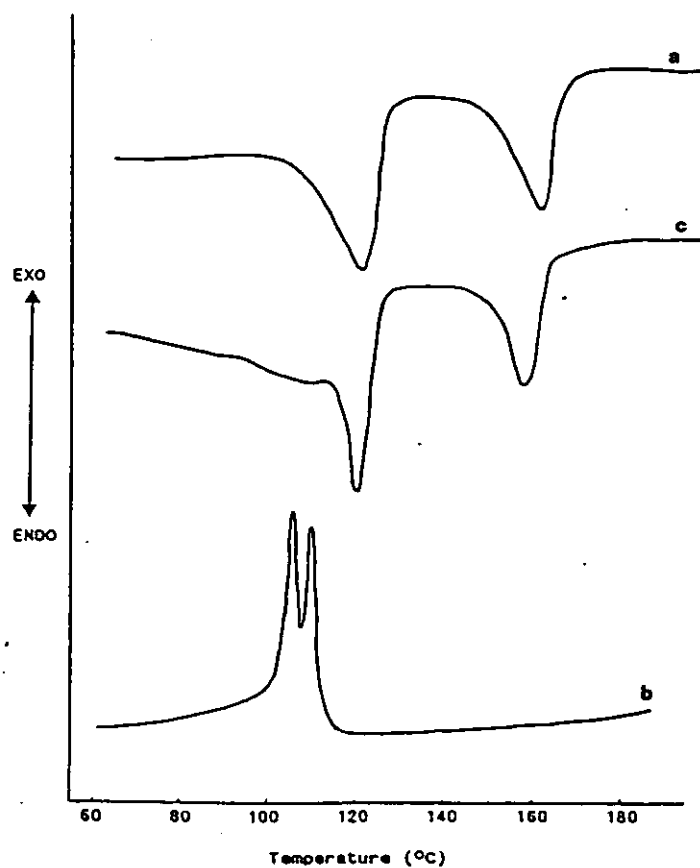


Fig. 6.21 Thermograms of LLDP(MFI=1)/PP-60/40 blend. (a) first heating, (b) cooling, and (c) second heating.

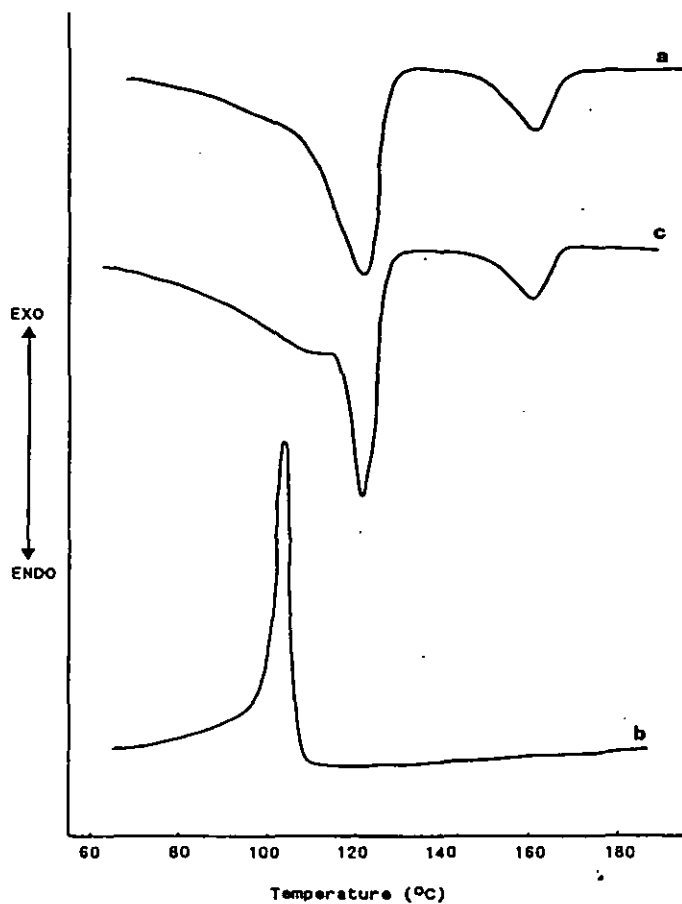


Fig. 6.22 Thermograms of LLDPE(HFI=1)/PP-80/20 blend. (a) first heating, (b) cooling, and (c) second heating.

