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COMPATIBILISATION OF POLY(ETHYLENE TEREPTHALATE) AND POLYOLEFINS WITH MIXTURES OF PHENOXY AND ACID FUNCTIONALISED ETHYLENE COPOLYMER

by

FATMA BELLAHDEB

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

Supervisor: Dr L Mascia

January 1993

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To the Memory of my Father
ACKNOWLEDGEMENTS

I would like to express my gratitude to my supervisor, Dr L Mascia, for the time and discussions devoted to this work. His help and encouragement has been a very important guidance throughout this project.

I would like to thank my friends and technical staff for their encouragement and assistance. My thanks also go to my husband Shahram for his moral support and the useful discussions we had.

A special thank you to Janet Smith for typing this thesis.

Finally, I would like to express my appreciation to Enichem Fibres SpA for funding the research programme without which this project would not have been possible.

F. Bellahdeb
Polyethylene terephthalate (PET) and polyolefins, such as high density polyethylene (HDPE), are important commodity polymers. PET is widely used for fibres and films but is also an attractive material for moulded products, owing to its high melting point and solvent resistance. Crystalline PET, however, is brittle and susceptible to hydrolytic degradation through water absorption. Polyolefins, on the other hand, are tough materials with low water absorption but have a relatively low melting point. Blending these two materials is expected to produce an attractive combination of properties. Blending PET with polyolefins, however, produces coarse microstructures and poor mechanical properties due to the lack of compatibility of the two polymers. Compatibility is expected to improve by reducing the interfacial tension and increasing the adhesion between the two phases; the first will reduce the size of the dispersed phase, while the latter would improve the mechanical properties. Compatibilisation of immiscible blends can be achieved by blending suitable functionalised polymers capable of reacting with the two components and/or by adding a compatibilising agent, e.g. block and graft copolymers with units along the main chains that are miscible and capable of strong interactions, such as H-bonds, with the two polymers in the blend.

In the present work, polyhydroxyether of bisphenol A (phenoxy), which is known to be compatible with polyesters [1,2] and anhydride/acid functionalised ethylene copolymers, i.e. copolymers and terpolymers of ethylene containing acrylic acid units or grafted maleic anhydride, as well as the corresponding sodium ionomers, were used as the base polymer components for the production of graft copolymer type of compatibilisers by reaction processing methods. Additives such as sodium ethoxide, sodium benzoate, sodium montanate and sodium p-toluene sulphonate were evaluated as reaction controller catalysts for
potential interactions between the OH groups in the phenoxy and acid and/or anhydride groups in the ethylene copolymers. The extent of interactions between the compatibiliser components were characterised by solubility tests, Fourier transform infrared spectroscopy (FTIR), rheological properties and optical microscopy. The efficiency of the compatibilisers was studied on blends of PET with several grades of HDPE differing in molecular weights, by scanning electron microscopy (SEM), rheological properties, differential scanning calorimetry (DSC), and by measuring the mechanical properties. The results show that the type of graft copolymers or co-ionomers of phenoxy with acid functionalised ethylene copolymers can be made and that sodium ethoxide is an effective catalyst for the production of these types of compatibilisers. These systems were found to be a very efficient compatibiliser for PET/HDPE blends as they produce fine dispersions and improve the mechanical properties. A correlation is found between the efficiency of the compatibilisers and the melt viscosity of the final blends. Furthermore this work has revealed that the further addition of sodium ethoxide to ionomers and ionomer based compatibilisers enhances considerably the nucleation of PET in the blend.
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CHAPTER 1
INTRODUCTION

1.1 GENERAL INTRODUCTION

Blending has long been recognised as an important route to the development of new polymeric products. Few polymers, however, form truly miscible blends characterised by a single Tg and structure homogeneity at a 5-10 nm scale [3]. The majority of blends are immiscible, i.e. possess a multiple phase morphology. Blends of this type are often preferred, however, over miscible systems since they may exhibit desirable properties derived from both constituents. Blend composition, viscoelastic properties of the components and interfacial adhesion are among the parameters known to control the domains size and morphology of the dispersed phase as well as morphology stability [4]. Heterogeneous blends of technological importance are termed "compatible" and they constitute the
majority of the commercial blends introduced in the past 20 years [5]. In such blends, satisfactory physical and mechanical properties depend on the achievement of a finely dispersed phase, either as discrete particles or as co-continuous domains.

Polymer compatibility can be improved in various ways [5,6]. Blending methods providing intensive mixing and the incorporation of compatibilisers, such as block copolymers, to stabilise the blend morphology have been used successfully to produce both fine dispersions and interpenetrating co-continuous phases. Strong interactions between the blend components, such as acid-base or ion-dipole, hydrogen bonding and transition metal complexation, have also been shown to enhance the miscibility of suitably functionalised polymers [7,8]. Another way to improve compatibility, which is the focus of this work, is by the incorporation of compatibilisers based on graft copolymers, whose chemical structures are chosen on the basis of their ability to exert specific physical interactions or chemical reactions with the blend components. The copolymers may be added separately or formed in situ using suitable functionalised polymers. It is presumed that compatibilisers tend to concentrate at the interface and act as emulsifiers in reducing interfacial tension and improving adhesion between the two phases.

1.2 BACKGROUND

1.2.1 Polyethylene Terephthalate (PET)
The discovery of polyethylene terephthalate, generally known as PET, was patented as a fibre forming polymer by J.R. Whinfield and J.T. Dickson while working in the laboratories of the Calico Printers Association in Accrington, Lancashire in 1941. The simplest route to produce PET is the esterification of
terephthalic acid with ethylene glycol forming a monomer (bis-β-hydroxyethyl terephthalate) which is polycondensed to yield PET.

Polyethylene terephthalate is widely used for synthetic fibres, packaging films, photographic films and also in electronics and other applications. In 1977 blow-moulded PET bottles became commercially available for carbonated soft drinks, wines, spirits etc. The advantages lie in the glass-like transparency, lightweight and high toughness. By 1985 the world annual consumption of PET for this purpose had grown to 470,000t. The rapid quenching of molten PET gives rise to an amorphous polymer; slow cooling, on the other hand causes crystallisation to large spherulitic forms, giving stiff but brittle solids. An important development in the exploitation of the polymer as a moulding plastic material was the disclosure in the late 1960s [9] that nucleation with inorganic particulate solids, such as sodium stearate, zinc stearate, talc, calcium benzoate, etc and plasticisers such as oligomeric esters or segmented, block polyesterethers [10], permit mould temperatures lower than 90-100°C, inducing rapid crystallisation of PET from the melt with a controlled morphology. With these developments, PET based plastics are gaining acceptance as injection-moulded parts for automotive, electrical, and electronic uses.

a) Properties

Melt and Transition Temperatures

The melting point of virgin, fully annealed PET can reach the value of 280°C, but commercial products generally melt at 255-265°C due to reduced crystallinity caused by comonomers, such as diethylene glycol, in the polymer backbone [11,12], the heat of fusion of PET is 39.7 cal/g [13], the specific gravity of the amorphous non-oriented polymer is 1.33, while for highly crystalline oriented
fibres is 1.39. The Tg of commercially available PET materials is in the temperature range 67-80°C depending on composition and degree of crystallinity.

**Molecular Weight**

PET with a weight-average molecular weight Mw of 35,000-40,000 is used for oriented films and textile fibres. However, this range of molecular weights is not suitable for injection moulding because the resulting moulded parts are brittle [14]. Higher molecular weight PET, with Mw = 80,000 is manufactured for injection moulding to give products with better impact strength [15].

The Mark-Houwink relationship between number-average molecular weight Mn and intrinsic viscosity [η] in a solvent is:

\[
[\eta] = K M_n^a
\]

where K and a are constants, depending on the solvent.

The intrinsic viscosity [η] for PET in a phenol-sym-tetrachloroethane (60:40) mixture at 25°C is given by Hergenrother et al.[10]:

\[
[\eta] = 3.72 \times 10^{-4} M_n^{0.73}
\]

Commercial PET products have intrinsic viscosities from 0.45 dl/g for certain film and textile fibre applications to as high as 0.9 dl/g for blow-moulded bottles, which correspond to Mn of 15,000 and 45,000 respectively.
Commercial Properties

PET is characterised by outstanding resistance to deformations at high temperatures to allow it to be used in a number of applications requiring exposure to elevated temperatures. The impact strength depends on the molecular weight and increases with the increasing Mw.

Chemical Resistance

Since PET is a crystalline material, it is stable to a wide range of chemicals. The polymer is resistant to water, ketones, alcohols, glycols, ether, aliphatic hydrocarbons, and chlorinated aliphatic hydrocarbons at room temperature. This polymer is also resistant to petrol, motor oil, and transmission/brake fluids at temperatures up to 60°C.

Electrical Properties

PET compounds exhibit good electrical insulation properties, allowing it to be used in many electrical applications owing also to the good balance of processability and physical properties, coupled with a good arc resistance and dielectric strength.

b) Hydrolysis

PET is hygroscopic and susceptible to hydrolysis, which causes chain scission and deterioration of mechanical properties [16,17]. Commercially supplied PET can have a moisture content up to 400 ppm and it is always recommended to dry the polymer to a moisture content <200 ppm to prevent hydrolysis during processing.
1.2.2 Development of Polymer Blends

Polymer blending is not a recent development, the lack of historical perspective in the commercial development of polymer blends is due to their rapid growth in importance during the 1980s. While during the late 1980s the annual growth rate of the plastics industry was 2 to 4%, that of polymer blends was 9 to 11% while the growth of engineering blends was 13 to 17% [18]. However, the first commercial thermoplastics blend PVC/NBR was introduced in 1942. In the same year Dow Chemical Company introduced Styralloy-22, a blend of polystyrene and polybutadiene. Not much later the development of mechanical mixtures of NBR with SAN (known as ABS type A) was an important step in starting a rapid expansion of styrenic blends, which still dominate the market. In 1986 sales were 74% of all polymer blends sales in Europe, 77% in Japan and 69% in North America [18].

The 1960s were important times for modern engineering polymer blends. In this period the addition of polystyrene (PS), to poly-2,6-dimethyl-1,4-phenylene ether (PPE) was found to improve the processing of this new polymer. PPE/PS are in fact miscible and as a result, several mechanical properties of these blends showed a significant synergistic behaviour [19].

In 1975 Du Pont de Nemours introduced a super tough polyamide (PA), Zytel-ST. The importance of this event extends beyond the development of PA blends. The observation that addition of a small amount of a finely dispersed polyolefin rubber dramatically changes the fracture behaviour of PA led also to improvement of impact properties for other engineering polymers, e.g. polyesters, polycarbonate, polyoxymethylene, etc. While in the past blending relied mostly on mechanical mixing of the ingredients, for instance, a ten fold improvement of notched Izod impact strength was reported to result from
addition of 5 wt% of immiscible high density polyethylene to polycarbonate [20]. Reactive blending has introduced a new level of sophistication in this field. Several patents on PA toughening already require addition of a reactive ingredient, e.g. ionomers and grafted copolymers with maleic or fumaric acids (or their anhydrides) etc. Reactive blending of engineering polymers with maleated copolymers provides in fact a direct method of toughness enhancement [21].

To appreciate the importance of polymer blends in the 1980s the following statistics have been quoted. During the years 1981-4 the number of patents issued for polybutylene terephthalate (PBT) blends was 597, those for polyethylene terephthalate (PET) 468, whereas the blends with polyamide-6,6 patented was 431, for polycarbonate 390, and for polyphenylene ether was 360. In comparing these numbers one notes that patenting activity is mostly in the field of thermoplastic polyesters.

1.2.3 Advantages of Blends

The general reasons for blending polymers are:

2. Developing cheaper materials with a wider range of desired properties.
3. Adjusting the composition of the blend to customer specifications.
4. Recycling industrial and/or municipal plastic scrap.

1.2.4 Methods of Blending

About 65% of polymer blends are produced by resin manufacturers; 25% by compounding companies and the remainder by processing companies. In general the preparation of polymer blends can be accomplished by:
1. Mechanical mixing or melt compounding.
2. Dissolution in co-solvent then film casting, freeze or spray drying.
3. Latex blending (e.g. SAN + AB→ABS).
4. Fine polymer powder mixing.
5. Use of monomer(s) as solvent for another blend component followed by polymerisation as in IPNs or HIPS manufacture.

For economic reasons mechanical blending predominates. The requirements for the polymer compounding of blends are: uniformity of shear and elongational stress field, flexible control of temperature, pressure and residence time, and efficient homogenisation. Most of the polymer blends have been produced using either internal mixers or single screw extruders (the latter are usually poor mixers and are unsuitable for reactive blending), and twin screw extruders, which are more expensive but easier to control. The twin screw extruder can be optimised for specific polymeric systems. As a result, the blend quality and run-to-run reproducibility are satisfactory.

1.2.5 Compatibility of Polymers

a) Definition of Compatibility

The definition of compatibility as miscibility on a molecular scale is only one of many definitions for polymer compatibility. As explained earlier, compatible polymers are polymer mixtures that have desirable physical properties when blended. Sometimes, however, compatible polymers are described as polymer mixtures that do not exhibit gross tendencies to phase separation when blended. These three definitions of polymer compatibility are somewhat interrelated since it is only reasonable to suppose that polymer blends exhibiting no gross propensity to phase separation on blending, and having desirable properties,
display at least a degree of mixing of polymer segments on a molecular scale. This implies the occurrence of either a certain amount of thermodynamic miscibility or physical constraints that prevent demixing such as grafting, crosslinking. The addition of block copolymers, the formation of interpenetrating network (IPN), or the quenching of a mixed system to a temperature at which demixing is thermodynamically but not kinetically favoured [4] are all methods used to achieve compatibility between polymers.

b) Thermodynamic Homogeneity in Liquid Mixtures
Homogeneity is the only requirement for miscibility [22]. To understand what constitutes the condition leading to homogeneous liquid mixtures, it is desirable to start with the principal objective, i.e. one wishes to know if \( N_A \) moles of liquid A and \( N_B \) moles of liquid B when mixed will form a one-phase homogeneous mixture or a two-phase heterogeneous mixture. For the latter case, one wishes to know what is the composition and the relative proportion of the two phases. Thermodynamics teaches that if the change in free energy \( \Delta F \) of a reaction or a physical process is negative, the phenomenon proceeds spontaneously to achieve the maximum negative \( \Delta F \). At that point, any further change would require expenditure of free energy, i.e. a positive change in free energy, so the system is forced to remain at this equilibrium position, i.e. there will be no further change in the relative amount and composition of the two phases in time. As to the exact composition of the two phases and their relative amounts, it would need a phase diagram representing the relationship between temperature and mole fraction of the two liquids. From thermodynamics \( \Delta F = \Delta H - T \Delta S \). [\( \Delta H \) is the change in heat content and \( \Delta S \) is the change of entropy of the process]. For the present purpose, if the magnitude of \( \Delta H \) and \( \Delta S \) of mixing and the temperature at which mixing takes place are known, one can calculate \( \Delta F \) and therefore predict if a homogeneous mixture will result or not. \( \Delta H \) for mixing is a measure of the
attraction between the molecules to be mixed. A negative $\Delta H$ means that heat is evolved during mixing and lost to the surroundings. $\Delta S$ of mixing is always positive and, therefore, $-T\Delta S$ will always be negative. Thus, the sign of $\Delta F$ will be determined by the sign and magnitude of $\Delta H$.

For quantitative calculations of the heat of mixing, the Scatchard-Hildebrand equation [23] gives:

$$\Delta H_m = V_M (\delta_S - \delta_B)^2 \phi_A \phi_B$$  \hfill (1)

where $V_M$ is the total volume of the mixture, $\phi$ is the volume fraction of the liquids, and $\delta$ is the solubility parameter of the liquids. The solubility parameter of the liquid is a measure of the cohesive energy of the liquid. $\Delta H_m$ depends also on concentration since $\phi_A \phi_B$ has maximum value when $\phi_A = \phi_B = 0.5$ and approaches zero when the liquid mixture is infinitely dilute. Note that $(\delta_A - \delta_B)^2$ is always positive when $\delta_A \neq \delta_B$, and $\Delta H_m$ is zero only when $\delta_A = \delta_B$. A positive $\Delta H_m$ will contribute to phase separation unless overcome by a large $T\Delta S$. If the solubility parameter of $A$ is very different from $B$, one may obtain a two-phase system. On the other hand, if $A$ and $B$ have equal solubility parameters, $\Delta H_m$ will be zero. In statistical mechanics, entropy is a measure of the randomness or disorder of a system. When $N_A$ moles of $A$ and $N_B$ moles of $B$ are mixed, the change in the entropy of mixing is represented by:

$$\Delta S_M = -R (N_A \ln X_A + N_B \ln X_B)$$  \hfill (2)

where $X_A$ and $X_B$ are the mole fractions of $A$ and $B$ in the mixture. Equation (2) represents the entropy change in a completely random mixing of $A$ and $B$. 

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Since \( \Delta F_M = \Delta H_M - T \Delta S_M \), then

\[
\Delta F_M = V_M (\delta_A - \delta_B)^2 \phi_A \phi_B + RT (N_A \ln X_A + N_B \ln X_B)
\]  

Since an ideal solution is characterised by a heat of mixing and an entropy of mixing both equal to zero, giving random and complete mixing of the molecules at the molecular level. An ideal solution requires the molecules of the liquids to have the same size, the same shape, and the same solubility parameters. They are miscible in all proportions at all temperatures and pressures. Thus, even among simple liquids, soluble mixtures in all composition and temperature ranges are exceptions rather than the rule. Therefore in describing a liquid mixture as miscible, it is necessary to specify the composition and temperature of the mixture.

c) Thermodynamic Compatibility in Polymer Blends

To study the phenomenon of compatibility of blends, one can extend the thermodynamic treatment of the mixing of liquids to systems involving two or more polymers. Eventually mixing will reach an equilibrium state at which any further mixing will not reduce the degree of heterogeneity. At this point, it is found out if the blend has a two-phase or a one-phase structure. It has to be noted that excessive mechanical mixing may cause degradation, chain scission, or even graft copolymer formation. All these side reactions will complicate the study of polymer compatibility. Thus, mixing of two polymers to reach an equilibrium state of distribution of one polymer in another is more complex than mixing of liquids. Thermodynamically the equation \( \Delta F_M = \Delta H_M - T \Delta S \) still applies to the mixing of polymers. Flory [24,25,26] has proposed methods to calculate these terms and stated that: "Two high polymers are mutually compatible with one another only if their free energy of interaction is favourable,
i.e. negative. Since the mixing of a pair of polymers, like the mixing of simple liquids, in the great majority of cases, is endothermic, incompatibility of chemical dissimilar polymers is the rule and the compatibility is the exception". By the author definition, compatibility implies complete miscibility across the entire composition range, whereas the system that shows any region of incomplete miscibility is regarded as incompatible.

Scott [27] and Tompa [28] were the first to show that the likelihood of any polymers, of appreciable degree of polymerisation, being thermodynamically miscible was very small. This was demonstrated by an extension of the Flory-Huggins theory of polymer solutions [29-30] with or without added solvent. A mixture of polymers in the molten state will form a miscible system only if mutual solution takes place during mixing and the resultant blend forms a thermodynamically stable single-phase system at room temperature.

The entropy term $T\Delta S$ is a measure of the increase in disorder of the system and, since the molecular weight of most polymers is high, the entropy is correspondingly low. As crystallisation in polymers is a process of ordering this leads to even lower values for the entropy after crystallisation, thus making miscibility among crystallisable polymers on cooling from the melt state even less likely. Since the solubility parameters are derived from the cohesive energy densities of the molecules, they are related to intermolecular distances, and are therefore temperature dependent. In considering the possible miscibility of polymers from such calculations, the values of the solubility parameter are usually compared at room temperature. Thermoplastics polymer blends are usually produced at high temperatures and therefore if miscibility is not obtained at the melt temperature, these are not likely to be homogeneous at room temperature because of the reduced mobility of molecules. For the majority of
amorphous rubbery polymer blends this factor is unlikely to be critical, because the low Tg of the blend gives them greater mobility. In the case where one or both of the components are crystalline polymers, the large specific volume changes that take place at the crystalline melting point will lead to similar large changes in the solubility parameter with changes in temperature. Therefore it is highly unlikely that the comparison of solubility parameters obtained at room temperature for crystalline polymers will give an indication of the miscibility of the polymers in the melt state. The situation can arise in which two different polymers may in fact be miscible at the melt temperature but immiscible at room temperature even if they remain homogeneous for kinetics reasons.

In general for blends involving one or two crystalline polymers, there are three major possibilities: (a) the polymers may co-crystallise and remain miscible (this very rarely happens); (b) both polymers may remain amorphous and homogeneous; or (c) crystallisation of one or both polymers may take place leading to phase separation. Cases of blends have been reported of polymers which normally exist in the crystalline state in isolation but on blending remain amorphous. For example, poly(vinylidene fluoride) with poly(methyl methacrylate) or with poly(ethyl methacrylate) form miscible blends [31]. The crystalline poly(vinylidene fluoride) remains amorphous and behaves as a plasticiser for the glassy methacrylate polymer. For the majority of crystalline polymer blends, on the other hand, phase separation and crystallisation take place.

As implied earlier it is unlikely for many amorphous polymer pairs, and even less likely for crystalline pairs, to exhibit mutual solubility and hence true thermodynamic compatibility, as in the sense of low Mw liquids. As explained earlier, from a technological point of view, on the other hand, blends do not have
to be thermodynamically compatible to be useful; HIPS and ABS have proven the importance of a two-phase morphology for impact resistance. Xanthos et al. pointed out the difference [32]. Conceptually compatibility is a representation of how close a blend can approach this ultimate state of molecular mixing. Phenomenologically, it is a relative measure of the degree of heterogeneity of the blend, i.e. how fine one polymer is dispersed in another. Compatibility of a blend is subject to differences in experimentation and in interpretation of results one should describe it by giving the sample history, method and instruments used to determine its degree of heterogeneity [22].

d) **Determination of Compatibility**

The literature has revealed that various methods have been used to determine compatibility of polymer blends and each method has its own advantages and disadvantages.

**Solubility Parameter:** It has been suggested that solubility parameters, despite the limitations outlined earlier, may be used to predict the miscibility of any two polymers of interest if two factors are known for each polymer: solubility parameter and molecular weight. For many homopolymers and some copolymers, solubility parameters have been listed in tables, some of which may be found in Brandrup and Immergut [33], Shvarts [34], Shvarts et al. [35], Gardon [36] and Burrell [37]. The experimental methods for determining the solubility parameters of polymers involve studies of polymers in solution. It has been found [38], however, that the most accurate predictions of miscibility are made when the solubility parameters are calculated rather than measured experimentally. One widely known method for the calculation of solubility parameters is by group contribution, i.e. Small’s method [39,40]. Bohn [41] has indicated that the prediction of miscibility by matching the solubility parameters
has had success with some pairs of polymers but resulted in complete failure with others and suggested that the common practice of measuring solubility parameters by interaction with a series of solvents can give different results depending on the solvents, which may be non-polar, polar, or hydrogen bonding.