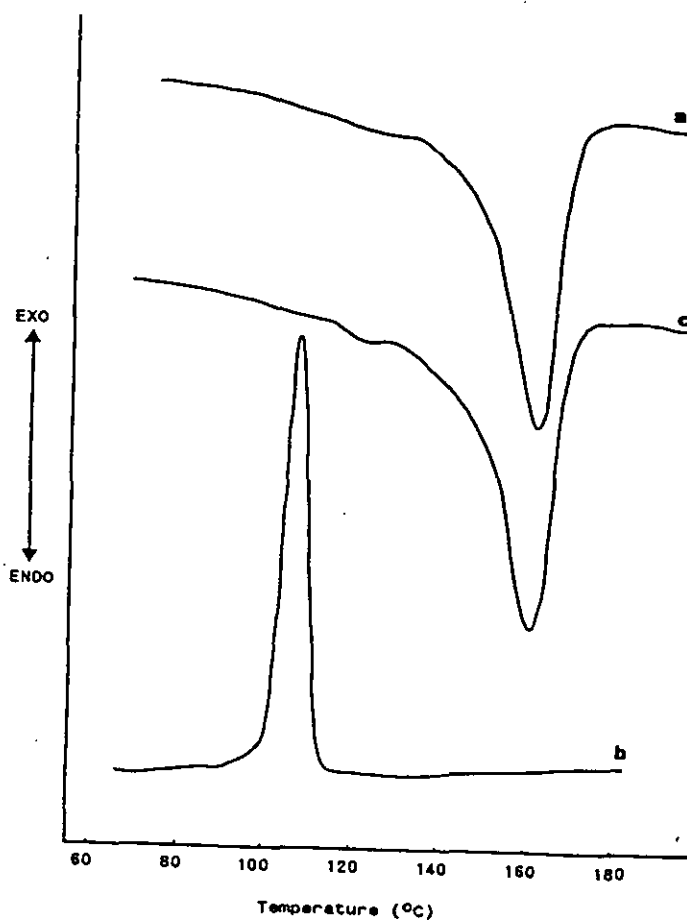


Fig. 6.32 Thermograms of Dowlex/PP-5/95 blend. (a) first heating, (b) cooling, and (c) second heating.

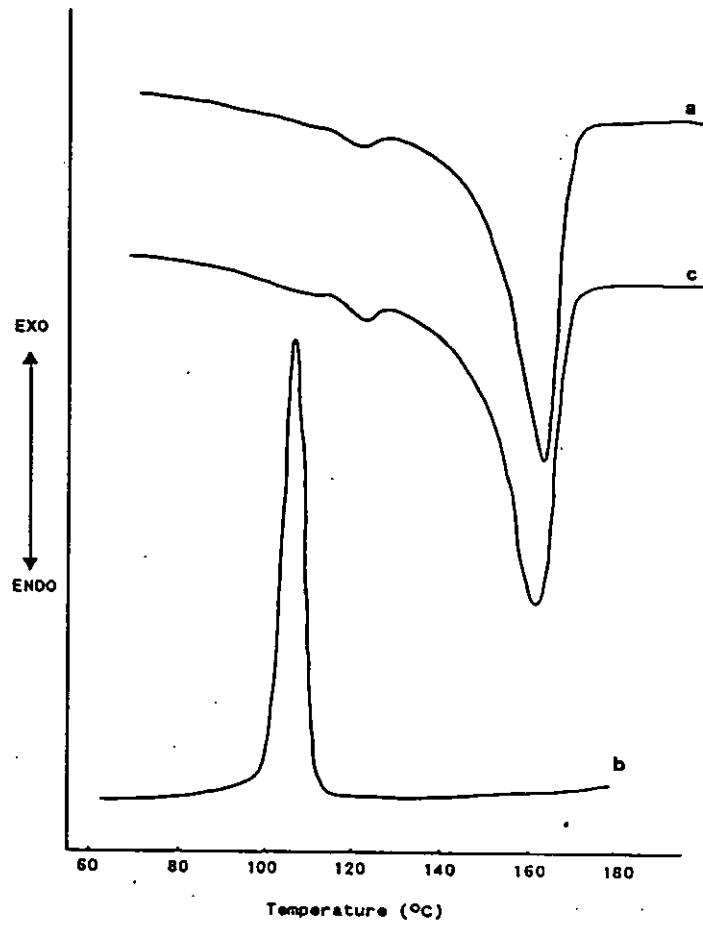


Fig. 6.33 Thermograms of Dowlex/PP-10/90 blend. (a) first heating, (b) cooling, and (c) second heating.

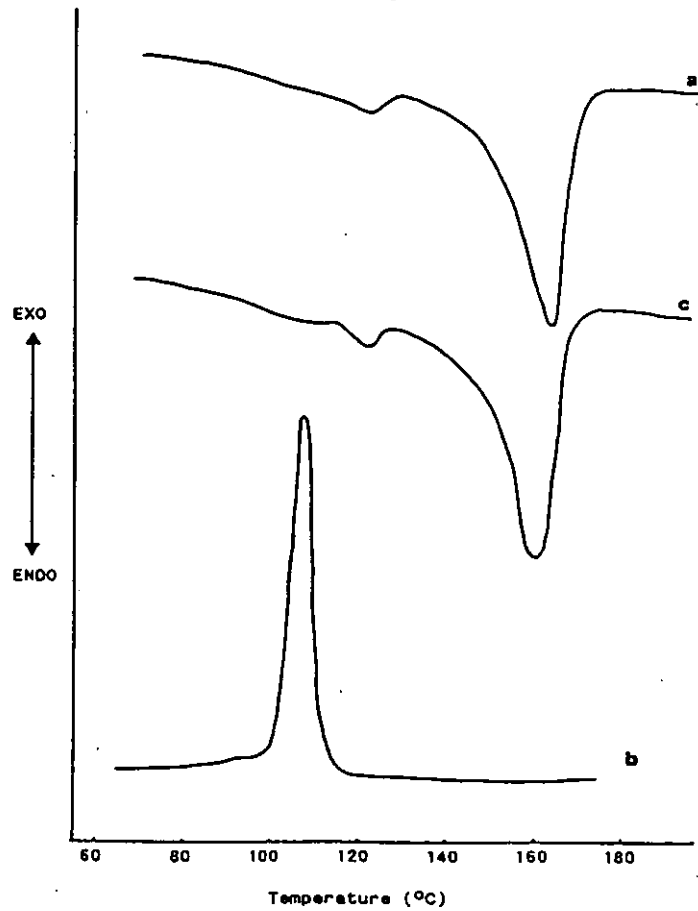


Fig. 6.34 Thermograms of Dowlex/PP-15/85 blend. (a) first heating, (b) cooling, and (c) second heating.

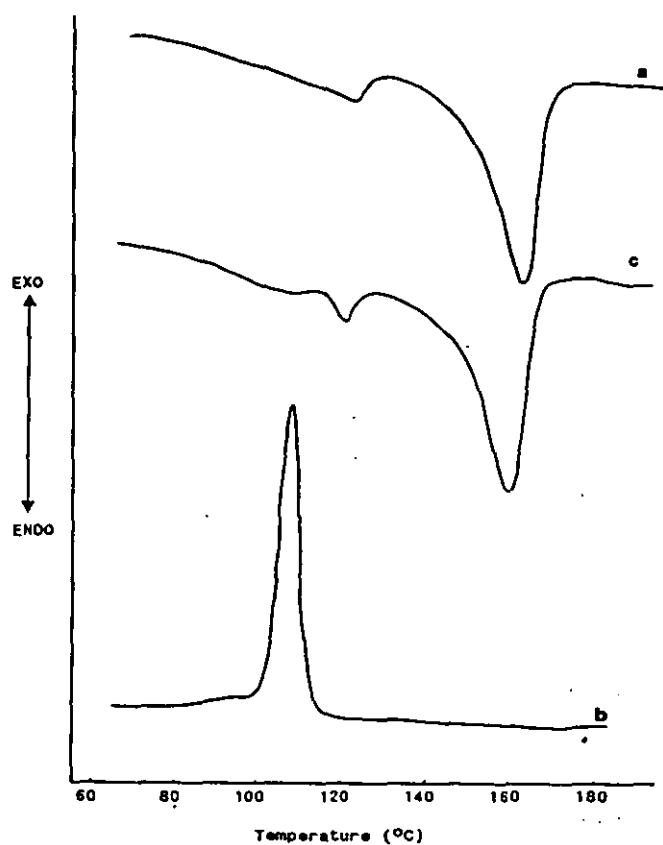


Fig. 6.35 Thermograms of Dowlex/PP-20/80 blend. (a) first heating, (b) cooling, and (c) second heating.

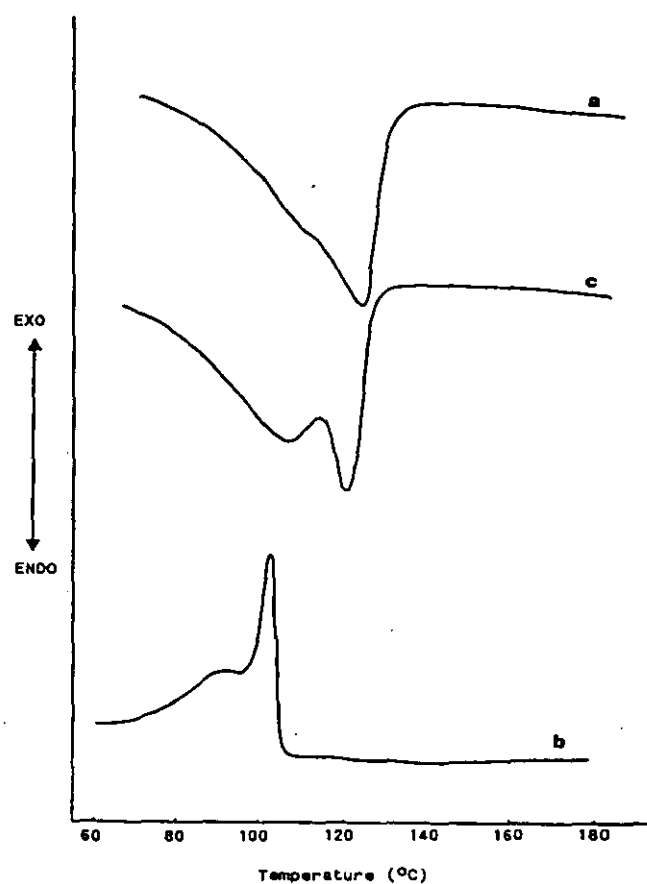


Fig. 6.36 Thermograms of Dowlex(LLDPE). (a) first heating, (b) cooling, and (c) second heating.

PUBLICATION

HAGHIGHAT, S, BIRLEY, A. W, "Blends of linear low density and low density polyethylene", *Plastics and Rubber Processing and Applications* Vol. 13, No.3, (1990)