**Solution in Common Solvent:** Dobry and Boyer-Kawenoki [42] and other workers [43,44] showed that the miscibility of polymer pairs could be assessed by solution in a common solvent. If phase separation occurs, the pair is immiscible. This test is arbitrary and gives only relative results since phase separation is affected by concentration and temperature. It has to be noted that Scott [27] showed that no matter how immiscible two polymers are, it is always possible to make a very dilute solution containing both, as long as a solvent which dissolves each lone polymer exists.

**Film Casting:** This technique has been suggested as a control for the previous method. Paterson et al. [44] showed that certain polymer pairs formed single phase solutions but failed to yield homogeneous films on casting from solution.

**Glass Transition Temperature:** In polymers the glass transition temperature is related to cooperative segmental motions. It was stated earlier that a miscible blend exhibits a single glass transition, whereas polymer pairs which are immiscible or partially miscible display two glass transition temperatures. Boyer [45] suggested that Tg involves 50 to 100 backbone chain carbon atoms, i.e. a domain with diameter Dd = 2-3 nm. This is in agreement with Warfield and Hartman [46] who estimated that the glass transition of amorphous thermoplastics involves 15 to 30 statistical segments (not mers) i.e. Dd = 15 nm, while values from 10 to less than 5 nm were assigned respectively by Kaplan [47] and by Barr and Warren [48].
The use of Tg for determining polymer/polymer miscibility therefore, is based on the premise that a single Tg indicates that the domain size is below the Dd values stated earlier, i.e. $2 \leq Dd \leq 15$ nm. Confirmation of this can be found in several publications on Tg of multiphase systems. Hence a single Tg is not a measure of miscibility (as defined in thermodynamic terms) but only of the state of dispersion. This was also clearly demonstrated in work by Shultz and Young [49].

**Dynamic Mechanical Tests:** This very sensitive technique has been used intensively by Nielsen [50] and by Takayanagi [51] to study compatibility, and who have shown that a compatible (i.e. miscible or partially miscible) polymer pair will show a damping maximum between those of the parent polymers, whereas a completely immiscible polymer pair gives two damping maxima at temperatures corresponding to those of the parent components. The modulus variation with temperature can also give an indication of compatibility of polymer mixtures. If the modulus temperature curve of a polymer blend is situated between those of the two parent polymers, the blend is miscible. If the modulus-temperature curve shows two points of inflexion, then the blend is immiscible or partially miscible (i.e. two phases are present, each containing small amounts of the other component).

**Microscopy:** Modern electron microscopy using vacuum tunnelling techniques allows resolution better than 1 A [52]. In polymer blends the main application of microscopy is not only to determine compatibility but to study their morphology. The microscopic methods can be divided into three categories: optical or light microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). In most cases some mode of sample preparation has to be used: staining, fracturing, etc. Staining is the preferred method of
identification and observation of phases in TEM. The other techniques that have been used are: phase contrast, polarised light, reflected and transmitted light OM [53,54].

SEM is becoming the most common method for studying the morphology of polymer blends. The main advantages of this technique are: rapidity, range of readily accessible magnifications, depth of field, and the ability to perform back scattered electron imaging and X-ray elemental analysis of the observed surface. In contrast to SEM analysis preparation of samples for TEM require great skill and expertise. The samples have to be hardened and stained with Br$_2$, OsO$_4$, or RuO$_4$, microtomed into thin (≥ 20 μm) slices, mounted on a grid and polymeric film support. The surface morphology can also be observed under TEM by cryogenic shadow casting and/or replication methods. Etching is frequently used to enhance the morphological details [55]. Both electron microscopy methods are frequently used in parallel.

Of the methods discussed, glass transition temperature measurements by dynamic mechanical tests and electron microscopy give the most useful information on the compatibility of polymer blends. However, it is possible that a polymer blend shown to be miscible by one method may be revealed to be immiscible or, more usually, partially miscible by another. For example, Matsuo [56] found in the blend of poly(vinyl chloride) and poly(butadiene-co-acrylonitrile) (60:40) that whereas dynamic mechanical measurement gave only one damping peak suggesting a miscible system, electron microscopy indicated heterogeneity.

A more difficult situation has been observed experimentally [38] for several polymer blends that are on the "edge" of miscibility, that is, the free energy change or driving force leading to phase separation is very small. For example,
some mixtures of polystyrene with poly(vinyl methylether) form transparent films with only a single glass transition temperature when cast from toluene, whereas they form cloudy films with two glass transition temperatures when cast from trichloroethylene [57]. It became known later that these mixtures, at room temperature, are close to both an upper and a lower critical solution temperature, so that small changes in temperature or other conditions could lead to phase separation [58]. (Heat treatment caused phase separation in a system that originally showed no phase separation, i.e. poly(vinyl acetate)-poly(methyl methacrylate) [59].

Thermodynamic predictions and experimental observations show that when polymers of different chemical composition are mixed, they will not intermix down to the molecular level and will not give a homogeneous single phase structure across the entire composition and temperature range. Therefore, the criterion of polymer blends compatibility should not depend on the attainment of a single phase homogeneous structure. Compatibility can best be described by the degree of homogeneity of the polymer blend measured and compared by the domain size of the dispersed phase. The finer the size of the dispersed phase, the better the compatibility. If two polymers have strong affinity for each other owing to strong intermolecular interaction, they will mix more intimately. Shultz [49] has reviewed the thermodynamic nature of this interaction. One can say that when two polymers show strong affinity for each other, they can be dispersed to small domain size. For the purpose of the present work, however, the distinction is made between miscibility and compatibility according to the following criterion. Miscibility is defined as complete solubilisation of two polymers on a molecular scale characterised by a single Tg and homogeneity at 5-10 nm scale, whereas the term compatibility denotes that the level of molecular mixing is
adequate to produce a "high level of dispersion" of the two components, which would in turn result in improved properties.

1.2.6 Two Phase Polymer Systems
From the practical point of view hetero-phase systems are preferred since the dispersed phase can improve the toughness of brittle polymer or have a reinforcing effect in flexible polymers. In other words, it is advantageous to produce heterogeneous blends which will be easy to handle and as stable and reproducible as single polymer systems. The way to obtain such systems is by stabilisation of the phases or by compatibilisation. The ultimate method of structure stabilisation is by chemical or physical crosslinking of the multiphase system as it is done in the rubber industry [60]. Temporary or reversible crosslinking can be achieved by block polymerisation or by introducing ionic interactions [61]. Another way is to generate various types of interpenetrating polymer networks [62,63]. However, the more common method of structure stabilisation is by compatibilisation which involves addition or generation of an agent which will modify the interfacial properties in polymer systems.

1.2.7 Compatibilisation Methods
Compatibilisation can be achieved through the following general routes:

a) addition of a third component (e.g. block, graft copolymers) with segments capable of specific interactions, and/or chemical reactions with the blend constituent.

b) by blending suitable functionalised polymers capable of enhanced specific interactions to generate in-situ either copolymers or interacting polymers, acting in a similar manner as the above compatibiliser added separately.
c) using IPN technology.

d) crosslinking the blend ingredients.

e) modification of homopolymers, e.g. through incorporation of acid/base groups, hydrogen bonding groups, charge-transfer complexes, ionic groups, etc.

f) addition of co-solvent.

1.3 **AIM OF THE INVESTIGATION**

Polyethylene terephthalate (PET) is widely used as an engineering thermoplastic polymer for packaging, electronics, and other applications. Blended with other polymers it could ideally offer an attractive balance of properties. Efforts to develop PET based blends and glass reinforced compounds have recently been intensified especially with the availability of high purity recycled resin. Blending PET with polyolefins is expected to produce an attractive combination of properties. However, these classes of polymers are incompatible and an effective compatibiliser would be needed to achieve adequate mechanical properties. The aim of this study is to improve the compatibility of the PET with HDPE by adding a third compatibilising component. The more specific objectives of the study are:
i) Manufacturing of compatibiliser with segments capable of specific interaction with the blend components i.e. PET and HDPE. Polyhydroxyether of bisphenol A (phenoxy) and acid functionalised ethylene copolymer have been chosen as the base components of the compatibilisers for the production of graft copolymers by reaction melt processing methods.

ii) Characterisation of the compatibilisers to determine the nature of interactions or chemical reactions between phenoxy and acid functionalised ethylene copolymer. Evaluation of mixture composition, catalysts, effect of viscosity, and phase morphology is carried out.

iii) Evaluation of the efficiency of the compatibilisers in PET/HDPE at different weight ratio blends. Also HDPE of different molecular weights are studied. Evaluation of phase morphology, effect of viscosity, crystallisation behaviour of the PET phase and mechanical properties of the blend is carried out.
CHAPTER 2
LITERATURE REVIEW

2.1 PHASE DISPERSION IN IMMISCIBLE POLYMER BLENDS

Since the great majority of polymers are immiscible in the melt they form multiphase domain structures when mixed in conventional compounding equipment. This gives rise to two problems: (a) sensitivity of structure to processing conditions, and (b) poor mechanical properties resulting from a lack of adhesion between the blend components [64,65].

Although there are various ways to mix polymers in order to achieve optimum properties (as discussed in the preceding pages), melt blending by extrusion is the most flexible and economical method. During melt blending operations the blend components are redistributed, producing either a particle dispersed morphology or an interconnected (co-continuous) phase structure [66,67]. In
subsequent shaping operations, the phase morphology of the blend, however, may change and the dispersed phase is frequently drawn or elongated. The size and shape of the dispersed phase are primarily controlled by the interfacial tension, rheological properties, and the complex strain field in the processing equipment used [68].

2.1.1 Interfacial and Rheological Considerations

Studies of the flow and break up of dispersed droplets of Newtonian fluids began with the work of Taylor [69] and continued through the work of Karam and Bellinger [70] among others. These studies frequently emphasised the influence of viscosity ratio and interfacial tension on droplet size and shape (dispersive mixing).

For a viscoelastic system, the phenomenon of droplet deformation and break up was investigated by Wu [68] for blends of both nylon and poly(ethylene terephthalate) with ethylene-propylene terpolymer, processed by twin screw extrusion at constant average shear rate (G). It was concluded that the relative influence of interfacial tension (v) and viscosity ratio ($\eta_r = \eta_d/\eta_m$, $m$ for matrix and $d$ for dispersed phase) on the dimension of the dispersed phase can be represented by the relations:

\[
\frac{(\eta_m aG)}{v} = 4 (\eta_r)^{0.84}: \quad \text{for } \eta_r > 1
\]

\[
\frac{(\eta_m aG)}{v} = 4 (\eta_r)^{-0.84}: \quad \text{for } \eta_r < 1
\]

where $a$ is the dispersed phase average particle size. According to equation 1, the deformation and break up of droplets during mixing are favoured by lowering the interfacial tension, and by increasing the shear rate and by choosing a matrix
(continuous) phase with the highest viscosity. For the same processing conditions and composition the minimum particle size is reached when the viscosity ratio for the two components is equal to unity. Van Oene [71] and Elmendorp and his co-workers [72,73] investigated the influence of melt elasticity and particularly normal stresses on phase morphologies in polymer blends. Van Oene proposes that normal stresses can alter the interfacial energy between the two phases in the melt state and exert an influence on the geometry of the dispersed phase. On the other hand, Elmendorp [72,73] shows that the viscoelastic nature of polymer melts enhances the stability of the droplets.

2.1.2 Morphological Considerations
The solid-state properties of multiphase systems clearly depend not only upon the obvious factors, such as the choice of the blend components and their relative amounts, but also upon morphological features developed during the melt mixing operation and subsequently by the moulding process. White and Min [66] have provided a brief overview of polymer blend morphology development, affirming that this aspect has received little attention. D. Quintens et al. [74] have reported that the phase morphology of intensively melt mixed and subsequently injection moulded blends of bisphenol-A polycarbonate (PC) and polystyrene-acrylonitrile copolymer (SAN) changes when the samples are annealed above the glass transition temperature (Tg) of both components. Changes in phase morphology result in changes of the macroscopic properties of the blend. An increase in the storage modulus at temperatures between the Tg of SAN and the Tg of PC was observed with the increase of coarsening of the phase structure until a continuous PC matrix was established. In contrast the coarsening of the phase structure of the blends gives rise to a transition from ductile to brittle fracture. The loss in ductility was related to a decrease in relative interface area and the setting up of tensions in the two phases, SAN becoming the continuous phase. For the
reduction in dimensions of the dispersed phase, the viscosity of the two components must be low and similar in magnitude, the interfacial interactions very strong, the interfacial surface tension very low, and shear forces must be large and applied for a long time [75].

With a sufficiently long processing time, therefore, the formation of very small particles should be achievable. This, however, has not been observed as an equilibrium average particle size is quickly reached and prevents further reduction in size with increasing shearing time. Hence there must be another mechanism which limits the particle size. One possibility is that particles can also coalesce and increase their size [64,65,73]. One frequently observes a coarsening of a quiescent blend morphology with time. The results of studies for a range of polyolefin-nylon and polystyrene-nylon blends by Chen et al. [76] show that coalescence is most important at low shear rates, with long residence times and with large interfacial tensions. Quintens et al. [74] have shown how different phase morphologies can be obtained and quantitatively defined by estimating the surface area per unit volume of the PC phase [74,77].

The general conclusion is that it is very difficult to quantify and to predict theoretically the dispersion of phases for a given polymer blend. The main reason is the lack of systematic data and reliable theories [75], which make use of measurable parameters. In addition, the measurements of surface tension and interfacial interaction are not easy to perform. It is thus necessary to rely on experimental measurements of phase dispersion for each polymer system and to correlate them with processing conditions.

A wide range of sizes and shapes can be obtained for the dispersed phase in polymer blends during processing. Generally the sizes range from about 0.1 to 50
μm and the shape can be spherical, ellipsoidal, cylindrical, or ribbon-like. It has to be noted also that the melt rheology of a system is sensitive to morphology [78,79]. In studying PS/PP blends, Han et al. [78] found that even moderately different modes of dispersion and particle size can give rise to pronounced differences in rheological properties in the molten state. It is also well known that the size and size distribution of the minor phase also have profound influence on the mechanical properties, especially impact strength [80].

The control of the shape of the dispersed phase is also of importance. Deformation of the dispersed phase in the direction of extrusion can significantly influence its final shape and mechanical properties of the blend, particularly ductility [81]. Another novel example of the importance of dispersed phase shape has been demonstrated for the ternary blend nylon/polyolefin/ionomer, where the ionomer is used as compatibiliser. In this case the dispersed phase can take the form of platelets, giving a significant improvement in barrier properties with respect to oxygen and hydrocarbons [82,83].

The blend morphology, which depends on a number of factors as discussed earlier, determines the macroscopic properties, rheological behaviour, barrier properties as well as the mechanical properties of the blend. Therefore the control of the morphology of multiphase blends during processing is of critical importance, but as yet remains poorly understood [84].

2.1.3 Compatibilisation and Control of the Multiphase Morphology
Polymer compatibility may be enhanced by various methods [5,6]. Co-crystallisation and co-crosslinking can often result in stable morphologies, i.e. they afford resistance to coalescence. Strong interactions such as acid-base or ion-dipole, hydrogen bonding and transition metal complexation have also been
shown to enhance thermodynamic miscibility of suitably functionalised components [85,86] as well as compatibility in a variety of systems of technological importance [87,88]. As mentioned earlier, more commonly, compatibility is promoted with the use of block or graft copolymers containing segments capable of specific interactions and/or chemical reactions with the blend components. The copolymers may be added separately or formed in situ by blending suitable functionalised polymers; they are thought to concentrate at the interface and act as emulsifiers thereby reducing the interfacial tension [6].

Paul [4] and Barlow and Paul [89] reviewed the use of block polymers and copolymers to compatibilise immiscible polymer blends. The beneficial effects of Kraton 16520 (tri-block polymer: 15% polystyrene - 70% central block - 15% polystyrene, where the central block is an alternating copolymer of ethylene and butene) or Epcar 847 (ethylene-propylene-ethylidene norborene copolymer with relatively long ethylene blocks, sufficient to crystallise) are of particular interest, for instance the addition of one or another of these block copolymers to polyethylene terephthalate/high density polyethylene blends have been claimed to affect the physical properties, viz modulus and yield strength [90]. A review article on the compatibilisation of polyethylene terephthalate (PET) with polypropylene has been published by Xanthos [88]. An acrylic acid functionalised polypropylene (PP-g-AA) was evaluated as the blend component in polyblends and compared with an unmodified polypropylene. Additives such as magnesium acetate and p-toluene-solfonic acid were evaluated as catalysts for potential interchange or esterification reactions that could occur in the melt. The authors have shown that functionalised polypropylene promotes a fine dispersed phase morphology, improves processability and mechanical properties, and at the same time it modifies the crystallisation behaviour of the polyester component. These effects are attributed to enhanced phase interactions resulting in reduced
interfacial tension. Earlier attempts to form compatible blends of PET with polypropylene (PP) using a potentially reactive acrylic acid grafted polypropylene as compatibiliser were also successful [91]. This approach is similar to that used with polyamide 6-6/PET blends [92] compatibilised with a carboxylic acid modified PP copolymer through transamidation reactions. Contrary to its effects on the properties of the polyamide/PP blends, the carboxylic acid modified PP copolymer was reported [91] to have little or no effect on the mechanical properties of the PP/PET blends. In fact, blends of this type exhibited a minimum in the property vs composition curves at about 40 percent by weight PET.

While co-reaction between the constituents of blends to improve the performance has for many decades been common practice in the rubber industry [93], this is only a recent happening within the plastics industry. For instance, compatibilisation via co-reaction between polyarylate and phenoxy has been reported [94] and compatibilisations of polyesters and polyamides via an exchange reaction have also been claimed. Transesterification has also been used to modify the properties of miscible polyester blends [95,96,97,94,98,99]. Devaux et al.[96,97,100] observed that in the initial stage of transesterification between polycarbonate and polybutyleneterephthalate block polymers with reduced solubility are produced. At a later stage, soluble random copolymers are formed. Significant changes of properties as a result of transesterification between polyethylene terephthalate and polyarylate have been reported [101]. Particularly interesting is the catalysed exchange reactions between polyamide-6,6 and polyethylene terephthalate occurring during a standard processing operation i.e. extrusion or injection moulding [102,103,104]. Due to the small interface area in these immiscible blends in the past the exchange reaction had to be carried out by heating the mixtures for 5 to 30 hours at 220 to 290°C. More
recently the use of organic phosphites to enhance co-reaction with the amine or hydroxyl end groups of the condensation polymers, polyamides or polyesters, has been reported by Aharoni [105]. Compatibilisation by the incorporation of ionic groups in polymers has been the method proposed by Eisenberg and co-workers [106,107]. Attaching about 5 mole % of $\text{SO}_3\text{H}$ groups to polystyrene and copolymerising about 5 mol % of vinyl pyridine with ethyl acrylate, then mixing the two polymers, resulted in a compatible blend. Similar results were obtained by blending sulfonated polyisoprene with styrene copolymerised with 5 mol % of vinyl pyridine [87]. Recently it was shown that compatibilisation can be obtained by securing ion-dipole interaction, as in poly(styrene-co-lithium methacrylate), containing 9.5 mol % of ionic groups, with a polyalkyleneoxides [108].

Subramanian [109] reported an investigation on blends of polyethylene-terephthalate to improve toughness while retaining its barrier properties. PET was modified with an ethylene methacrylic acid copolymer (EMAA). The impact toughness properties of the crystallised blends showed some improvements, but the use of the sodium salt of the ethylene copolymer resulted in greater improvements, and the zinc salt proved to be an even better impact modifier. It was also reported that when the ionomer of the EMAA copolymer contained termonomer, such as isobutylacrylate, the PET compositions were even tougher. The coarser morphology of the PET/ethylene copolymer blends explains the lower impact strength obtained with the EMAA/PET blend. The zinc ionomer of the ethylene-isobutyl acrylate-methacrylic acid copolymer, on the other hand, disperses into very fine particles, reflecting the higher toughness of these blends. This is in contrast to the large particles obtained with the sodium ionomer, but the improved toughness of the composition containing the sodium ionomer over those containing the zinc ionomer could not be explained.
The other method of compatibilisation, by high shear mixing, has been reported by Maxwell and co-workers [110,111,112]. The authors blended immiscible polymers in an elastic melt extruder (otherwise known as "Maxwell normal stress extruder") generating blends with continuous-phase morphologies. Polystyrene (PS), polymethylmethacrylate (PMMA) and polyethylene (PE) were blended each with another. Extraction by a selective solvent indicated a three-dimensional intertwined network of homopolymeric strands with diameter 1 to 50 μm. While the blends are known to be immiscible the generated structure was found to be surprisingly stable. Craubner and Illing [113] succeeded in compatibilising polyamide (PA) and functionalised polyethylene by means of suitable processing techniques. The action of high shear forces and temperatures causes a mechanical-chemical chain degradation. These mechanically initiated chemical reactions lead to the formation of graft copolymers of PA and polyolefin. The particle size of the dispersed phase, i.e. the polyolefin, depends on the functional groups in the polyolefin copolymers used [113]. The impact strength of the corresponding blend increased as particle size decreases.

The interpenetrating polymer network (IPN) is a diverse, rapidly developing branch of polymer blends technology. At least one of these polymers is synthesised and/or crosslinked in the immediate presence of the other. Crosslinks in thermoplastic IPNs can be of a physical nature: hard blocks, ion clusters or crystalline regions [114]. Most of the IPNs can be classified as compatibilised, immiscible polymer blends or alloys. Single phase IPN are also known. Polymerisation of vinyl chloride (VC) in the presence of polyethylacrylate, PEA, resulted in a homogeneous system, whereas the physical blending of polyvinylchloride (PVC) with PEA produced immiscible blends [115].
The methods used to achieve compatibilisation are hardly exhausted. Out of all the methods used, the whole domain of reactive compatibilisation during the melt mixing operation [116] is where rapid technological progress must be expected [117,118]. The wide availability of polymers functionalised with a variety of reactive groups, and the versatility of extruders as continuous reactors are among the factors contributing to such growth.
CHAPTER 3
EXPERIMENTAL

3.1 MATERIALS SELECTION

For the purposes of this study the selection of suitable materials to prepare the compatibilisers for PET and polyolefins were based on the following considerations:

a) the polymer must not degrade (chemically decompose) under the processing conditions

b) suitable chemical sites must be present and reaction conditions exist (including the use of catalysts) to provide the possibility of chemical reaction between the two polymers without excessive crosslinking.
The above criterion resulted in the choice of combinations polyhydroxyether of bisphenol-A (phenoxy), which would react via the OH groups, with ethylene copolymers containing carboxyl groups to produce either graft copolymers through specific condensation reactions, or highly interactive polymer associations. Three ethylene based polymers were chosen for this study, i.e. ethylene copolymer with acrylic acid as a comonomer (EAA₁), an ethylene terpolymer containing tert-butyl acrylate units and acrylic acid (EAA₂) and a copolymer of ethylene and partially neutralised methacrylic acid (Surlyn A), Ionomer. Two anhydride functionalised ethylene based polymers, i.e. ethylene-ethylacrylate-maleic anhydride (EMA) and ethylene-propylene elastomer grafted maleic anhydride (EP-gMA).

The polyolefins chosen to be blended with PET were grades of HDPE of different molecular weight.

3.2 RAW MATERIALS

The general characteristics of the materials used in this study are summarised in Table 3.1 on the following page.
<table>
<thead>
<tr>
<th>Materials Code</th>
<th>Grade</th>
<th>Company</th>
<th>Density (g/cm(^3))</th>
<th>MFI (g/10 mm)</th>
<th>T(_m) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenox</td>
<td>PKHH</td>
<td>Union Carbide</td>
<td>1.17</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>EAA(_2)</td>
<td>Lupolen A2910M</td>
<td>BASF</td>
<td>0.924</td>
<td>-</td>
<td>91-101</td>
</tr>
<tr>
<td>EAA(_1)</td>
<td>Lupolen A371OMX</td>
<td>BASF</td>
<td>0.932</td>
<td>-</td>
<td>100-140</td>
</tr>
<tr>
<td>E-MA</td>
<td>Lotader 4700</td>
<td>CDF</td>
<td>-</td>
<td>-</td>
<td>65</td>
</tr>
<tr>
<td>EP-gMA</td>
<td>Exxelor VA-1801</td>
<td>Exxon</td>
<td>-</td>
<td>-</td>
<td>62</td>
</tr>
<tr>
<td>Ionomer</td>
<td>Surlyn 8660</td>
<td>Du Pont</td>
<td>0.945</td>
<td>-</td>
<td>95</td>
</tr>
<tr>
<td>Na-Mont</td>
<td>Hostalub VPNAW2</td>
<td>Hoechst</td>
<td>1.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na-Bzt</td>
<td>-</td>
<td>Aldrich</td>
<td>-</td>
<td>-</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Na.P-T-S</td>
<td>-</td>
<td>Aldrich</td>
<td>-</td>
<td>-</td>
<td>&gt;300</td>
</tr>
<tr>
<td>Na-OEt</td>
<td>-</td>
<td>Aldrich</td>
<td>-</td>
<td>-</td>
<td>&gt;300</td>
</tr>
<tr>
<td>PET</td>
<td>-</td>
<td>Enichem</td>
<td>1.455</td>
<td>-</td>
<td>254</td>
</tr>
<tr>
<td>HDPE</td>
<td>Eraclere AB5015</td>
<td>Enichem</td>
<td>0.951</td>
<td>0.3</td>
<td>133</td>
</tr>
<tr>
<td>HDPE(1)</td>
<td>Hostalen GD6250</td>
<td>Hoescht</td>
<td>0.941</td>
<td>4.5</td>
<td>128</td>
</tr>
<tr>
<td>HDPE(2)</td>
<td>Hostalen GB7250</td>
<td>Hoescht</td>
<td>0.953</td>
<td>28</td>
<td>127</td>
</tr>
<tr>
<td>Talc</td>
<td>Microtal 10H</td>
<td>Microfine</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Irganox</td>
<td>Irganox 1010</td>
<td>Ciba Geigy</td>
<td>-</td>
<td>-</td>
<td>110-125</td>
</tr>
</tbody>
</table>

The chemical constitution of these materials is shown in the following pages:

34
Phenoxy: Polyhydroxyether of bisphenol A:

\[
\begin{align*}
&\text{CH}_3 \\
&\text{CH}_3
\end{align*}
\]

EAA\(_1\): Copolymer of ethylene with acrylic acid as a comonomer

\[
\left\{(\text{CH}_2 - \text{CH}_2)\right\}_x \left\{(\text{CH}_2 - \text{CH})\right\}_y \left\{(\text{CH}_2 - \text{CH} - \text{CH})\right\}_z
\]

(Believed to contain 8% acrylic acid)

E-MA: Ethylene-ethylacrylate-maleic anhydride terpolymer

\[
\left\{(\text{CH}_2 - \text{CH}_2)\right\}_x \left\{(\text{CH}_2 - \text{CH})\right\}_y \left\{(\text{CH}_2 - \text{CH} - \text{CH})\right\}_z
\]

(Believed to contain 32% acrylic units and about 2% maleic anhydride)

EAA\(_2\): Ethylene terpolymer that contains tert-butyl acrylate unit and acrylic acid

Believed to contain about 4% acrylic acid and about 19% acrylate units).
Surlyn (Ionomer): Terpolymer of ethylene - sodium methacrylate and methacrylic acid

\[
\left\{ (CH_2-CH_2)_x (CH_2-C=O)_y (CH_2-C=O)_z \right\}_n \\
\text{Believed to contain about 12-15\% acrylic units, neutralised approximately 50\%})\.
\]

EPgMA: Ethylene-propylene elastomer grafted with maleic anhydride

\[
\left\{ (CH_2-CH_2)_x CH_2-CH_2-C \right\}_n
\]

(Believed to contain 77\% ethylene and 0.7\% maleic anhydride).

NaOEt: Sodium ethoxide (purity 97\%) (catalyst)

\[
CH_3-CH_2-O^-Na^+
\]

NaBzt: Sodium benzoate (purity 99\%) (catalyst)

\[
\text{[benzoate]}^-
\]
Na.P.T.S: Sodium p-toluene sulfonate (purity 95%) (catalyst)

\[
\text{CH}_3\text{(O)}-\text{SO}_3^\text{N}_\text{a}^+ \quad 0
\]

Technical Na-Montanate: \( \text{CH}_3-\left(\text{CH}_2\right)_n-\overset{\text{C}}{\text{C}}-\overset{\text{O}^-}{\text{O}^+}_\text{N}_\text{a}^+, n = 26 - 32 \)

PET: Polyethylene terephthalate (IV = 0.74)

\[
\overset{\text{0}}{\text{CH}_2-\text{CH}_2-\text{O}-\overset{\text{C}}{\text{C}}-\overset{\text{O}}{\text{O}}}_n \quad 0
\]

HDPE: High density polyethylene with high molecular weight MFI = 0.3

\[
\overset{\text{0}}{\text{CH}_2-\text{CH}_2}_n \quad 0
\]

HDPE (1): High density polyethylene with intermediate molecular weight MFI = 4.5

HDPE (2): High density polyethylene with low molecular weight MFI = 28

3.3 DRYING OF MATERIALS

For the compatibilisers preparation, phenoxy and ethylene copolymers were dried prior to any processing step. The materials were dried at 60°C under vacuum, for a period not less than eight hours. Due to the susceptibility of PET to hydrolytic degradation in the melt, the polymer was also thoroughly dried prior to mixing with HDPE and the respective compatibilisers. The compatibilisers were also dried at 60°C. The procedure adopted was to dry the
PET at 120°C for a period of eight to ten hours. The material was then cooled to 100°C and maintained at this temperature in the hopper during the subsequent processing step.

3.4 BLENDING

3.4.1 Melt Blending in an Internal Mixer

For the preliminary studies a Brabender mixer with 30 cc volume capacity was employed to prepare the compatibilisers based on phenoxy and functionalised ethylene copolymers. Two different sets of processing conditions were used i.e. temperature 180 and 260°C; rotational speed 50 and 100 rpm; mixing time 5 mins in each case.

a) Phenoxy/EAA Mixtures

The first series of compatibilisers were prepared with the two ethylene copolymers, coded respectively EAA₁ and EAA₂ (see Table 3.1). Most of the experiments were, however, carried out on EAA₂ i.e. the ethylene tert-butyl acrylate-acrylic acid terpolymer. The mixes were studied at different weight ratios of phenoxy to EAA: i.e. 25:75, 50:50 and 75:25.

b) Phenoxy/EAA₂ mixtures containing sodium ethoxide

Sodium ethoxide (Na-OEt) was introduced in the phenoxy/EAA₂ blend in an attempt to catalyse the interaction or reaction between the two components maintaining to a minimum the level of crosslinking. For the purpose of this work a reaction constitutes the formation of ester groups, while interactions denote the occurrence of H-bonds or ionomeric species. The appropriate amount of catalyst used in 50:50 phenoxy/EAA₂ mixtures was varied from 0.5 to 4% by weight at the two processing conditions described earlier.
Mixture of EAA2/Na-OEt and phenoxy/Na-OEt were also prepared in the Brabender at 2 and 4% Na-OEt level in order to investigate the likelihood of Na-OEt producing grafting or ionomeric interactions in the individual polymer components.

c) Blends phenoxy/ various ethylene copolymers
Anhydride functionalised ethylene copolymers i.e. E-MA and EPGMA, and Surlyn 8660 (Ionomer) (see Table 3.1) were blended with phenoxy in 50:50 weight ratio. Sodium ethoxide was added to the various blends in amounts of 0.5 and 2% by weight.

d) Effects of base strength of sodium salts
Various types of sodium salts exhibiting different base strengths i.e. Sodium Benzoate (Na-Bzt), Sodium Montanate (Na-Mont) and Sodium p-Toluene Sulfonate (Na-P-TS), were investigated as catalysts for the possible interaction or reaction between phenoxy and various ethylene copolymers.

3.4.2 Melt Blending in Twin Screw Extruder
A twin screw compounding extruder APV (MP 2000) was used to produce both the compatibilisers and the various PET/HDPE blends. The specifications of the compounder are shown in Table 3.2.

<table>
<thead>
<tr>
<th>TABLE 3.2: SPECIFICATIONS FOR APV (MP 2000) TWIN SCREW EXTRUDER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length:Diameter ratio</td>
</tr>
<tr>
<td>Drive power</td>
</tr>
<tr>
<td>Screw speed</td>
</tr>
<tr>
<td>Barrel diameter</td>
</tr>
<tr>
<td>Direction of screw rotation</td>
</tr>
</tbody>
</table>
The screw configuration for mixing the various phenoxy and ethylene acid functionalised copolymer and also PET with HDPE was designed with the help of the machinery manufacturers and previous experience. Therefore the designed screw configuration is as follows:

<table>
<thead>
<tr>
<th>Die</th>
<th>Camel</th>
<th>Feed</th>
<th>Thin</th>
<th>Mixing</th>
<th>Mixing</th>
<th>6D Feed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Back</td>
<td>5.5D</td>
<td>Orifice Plugs</td>
<td>4x90°</td>
<td>6x60°</td>
<td>Feed Screws</td>
<td></td>
</tr>
</tbody>
</table>

The dried materials i.e. (phenoxy/ethylene copolymers and/or PET/HDPE) were tumble blended in the required ratios before being mixed in the extruder. The polymer passed from the metered volumetric feed hopper to the barrel where the melt mixing took place. The material was discharged to the four strand dies, then into the cooling water bath and out through the pelletizer. For the preparation of the various compatibilisers (see Table 3.3), the temperature profile was: feeding zone 100°C, mixing zone 180°C, metering zone 190°C and die temperature 200°C. The rotational speed was 250 rpm. The temperature profile used for the production of various PET/HDPE blends was: feeding zone 200°C, mixing zone 270°C, metering zone 270°C and die temperature 260°C. The rotational speed was 250 rpm. The blends of PET with HDPE were produced at 77.5/22.5 ratio for the control and for those containing compatibilisers the ratio was 75/20/5 PET/HDPE/compatibiliser respectively. Control experiments were also carried out using compatibilisers in each individual polymer of the blend i.e. 5% and 20% were separately added to PET and HDPE respectively. Additional control experiments were produced using the individual components of the compatibilisers (i.e. phenoxy and ethylene copolymers), also at 5 and 20% in PET and HDPE respectively. It has to be noted that all PET/HDPE blends with or without compatibiliser contain 1% talc as nucleating agent and 0.5% Irganox 1010 as stabiliser. These additives were used to increase the crystallisation rate of PET and to minimise hydrolytic and thermal degradation.
### TABLE 3.3: DIFFERENT COMPATIBILISERS

<table>
<thead>
<tr>
<th>Compatibilisers Code</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Surlyn 8660</td>
</tr>
<tr>
<td>C₁</td>
<td>Surlyn 8560 + 2% Na-OEt</td>
</tr>
<tr>
<td>C₂</td>
<td>Surlyn/phenoxy (25:75)</td>
</tr>
<tr>
<td>C₃</td>
<td>Surlyn/phenoxy (25:75) + 2% Na-OEt</td>
</tr>
<tr>
<td>C₄</td>
<td>Surlyn/phenoxy (50:50)</td>
</tr>
<tr>
<td>C₅</td>
<td>Surlyn/phenoxy (50:50) + 2% Na-OEt</td>
</tr>
<tr>
<td>C₅*</td>
<td>Surlyn/phenoxy (50:50) + 2% Na-OEt extruded twice</td>
</tr>
<tr>
<td>C₆</td>
<td>Surlyn/phenoxy (50:50) + 2% Na-Bzt</td>
</tr>
<tr>
<td>C₇</td>
<td>Surlyn/phenoxy (75:25)</td>
</tr>
<tr>
<td>C₈</td>
<td>Surlyn/phenoxy (75:25) + 2% Na-OEt</td>
</tr>
<tr>
<td>C₉</td>
<td>EPgMA/phenoxy (25:75)</td>
</tr>
<tr>
<td>C₁₀</td>
<td>EPgMA/phenoxy (50:50)</td>
</tr>
<tr>
<td>C₁₁</td>
<td>EPgMA/phenoxy (75:25)</td>
</tr>
<tr>
<td>C₁₂</td>
<td>EPgMA/phenoxy (25:75) + 2% Na-OEt</td>
</tr>
<tr>
<td>C₁₃</td>
<td>EPgMA/phenoxy (75:25) + 2% Na-OEt</td>
</tr>
<tr>
<td>C₁₄</td>
<td>EAA₂/phenoxy (25:75)</td>
</tr>
<tr>
<td>C₁₅</td>
<td>EAA₂/phenoxy (25:75) + 2% Na-OEt</td>
</tr>
<tr>
<td>C₁₆</td>
<td>EAA₂/phenoxy (25:75) + 2% Na-Bzt</td>
</tr>
<tr>
<td>C₁₇</td>
<td>EAA₂/phenoxy (50:50)</td>
</tr>
<tr>
<td>C₁₈</td>
<td>EAA₂/phenoxy (50:50) + 2% Na-Bzt</td>
</tr>
<tr>
<td>C₁₉</td>
<td>EAA₂/phenoxy (75:25)</td>
</tr>
<tr>
<td>C₂₀</td>
<td>EAA₂/phenoxy (75:25) + 2% Na-Bzt</td>
</tr>
</tbody>
</table>
3.5 SAMPLE PREPARATION

For the preliminary characterisation of the different prepared compatibilisers, compression moulding was used to prepare the specimens. The PET/HDPE blend samples, on the other hand, were prepared by injection moulding.

3.5.1 Specimens Preparation by Compression Moulding
The Brabender blended compatibilisers were compression moulded into 1 mm thick plaques at a moulding temperature of 180°C, with 2 min preheating followed by 5 min hold under pressure of 0.5 MPa; the mould was transferred to a cold press and allowed to cool down under the same pressure, in order to avoid deformation of the plaques. Specimens were cut from these plaques to characterise the compatibilisers.

3.5.2 Specimens Preparation by Injection Moulding
Injection moulding of the blends carefully dried was carried out on the Negri Bossi NB55 injection moulding machine. The specimens were moulded in a four tensile bars mould. A chiller was used to cool the mould to 5°C in order to produce amorphous specimens. All the moulding conditions were kept as constant as possible for all the blend series in order to minimise the influence of processing conditions. The injection moulding of the testing specimens was carried out under the following conditions: the barrel temperatures were 248, 260 and 265°C, the nozzle temperature was 268°C, injection time was 2.2 sec, hold on time 18 sec and the cooling time was 40 sec. The crystalline test samples were produced by annealing the moulded samples at 120°C for 4 hours.
3.6 CHARACTERISATION AND TESTING

3.6.1 Chemical Characterisation of Compatibilisers
The occurrence of grafting and/or crosslinking reaction between phenoxy and the different types of ethylene copolymers were evaluated by means of solubility testing and quantitative measurements of the residue (gel), using the procedures outlined below.

Procedure 1
Using reflux-extraction in a Soxhlet, the samples were extracted with DMF for 24 hours and then with xylene for another 24 hours in order to selectively dissolve the phenoxy and the ethylene copolymer respectively. In a second series of extraction tests, cyclohexanone was used instead of DMF.

Procedure 2
By this procedure 80-100 mg of material, in the form of small thin plaques (0.5 mm thick) were placed within a 200 mesh stainless steel gauze, using two different solvent mixtures, i.e. 50/50 DMF/xylene and 50/50 cyclohexanone/xylene. To establish the required extraction time the residue was measured at different time intervals. This procedure provided a means of assessing the effect of using a solvent mixture with solubility parameter intermediate between the individual solvents used in the sequential Soxhlet extraction tests. This procedure offers also a practical advantage in being much less time consuming.

3.6.2 Fourier Transform Infrared (FTIR) Characterisation
The Fourier transform infrared spectroscopy analysis was carried out using the spectrophotometer Nicolet 20DXC in order to illustrate the possible occurrence
Chapter 3: Experimental

of esterification reactions or H-bonding interactions and salt formation in the various compatibilisers.

a) Sample Preparation
The blends under examination were prepared in the Brabender at 180°C, 100 rpm rotational speed and 5 min mixing time. The samples required for FTIR analysis have to be very thin, i.e. around 5 μm thickness. The first method adopted was to compress a small amount of the material between two plates at 160°C for 5 mins, using "Melinex" film (biaxially drawn PET) to prevent sticking on the plates. This method, however, was not suitable for all the materials used in this study. It was not possible, for instance, to prepare Surlyn samples by this method as adhesion to the "Melinex" film could not be prevented. A second method was adopted in this case by using a microtoming technique to produce thin films. This method consists of preparing sample bars, 25 x 10 x 6 mm, by compression moulding at 140°C for 25 min under pressure, which were then microtomed on a mechanical microtome (Polycut E) with a tungsten carbide blade that could be set to take slices at 5 μm. Even so the minimum thickness achieved was about 10-15 μm due to the blade not being sufficiently sharp and causing recovery of the rubbery Surlyn material after being deformed by the microtome. In some cases, where the microtome method did not produce samples, sufficiently thin, the hot press method was used as a follow up stage. The ethylene-propylene elastomer grafted maleic anhydride (EP-gMA) samples, being even more rubbery than Surlyn made microtoming extremely difficult.

3.6.3 Scanning Electron Microscopy (SEM)
To study the morphology of the different blends prepared, SEM examinations were carried out on the Cambridge Stereoscan 360 electron microscope, using fractured specimens in liquid nitrogen taken from injection moulded tensile bars

44
as well as from the extruded pellets. Each specimen was gold coated and images of the fractured surfaces were taken. The average particle diameter of the dispersed phase was determined by measurements from SEM micrographs of fractured surfaces.

3.6.4 Differential Scanning Calorimetry (DSC)

a) Description

A Du Pont DSC Instruments, Model 2000, was used. It consisted of a constantan disc from which heat is transferred to the sample and reference position. The sample which may vary in weight from 0.1 mg to 25 mg is placed in a small aluminium pan with a lid; a similar pan and lid is normally used as a reference. The sample holders can be cooled or heated at various fixed rates (from 0.5°C/min to 50°C/min) in an atmosphere of nitrogen. In the course of an experiment even a slight change in heat content of the sample produces a high voltage output. This means that when some thermal transition takes place in the sample, the differential heat is monitored. This difference in heat flow per unit of time is recorded as a function of the temperature or time. Also this equipment is attached to a computer that calculates Tg values, Tc values, Tm values as well as the heat of crystallisation (ΔHc) and heat of fusion (ΔHf) of the sample.

b) DSC Analysis

DSC measurements were carried out on the specimens cut from both the extruded pellets and injection moulded samples (made with 5°C mould temperature). For the extruded compatibilisers pellets (phenoxy/ethylene copolymers) the temperature range used was 20°C-180°C at a scanning rate of 10°C/min. For the PET blends the temperature range of the heating scan was 20°C-280°C, at a heating scan of 5°C/min. This was followed by cooling down to 50°C at a cooling rate of 10°C/min. One to two minutes were allowed between the heating and cooling scans.
The thermal analysis data such as crystallisation temperature ($T_c$), melting temperature ($T_m$), heat of crystallisation ($\Delta H_c$) and heat of fusion ($\Delta H_m$) were measured and a typical trace of the thermogram obtained is illustrated in Figure 3.1. The degree of crystallinity was calculated assuming a heat of fusion of the pure PET crystal of 32.5 cal/g [88].

**FIGURE 3.1: TYPICAL DSC TRACE**

![TYPICAL DSC TRACE](image-url)
3.6.5 Rheological Characterisation

The melt rheology characterisation of the compatibilisers and PET blends were investigated using a conventional capillary rheometer (Davenport). On this equipment one measures the pressure at the die entry as a function of the speed at which the plunger travels down the barrel to extrude the melt through a capillary die. The experimental results were expressed first in terms of the uncorrected shear stress $\tau$, using the formula

$$\tau = \frac{\Delta P}{4L/D}$$

where $\Delta P$ is the pressure of the melt in the reservoir, $D$ is the die diameter (2 mm) and $L$ the die length (20 mm). The "apparent shear rate" is

$$\gamma_a = \frac{4Q}{\pi R^3}$$

where $Q$ is the volumetric flow rate through the die, and $R$ is the radius of the capillary.

The pressure drop across a zero length die ($\Delta P_0$) with the same diameter as the capillary die was also measured to make the necessary corrections for the entry pressure drop. Therefore the true shear stress is given by:

$$\tau = \frac{\Delta P - \Delta P_0}{4L/D}$$

The apparent viscosity, $\eta_a$ (at any shear rate $\gamma$) is, therefore, calculated as the ratio of shear stress to shear rate, i.e.
3.6.6 Tensile Test

The injection moulded tensile bars were tested on a tensile testing machine (Nene modified Instron). The test was carried out at room temperature and the samples were conditioned for at least 24 hours. Also a clip-on extensometer was used to obtain accurate measurements of the modulus. From this test, tensile strength at yield or at break (for brittle failures), modulus and elongation at break were determined at a crosshead speed of 20 mm/min. The reported values of all properties are the average of at least five determinations.

**FIGURE 3.2: TENSILE TEST BARS**

Dimensions are in millimetres.

\[
\eta = \frac{\tau}{\gamma}
\]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>L₀</td>
<td>Overall length</td>
<td>190</td>
</tr>
<tr>
<td>W₀</td>
<td>Width</td>
<td>19</td>
</tr>
<tr>
<td>G</td>
<td>Length of narrow parallel portion</td>
<td>70</td>
</tr>
<tr>
<td>Wₑ</td>
<td>Width of narrow parallel portion</td>
<td>13</td>
</tr>
<tr>
<td>T</td>
<td>Thickness</td>
<td>3</td>
</tr>
</tbody>
</table>
A typical load/extension and stress/strain curve are shown in Figures 3.3 and 3.4 respectively.

FIGURE 3.3: TYPICAL LOAD-EXTENSION CURVE
(produced with an extensometer of the PET/HDPE + 5% [phenoxy/Surlyn (50:50) + 2% Na-OEt] blend)

FIGURE 3.4: TYPICAL STRESS-STRAIN CURVE
(produced without an extensometer of the PET/HDPE + 5% phenoxy blend)
CHAPTER 4
RESULTS

In this section are presented the main results of the investigation.

4.1 CHEMICAL CHARACTERISATION OF COMPATIBILISERS

4.1.1 Solubility Tests
The quantitative estimation of grafting and crosslinking reactions between phenoxy and the different types of ethylene copolymers used are presented in this section in terms of its solubility in appropriate solvents.

a) **Solubility tests by reflux extraction in a Soxhlet apparatus**
*Phenoxy/ethylene acrylic acid terpolymers (EAA):* All the blends of phenoxy/ethylene copolymer with acrylic acid as a comonomer (EAA₁) prepared at various compositions in the Brabender at both processing conditions (i.e. temperature 180°C and 260°C; rotational speed 50 and 100 rpm; mixing time 5
mins in each case) were found to dissolve by sequential extraction in DMF followed by xylene. A similar situation was found for the case of phenoxy/ethylene terpolymer containing tert-butyl acrylate units and acrylic acid (EAA₂) blends indicating that in both cases no crosslinking reactions have taken place. However the blends produced in the presence of small amounts of sodium ethoxide (Na-OEt) as catalyst displayed an appreciable amount of residue in the sequential extraction tests as indicated in Figure 4.1.

These results show, therefore, that reactions or physical interactions between the two polymer components of these compatibilisers have taken place in the presence of NaOEt but without causing crosslinking. The results also show that the amount of residue increases monotonically with the increase of concentration of Na-OEt.

*Phenoxy/different ethylene copolymer blends*: The use of different ethylene copolymers i.e. the terpolymer of ethylene methyl acrylate and partially neutralised acrylic acid (Surlyn A), Ionomer and the ethylene-ethylacrylate-maleic anhydride (E-MA) blended with phenoxy at 50% by weight has shown similar trends to those obtained with phenoxy/EAA₂ blends but the % residue is lowest for the phenoxy/E-MA system, see Table 4.1.

However the use of the ethylene-propylene elastomer grafted with maleic anhydride copolymer (EP-gMA) at different weight ratios 25, 50 and 75 percent shows different behaviour than the other functionalised copolymers i.e. the percentage residue increases with increasing EP-gMA weight ratio in the EP-gMA/phenoxy mixtures, as shown in Figure 4.2.
Fig. 4.1 The Effect of Sodium Ethoxide on the Residue of Phenoxy/EAA2 (50:50) in Sequential Extraction.
Fig. 4.2 The Effect of EP-gMA Content and Sodium Ethoxide on the Residue of Phenoxy/EP-gMA.
### TABLE 4.1: THE RESIDUE OF PHENOXY/DIFFERENT ETHYLENE COPOLYMER BLENDS

<table>
<thead>
<tr>
<th>Blends</th>
<th>% Na-OEt</th>
<th>% Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surlyn/phenoxy (50:50)</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50)</td>
<td>2</td>
<td>17.7</td>
</tr>
<tr>
<td>E-MA/phenoxy (50:50)</td>
<td>0.5</td>
<td>2.7</td>
</tr>
<tr>
<td>E-MA/phenoxy (50:50)</td>
<td>2</td>
<td>8.7</td>
</tr>
</tbody>
</table>

*Surlyn = Terpolymer of ethylene, ethyl acrylate and partially neutralised acrylic acid (Ionomer)*

*E-MA = Ethylene-ethylacrylate-maleic anhydride*

**Effects of sodium catalysts:** The results obtained from the Soxhlet extraction for the blends of phenoxy/ethylene tert-butyl acrylate and acrylic acid terpolymer (EAA₂) using different types of sodium catalysts i.e. sodium ethoxide (Na-OEt), sodium p-toluene sulfonate (Na-PTS) and sodium benzoate (Na-Bzt) in DMF/xylene solvent are shown in Table 4.2. Note that these blends were prepared in the Brabender at 260°C temperature, 100 rpm rotational speed and 5 min mixing time.
TABLE 4.2 RESIDUE OF PHENOXY/EAA, (50:50) WITH DIFFERENT SODIUM COMPOUNDS IN DMF, XYLENE SEQUENTIAL EXTRACTION

<table>
<thead>
<tr>
<th>Sodium Salts</th>
<th>% Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>2% (Na-OEt)</td>
<td>27.2</td>
</tr>
<tr>
<td>4% (Na-OEt)</td>
<td>34.4</td>
</tr>
<tr>
<td>2% (Na-PTS)</td>
<td>0</td>
</tr>
<tr>
<td>4% (Na-PTS)</td>
<td>0</td>
</tr>
<tr>
<td>2% (Na-Bzt)</td>
<td>10.3</td>
</tr>
<tr>
<td>4% (Na-Bzt)</td>
<td>13.0</td>
</tr>
</tbody>
</table>

EAA$_2$ = Ethylene tert-butyl acrylate and acrylic acid terpolymer
(NaOEt) = Sodium ethoxide
(Na-PTS) = Sodium p-toluene sulfonate
(Na-Bzt) = Sodium benzoate

b) Solubility of compatibilisers in Boiling Solvent Mixtures
As reported in the experimental section, thin plaques (80-100 mg) of compatibilisers were boiled for different lengths of time in two different solvent mixtures respectively (1:1) DMF/xylene and (1:1) cyclohexanone/xylene. The mixtures treated by this method were prepared in the Brabender. The results are shown in Tables 4.3, 4.4 and 4.5.
Chapter 4: Results

TABLE 4.3: RESIDUE (%) FOR DIFFERENT BOILING TIMES IN (1:1) DMF/XYLENE SOLVENT

<table>
<thead>
<tr>
<th>Blends</th>
<th>2 hrs</th>
<th>4 hrs</th>
<th>6 hrs</th>
<th>10 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAA-phenoxyl (50:50) + 2% NaOEt</td>
<td>20</td>
<td>22</td>
<td>24</td>
<td>23.8</td>
</tr>
<tr>
<td>EP-gMA/phenoxyl (25:75) + 2% NaOEt</td>
<td>30.7</td>
<td>26.9</td>
<td>35</td>
<td>38</td>
</tr>
<tr>
<td>Surlyn/phenoxyl (50:50) + 2% NaOEt</td>
<td>51.4</td>
<td>27</td>
<td>25.5</td>
<td>24.5</td>
</tr>
</tbody>
</table>

EP-gMA = Ethylene-propylene elastomer grafted maleic anhydride
Surlyn = Terpolymer of ethylene, methyl acrylate and partially neutralised acrylic acid.

Table 4.3 shows that there is no significant change in the amount of residue obtained after 2 hours boiling without changing the solvent, except for the Surlyn/phenoxyl (50:50) + 2% Na-OEt, which requires at least 4 hours to obtain a reasonably constant residue. Hence 4 hours boiling was chosen for all systems to standardise the solubility test.

Comparison of Solubility Methods: Table 4.4 compares the different methods used to evaluate the residue i.e. reflux extraction in Soxhlet and liquid extraction in two different solvent mixtures (1:1) DMF/xylene and (1:1) cyclohexanone/xylene. The effect of different boiling times was also compared at 2 hrs, 4 hrs with changing solvent every 2 hrs (2 + 2 hrs) and 4 hrs continuous boiling.
### TABLE 4.4: COMPARISON OF METHODS USED FOR RESIDUE DETERMINATION

<table>
<thead>
<tr>
<th>Blends</th>
<th>Sequential Soxhlet (DMF/xylene) 24/24 hrs</th>
<th>Liquid extraction in mixed solvent (1:1)</th>
<th>2 hrs</th>
<th>2+2 hrs</th>
<th>4 hrs</th>
<th>Cyclohexane-xylene 4 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAA₉/phenoxy (50:50)</td>
<td>0</td>
<td>8.8</td>
<td>1.2</td>
<td>2</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>EAA₉/phenoxy (50:50) + 2% Na-OEt</td>
<td>27.2</td>
<td>20</td>
<td>18</td>
<td>22</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50)</td>
<td>0</td>
<td>30.6</td>
<td>4.2</td>
<td>4.6</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 2% NaOEt</td>
<td>17.7</td>
<td>51.0</td>
<td>24.6</td>
<td>27.0</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>EP-gMA/phenoxy (25:75)</td>
<td>0.0</td>
<td>30</td>
<td>9.2</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>EP-gMA/phenoxy (25:75) + 2% Na-OEt</td>
<td>24</td>
<td>30.7</td>
<td>24.5</td>
<td>26.9</td>
<td>20.3</td>
<td></td>
</tr>
<tr>
<td>EPgMA/phenoxy (50:50)</td>
<td>4.12</td>
<td>35.0</td>
<td>14.0</td>
<td>16.0</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>EPgMA/phenoxy (50:50) + 2% Na-OEt</td>
<td>36.0</td>
<td>42.3</td>
<td>28.4</td>
<td>30.0</td>
<td>22.0</td>
<td></td>
</tr>
<tr>
<td>EPgMA/phenoxy (75:25)</td>
<td>23.0</td>
<td>45.2</td>
<td>34.0</td>
<td>39</td>
<td>23.9</td>
<td></td>
</tr>
<tr>
<td>EPgMA/phenoxy (75:25) + 2% Na-OEt</td>
<td>59.8</td>
<td>72.0</td>
<td>64.7</td>
<td>69</td>
<td>55.0</td>
<td></td>
</tr>
</tbody>
</table>

2+2 hrs = 4 hrs total boiling in solvent; fresh solvent used after 2 hrs.

The different methods used to determine the residue gave different values, but both methods show qualitatively the same trends, i.e. the addition of sodium ethoxide produces a higher amount of residue in both the reflux extraction as
well as in the liquid extraction in (1:1) DMF/xylene solvent. On the other hand the liquid extraction in (1:1) cyclohexanone/xylene solvent seems to always give lower amounts of residue. It was found that the addition of 2% Na-OEt to both mixtures EAA₂/phenoxy (50:50) and Surlyn/phenoxy (50:50) did not produce a residue in extraction tests with (1:1) cyclohexanone/xylene solvent, whereas an appreciable amount of residue is obtained with EP-gMA/phenoxy (75:25) mixtures and all the EP-gMA/phenoxy mixtures containing 2% Na-OEt. From these results it can be said that the amount of residue obtained from the sequential reflux extraction in DMF/xylene and liquid extraction in mixed DMF/xylene gives an indication of the extent of grafting, or formation of coionomers, while the true gel content, which indicates crosslinking, is obtained with the cyclohexanone/xylene extraction method. The results in Table 4.4 have shown that 4 hrs boiling time, with solvent change after 2 hrs, did not show any significant difference in the amount of residue compared to that of 4 hrs continuous boiling, in other words the amount of solvent used is sufficient for the liquid extraction tests.

**TABLE 4.5: RESIDUE OF PHENOXY/EAA₂ (50:50) WITH DIFFERENT SODIUM COMPOUNDS FROM 4 HRS LIQUID EXTRACTION IN (1:1) DMF/XYLENE**

<table>
<thead>
<tr>
<th>Sodium Salts</th>
<th>% Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Na compound</td>
<td>2.3</td>
</tr>
<tr>
<td>2% Na-OEt</td>
<td>22.0</td>
</tr>
<tr>
<td>2% Na-Bzt</td>
<td>11.0</td>
</tr>
<tr>
<td>2% Na-PTS</td>
<td>2.8</td>
</tr>
<tr>
<td>2% Na-Mont</td>
<td>5.6</td>
</tr>
</tbody>
</table>

EAA₂: = Ethylene tert-butyl acrylate and acrylic acid terpolymer
NaOEt = Sodium ethoxide
Na-Bzt = Sodium benzoate
Na-PTS = Sodium p-toluene sulfonate
Na Mont = Sodium Montanate
Chapter 4: Results

The residue of phenoxy/EAA₂ (50:50) with different sodium compounds obtained from 4 hrs liquid extraction in (1:1) DMF/xylene does not show a significant difference from those obtained with the sequential extraction in DMF/xylene, see Table 4.2 and Table 4.5. The results in Table 4.5 show that the most effective sodium compound to produce a considerable amount of grafting or coionomers is sodium ethoxide (Na-OEt) i.e. the strongest base. On the other hand an appreciable amount of residue is obtained also with 2% of sodium benzoate (Na-Bzt) i.e. a weak base, while practically no residue is obtained with the neutral Na-PTS salt and in the absence of any sodium compound.

Solubility of compatibilisers produced by twin screw extrusion: The amount of residue for different extruded compatibilisers was determined as the processing conditions are different from those used in the Brabender (see experimental section) which might affect the amount of grafting in the mixture. The results obtained are presented in Tables 4.6, 4.7 and 4.8.

**Table 4.6: Residue (%) for the Extruded Phenoxy/EAA₂ Compatibilisers After 4 hrs boiling in different solvent mixtures**

<table>
<thead>
<tr>
<th>Compatibilisers</th>
<th>Liquid Extraction in Mixed Solvent</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF/xylene (1:1)</td>
<td>Cyclohexanone/xylene (1:1)</td>
</tr>
<tr>
<td>EAA₂/phenoxy (27:75)</td>
<td>2.3</td>
<td>0.0</td>
</tr>
<tr>
<td>EAA₂/phenoxy (25:75) + 2% Na-OEt</td>
<td>20.0</td>
<td>1.3</td>
</tr>
<tr>
<td>EAA₂/phenoxy (25:75) + 2% Na-Bzt</td>
<td>10.0</td>
<td>0.0</td>
</tr>
<tr>
<td>EAA₂/phenoxy (50:50)</td>
<td>2.9</td>
<td>0.0</td>
</tr>
<tr>
<td>EAA₂/phenoxy (50:50) + 2% Na-Bzt</td>
<td>12.0</td>
<td>1.1</td>
</tr>
<tr>
<td>EAA₂/phenoxy (75:25)</td>
<td>4.3</td>
<td>0.0</td>
</tr>
<tr>
<td>EAA₂/phenoxy (75:25) + 2% Na-Bzt</td>
<td>10.2</td>
<td>1.2</td>
</tr>
</tbody>
</table>
### TABLE 4.7: RESIDUE (%) FOR THE EXTRUDED PHENOXY/ EP-gMA COMPATIBILISERS AFTER 4 HRS BOILING IN DIFFERENT SOLVENT MIXTURES

<table>
<thead>
<tr>
<th>Compatibilisers</th>
<th>Liquid Extraction in Mixed Solvent</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF/xylene (1:1)</td>
<td>Cyclohexanone/xylene (1:1)</td>
<td></td>
</tr>
<tr>
<td>EP-gMA/phenoxy (25:75)</td>
<td>18.5</td>
<td>1.9</td>
<td></td>
</tr>
<tr>
<td>EP-gMA/phenoxy (25:75) + 2% Na-OEt</td>
<td>26.5</td>
<td>20.2</td>
<td></td>
</tr>
<tr>
<td>EP-gMA/phenoxy (50:50)</td>
<td>30.0</td>
<td>4.2</td>
<td></td>
</tr>
<tr>
<td>EP-gMA/phenoxy (75:25)</td>
<td>48.0</td>
<td>25.0</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 4.8: RESIDUE (%) FOR THE EXTRUDED PHENOXY/ SURFLYN COMPATIBILISERS AFTER 4 HRS BOILING IN DIFFERENT SOLVENT MIXTURES

<table>
<thead>
<tr>
<th>Compatibilisers</th>
<th>Liquid Extraction in Mixed Solvent</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMF/xylene (1:1)</td>
<td>Cyclohexanone/xylene (1:1)</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (25:75)</td>
<td>7.0</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (25:75) + 2% Na-OEt</td>
<td>15.0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50)</td>
<td>8.5</td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 2% Na-OEt</td>
<td>28.0</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 2% Na-Bzt</td>
<td>12.3</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (75:25)</td>
<td>10.0</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Surlyn/phenoxy (75:25) + 2% Na-OEt</td>
<td>17.0</td>
<td>0.7</td>
<td></td>
</tr>
</tbody>
</table>
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The results in Tables 4.6, 4.7 and 4.8 show that the amount of residue is more or less the same as for the samples produced in the Brabender, except for the EP-gMA/phenoxy blends which display an increase in graft copolymer formation. Furthermore the only crosslinked polymer formed is from the (25:75) EP-gMA/phenoxy + 2% Na-OEt and from the (75:25) EP-gMA/phenoxy blend which exhibits a considerable amount of gel after 4 hrs boiling in (1:1) cyclohexanone/xylene solvent mixture. These results are also similar to those obtained when the above mentioned blends were produced in the Brabender. In other words it is primarily the nature of the polymers used and type of catalyst, rather than processing method, that determines whether grafting and crosslinking reactions may take place. The selection of suitable compatibilisers was made according to the residue obtained. Since E-MA gave the lowest amount of residue when reacted with phenoxy, it was not used for the production of compatibilisers. Similarly neither Na-PTS nor Na-Mont were used as catalysts.

4.1.2 Fourier Transform Infrared (FTIR) Characterisation

As explained in Section 3.4.2, FTIR spectroscopy was used to characterise the possible reactions, such as crosslinking and grafting, occurring between phenoxy and the different types of ethylene copolymers.

a) Phenoxy/ethylene tert-butyl acrylate and acrylic acid terpolymer (EAA₂) mixtures

Figure 4.3 shows the FTIR spectra of phenoxy, EAA₂ phenoxy/EAA₂ (50:50), EAA₂ + 2% Na-OEt, and phenoxy/EAA₂ (50:50) + 2% Na-OEt mixtures. The phenoxy spectrum obtained at 1850-1550 cm⁻¹ shows peaks referable to the stretching modes of the unsaturated C-C bonds of the aromatic rings at the following wavebands:
Fig. 4.3 FTIR Spectra of (a) Phenoxy, (b) EAA2, (c) EAA2/Phenoxy (50:50)
(d) EAA2 + 2% Na - OEt and (e) EAA2/Phenoxy (50:50) + 2% Na - OEt.
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i) 1625-1575 cm\(^{-1}\)

ii) 1581 cm\(^{-1}\): normal aromatic vibration [119].

The spectra of the EAA\(_2\) (1880-1400 cm\(^{-1}\)) show the C=O stretching vibration of the acid groups. The tert-butyl acrylate at 1730 cm\(^{-1}\) and the acrylic acid at 1706 cm\(^{-1}\) are clearly distinguished. Also typical CH\(_2\) deformation of the polyethylene backbone is observed at 1465 cm\(^{-1}\). The phenoxy/EAA\(_2\) (50:50) mixtures in Figure 4.3(c) display a spectrum showing a direct combination of the two components spectra, i.e. showing no shifts of peaks to different wavenumber or changes in their intensity. The addition of 2% Na-OEt to the phenoxy/EAA\(_2\) (50:50) mixtures shows a reduction in the height of the acrylic acid peak (1706 cm\(^{-1}\)) and a new peak is observed at 1570 cm\(^{-1}\), which is attributed to the salt formation (C-ONa\(^+\)). These results are clearly shown in the spectrum of EAA\(_2\) containing 2% Na-OEt, i.e. without the interference of the phenoxy component. The reduction in the height of the acrylic acid peak, and the formation of the broad salt peak centred at 1550 cm\(^{-1}\) are observed (Figure 4.3(d)).

b) Phenoxy/Surlyn Mixtures

Figure 4.4 illustrates the FTIR spectra of the Surlyn, phenoxy/Surlyn (50:50), and phenoxy/Surlyn (50:50) + 2% Na-OEt. The FTIR spectrum for Surlyn in the region investigated (1800-1400 cm\(^{-1}\)) (Figure 4.4(a)) shows typical peaks at the following wavenumbers:

i) 1700 cm\(^{-1}\): identifiable with the C=O stretching vibrations of the acid group.

ii) 1545 cm\(^{-1}\): a broad peak typical of carbonate groups.
Fig. 4.4 FTIR Spectra of Surlyn and Surlyn/Phenoxy Mixtures.
iii) 1470 cm\(^{-1}\): typical of \(>\text{CH}_2\) deformation of the polyethylene backbone [119].

iv) 1404 cm\(^{-1}\): identifiable with C-O vibration coupled with O-H [119].

The spectrum of the Surlyn/phenoxy (50:50) (Figure 4.4(b)) represents a physical combination of the two mixture components. The analysis of the spectrum, however, does not reveal any shift of the acid peak or the peak corresponding to the formation of esters.

The addition of Na-OEt causes only the broadening of the salt peak at 1550 cm\(^{-1}\) (Figure 4.4(c), 4.4(d)). Once again, no clear evidence of chemical reactions between the two components of the mixtures can be obtained.

It was concluded that the above uncertainties were due to the difficulties in obtaining sufficiently thin films, which enabled only major changes in the spectra to be detected. Therefore FTIR examinations were not carried further in this study, and inferences were made mainly on the basis of the solubility tests and rheological measurements. However, a thorough investigation by infrared spectroscopy on the various prepared compatibilisers has been carried out by A. Moggi for work towards an MPhil degree at Loughborough University.

### 4.2 RHEOLOGICAL CHARACTERISATION

The melt viscosity and entry pressure drop for the compatibilisers and PET blends are presented as function of shear rate.
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Fig. 4.5 Viscosity vs Shear rate at 180°C of the Compatibiliser prepared in the Brabender.

Phenoxy
EAA2
Phenoxy/EAA2
Phenoxy/EAA2+2NaOEt

Shear Rate (sec⁻¹)

Viscosity (Pa·Sec)
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Fig. 4.6 Viscosity vs Shear rate at 180°C of the Compatibilisers Prepared in the Brabender.
Fig. 4.7 Viscosity at 180°C of EP-gMA/Phenoxy Compatibilisers Prepared in the Brabender.
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4.2.1 Compatibilisers Produced on the Brabender

The rheological measurements were carried out on the different compatibilisers to study further the possible interactions between the two components of the compatibilisers. The melt viscosity of the compatibilisers was measured at 180°C.

The melt viscosity results are shown in Figures 4.5, 4.6 and 4.7. The viscosity vs shear rates curve for the 50:50 ethylene tert-butyl acrylate and acrylic acid terpolymer (EAA₂)/phenoxy blend falls between the curves for the phenoxy and EAA₂, while the addition of 2% Na-OEt shows an appreciable increase in viscosity at all shear rates, approaching closely that of the phenoxy component.

Figure 4.6 shows the viscosity data for the ethylene-propylene elastomer grafted with maleic anhydride (EP-gMA), the 50:50 EP-gMA/phenoxy and the 50:50 EP-gMA/phenoxy + 2% Na-OEt mixtures. The same behaviour as in the previous case is observed i.e. the viscosity of the 50:50 EP-gMA/phenoxy mixture increases significantly with the addition of 2% Na-OEt. Furthermore similar results are also obtained at different ratios of EP-gMA/phenoxy i.e. 25:75 and 75:25, see Figure 4.7.

4.2.2 Compatibilisers and PET Blends Prepared in the Twin Screw Extruder

The melt viscosity of the different compatibilisers was measured at 280°C as this is the temperature at which they are mixed in the PET blends and is also the moulding temperature used for the preparation of specimens. The rheological measurements show that at this temperature the viscosity ratio of PET and HDPE (AB5015) is approximately equal to 1 when the shear rate is about 2000 sec⁻¹, i.e. in the range of shear rate for injection moulding, (see Figure 4.8). However, the
Fig. 4.8 Viscosity VS Shear Rates at 280°C for PET/HDPE Blend and its Individual Components.
Fig. 4.9 Viscosity vs Shear Rate. at 280°C.

(a). Phenoxy and Various Ethylene Copolymers.

(b). PET/HDPE Blends Containing 5% Phenoxy and Various Ethylene Copolymers.
viscosity of PET/HDPE (77.5:22.5) blends is lower than that of PET and HDPE i.e. shows a negative deviation from the additivity rule. Figure 4.9(a) shows the viscosity vs shear rate data of phenoxy and different ethylene copolymers. The EP-gMA has the highest viscosity at all shear rates, whereas that of the Surlyn (I) is the lowest. Figure 4.9(b) shows the PET/HDPE blend and the corresponding PET/HDPE containing 5% of the above different polymer components used for the production of compatibilisers. The PET/HDPE + 5% Surlyn shows the lowest viscosity i.e. even lower than the PET/HDPE. An increase in viscosity of the PET/HDPE blend is obtained, on the other hand, with the addition of 5% either phenoxy or EP-gMA. Figure 4.10(a) shows the viscosity for different Surlyn based compatibilisers i.e. Surlyn + 2% Na-OEt (C_1), Surlyn/phenoxy (50:50) (C_2), Surlyn/phenoxy (50:50) + 2% Na-OEt (C_3) and Surlyn/phenoxy (50:50) + 2% Na-OEt extruded twice (C_5*). The addition of 2% Na-OEt to Surlyn systems has shown a considerable increase in viscosity in both the pure Surlyn (C_1) and in the blend PET/HDPE/C_1. A considerable increase in viscosity is obtained with the addition of 2% Na-OEt to Surlyn/phenoxy (50:50) mixture. Further increase in viscosity is obtained when the above blend is extruded for a second time, confirming the occurrence of further interactions or grafting. However a difference in viscosity, at low shear rates, is noted with all these systems when they are used as compatibilisers for PET/HDPE blends (see Figure 4.10(b)). At low shear rates the viscosity of PET/HDPE blends is highest for blends containing 5% C_5* (i.e. (50:50) Surlyn/phenoxy + 2% Na-OEt extruded twice), while the lowest viscosity is exhibited by the blend containing 5% C_1 (i.e. Surlyn + 2% Na-OEt) when comparing the compatibilised PET/HDPE blends.

Figure 4.11(a) shows the effect of increasing the Surlyn content in the compatibilisers produced with the addition of sodium ethoxide i.e. 25:75
Fig. 4.10 Viscosity vs Shear Rate at 280°C.

(a). Various Surlyn/Phenoxy Compatibilisers Containing Na-OEt.

(b). PET/HDPE Blends Containing 5% Various Surlyn based Compatibilisers.
Fig. 4.11 Viscosity vs Shear Rate at 280°C.

(a) Compatibilisers Containing Different Levels of Surlyn.

(b) PET/HDPE Blends Containing 5% Compatibiliser With Different Level of Surlyn.
Fig. 4.12 Viscosity vs Shear Rate: at 280°C.

(a). Compatibilisers Containing Different Level of EP-gMA.

(b). PET/HDPE Blends Containing 5% Compatibiliser with Different Level of EP-gMA.
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Surlyn/phenoxy + 2% Na-OEt (C₃), 50:50 Surlyn/phenoxy + 2% Na-OEt (C₅), and 75:25 Surlyn/phenoxy + 2% Na-OEt (C₇). The plots show that the compatibiliser viscosity increases as the percentage of Surlyn decreases and this behaviour is also reflected in the corresponding blends PET/HDPE containing 5% compatibiliser at low shear rates, see Figure 4.11(b).

In Figure 4.12(a) are shown plots of viscosity vs shear rate for EP-gMA, EP-gMA/phenoxy (25:75) (C₉) and EP-gMA/phenoxy (50:50) (C₁₀). Although these indicate that EP-gMA has the highest viscosity, the data for the blends of PET/HDPE containing these compatibilisers show that there is no clear difference between the various blends, see Figure 4.12(b).

Figure 4.13(a) shows the effect of Na-OEt on the viscosity of different compatibilisers, namely Surlyn/phenoxy, EAA₂/phenoxy and EP-gMA/phenoxy at weight ratio 25:75 and with 2% Na-OEt, i.e. compatibiliser, C₃, C₁₅ and C₁₂ respectively. In the same figure are shown also the data for blends of PET/HDPE containing 5% compatibiliser. The compatibiliser EP-gMA/phenoxy (25:75) + 2% Na-OEt (C₁₂) exhibits the lowest viscosity at all shear rates. It is important to note that this system was found from solubility tests to be crosslinked, (see Table 4.4). On the other hand Figure 4.13(b) shows that in blends PET/HDPE it is compatibiliser C₁₅ i.e. EAA₂/phenoxy (25:75) + 2% Na-OEt that displays the lowest viscosity characteristics. Figure 4.14(a) compares the effect of Na-OEt with that of Na-Bzt (sodium benzoate) as catalysts for the compatibilisers. The plots shown are for viscosity vs shear rate of PET/HDPE with 5% C₄, C₅ and C₆ i.e. [Surlyn/phenoxy (50:50), [Surlyn/phenoxy (50:50) + 2% Na-OEt] and [Surlyn/phenoxy (50:50) + 2% Na-Bzt] respectively. It is clear that the PET/HDPE + 5% C₆ has the lowest viscosity compared to the blends with C₄ and C₅. However the viscosity of PET/HDPE + 5% C₁₈ i.e. EAA₂/phenoxy (50:50) +
Fig. 4.13 Viscosity vs Shear Rate at 280°C.

(a). Effect of Na-OEt on Different Ethylene Copolymer based Compatibilisers.

(b). PET/HDPE Blends Containing 5% Ethylene Compatibilisers.
Fig. 4.14 Viscosity vs Shear Rate at 280°C.

(a). Effect of Sodium Benzoate in Surlyn based Compatibilisers on the Viscosity of PET/HDPE Blends.

(b). Effect of Sodium Benzoate in EAA2 based Compatibiliser on the Viscosity of PET/HDPE Blends.
Fig. 4.15 Viscosity vs Shear Rate at 280°C.

(a). PET/HDPE Blends at Different Weight Ratios.

(b). PET/HDPE Blends at Different Weight Ratios Containing 5%[Surlyn/Phenoxy(50:50)+2%NaOEt] (C5).
Fig. 4.16 Effect of PET/HDPE ratio and the Compatibiliser C5 on Viscosity of PET/HDPE Blends at 280°C.

(a). Viscosities at 133 Sec-1 Shear Rate.

(b). Viscosity at 2667 Sec-1 Shear Rate.
Fig. 4.17 Viscosity vs Shear Rate at 280°C.

(a). PET and HDPE of Different Molecular Weight.

(b). PET/HDPE Blends using HDPE with Different Molecular Weight and Effect of 5% Surlyn based Compatibiliser.
Fig. 4.18 Entry Pressure vs Shear Rate: for Different Ratio of PET/HDPE Blends.

(a). PET/HDPE Blends (77.5:22.5)

(b). PET/HDPE Blends (50:50)

(c). PET/HDPE Blends (22.5:75)
2% Na-Bzt) is higher than that of PET/HDPE, PET/HDPE + 5% C$_{17}$ i.e. (EAA$_2$/phenoxy 50:50).

In Figure 4.16 is shown viscosity at 133 sec$^{-1}$ vs % HDPE in PET/HDPE blends i.e. 77.5:22.5, 50:50 and 22.5:77.5 and the effect of 5% compatibiliser C$_5$ i.e. (Surlyn/phenoxy (50:50) + 2% Na-OEt). The viscosity of the blend with a higher amount of HDPE is the highest, while for the blend with 50:50 ratio the viscosity is the lowest over all the measured shear rates, see Figure 4.15(a) and (b). A significant increase in viscosity on the other hand is noted with the addition of C$_5$ at all ratios of PET/HDPE in the blends. In Figures 4.17(a) and 4.17(b) are compared the viscosity vs shear rate curves for the different grades of HDPE used in this investigation, i.e. HDPE, (MFI = 0.3); HDPE (1), (MFI = 4.5); HDPE (2) (MFI = 28) and for corresponding PET/HDPE blends, showing in all cases the effect of the compatibilisers.

The effect of the compatibiliser Surlyn/phenoxy (50:50) + 2% Na-OEt on the PET/HDPE blends is also seen with respect to the entry pressure drop, $\Delta P_0$, as function of shear rates. An increase in entry pressure is observed on all shear rates for the PET/HDPE (75:20) and (20:75) ratios, whereas the increase in $\Delta P_0$ for the PET/HDPE (50:50) ratio is not so pronounced (see Figure 4.18(a,b,c)).

4.3 PHASE MORPHOLOGY OF BLENDS

The microstructure of the compatibilisers and the various PET/HDPE blends was studied by means of electron microscopy.
4.3.1 Scanning Electron Microscopy (SEM)

a) Phase Morphology of the Compatibilisers

Samples of compatibilisers produced on the twin screw extruder were fractured in liquid nitrogen and then observed under the scanning electron microscope. The micrographs for the various types of compatibilisers are shown in Figures 4.19 to 4.21. In Figure 4.19 is shown that there is no considerable differences in phase morphology between (a) EAA$_2$/phenoxy (50:50), and (b) Surlyn/phenoxy (50:50). However a considerable decrease in particle size is obtained with the addition of 2% Na-OEt to the Surlyn/phenoxy (50:50) blend (c) and to the EAA$_2$/phenoxy (25:75) compatibilisers (Figure 4.20). This may be due to the occurrence of grafting, or ionic interactions within the compatibiliser as by the considerable amount of residue obtained in DMF/xylene solubility tests. Ionomeric bonds could still exist in the melt state and therefore would exert a compatibilising effect similar to graft copolymers.

However the use of 2% sodium benzoate (Na-Bzt) does not show the same effect, suggesting that the Na ions are not sufficiently dissociated to produce ionic interactions between the two polymer components of the compatibiliser. In Figure 4.21 is shown the phase morphology micrographs for the EP-gMA/phenoxy compatibilisers. These demonstrate that the EP-gMA/phenoxy systems are more finely mixed at 25:75 ratio than at 50:50 ratio. However the addition of 2% Na-OEt to the EP-gMA/phenoxy (25:75) system produces a "brittle phase" morphology instead of a ductile one obtained with EP-gMA/phenoxy (25:75), which is to be expected from the occurrence of crosslinking reactions revealed by the formation of a gel in cyclohexanone/xylene solubility tests.
FIGURE 4.19: Scanning electron micrographs obtained from cryogenically fractured extruded pellets of compatibilisers: (a) EAA/phenoxy (50:50), (b) Surlyn/phenoxy (50:50), (c) Surlyn/phenoxy (50:50) + 2% Na-OEt
FIGURE 4.20: Scanning electron micrographs obtained from cryogenically fractured extruded pellets of compatibilisers: (a) EAA_{j} phenoxy (25:75), (b) EAA_{j}phenoxy (25:75) + 2% Na-OEt, (c) EAA_{j}phenoxy (25:75) + 2% Na-Bzt
b) Phase Morphology of PET Blends

The effect of phenoxy, ethylene copolymers and various compatibilisers on the microstructure of PET and HDPE separately are shown in Figures 4.22 to 4.25. Figure 4.22 shows that the addition of 5% EP-gMA/phenoxy (50:50) to PET produces a more homogeneous system than the addition of 5% EP-gMA. However the greatest level of homogeneity appears to occur for systems containing 5% Surllynpseudoxy (50:50) + 2% Na-OEt (Figure 4.23).

Figures 4.24 and 4.25 show the phase morphology of HDPE containing 25% of each of the following: Surllyn, EAA₂, EP-gMA and Surllyn/pseudoxy (50:50) + 2% Na-OEt. Both HDPE/EAA₂ and HDPE/Surllyn show a homogeneous phase morphology similar to that of HDPE. EP-gMA shows to be completely compatible in HDPE as it gives transparent plaques. On the other hand the Surllyn/pseudoxy (50:50) + 2% Na-OEt disperses into very fine particles (i.e. 0.7 μm) in HDPE, showing a reduced level of compatibility over the pure Surllyn system (see Figure 4.25).

In Figures 4.26 to 4.32 are shown phase morphology micrographs for various PET/HDPE and those containing 5% compatibiliser. A very coarse dispersed phase is obtained with PET/HDPE (77.5:22.5) blend, i.e. average particle size about 12.7 μm. However with the addition of 5% EP-gMA/pseudoxy (50:50) a drastic decrease in particle size of the dispersed phase takes place. It was noted that the (50:50) EP-gMA/pseudoxy (C₁₀) produces finer dispersed particles in PET/HDPE blend than the (50:50) Surllynpseudoxy (see Figure 4.26). In Figure 4.27 it is seen that the particle size of the dispersed phase in PET/HDPE (75:20) + 5% Surllynpseudoxy is determined by the composition of the Surllynpseudoxy compatibiliser and that the particle size is larger when larger amounts of Surllyn are present in the compatibiliser.
FIGURE 4.21: Scanning electron micrographs obtained from cryogenically fractured extruded pellets of compatibilisers: (a) EP-gMA/phenoxo (50:50), (b) EP-gMA/phenoxo (25:75), (c) EP-gMA/phenoxo (25:75) + 2% Na-OEt
FIGURE 4.22: Scanning electron micrographs obtained from cryogenically fractured extruded pellets of (a) PET and PET containing: (b) 5% phenoxy, (c) 5% EP-gMA, (d) 5% EP-gMA/phenoxy (50:50)
FIGURE 4.23: PET + 5% Surlyn/phenoxyl (50:50) + 2% Na-OEt
FIGURE 4.24: Scanning electron micrographs obtained from cryogenically fractured extruded pellets of (a) HDPE and HDPE containing: (b) 25% Surlyn, (c) 25% EAA₂, (d) 25% EP-gMA
FIGURE 4.25: HDPE + 25% Surlyn/phenox (50:50) + 2% Na-OEt
Figure 4.28 shows PET/HDPE (75:20) + 5% Surlyn/phenoxy compatibiliser produced with 2% Na-OEt at different ratios of Surlyn/phenoxy. It is found that the addition of 2% Na-OEt decreases substantially the particle size of the dispersed phase at all Surlyn/phenoxy ratios. However the addition of 5% Surlyn/phenoxy (75:25 + 2% Na-OEt) to the PET/HDPE (75:20) induces a brittle failure with fracture propagating through the dispersed particles. This has been supported by the poor mechanical properties obtained. It was noted that the dispersion behaviour of Surlyn/phenoxy in PET/HDPE (75:20) (i.e. the increase in particle size with increasing the Surlyn ratio in the compatibiliser), is observed also with Surlyn + 2% Na-OEt.

The PET/HDPE (75:20) blend with 5% EP-gMA/phenoxy compatibiliser shows a much finer dispersed phase than PET/HDPE (75:25) alone. Furthermore it was noticed that the particle size of the dispersed phase decreases with increasing the EP-gMA ratio in the compatibiliser. The addition of 5% pure EP-gMA to the PET/HDPE (75:20) shows a ductile failure of the matrix phase, (see Figure 4.29(d)) in the cryogenically broken samples, which is in accordance with the large increase in elongation at break recorded in the tensile tests. However, the addition of 5% of EP-gMA/phenoxy (25:75) + 2% Na-OEt) in PET/HDPE (75:20) produces a brittle failure of the matrix and a very coarse dispersed phase compared to the effect of the EP-gMA/phenoxy (25:75). This system was also found to result in a decrease of tensile strength, attributed to the crosslinked nature of the compatibiliser (as discussed earlier). On the other hand a very poor adhesion of dispersed phase to the matrix is obtained with PET/HDPE (75:20) + 5% EAA₂/phenoxy (25:75) showing signs of microyielding in the matrix, but with the addition of 2% Na-OEt to the EAA₂/phenoxy (25:75) compatibiliser the occurrence of brittle failure predominates, including an increase in the incidence of fractured particles, (see Figure 4.30). Different ratios of PET and HDPE were
FIGURE 4.26: Scanning electron micrographs obtained from cryogenically fractured injection moulded tensile bars of: (a) PET/HDPE (77.5:22.5) blend and PET/HDPE (75:20 blends) containing (b) 5% Surlyn/phenox (50:50), (c) 5% EP-gMA/phenox (50:50)
FIGURE 4.27: Scanning electron micrographs obtained from cryogenically fractured injection moulded tensile bars of: PET/HDPE (75:20) blends containing (a) 5% phenoxy, (b) 5% Surlyn/phenoxy (25:75), (c) 5% Surlyn/phenoxy (50:50), (d) 5% Surlyn/phenoxy (75:25), (e) 5% Surlyn
FIGURE 4.28: Scanning electron micrographs obtained from cryogenically fractured injection moulded tensile bars of: PET/HDPE (75:20) blends containing (a) 5% Surlyn/phenoxy (25:75) + 2% Na-OEt, (b) 5% Surlyn/phenoxy (50:50) + 2% Na-OEt, (c) Surlyn/phenoxy (50:50) + 2% Na-OEt extruded twice, (d) 5% Surlyn/phenoxy (75:25 + 2% Na-OEt, (e) 5% Surlyn + 2% Na-OEt
FIGURE 4.29: Scanning electron micrographs obtained from cryogenically fractured injection moulded tensile bars of PET/HDPE (75:20) blends containing: (a) 5% EP-gMA/phenoxy (25:75), (b) 5% EP-gMA/phenoxy (50:50), (c) 5% EP-gMA/ phenoxy (25:75) + 2% Na-OEt, (d) 5% EP-gMA
studied including the effects of adding 5% Surlyn/phenoxy (50:50) + 2% Na-OEt (C₃) compatibiliser. It is shown in Figure 4.31 that at higher amounts of HDPE in PET i.e. PET/HDPE (50:50) and (22.5:77.5) a coalescence of phases is likely to occur and it seems that the addition of 5% C₃ does not have a significant effect on phase morphology of these blends. In Figure 4.32 it is shown that increasing the MFI of the HDPE in the blends i.e. from 0.3 for HDPE (AB5015) to 4.5 for HDPE (1) and to 28 for HDPE (2) produces an increasingly finer dispersed phase. Once more much finer particles are obtained with the addition of 5% Surlyn/phenoxy (50:50) + 2% Na-OEt).

4.4 MECHANICAL PROPERTIES OF THE BLENDS

In this section tensile results of the PET/HDPE blends are presented. The tensile strength, modulus and elongation to break of the injection moulded and the annealed samples are shown in the following sections:

4.4.1 Tensile Strength
Typical examples of force/extension curves are shown in Figures 3.3 and 3.4 from which tensile strength and elongation at break were calculated. In all cases the elongation at yield was estimated to be in the region of 7%, hence tensile strength values quoted when elongation at break is larger than 7% represent the yield strength.

The results show that a considerable improvement in tensile strength is obtained when 5% of Surlyn/phenoxy compatibiliser (at all Surlyn/phenoxy weight ratios) is added to the PET/HDPE (75:20) blend. The largest improvement in tensile strength is achieved for both PET/HDPE + 5% Surlyn/phenoxy (25:75 + 2% Na-OEt) (C₃) and PET/HDPE + 5% Surlyn/phenoxy (50:50 + 2% Na-OEt) (C₅)
FIGURE 4.30: Scanning electron micrographs obtained from cryogenically
fractured injection moulded tensile bars of PET/HDPE (75:20) blends containing: (a) 5% EAAJphenoxy (25:75),
(b) EAAJphenoxy (25:75) + 2% Na-OEt
FIGURE 4.31: Scanning electron micrographs obtained from cryogenically fractured injection moulded tensile bars of PET/HDPE blends containing: (a) PET/HDPE (77.5:22.5), (b) PET/HDPE (50:50), (c) PET/HDPE (22.5:77.5), (d) PET/HDPE (47.5:47.5) + 5% Surlyn/phenoxy (50:50) + 2% Na-OEt, (e) PET/HDPE (20:75) + 5% Surlyn/phenoxy (50:50) + 2% Na-OEt
FIGURE 4.32: Scanning electron micrographs obtained from cryogenically fractured injection moulded tensile bars of PET/HDPE blends containing: (a) PET/HDPE (1), MFI=4.5 (77.5:22.5), (b) PET/HDPE (2), MFI=28 (77.5:22.5), (c) PET/HDPE (1) (75:20) + 5% Surlyn/phenoxy (50:50) + 2% Na-OEt, (d) PET/HDPE (2) (75:20) + 5% Surlyn/phenoxy (50:50) + 2% Na-OEt
(Figure 4.33). Furthermore the addition of 5% Surlyn + 2% Na-OEt (C₁) to the PET/HDPE blend shows also a substantial improvement in tensile strength over that containing 5% pure Surlyn (I), but not as large as that of C₃ and C₅ compatibilisers. However, 5% of Surlyn/phenoxy (75:25) + 2% Na-OEt (C₈) in PET/HDPE shows a decrease in tensile strength compared to all the other Surlyn compatibilisers. It is important to note, however, that a small decrease in tensile strength is observed also with the addition of 5% Surlyn/phenoxy + (50:50 2% Na-OEt) extruded twice (C₅*) to the PET/HDPE (Tₛ = 41 MPa) compared to that containing 5% (50:50 Surlyn/phenoxy + 2% Na-OEt) (C₅) (Tₛ = 47 MPa), despite the larger melt viscosity displayed by the former (C₅*). Furthermore a greater extent of interactions taking place when C₅ was extruded for a second time, as confirmed by measurements of gel contents of the two compatibilisers. The gel contents of C₅ and C₅* in DMF/xylene solvent were found to be 17.5 and 30.45% respectively whereas in cyclohexanone/xylene solvent the gel content values were 7.62% and 10% respectively. It is difficult to explain this behaviour, but it is possible that it may be related to the greater associations of the polymer molecules criteria of the compatibilisers which may have the same effect as if the two polymers were crosslinked. All the annealed samples of PET/HDPE (77.5:22.5) blends show a substantial increase in tensile strength (16-20%) but the largest increase occurs also with the most efficient compatibilisers with respect to particle size reduction i.e. C₃ and C₅ (see Figure 4.34).

In Figure 4.35 is shown the tensile strength of PET/HDPE with 5% EP-gMA/phenoxy compatibilisers at different weight ratios of EP-gMA in the compatibiliser. The tensile strength of these blends is seen to decrease with increasing the weight ratio of the EP-gMA component in the compatibilisers. This could be associated with the presence of flexible chains of the EP-gMA in
Fig. 4.33 Tensile Strength of PET/HDPE (75:20) Blends Containing 5% Surlyn/Phenoxy Compatibilisers.
Fig. 4.34. Tensile Strength of PET/HDPE (75:20) and Effect of Annealing

(a) Containing 5% Surlyn/Phenoxy Compatibilisers.

(b) Containing 5% Surlyn/Phenoxy+2%NaOEt Compatibilisers
the PET/HDPE blends. The addition of 5% EP-gMa/phenoxy (25:75) with 2% Na-OEt to the PET/HDPE blend shows a substantial drop in tensile strength (33.9 MPa) compared to that containing 5% EP-gMa/phenoxy (25:75) (37.8 MPa) (see Figure 4.36). However all the annealed samples of PET/HDPE (75:20) containing 5% EP-gMa/phenoxy compatibiliser show an increase of ca. 30 to 35% in tensile strength, confirming that crystallisation rate is reduced in PET/HDPE blends in the presence of EP-gMa/phenoxy compatibiliser, and that the addition of Na-OEt does not alter this behaviour. Figure 4.37 shows the tensile strength of PET/HDPE containing 5% EAA₂/phenoxy compatibilisers and the effect of using 2% Sodium Benzoate (Na-Bzt) in comparison with PET/HDPE (77.5:22.5) uncompatibilised blends. It is noted that only a slight improvement in tensile strength is achieved with the addition of 5% EAA₂/phenoxy compatibilisers (i.e. without the use of a catalyst) at all the weight ratios of EAA₂. The effect of using Na-Bzt as catalyst is also negligible. Higher tensile strength is obtained on the other hand with 5% EAA₂/phenoxy (25:75 + 2% Na-OEt) but the improvement is lower than that obtained with 5% Surlyn/phenoxy (25:75 + 2% Na-OEt), see Figure 4.36. Figure 4.38 shows tensile strength in function of varying amounts of HDPE and effect of adding the compatibiliser C₅ (i.e. 50:50 Surlyn/phenoxy + 2% Na-OEt). As expected, the tensile strength of the PET/HDPE blend decreases as the amount of HDPE increases. Furthermore it is observed that the efficiency of the C₅ compatibiliser decreases with the increase of HDPE ratio in the PET/HDPE blends. In Table 4.9 are presented results of tensile strength of PET/HDPE (77.5:22.5) for different grades of HDPE, showing that a slight increase in tensile strength of PET/HDPE (77.5:22.5) blends is obtained with increasing the MFI of HDPE. Moreover the addition of 5% [50:50 Surlyn/phenoxy + 2% Na-OEt] (C₅) to different PET/HDPE blends results in an appreciable improvement in tensile strength for all grades of HDPE, but the largest improvement in tensile strength is
Fig. 4.36 Comparison of Different Ethylene Copolymers Used in Compatibilising PET/HDPE(75:20) Blends.

1. PET/HDPE
2. PET/HDPE+5%[Surlyn/Phenoxy(25:75)]
3. PET/HDPE+5%[EP-gMA/Phenoxy(25:75)]
4. PET/HDPE+5%[EAA2/Phenoxy(25:75)]
Fig. 4.35  Tensile Strength of PET/HDPE(75:20) Blends Containing 5% EP-gMA/Phenoxy Compatibilisers.
Fig. 4.37  Tensile Strength of PET/HDPE(75:20) Blends
Containing 5\% EAA2/Phenoxy Compatibilisers.
Fig. 4.38 Tensile Strength of PET/HDPE Blends Containing Various Amount of HDPE and Effect of Compatibiliser (C5).
achieved for PET/HDPE (AB5015, MFI = 0.3) blend (see Table 4.9). The annealed samples, on the other hand, show the largest tensile strength for both PET/HDPE blends containing higher MFI grades of HDPE (i.e. MFI = 4.5 and 28). However the same level of improvement in tensile strength is obtained for all grades of HDPE with the addition of 5% (50:50 Surlyn/phenoxy + 2% Na-OEt) (C₅) to PET/HDPE (75:20) blends.

**TABLE 4.9: TENSILE STRENGTH OF PET/HDPE (77.5:22.5) FOR DIFFERENT HDPE GRADES AND EFFECT OF 5% COMPATIBILISER (C₅)**

<table>
<thead>
<tr>
<th>Blends</th>
<th>(MFI) of HDPE</th>
<th>Tensile Strength (MPa)</th>
<th>Non-Annealed Samples</th>
<th>Annealed Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/HDPE</td>
<td>0.3</td>
<td>32.64</td>
<td>37.82</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C₅</td>
<td>0.3</td>
<td>46.83</td>
<td>56.69</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE</td>
<td>4.5</td>
<td>33.20</td>
<td>44.38</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C₅</td>
<td>4.5</td>
<td>43.02</td>
<td>54.31</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE</td>
<td>28.0</td>
<td>35.44</td>
<td>48.86</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C₅</td>
<td>28.0</td>
<td>44.22</td>
<td>54.69</td>
<td></td>
</tr>
</tbody>
</table>

C₅ = 50 Surlyn/phenoxy (50:50) + 2% Na-OEt

4.4.2 Youngs Modulus

A very consistent behaviour of the modulus is recorded for blends of PET/HDPE with various compatibilisers (i.e. using various ethylene copolymers/phenoxy). The results show a decrease in Young's modulus with increasing the amount of the ethylene copolymer in the compatibilisers. However an increase in Young's modulus is obtained when 2% Na-OEt is added to ethylene copolymer/phenoxy compatibilisers, (see Figures 4.39 and 4.40).
4.4.3 Elongation to Break

The brittle behaviour of the PET/HDPE (77.5:22.5) blend is transformed to ductile behaviour with the addition of 5% compatibilisers e.g. (25:75 Surlyn/phenoxy + 2% Na-OEt) (C_3), (50:50 Surlyn/phenoxy + 2% Na-OEt) (C_5) and EP-gMA, (see Figures 4.41, 4.42 and 4.43), giving a ca. 300% increase in elongation at break with the addition of 5% C_3 and C_5 to the blend and a ca. 500% increase with 5% EP-gMA. It has to be noted that the addition of 5% (50:50 Surlyn/phenoxy + 2% Na-OEt extruded twice) (C_5*) to the PET/HDPE blend does not show any considerable improvement in elongation at break (see Figure 4.43). The addition of 5% 25:75 EP-gMA/phenoxy with 2% Na-OEt (C_12) to the blend shows no difference in elongation at break to the corresponding compatibiliser without Na-OEt. The EAA_2/phenoxy (with and without Na-OEt or Na-Bzt) compatibilisers do not show any considerable effect on elongation at break of PET/HDPE blends. Annealed PET/HDPE (77.5:22.5) shows an increase in elongation at break. However with the addition of 5% (Surlyn/phenoxy + 2% Na-OEt) and (EP-gMA/phenoxy) compatibilisers a decrease in elongation at break is predominating, after annealing (see Figures 4.42 and 4.43. Table 4.10 shows the elongation at break of PET/HDPE blends at different ratios and the effects of various compatibilisers, i.e. Surlyn (I), (50:50 Surlyn/phenoxy + 2% Na-OEt) (C_3) (which are also shown in Figure 4.44) and (50:50 EP-gMA/phenoxy (C_10). The elongation at break of PET/HDPE blends is not much different for all concentrations of HDPE; while a 5% addition of both C_5 and C_10 compatibilisers to PET//HDPE (20:75) shows a very large increase in elongation at break in all cases. The addition of 5% Surlyn (I) to the PET/HDPE (20:75) however also provides a considerable improvement in elongation at break over that of uncompatibilised PET/HDPE (25:75).
**Fig. 4.39** Young's Modulus of PET/HDPE (75:20) Containing 5% Surlyn/Phenoxy Compatibilisers.

1- PET/HDPE
2- PET/HDPE + 5%[Surlyn/Phenoxy (25:75)]
3- PET/HDPE + 5%[Surlyn/Phenoxy (50:50)]
4- PET/HDPE + 5%[Surlyn/Phenoxy (75:25)]
Fig. 4.40 Young's Modulus of PET/HDPE (75:20) Containing 5% EP-gMA/Phenoxy Compatibilisers.

1- PET/HDPE
2- PET/HDPE + 5% [EP-gMA/Phenoxy (25:75)]
3- PET/HDPE + 5% [EP-gMA/Phenoxy (25:75) + 2% NaOEt]
4- PET/HDPE + 5% [EP-gMA/Phenoxy (50:50)]
5- PET/HDPE + 5% EP-gMA
Fig. 4.41 Elongation to Break of PET/HDPE(75:20) Blends Containing 5% Surlyn/Phenoxy Compatibilisers.
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Fig. 4.42 Elongation to Break of PET/HDPE(75:20) Blends Containing 5% EP-gMA/Phenoxy Compatibilisers.

Elongation to Break (%) vs %EPgMA

- Non-annealed
- Annealed
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Fig. 4.43 Elongation to Break of PET/HDPE (75:20) and Effect of Annealing

(a) Containing 5% Surlyn/Phenoxy Compatibilisers.

(b) Containing 5% Surlyn/Phenoxy+2%NaOEt Compatibilisers.
Fig. 4.44 Elongation at Break of PET/HDPE Blends Containing Various Amount of HDPE and Effect of Compatibiliser (C5).
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It is important to note that the above results were obtained from amorphous samples i.e. moulded at 5°C mould temperature. When the samples of PET/HDPE (25:75) blends are subsequently annealed they show a considerable decrease in elongation at break, especially those with 5% compatibilisers, see Table 4.11. It has to be noted however that even with the decrease in elongation at break after annealing the overall improvement is still very large compared to the PET/HDPE (20:75) without compatibilisers.

<table>
<thead>
<tr>
<th>Blends</th>
<th>Elongation at break (%)</th>
<th>Non-Annealed Samples</th>
<th>Annealed Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET</td>
<td>49.66</td>
<td>7.32</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE (77.5:22.5)</td>
<td>4.68</td>
<td>9.78</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + (I)</td>
<td>5.87</td>
<td>5.66</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_5</td>
<td>17.68</td>
<td>10.76</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_{10}</td>
<td>9.91</td>
<td>9.84</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + EP</td>
<td>13.1</td>
<td>28.5</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE (50:50)</td>
<td>4.81</td>
<td>4.81</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_5</td>
<td>7.42</td>
<td>6.41</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE (22.5:775)</td>
<td>9.61</td>
<td>8.59</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + (I)</td>
<td>27.25</td>
<td>16.72</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_{5}</td>
<td>306.45</td>
<td>88.65</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_{10}</td>
<td>249.06</td>
<td>88.65</td>
<td></td>
</tr>
</tbody>
</table>

(I) Surlyn (Ionomer); C_5 Surlyn/phenoxy (50:50) + 2% Na-OEt; C_{10} EP-gMA/phenoxy 50:50.
In Table 4.11 the results show that the elongation at break of PET/HDPE (77.5:22.5) increases substantially with increasing the MFI of the HDPE component. Moreover it has to be noted that both compatibilised PET/HDPE blends containing HDPE with MFI of 4.5 and 28, exhibit cold drawing. On the other hand, the addition of 5% (50:50 Surlyn/phenoxy + 2% Na-OEt) \((C_5)\) increases the elongation at break only for blends containing HDPE of MFI = 0.3, but decreases the elongation for blends containing HDPE with MFI of 4.5 and 28 by suppressing the cold drawing phenomenon. It has been noted annealing causes a decrease in elongation at break of PET/HDPE blends containing compatibilisers, bringing all the different PET/HDPE samples, irrespective of whether they contain compatibilisers or not, to the same level of elongation at break, by suppressing; the occurrence of cold drawing (Table 4.11).

**Table 4.11: Elongation at Break of PET/HDPE (77.5:22.5) for Different HDPE Grades and Effect of 5% Compatibiliser \((C_5)\)**

<table>
<thead>
<tr>
<th>Blends</th>
<th>MFI of HDPE</th>
<th>Elongation at Break (%)</th>
<th>Non-Annealed Samples</th>
<th>Annealed Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>PET/HDPE</td>
<td>0.3</td>
<td>4.68</td>
<td>9.78</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_5</td>
<td>0.3</td>
<td>17.68</td>
<td>10.76</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE</td>
<td>4.5</td>
<td>13.50</td>
<td>7.78</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_5</td>
<td>4.5</td>
<td>11.95</td>
<td>8.18</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE</td>
<td>28.0</td>
<td>27.81</td>
<td>8.18</td>
<td></td>
</tr>
<tr>
<td>PET/HDPE + C_5</td>
<td>28.0</td>
<td>11.22</td>
<td>7.61</td>
<td></td>
</tr>
</tbody>
</table>

\(C_5 = (\text{Surlyn/phenoxy (50:50) + 2\% Na-OEt})\)
4.5 DIFFERENTIAL SCANNING CALORIMETRY

In this section the DSC results are presented for the various compatibilisers and PET/HDPE blends.

4.5.1 Thermal Analysis of the Compatibilisers

It is clear from the results obtained that the addition of sodium ethoxide to the compatibilisers affects the thermal behaviour of the components. For example, the addition of 2% and 4% Na-OEt to the phenoxy component alone shows an increase in its transition temperature (Tg) (see Table 4.12). Also the addition of the same amount of Na-OEt to Surlyn reduces significantly its heat of fusion (ΔHm), the heat of recrystallisation (ΔHc) and temperature of recrystallisation (Tc). The addition of sodium ethoxide to the phenoxy/Surlyn compatibiliser mixture induces a considerable depression in the melting point and recrystallisation temperature of the Surlyn phase, specially when 4% of Na-OEt is added. This is accompanied by a significant reduction in heat of fusion (ΔHm) and heat of recrystallisation (ΔHc), as a result of the reduction in the level of crystallinity and crystallisation rate (see Table 4.12). The addition of sodium ethoxide to phenoxy/EAA₂ and phenoxy/EP-gMA shows also a significant effect on thermal properties of the EAA₂ and EP-gMA phases (see Table 4.13). The presence of 50% phenoxy in the EP-gMA based compatibiliser induces a decrease in crystallinity of the EP-gMA, indicated by the reduction in heat of fusion and heat of crystallisation. Also the presence of higher portions of phenoxy in the phenoxy/Surlyn and phenoxy/EP-gMA i.e. at 75:25 ratio, masks the melting point and heat of fusion of the two copolymers since the melting peak of the ethylene copolymer coincides with the Tg of the phenoxy. However, the melting peak of both ethylene copolymers becomes clearly detectable with the addition of 2% Na-OEt in phenoxy/Surlyn and phenoxy/EP-gMA at 75:25 ratio. This might
be due to the increase in Tg of the phenoxy so that it no longer coincides with the melting peak of the copolymers, (see Tables 4.12 and 4.13).

4.5.2 Thermal Analysis of Various PET Blends

The results obtained from DSC show that the exothermic peak of the PET cold crystallisation occurs close to the endothermic melting of HDPE (see DSC thermogram in Appendix A). This makes it impossible, therefore, to quantify cold crystallisation phenomena of the PET phase in the various blends. To study the effect of the compatibilisers on the PET thermal properties, the onset temperature ($T_{se}$) of cold crystallisation, and the heat of fusion ($\Delta H_m$) on heating; the crystallisation temperature ($T_c$) and heat of crystallisation ($\Delta H_c$) on cooling are compared. The results indicate that for all the blends examined PET has not attained its maximum degree of crystallinity in the moulding process, as it undergoes further cold crystallisation on heating. The results show that the presence of Surlyn in PET/HDPE 75:20 blend increases the crystallisation rate of the PET. When 5% Surlyn is added to this blend the onset temperature of the cold crystallisation decreases by almost 4°C, while the recrystallisation temperature ($T_r$) increases. The addition of 2% Na-OEt to Surlyn increases the crystallisation rate even further, with the onset temperature of the cold crystallisation ($T_{se}$) being reduced from 110°C to 99.9°C. The same behaviour is also observed with the addition of the compatibiliser based on phenoxy/Surlyn + 2% Na-OEt to the PET/HDPE at different weight ratios and based on various grades of HDPE, (see Figures 4.45 and Table 4.14). When HDPE is the major phase in the PET/HDPE blend the PET peaks are not clearly detectable especially with the addition of the compatibiliser Surlyn/phenoxy (50:50) + 2% Na-OEt ($C_2$). Tables 4.15 and 4.16 show the effects of compatibilisers on PET and HDPE individually. The DSC traces for HDPE containing 25% EAA$_2$, EP-g-MA and phenoxy/Surlyn (50:50) + 2% Na-OEt ($C_2$) respectively, show one melting
Fig. 4.45 Onset Crystallisation Temperature ($T_{sc}$) for the PET Phase as Function of Surlyn Content.

![Graph showing the relationship between %Surlyn and $T_{sc}$ with and without Na-OEt.](image)

- Without Na-OEt
- With Na-OEt
### TABLE 4.12: DSC DATA OF VARIOUS COMPATIBILISERS BASED ON SURLYN/PHENOXY

<table>
<thead>
<tr>
<th>Compatibilisers</th>
<th>Surlyn Component</th>
<th>Phenoxo</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Tm(°C)</td>
<td>Tc(°C)</td>
</tr>
<tr>
<td>Surlyn</td>
<td>99.85</td>
<td>59.99</td>
</tr>
<tr>
<td>Surlyn + 2% Na-OEt</td>
<td>101.86</td>
<td>59.4</td>
</tr>
<tr>
<td>Surlyn + 4% Na-OEt</td>
<td>97.97</td>
<td>48.73</td>
</tr>
<tr>
<td>Phenoxy</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phenoxy + 2% Na-OEt</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Phenoxy + 4% Na-OEt</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50)</td>
<td>101.05</td>
<td>63.34</td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 2% Na-OEt</td>
<td>96.27</td>
<td>59.8</td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 2% Na-OEt*</td>
<td>95.68</td>
<td>58.81</td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 4% Na-OEt</td>
<td>93.09</td>
<td>44.16</td>
</tr>
<tr>
<td>Surlyn/phenoxy (50:50) + 2% Na-OEt</td>
<td>100.79</td>
<td>68.32</td>
</tr>
<tr>
<td>Surlyn/phenoxy (75:25) + 2% Na-OEt</td>
<td>101.21</td>
<td>60.03</td>
</tr>
<tr>
<td>Surlyn/phenoxy (75:25) + 2% Na-OEt</td>
<td>101.21</td>
<td>54.81</td>
</tr>
<tr>
<td>Surlyn/phenoxy (25:75) + 2% Na-OEt</td>
<td>-</td>
<td>65.01</td>
</tr>
<tr>
<td>Surlyn/phenoxy (25:75) + 2% Na-OEt</td>
<td>96.3</td>
<td>60.11</td>
</tr>
</tbody>
</table>

* The compatibiliser has been extruded twice

All the heat of fusion (ΔH<sub>m</sub>) and heat of crystallisation (ΔH<sub>c</sub>) have been normalised
<table>
<thead>
<tr>
<th>Compatibilisers</th>
<th>Tm(°C)</th>
<th>Te(°C)</th>
<th>( \Delta H_m ) (cal/g)</th>
<th>( \Delta H_c ) (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EAA₂</td>
<td>103.47</td>
<td>76.14</td>
<td>21.68</td>
<td>21.33</td>
</tr>
<tr>
<td>EAA₂/phenoxy (25:75)</td>
<td>104.89</td>
<td>75.92</td>
<td>14.16</td>
<td>10.52</td>
</tr>
<tr>
<td>EAA₂/phenoxy (25:75) + 2% Na-OEt</td>
<td>100.86</td>
<td>66.87</td>
<td>9.55</td>
<td>13.87</td>
</tr>
<tr>
<td>EPg-MA</td>
<td>62.24</td>
<td>33.63</td>
<td>10.06</td>
<td>6.33</td>
</tr>
<tr>
<td>EPg-MA/phenoxy (25:75)</td>
<td>-</td>
<td>44.85</td>
<td>-</td>
<td>4.12</td>
</tr>
<tr>
<td>EPg-MA/phenoxy (25:75) + 2% Na-OEt</td>
<td>61.76</td>
<td>44.3</td>
<td>3.12</td>
<td>2.94</td>
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<tr>
<td>EPg-MA/phenoxy (50:50)</td>
<td>63.3</td>
<td>37.4</td>
<td>4.9</td>
<td>4.16</td>
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</tbody>
</table>

*Are these unusual?*
<table>
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<tr>
<th>Blends</th>
<th>HDPE Phase</th>
<th>PET Phase</th>
<th>PET Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tm(°C)</td>
<td>Tc(°C)</td>
<td>$\Delta H_c$(cal/g)</td>
</tr>
<tr>
<td>PET + Talc</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heating</td>
<td>131.6</td>
<td>110.2</td>
<td>253.9</td>
</tr>
<tr>
<td>Cooling</td>
<td>-</td>
<td>116.7</td>
<td>38.67</td>
</tr>
<tr>
<td>HDPE</td>
<td>133.7</td>
<td>114.1</td>
<td>42.3</td>
</tr>
<tr>
<td>Heating</td>
<td>-</td>
<td>116.7</td>
<td>38.67</td>
</tr>
<tr>
<td>Cooling</td>
<td>-</td>
<td>116.7</td>
<td>38.67</td>
</tr>
<tr>
<td>PET/HDPE (77.5:22.5)</td>
<td>131.1</td>
<td>106.7</td>
<td>252.9</td>
</tr>
<tr>
<td>Heating</td>
<td>-</td>
<td>115.7</td>
<td>34.5</td>
</tr>
<tr>
<td>Cooling</td>
<td>-</td>
<td>117.0</td>
<td>37.0</td>
</tr>
<tr>
<td>PET/HDPE+C_1</td>
<td>130.5</td>
<td>99.9</td>
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<td>117.0</td>
<td>37.0</td>
</tr>
<tr>
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<td>-</td>
<td>116.4</td>
<td>39.5</td>
</tr>
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</tr>
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<td>-</td>
<td>116.4</td>
<td>39.5</td>
</tr>
<tr>
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<td>-</td>
<td>116.4</td>
<td>37.0</td>
</tr>
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<td>PET/HDPE+C_3</td>
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<td>104.0</td>
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<td>-</td>
<td>116.4</td>
<td>37.0</td>
</tr>
<tr>
<td>Cooling</td>
<td>-</td>
<td>116.4</td>
<td>37.0</td>
</tr>
<tr>
<td>Blends</td>
<td>HDPE Phase</td>
<td>PET Phase</td>
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<tr>
<td></td>
<td>Tm(°C)</td>
<td>Tc(°C)</td>
<td>ΔH_v(cal/g)</td>
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<tr>
<td>PET/HDPE+C_4</td>
<td>130.9</td>
<td>-</td>
<td>33.0</td>
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<td>116.1</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td></td>
<td></td>
<td>116.1</td>
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<td>130.8</td>
<td>-</td>
<td>38.5</td>
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<tr>
<td>Heating</td>
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<td>115.7</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td></td>
<td></td>
<td>115.7</td>
</tr>
<tr>
<td>PET/HDPE+C_5*</td>
<td>130.3</td>
<td>-</td>
<td>30.5</td>
</tr>
<tr>
<td>Heating</td>
<td></td>
<td>117.1</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
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<td></td>
<td>117.1</td>
</tr>
<tr>
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<td>16.5</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
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<td></td>
<td>16.5</td>
</tr>
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<td>-130.5</td>
<td>-</td>
<td>36.0</td>
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<td></td>
</tr>
<tr>
<td>Cooling</td>
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<td></td>
<td>117.4</td>
</tr>
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<td>-</td>
<td>39</td>
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<tr>
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<td></td>
<td>117.4</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
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<td></td>
<td>117.4</td>
</tr>
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<td>PET/HDPE+C_12</td>
<td>131.3</td>
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<td>39.5</td>
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<td>116.2</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td></td>
<td></td>
<td>116.2</td>
</tr>
<tr>
<td>PET/HDPE+Ph</td>
<td>130.6</td>
<td>-</td>
<td>36.5</td>
</tr>
<tr>
<td>Heating</td>
<td></td>
<td>115.6</td>
<td></td>
</tr>
<tr>
<td>Cooling</td>
<td></td>
<td></td>
<td>115.6</td>
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TABLE 4.15: EFFECT OF VARIOUS COMPONENTS OF THE COMPATIBILISERS ON THE CRYSTALLINITY AND CRYSTALLISATION CHARACTERISTICS OF PET

<table>
<thead>
<tr>
<th>Blends</th>
<th>Tm(°C)</th>
<th>Tc(°C)</th>
<th>$\Delta H_m$ (cal/g)</th>
<th>$\Delta H_c$ (cal/g)</th>
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<tbody>
<tr>
<td>PET Heating</td>
<td>255.6</td>
<td>120.9</td>
<td>11.14</td>
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<tr>
<td>PET Heating</td>
<td>-</td>
<td>206.0</td>
<td>-</td>
<td>10.85</td>
</tr>
<tr>
<td>PET+5% Ph Heating</td>
<td>251.5</td>
<td>127.9</td>
<td>9.37</td>
<td>5.9</td>
</tr>
<tr>
<td>PET+5% Ph Cooling</td>
<td>-</td>
<td>205.9</td>
<td>-</td>
<td>8.95</td>
</tr>
<tr>
<td>PET+5% EPg-MA Heating</td>
<td>253.4</td>
<td>125.0</td>
<td>8.74</td>
<td>5.6</td>
</tr>
<tr>
<td>PET+5% EPg-MA Cooling</td>
<td>-</td>
<td>199.7</td>
<td>-</td>
<td>8.6</td>
</tr>
<tr>
<td>PET+5% C_{10} Heating</td>
<td>251.0</td>
<td>128.8</td>
<td>9.9</td>
<td>6.95</td>
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<tr>
<td>PET+5% C_{10} Cooling</td>
<td>-</td>
<td>203.5</td>
<td>-</td>
<td>9.2</td>
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<tr>
<td>PET+5% C_{5} Heating</td>
<td>250.7</td>
<td>113.9</td>
<td>8.95</td>
<td>5.4</td>
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<tr>
<td>PET+5% C_{5} Cooling</td>
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<td>208.5</td>
<td>-</td>
<td>9.05</td>
</tr>
<tr>
<td>Blends</td>
<td>Tm(°C)</td>
<td>Tc(°C)</td>
<td>$\Delta H_\text{m}$ (cal/g)</td>
<td>$\Delta H_\text{c}$ (cal/g)</td>
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</tr>
<tr>
<td>HDPE</td>
<td></td>
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</tr>
<tr>
<td>Heating</td>
<td>133.7</td>
<td>-</td>
<td>43.0</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>-</td>
<td>114.1</td>
<td>-</td>
<td>42.3</td>
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<td>HDPE+25% Surlyn</td>
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<tr>
<td>Heating</td>
<td>133.2</td>
<td>-</td>
<td>34.93</td>
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</tr>
<tr>
<td></td>
<td>97.04</td>
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<td>70.93</td>
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<tr>
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<tr>
<td>Cooling</td>
<td>-</td>
<td>115.9</td>
<td>-</td>
<td>38.8</td>
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<td>HDPE+25% EAA$_2$</td>
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<tr>
<td>Heating</td>
<td>134.3</td>
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<td>41.06</td>
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<tr>
<td>Cooling</td>
<td>-</td>
<td>114.1</td>
<td>-</td>
<td>42.27</td>
</tr>
<tr>
<td>HDPE+25% C$_5$</td>
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<td></td>
</tr>
<tr>
<td>Heating</td>
<td>135</td>
<td>-</td>
<td>39.6</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>-</td>
<td>114.3</td>
<td>-</td>
<td>41.73</td>
</tr>
</tbody>
</table>

128
peak, corresponding to that of HDPE. However the addition of 25% Surlyn shows two melting points one at 97.04°C corresponding to the Surlyn phase, the other at 133.2°C corresponding to the HDPE. Furthermore the addition of Surlyn to the HDPE induces a reduction in level of crystallinity, shown by the reduction in heat of fusion ($\Delta H_m$) and heat of crystallisation ($\Delta H_c$) (see Table 4.16). It is observed that the addition of phenoxy to the PET shows a considerable increase in the crystallisation temperature ($T_c$) on heating as a result of reduction in crystallisation rate. This behaviour is seen also with the addition of EP-gMA and phenoxy/EP-gMA (50:50), both showing a reduction in crystallisation temperature of PET (see Table 4.15). On cooling the PET containing 5% EP-gMA shows a decrease in recrystallisation temperature ($T_r$), indicating the slow crystallisation of the PET in the presence of EP-gMA.
5.1 CHEMICAL CHARACTERISATION OF COMPATIBILISERS

5.1.1 Solubility Tests

The expected esterification reactions between phenoxy and ethylene copolymers with acrylic acid as a comonomer, EAA₁, or EAA₂ has not been ascertained neither for samples prepared in the Brabender nor in the twin screw extruder. However the addition of small amounts of sodium ethoxide produced an appreciable amount of residue in sequential reflux extraction (DMF followed by xylene) and liquid extraction in mixed solvents DMF/xylene (1:1) (see Results section 4.1). The phenoxy/EAA₁ and phenoxy/EAA₂ mixtures containing sodium ethoxide were completely dissolved, however, by liquid extraction in mixed solvents (1:1) cyclohexanone/xylene, showing that no crosslinking has taken place.
The criterion used for the solubility tests was that the occurrence of a residue from the sequential reflux extraction and liquid extraction in DMF/xylene was taken to indicate the possible formation of graft copolymer, while a residue after boiling in the (1:1) cyclohexanone/xylene mixture was taken to indicate the formation of a crosslinked polymer structure. The use of a terpolymer of ethylene, methyl acrylate and partially neutralised acrylic acid (Surlyn A) Ionomer and of the ethylene-ethylacrylate maleic anhydride (E-MA) in mixtures with phenoxy has shown a similar behaviour to the ethylene acrylic acid copolymer EAA\textsubscript{1}, and the ethylene, t-butyl acrylate, acrylic acid terpolymer EAA\textsubscript{2}. However, the use of the ethylene propylene copolymer, grafted with maleic anhydride (EP-gMA) has shown a formation of graft copolymer in amounts which increased with the increase of EP-gMA ratio in the EP-gMA/phenoxy blends. Furthermore the addition of sodium ethoxide to the EP-gMA/phenoxy blends resulted in the formation of a crosslinked polymer structure. These results have shown the importance of the accessibility of the reactive groups attached to the polymer, which makes one polymer more reactive than another (i.e. compare results on E-MA with EP-gMA). The studies on the use of various types of sodium compounds as possible catalysts for the various ethylene copolymers and phenoxy mixtures have revealed that sodium compounds with strong base character i.e. Na-OEt, when added to the phenoxy-ethylene copolymer produce the highest residue in DMF/xylene (1:1) solvent. A lower residue amounts being obtained with the salt of weak base, i.e. sodium, benzoate, while the lowest amounts of residue being obtained with the neutral sodium p-toluene sulfonate (Na-P-TS) and in the absence of sodium compounds (see Table 4.5). The formation of grafts and crosslinks was found not to depend on the processing method used, i.e. the Brabender or twin screw extruder. This is somewhat at variance with some work in the literature claiming that the use of high shear action can be effective in producing graft copolymer [113].
work the nature of polymers used and type of catalysts seem to be more important than processing method for the production of suitable graft copolymers to be used as compatibilisers for the PET/HDPE blends, although the second extrusion pass for the Surlyn based compatibilisers has shown to induce further changes.

5.1.2 Fourier Transform Infrared (FTIR) Characterisation

The results obtained have shown that mixtures of ethylene copolymers, EAA₂, Surlyn and EP-gMA with phenoxy produces spectra corresponding to the direct combination of the individual spectra of the two components. The EAA₂/phenoxy (50:50) mixture containing 2% Na-OEt showed the formation of sodium carboxylates, which in turn have been clearly identified also with the addition of 2% Na-OEt to the EAA₂ alone. However, no chemical interaction, such as hydrogen bonding or formation of esters have been detected between EAA₂ and phenoxy even in the presence of Na-OEt. The Surlyn/phenoxy 50:50 containing 2% Na-OEt has also shown an increase in the area of the sodium carboxylate peak, but no evidence of H-bond interactions or ester formation was apparent.

5.2 Rheological Characterisation

5.2.1 Compatibilisers

Viscosity measurements on the various compatibilisers based on ethylene copolymer/phenoxy mixtures were used to investigate further the possible interaction between the components of the compatibilisers. Both the compatibilisers prepared in the Brabender and the twin screw extruder have shown that the addition of sodium ethoxide increases the viscosity of the mixtures EAA₂/phenoxy, EP-gMA/phenoxy and Surlyn/phenoxy at all shear
rates. The fact that the viscosity increased is an indication that there are possible stronger interactions at the interface of the two polymers when sodium ethoxide is added to the mixture [120], see Figures 4.5, 4.6, 4.7 and 4.10(a).

Martuscelli et al [121] have prepared blends of maleic anhydride grafted ethylene propylene rubber (EPR) with dimethylamino maleimide-grafted EPR by solution blending. At low grafting levels, they obtained FTIR spectra superimposable with the sum of the components, but also observed an increase in the solution viscosity. They concluded that only strong polar interactions between anhydride and dimethylamino groups occur. They also found that such interactions are effective in enhancing the compatibility in a melt blend of dimethyl maleimide grafted polyethylene with styrene-maleic anhydride (S-MA) [122]. This is in agreement with the results of this study which show that while there is no real evidence of chemical reactions between the compatibilisers components, i.e. ethylene acrylic acid copolymer and phenoxy in the presence of sodium ethoxide, an increase in viscosity is clearly observed with the addition of sodium ethoxide and that such mixtures have shown to be effective in compatibilising blends of PET with HDPE (see Sections 5.3 and 5.4). The EP-gMA/phenoxy mixture 50:50 containing 2% sodium ethoxide shows a positive deviation in viscosity at 180°C (see Figure 4.6). According to the literature [89], the positive deviation in viscosity generally occurs when there are strong interactions. This is in agreement with the solubility results showing that the EP-gMA/phenoxy containing 2% sodium ethoxide form a crosslinked polymer structure. Furthermore it has been observed that the addition of 2% sodium ethoxide to the EP-gMA/phenoxy mixture with high ratio of EP-gMA i.e. (75:25) produces a decrease in viscosity compared to mixtures at lower ratios i.e. 25:75 and 50:50, of EP-gMA/phenoxy (see Figure 4.7). This might be attributed to excessive crosslinking reactions.
It has been proved that such crosslinking reactions in mixtures of EP-gMA/phenoxy containing 2% sodium ethoxide are not effective in enhancing the compatibility of blends of PET and HDPE. On the other hand, the effect of processing history has been shown by mixing twice the (50:50) Surlyn/phenoxy + 2% Na-OEt compatibiliser in the twin screw extruder. The re-extruded mixtures show a further increase in viscosity, which means further interactions have taken place (see Figure 4.10(a)), while the solubility tests in cyclohexanone/xyylene confirmed the absence of crosslinks.

5.2.2 PET/Polyolefins Blends

At all shear rates, the viscosity of PET/HDPE blends show a negative deviation from the simple additivity rule, which is characteristic of incompatibility [123,124] but the blend retains the same shear rate dependence as the PET component in isolation (see Figure 4.8). The viscosity as a function of composition at two different shear rates of PET/HDPE blend shows negative deviation for all three compositions tested (see Figure 4.16). It is also noted that the negative deviation becomes greater as the shear rate increases and results in a shallow viscosity minimum at high shear rate. A similar behaviour has also been reported for other blends [125] and has been associated with the elongation of the droplet phase along the flow direction during capillary flow at high shear rates. In agreement with the above findings, the results of this work show that viscosity at high shear rate (2667 sec⁻¹) displays a maximum negative deviation from the additive rule at the 50:50 ratio of the two components (HDPE and PET) (see Figure 4.16(b)).

The addition of 5% compatibiliser, i.e. Surlyn/phenoxy, EP-gMA/phenoxy and EAA₂/phenoxy, to the PET/HDPE blend shows an increase in viscosity, especially at low shear rates where the dispersed particles are subjected only to
small deformations and the viscosity is primarily determined by the size of the dispersed particles and not their geometry during flow [125,126,127]. At low shear rate (i.e. about 100 sec\(^{-1}\)) the addition of compatibiliser C\(_5\), i.e. 50:50 Surlyn/phenoxy + 2\% Na-OEt, to PET/HDPE blends shows an increase in viscosity over that containing compatibiliser C\(_4\) i.e. Surlyn/phenoxy (50:50) without sodium ethoxide. Furthermore higher viscosity for PET/HDPE blends is obtained with the addition of the C\(_5^*\) compatibiliser, i.e. extruded twice. These viscosity results are in agreement with the reduction in particle size obtained with the addition of compatibiliser C\(_5\), i.e. (50:50) Surlyn/phenoxy + 2\% Na-OEt, to the PET/HDPE (75:20) blend (see Figures 4.26 and 4.27). The viscosity as function of composition of the PET/HDPE containing 5\% compatibiliser C\(_5\) in Figures 4.15 and 4.16 show a positive deviation at high concentrations of HDPE for low shear rates. Positive deviation from the additive rule generally occurs either at low shear rates when there are strong interactions between the two phases or when the blend has an interlocked morphology [125].

The addition of sodium ethoxide to the different systems used as compatibilisers has resulted in the largest increase in viscosity for the PET/HDPE (75:20) Surlyn/phenoxy ratio compared to the EAA\(_2\)/phenoxy and EP-gMA/phenoxy at (25:75) ratio. This is probably due to the structure of the Surlyn already containing sodium clusters. The use of sodium benzoate as a catalyst for the compatibilisers has shown no appreciable change in the melt viscosity of the PET/HDPE blends, suggesting that no change in phase morphology has taken place, Figures 4.13(b) and 4.14(b).

The addition of (50:50) Surlyn/phenoxy + 2\% Na-OEt (C\(_5\)) to the PET/HDPE (2) high molecular weight grade of HDPE shows a positive deviation in viscosity at low shear rates. This can be related to the smaller particle size obtained with
PET/HDPE (2) than that of PET/HDPE (1), showing further reduction in particle size with the addition of (C₅) (see Figure 4.32). A relationship has been found between viscosity and particle size of the dispersed phase of the compatibilised PET/HDPE blends. Figure 5.1 shows that the increase in viscosity of the PET/HDPE blends is accompanied by a decrease in the particle size of the dispersed phase, confirming the compatibilisation of the blend [123] PET/HDPE (75:20) containing 5% Surlyn/phenoxy at (50:50) and (25:75). These results are in agreement with the improved tensile strength and elongation to break of the PET/HDPE containing the same compatibiliser (see Section 5.4). Also Figure 5.2 illustrates the relationship between viscosity and particle size for the three different ethylene copolymers used in the compatibiliser with Na-OEt i.e. Surlyn/phenoxy, EP-gMA/phenoxy, and EAA₂/phenoxy at (25:75). The most effective compatibiliser i.e. Surlyn/phenoxy (25:75) + 2% Na-OEt, is characterised by the highest viscosity and lowest particle size of the compatibilised PET/HDPE blends.

It has been observed that the addition of 5% Surlyn/phenoxy (50:50) + 2% Na-OEt (C₅) to the PET/HDPE blends gives higher values for the entry pressure drop, ΔPₒ, than PET/HDPE blends without compatibiliser. According to Han [128] ΔPₒ can be used as a rough measure of the relative elasticity of single polymer systems. The above author states, however, that the ΔPₒ parameter cannot be used with certainty to predict melt elasticity for a multiphase polymer blend, in view of the fact that the rheological properties of dispersed multiphase blends depends very much on the state of dispersion [124]. The results are, however, indicative of a possible increase in melt elasticity for the case of compatibilised polymer blends.
Fig. 5.1 Relationship between Viscosity and Particle Size of PET/HDPE Blends Containing 5% Surlyn/Phenoxy + 2% Na-OEt Compatibilisers.

a) Viscosity at 133 Sec-1 Shear Rate.

b) Viscosity at 2667 Sec-1 Shear Rate.
5.3 PHASE MORPHOLOGY OF BLENDS

The SEM micrographs of the phenoxy/ethylene copolymers compatibiliser mixtures shown in Figures 4.19 to 4.21, illustrate the type of morphology obtained with these systems. Phenoxy/EP-gMA shows to be a more homogeneous mixture, especially at 75:25 ratio, than those of phenoxy/EAA₂ and phenoxy/Surlyn. The latter two mixtures show the presence of elongated particles (see Figure 4.19). The addition of 2% sodium ethoxide (Na-OEt) to the above mentioned mixtures has different effects on the various mixtures. The addition of 2% Na-OEt to the phenoxy/Surlyn (50:50) system results in a reduction in particle size, an increase in the population of spherical dispersed phase and an increase in interphase bond strength which is reflected in the topology of the fractured surfaces. This can be seen in Figure 4.19(b), the phenoxy/Surlyn 50:50 mixture produced a fracture along the boundaries of the co-continuous phases, while the fracture of the mixture containing 2% Na-OEt occurred right through the two phases (see Figure 4.19(c)).

The phenoxy/EAA₂ 75:25 mixture shows a coarser dispersed phase than both the phenoxy/EAA₂ 50:50 and Surlyn/phenoxy 50:50 systems. The addition of 2% Na-OEt to the phenoxy/EAA₂ 75:25, however, produces a substantial reduction in particle size of the dispersed phase, while the addition of 2% of sodium benzoate produces no improvements (see Figure 4.20). The addition of sodium ethoxide to the phenoxy/EP-gMA 75:25 produces a brittle morphology (see Figure 4.21(c)). This observation has to be considered in parallel to the lower viscosity of this compatibiliser at 280°C and the high gel content in xylene/cyclohexanone, i.e. the evidence for the formation of crosslinked polymer, and finally with respect to its failure to compatibilise the PET/HDPE blend.
In order to gain a better understanding of the compatibilisation behaviour of these mixtures it is important to consider the effect of each component of the compatibilisers and their combination on the morphology in both PET and HDPE polymer components. The addition of 5% phenoxy to PET (Figure 4.22) produces a completely homogeneous system, while the combination of the phenoxy with EP-gMA at 50:50 ratio results in a well compatibilised PET/EP-gMA mixture. On the other hand both mixtures of EAA₂ and Surlyn with HDPE (shown in Figure 4.24) seems to form a homogeneous morphology.

Also the Surlyn/phenoxy 50:50 + 2% Na-OEt seems to produce a homogeneous phase structure at 5% level in PET, but shows phase separation at 25% in HDPE, albeit with a finely dispersed morphology (see Figures 4.23 and 4.25).

The addition of 5% phenoxy/Surlyn 50:50 and 75:25 containing 2% Na-OEt to the PET/HDPE (75:20) blend has produced a finer dispersed phase morphology, and has resulted in considerable improvements in mechanical properties. On the other hand, it has been observed that the higher the Surlyn content in the compatibiliser the larger are the particle sizes of the dispersed phase in PET/HDPE blends (see Figure 5.1). At the same time the viscosity of the Surlyn/phenoxy compatibilisers and the PET/HDPE blends containing these compatibilisers decreases with the increase of Surlyn content in the compatibiliser (see Figures 5.11(a) and 5.11(b)). A possible explanation for this is that the compatibiliser with high Surlyn content tends to migrate into the HDPE phase of the blend and therefore is not available in sufficient amount at the interphase. The preferential migration of the Surlyn in HDPE phase is not only favoured by thermodynamics, but also by the fact that it has a low viscosity and can diffuse rapidly. Therefore it has to be remembered that to obtain an effective interfacial agent, it is necessary to avoid the migration of the
compatibiliser to one of the blend components. Viscosity of the compatibilisers could be related to the efficiency of the compatibilisers. These results appear to be at variance, however, with those of M. Joshi et al.[129] who suggested that the addition of Surlyn to PBT/HDPE blend acts as an effective surfactant. Unlike PET the crystallisation behaviour of PBT is probably not affected by Surlyn.

The phenoxy/EP-gMA compatibilisers promote much finer particles of the dispersed phase in PET/HDPE than the phenoxy/Surlyn mixtures. The finest phase dispersion being obtained with 5% EP-gMA in PET/HDPE 75:20 blend, which in turn shows ductile failure of the matrix phase (see Figure 4.29(d)) and a large increase in elongation at break for the blends. However the addition of sodium ethoxide to the phenoxy/EP-gMA system shows the opposite effect to that of phenoxy/Surlyn systems i.e. it promotes a brittle failure of the matrix and an increase in particle size of the dispersed phase, see Figure 4.29(c). Similarly the addition of sodium ethoxide is shown to be ineffective when used with phenoxy/EAA\textsubscript{2} to improve the compatibilisation of PET/HDPE blends, although the addition of 5% phenoxy/EAA\textsubscript{2} in PET/HDPE blends promotes a finer dispersed phase (see Figure 4.30). These observations on phase morphology are reflected in the poor mechanical properties obtained when sodium ethoxide is used in phenoxy/EP-gMA and phenoxy/EAA\textsubscript{2} compatibilisers. For the case of phenoxy/EP-gMA the occurrence of crosslinking with the addition of sodium ethoxide might be the cause of such a behaviour, whereas for phenoxy/EAA\textsubscript{2} the only explanation could be that sodium ethoxide in these systems is not so effective in producing ionomers and that the non-ionomerised free base Na-OEt causes degradation of PET.

The 50:50 PET/HDPE blend shows a co-continuous phase morphology where the dispersed phase and the matrix cannot be distinguished (see Figure 4.31b).
Chapter 5: Discussion

Fig. 5.2 Relationship between Viscosity and Particle Size of PET/HDPE Blends Containing different Ethylene/Phenoxy + 2% Na-OEtCompatibilisers.

a) Viscosity at 133 Sec-1 Shear rate.

b) Viscosity at 2667 Sec-1 Shear Rate

c) Particle Size of Dispersed Phase.
Injection moulded samples of these blends show an onion skin effect and a rapid deterioration in mechanical properties. The addition of 5% Surlyn/phenoxy 50:50 + 2% Na-OEt compatibiliser converts this morphology into a dispersed phase microstructure with large elongated particles, giving a brittle fracture through both the matrix and the dispersed particles, (see Figure 4.31(d)). In the PET/HDPE 22.5:77.5 blend the dispersed phase displays a variety of size and shape of particles. The addition of 5% Surlyn/phenoxy (50:50) + 2% Na-OEt does not cause appreciable changes in phase morphology of the blend but produces large improvements in mechanical properties and a large increase in viscosity of blends at all shear rates, see Figure 4.31(e). Reducing the molecular weight of HDPE has resulted in a finer morphology of both PET and HDPE as dispersed phases, but an even finer dispersion is induced with the addition of the compatibiliser Surlyn/phenoxy (50:50) + 2% Na-OEt (Figure 4.32). The reduction in the MW of HDPE may have resulted in a more favourable match of viscosity characteristics with improvements in interface energy by the compatibiliser.

5.4 MECHANICAL PROPERTIES OF PET/HDPE BLENDS

The preliminary studies on injection moulding the various PET/HDPE blends has shown that the use of a chilled mould gives the most appropriate conditions to obtain good specimens. The use of a hot mould has shown different effects on different blends. For example, the PET/HDPE + 5% phenoxy produced very brittle specimens when moulded with a mould temperature of 90°C, while the PET/HDPE + 5% [phenoxy/EP-gMA (50:50)] blend exhibited poor moulding characteristics and produced distorted specimens when moulded with a mould temperature of 90°C. In contrast, the PET/HDPE + 5% [phenoxy/Surlyn (50:50)] and PET/HDPE + 5% [phenoxy/Surlyn (50:50) + 2% Na-OEt] blends showed
good moulding characteristics and produced testing specimens with improved surface finish.

To minimise the effects of moulding conditions the specimens were also annealed in order to develop the maximum level of crystallinity. Figure 4.33 shows the effect of the phenoxy/Surlyn compatibiliser on the tensile strength of the PET/HDPE blend. Clearly the addition of 5% phenoxy/Surlyn at all weight ratios to PET/HDPE (75:20) produces considerable improvements in tensile strength. The extent of improvement appears to be independent of the ratio of Surlyn/phenoxy in the compatibiliser. However when 5% Surlyn or phenoxy alone are used as compatibilisers, lower tensile strength of compatibilised PET/HDPE blends is obtained (see Figure 4.33). The increase in tensile strength can be explained by considering the relatively finer dispersed phase obtained with the addition of 5% phenoxy/Surlyn specially at 50:50 and 75:25 ratios. It is worth noting that the addition of these compatibilisers results in a slight decrease of modulus with the increase of Surlyn content in the compatibiliser (see Figure 4.39). This is expected in view of the low modulus Surlyn. The addition of phenoxy/Surlyn compatibiliser to the PET/HDPE blend shows an appreciable increase in the elongation at break (see Figure 4.41), while the presence of 2% sodium ethoxide in 5% phenoxy/Surlyn 75:25 and 50:50 compatibilisers added to the PET/HDPE (75:20) changes the failure mechanism from brittle to ductile, with a considerable increase in tensile strength and modulus (see Figures 4.33, 4.34 and 4.39). This combination of properties enhancement is a considerable achievement with respect to the compatibilisation of PET/HDPE blends. When compared with previously reported work [90] which has shown that the compatibilisation of this blend required 20% triblock copolymer (15% polystyrene, 70% random copolymer of ethylene and butene, 15% polystyrene), (Kraton 1652G), to produce an appreciable increase in ductility, but this occurred
at the expense of large reductions in tensile strength and modulus. The addition of phenoxy/Surlyn 50:50 + 2% Na-OEt compatibiliser to PET alone produces a homogeneous phase morphology (see Figure 4.23). Surlyn is known to be capable of exerting physical interactions with PET [8] while phenoxy becomes highly compatible with PET through chemical reactions. The addition of 25% Surlyn to HDPE has shown a homogeneous phase morphology indicating the high level of compatibility (but not entirely miscible) between HDPE and Surlyn. These results appear to satisfy the criterion of an effective compatibiliser i.e. that the compatibiliser acts as an emulsifier [6], resulting in a finer dispersed phase and improved overall properties.

The addition of 5% [phenoxy/Ep-gMA (25:75) + 2% Na-OEt] to the PET/HDPE blend does not show any improvements over the addition of 5% [phenoxy/Ep-gMA (25:75) without sodium ethoxide] (see Figure 4.36). The phase morphology of this blend displays larger particles of the dispersed phase and brittle fractures.

It is observed from an inspection of Figure 4.33 that the higher the Surlyn content the less effective is the compatibiliser. No appreciable increase in tensile strength, modulus and elongation at break is obtained with the addition of either phenoxy/Surlyn (25:75) + 2% Na-OEt or Surlyn + 2% Na-OEt to the PET/HDPE blend and, at the same time, these blends show the coarsest dispersed phase morphology.

The annealed samples of PET/HDPE with 5% of any phenoxy/Surlyn compatibilisers display an appreciable increase in tensile strength. However the highest increase in tensile strength after annealing is obtained with the two most effective compatibilisers [i.e. phenoxy/Surlyn (50:50) and (75:25) both with 2% Na-OEt], see Figure 4.34, annealing the samples of PET/HDPE containing 5%
phenoxy/Surlyn + 2% Na-OEt induces a reduction in elongation at break (see Figure 4.43). Note that both the pure PET/HDPE and the blend containing 5% phenoxy show instead an increase in elongation at break after annealing, while the PET/HDPE containing 5% Surlyn does not show any difference in elongation at break. Hence the decrease in elongation at break after annealing has to be associated with the presence of sodium ethoxide in the compatibiliser, which may give rise to further crystallisation or degradation in the PET phase. The addition of 5% phenoxy/EP-gMA to the PET/HDPE blend, on the other hand, shows a slight decrease in tensile strength and modulus with the increase of EP-gMA content, which is to be expected owing to flexibilising effect of the elastomer (see Figures 4.35 and 4.40). The elongation at break of the blend increases with the increase of the EP-gMA content in the phenoxy/EP-gMA compatibiliser with the highest increase being obtained with the addition of 5% EP-gMA to the PET/HDPE blend. Furthermore the latter shows also the finest dispersion (see Figures 4.42 and 4.29(d)). Annealing the samples of PET/HDPE blends containing 5% phenoxy/EP-gMA produces a considerable increase in tensile strength at all phenoxy/EP-gMA ratios, over that exhibited by the pure PET/HDPE blend. However a reduction in elongation at break is observed with the annealed samples of PET/HDPE containing high amounts of EP-gMA in the compatibiliser (i.e. phenoxy/EP-gMA (25:75) and pure EP-gMA) (see Figures 4.35 and 4.42). The phenoxy/EP-gMA compatibilisers induce a decrease in the crystallisation rate of the PET phase which is deduced from the DSC thermograms by the rising in the cold crystallisation temperature ($T_c$) and in the recrystallisation temperature of the PET containing 5% EP-gMA. This behaviour is probably the cause of the significant increase in tensile strength of the blends after annealing. It is noted, on the other hand, that the addition of 5% phenoxy/EP-gMA (75:25) + 2% Na-OEt to the PET/HDPE blend reduces both the tensile strength and the elongation at break (see Figure 4.36). This blend
shows the coarsest dispersed phase morphology compared to all the other PET/HDPE blends containing + 5% phenoxy/EP-gMA compatibiliser. The addition of sodium ethoxide to the phenoxy/EP-gMA (75:25) produces a crosslinked copolymer which is evidenced by the high gel content in cyclohexanone/xylene solvent. This highly crosslinked mixture is, therefore, ineffective as a compatibiliser for the PET/HDPE blend.

The use of phenoxy/EAA₂ as compatibiliser for the PET/HDPE blend shows, on the other hand a moderate increase in tensile strength especially at phenoxy/EAA₂ 75:25 and 50:50 ratios (see Figure 4.37). The increase in tensile strength becomes less significant at higher content of EAA₂. However the addition of 2% sodium ethoxide to the phenoxy/EAA₂ compatibiliser produces only small further increase in tensile strength (Figure 4.36). It has to be noted that the values of tensile strength obtained with PET/HDPE + 5% phenoxy/EAA₂ compatibilisers are much lower than those obtained with 5% phenoxy/Surlyn compatibilisers, especially when sodium ethoxide is used for the production of the latter compatibilisers. Furthermore it has been found that no appreciable improvements are obtained in the elongation at break of the PET/HDPE containing phenoxy/EAA₂ irrespective of whether sodium ethoxide is present or not. Once again the use of sodium ethoxide has been shown not to be as effective as it is with the Surlyn system (see Figure 4.36).

The phenoxy/Surlyn 50:50 + 2% Na-OEt system, being an effective compatibiliser for the PET/HDPE blend, was then selected for more detailed studies to consider various ratios of PET/HDPE in the blends and to study the effect of decreasing the molecular weight of HDPE. Reducing the molecular weight of the HDPE component has resulted in an improvement in tensile strength for compositions where the strength was lowest i.e. 50:50, but no
appreciable change in tensile strength was obtained for PET/HDPE 20:75 blends (see Figure 4.38). In all cases, however, a dramatic increase in elongation at break is achieved with the addition of 5% phenoxy/Surlyn 50:50 + 2% Na-OEt to the PET/HDPE (20:75) blend, while no significant increase in elongation at break is obtained with the PET/HDPE 50:50 system (see Figure 4.44). The addition of either phenoxy/EP-gMA 50:50 or Surlyn to the blends with high content of HDPE i.e. PET/HDPE 20:75 shows a considerable increase of elongation at break similar to the effect obtained with the phenoxy/Surlyn 50:50 + 2% Na-OEt (see Table 4.10). Annealing the samples, however, shows a decrease in elongation at break for all the compatibilised PET/HDPE blends. The overall improvement, however, is still very significant compared to the unmodified blends (see Table 4.10). From these data one can see that the compatibilisers always have some beneficial effect for all ratios of PET/HDPE blends, especially with respect to the elongation at break at high HDPE contents, e.g. PET/HDPE 20:75, even though the effect on tensile strength is not significant. On the other hand, the addition of 5% phenoxy/Surlyn 50:50 + 2% Na-OEt to the PET/HDPE blends based on different molecular weights of HDPE, has produced a compatibilisation effect on all the blends. The tensile strength of this blend has improved significantly with the addition of the compatibiliser, especially after annealing, see Table 4.9. However, the addition of the compatibiliser to the PET/HDPE blends with lower molecular weight HDPE shows a reduction in elongation at break by suppressing the cold drawing of the samples. Further reduction has taken place after annealing (see Table 4.11). The reduction in elongation at break can be associated with the increase in crystallinity induced by the compatibiliser and annealing. It is clear from these results that the compatibiliser phenoxy/Surlyn 50:50 + 2% Na-OEt is not as effective at all ratios of the PET/HDPE blends nor for all types of HDPE used in the blends. In order to understand these observations it is important to consider
the interfacial characteristics and rheological properties of the various PET/HDPE blends, which can vary from one composition to another and from one type of component to another.

5.5 THERMAL ANALYSIS OF COMPATIBILISERS AND BLENDS

The results obtained from the DSC measurements show that the most important changes in the thermal properties of the compatibilisers and the PET/HDPE blends seem to be obtained with systems containing sodium ethoxide. The presence of Na-OEt in the phenoxy/Surlyn compatibilisers causes a decrease in the crystallisation rate and level of crystallinity of the Surlyn, whereas the addition of phenoxy/Surlyn compatibiliser containing Na-OEt in the PET/HDPE blends increases the crystallisation rate of the PET phase (see Figure 4.45). The fact that the level of crystallinity of the Surlyn phase decreases with the addition of Na-OEt could be explained by the further formation of ionomeric clusters. A larger decrease in heat of fusion ($\Delta H_m$) and heat of recrystallisation is also induced by the presence of Na-OEt in Surlyn/phenoxy blend than for Surlyn alone (see Table 4.12). This could be related to some kind of interaction taking place between phenoxy and Surlyn in the presence of Na-OEt. The gel content of these phenoxy/Surlyn + Na-OEt mixtures when dissolved in DMF/xylene (1:1) was, in fact, found to be substantially greater. However, since they were found to dissolve completely in cyclohexanone/xylene (1:1) solvent, (see Section 4.1) any possibility of crosslinked products being present has to be excluded. In the light of these observations the interaction taking place between phenoxy and Surlyn in the presence of Na-OEt could be a formation of ionomeric species consisting of clusters of Na$^+$ ions surrounded by carboxylate counter-ions and associated hydroxyl groups [130]. The addition of 25% Surlyn in HDPE shows two melting points as explained in results.
(Section 4.5), indicating that the two polymers are not completely miscible. Furthermore the presence of Surlyn causes a decrease in the level of crystallinity of HDPE (see Table 4.16). This behaviour can probably explain the increase in tensile strength of the PET/HDPE containing 5% phenoxy/Surlyn since Surlyn is expected to reduce the crystallisation of the HDPE as a dispersed phase, resulting in a lower shrinkage of the dispersed particles and consequently reducing the gap created between the matrix (PET) and the particles (HDPE) [131]. On the other hand, from the moulding characteristics and tensile properties of the PET/HDPE blends containing 5% EP-gMA and phenoxy/EP-gMA, it is inferred that the addition of the EP-gMA decreases the crystallisation rate of the PET (see Table 4.15). The DSC results, however, can be used to account for the crystallisation behaviour of the compatibilisers and the PET blends, but are insufficient to explain the different results obtained with respect to interaction tensile test and morphology, etc. For example the phenoxy/Surlyn (50:50) + 2% Na-OEt extruded twice (C_5*) shows a significant decrease in crystallinity of the mixture indicating the occurrence of further interactions in the mixture. However the addition of 5% of this compatibiliser to the PET/HDPE (75:20) shows more or less the same crystallisation behaviour as that obtained with phenoxy/Surlyn (50:50) + 2% Na-OEt extruded only once (compatibiliser C_5) see Tables 4.12 and 4.14. Knowing that the PET/HDPE blends containing 5% of C_5* compatibiliser show lower tensile strength, elongation at break and a coarser morphology, compared to that containing 5% C_5 (see Sections 4.3 and 4.4). Furthermore it has been found that the crystallinity of the PET/HDPE blends compatibilised with Surlyn/phenoxy + 2% NA-OEt systems do agree with the results obtained from tensile tests (see Figure 5.3).
Fig. 5.3 PET/HDPE Blends Containing 5% Surlyn/Phenoxy (50:50)+2% NaOEt Compatibiliser.
CHAPTER 6
CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

6.1 CONCLUSIONS

There are several major conclusions that can be drawn from this study in relation to the main aspects of the work:

1. Preparation of Compatibilisers
   a) The formation of graft copolymers in EP-gMA/phenoxy mixtures has been confirmed from solubility tests, while the addition of Na-OEt has been found to produce crosslinked products exhibiting a decrease in compatibilisation efficiency. Mixtures of Surlyn/ phenoxy and EAA₂/phenoxy have been found not to produce crosslinked products even when substantial amounts of Na-OEt has been added. The high level of residues from solubility tests for these mixtures has been attributed to the formation of ionomeric associations, as no evidence of formation of ester groups was found and by the fact that these systems are unable to form crosslinked products.
b) The amount of residue and therefore co-ionomeric species in Surlyn/phenoxy and EAA₂/phenoxy mixtures is related to the strength of the base of the sodium compound used as catalyst. The evidence for this is derived from the observation that Na-OEt (a strong base) gave the highest level of residue while no effect was found with Na p-toluene sulphonate (a very weak base).

c) Infrared studies have failed to reveal the formation of ester groups or any other type of interactions in Surlyn/phenoxy and EAA₂/phenoxy systems but this could be due to experimental difficulties.

d) Rheological studies have confirmed the formation of graft copolymers for EP-gMA/phenoxy and co-ionomeric species for Surlyn/phenoxy + Na-OEt mixtures from evidence of increased viscosities. The increase in viscosity for the compatibilisers causes an increase in viscosity of the PET/HDPE containing these compatibilisers, the latter resulting primarily from the smaller particle size of the dispersed phase.

e) The addition of Na-OEt to the Surlyn/phenoxy mixtures causes a reduction in the degree of crystallinity and crystallisation rate of the Surlyn phase whereas an increase in the transition temperature (Tg) of the phenoxy is obtained.

2. Efficiency of Compatibilisers in PET/HDPE Blends

a) Compatibilisation of PET/HDPE blends by EP-gMA/phenoxy Surlyn/phenoxy and EAA₂/phenoxy mixtures has been confirmed from observations of the size of dispersed particles and mechanical properties evaluations.
Although all systems, e.g. EP-gMA/phenoxy, Surlyn/phenoxy + Na-OEt and EAA<sub>2</sub>/phenoxy + Na-OEt, display a compatibilisation behaviour for PET/HDPE blends the greatest compatibilisation effect is achieved with EP-gMA/phenoxy and Surlyn/phenoxy + Na-OEt. The latter shows, however, better improvements in mechanical properties which could be due to the nucleation effect exerted on the PET and HDPE phases, as evidenced from the DSC results. For the case of Surlyn/phenoxy the effective ratio for the two components appears to be 25/75 and 50/50. For the case of EP-gMA/phenoxy, on the other hand, a higher amount of EP-gMA in the compatibiliser shows to be more effective.

b) The comparison of the effect of different ethylene copolymers in compatibilisers on the viscosity of the PET/HDPE blends shows a correlation between efficiency of the compatibilisers and the viscosity of the compatibilised PET/HDPE blends. Higher melt viscosity is obtained with the use of Surlyn/phenoxy than with EAA<sub>2</sub>/phenoxy, both containing Na-OEt. The lowest melt viscosity for PET/HDPE blends is obtained with the addition of EP-gMA/phenoxy containing Na-OEt, which is also further evidence of the reduction in compatibilisation efficiency with crosslinked compatibilisers.

c) The use of sodium ethoxide in the different compatibilisers causes a reduction in the onset temperature of cold crystallisation in PET/HDPE blends, indicating a nucleating effect of the PET phase.

d) The addition of Surlyn/phenoxy + Na-OEt to the PET/HDPE blends containing large amounts of HDPE produces only a marginal improvement in tensile strength. However the increase in elongation to
break is extremely high with the use of either Surlyn/phenoxy + Na-OEt or EP-gMA/phenoxy compatibiliser. The lowest compatibiliser efficiency is exhibited, however, in blends of PET/HDPE at 1:1 ratio, where the two components form a co-continuous phase. On the other hand, the use of lower molecular weight HDPE in PET/HDPE shows an appreciable reduction in particle size of the dispersed phase. The addition of Surlyn/phenoxy + Na-OEt to these PET/HDPE blends containing low amounts of HDPE shows a further reduction in particle size with improvements of tensile strength, but this is accompanied by a decrease in elongation to break.

e) Annealing of the injection moulded samples of PET/HDPE blends produces an increase in tensile strength in all cases. The highest increase in tensile strength, however, is achieved in the case of PET/HDPE blends containing the Surlyn/phenoxy + Na-OEt. This might be due to an increase in crystallinity of the PET matrix, since it has been found that when crystallinity of the mentioned blends increases, the tensile strength also increases. On the other hand, the addition of EP-gMA/phenoxy to PET/HDPE blends causes an increase in ductility and a decrease in tensile strength and modulus. The effect is greater when the EP-gMA content in the compatibiliser is highest. Alongside these effects, the DSC measurements have shown that the presence of EP-gMA in the PET phase reduces its crystallisation rate. Annealing the PET/HDPE blends containing EP-gMA/phenoxy compatibilisers causes a substantial increase in tensile strength accompanied by a decrease in elongation to break.

Similar behaviour is obtained when annealing the PET/HDPE blends containing higher amounts of HDPE and/or different HDPE molecular weights.
6.2 SUGGESTIONS FOR FUTURE WORK

Several aspects of this work remain unclear, hence the following suggestions are offered as a possible route to improve the compatibilising efficiency of mixtures of phenoxy/acid functionalised ethylene copolymers:

a) The interaction of phenoxy with ethylene acrylic acid copolymers, or the sodium ionomers of ethylene acrylic acid copolymers, do not appear to produce crosslinked products even when large amounts of sodium ethoxide are used. To account for the large increase in melt viscosity it is suggested that ionomer clusters are formed, hence a more thorough investigation to elucidate this point would be very useful and to determine whether their compatibilisation efficiency can be increased further by increasing the concentration of the cation.

b) Sodium ethoxide was found to produce crosslinked products in compatibilisers based on mixtures of phenoxy and EP-gMA. A much weaker base, such as sodium benzoate or Zn ethoxide, may increase the yield of graft copolymers without the formation of crosslinked products.

c) The compatibilisation efficiency of the compatibilisers studied in this work should also be assessed in blends based on PBT as the crystallisation behaviour of this polymer is very different from that of PET.
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LIST OF PUBLICATIONS


3. L. Mascia and F. Bellahdeb: 'Graft Copolymers and Co-Ionomers Produced by Reactive Mixing of Phenoxy Polymers with Acid/Anhydride Functionalised Ethylene Copolymers' (Part I). In course of preparation, to be submitted to Advances in Polymer Technology.

4. L. Mascia and F. Bellahdeb: 'Compatibilisation of PET/HDPE blends by Mixtures of Phenoxy and Acid/Anhydride Functionalised Ethylene Copolymers (Part II). In course of preparation, to be submitted to Advances in Polymer Technology.
Fig. A1 DSC Trace for PET/HDPE Blend.