Compatibilisation of polysulphones/polyester blends

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COMPATIBILISATION OF POLYSULPHONES/POLYESTER BLENDS

by

LEE MARTIN

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of DOCTOR OF PHILOSOPHY of the LOUGHBOROUGH UNIVERSITY OF TECHNOLOGY

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Supervisor: Dr L. Mascia

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Dedicated to Sandy,
Danielle and Katie Louise.
ABSTRACT

Ternary blends comprising Polysulphones [Polyethersulphone (PES) and Polysulphone (PSO)], the Polyhydroxyether of bisphenol-A (Phenoxy), and Polyesters [Poly(ethylene terephthlate) (PET) and Poly(butylene terephthlate) (PBT)] have been studied particularly with the aim in mind of elucidating the factors determining their miscibility and morphology. Binary and ternary combinations, including equivalent systems based on a butylene terephthlate-tetramethylene oxide block copolymer (PBT-TMO), were prepared from solution and by mixing in the melt state using both an internal mixer and a twin screw extruder.

Scanning electron microscopy was employed to examine the morphology of these blends. A co-continuous, (interpenetrating), dual-phase morphology was displayed by both the PSO/PBT and PSO/PBT-TMO (70/30) combinations. The compatibility was further increased by the addition of Phenoxy, which was evidenced by the formation of a very fine dispersion of the two phases for both PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO blends, in the weight ratio of (60/15/25). A lower level of compatibility was displayed by the equivalent blends based on PES and PET, as a matrix/dispersed particle type of morphology was usually observed.

Differential thermal analysis and dynamic mechanical analysis measurements were also employed to ascertain the level of miscibility in these systems. A single composition dependent glass transition temperature was displayed by the binary PBT/Phenoxy and PBT-TMO/Phenoxy melt blends, and the binary PES/Phenoxy and PSO/Phenoxy solution blends. The remaining blends displayed two separate glass transition temperatures that were often broader and closer together than those of the homopolymers. This effect was more significant for blends containing the Phenoxy compatibiliser, confirming that these systems are semi-miscible.

Solvent resistance measurements were made on 500μm thick extruded sheets by measuring the time to failure at stress levels corresponding to 30% and 50% of the tensile strength. The blends displaying a matrix/dispersed particle type of morphology revealed poor solvent resistance and mechanical properties. The blends displaying a co-continuous interpenetrating dual-phase morphology on the other hand displayed a much higher solvent resistance and enhanced mechanical properties.

KEYWORDS: Polymer Blends, Miscibility, Compatibiliser, Polysulphones, Polyesters, Phenoxy, Morphology, Interpenetrating Network.
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INTRODUCTION

The scientific and commercial progress in the area of polymer blends during the past two decades has been enormous. The current and potential technological importance of polymer blends is remarkable and their ubiquitous presence in consumer products is testimony to their commercial importance.

The annual growth of polymer blends worldwide is estimated to be about 8%. Thus, the 800,000 tonnes consumption figure quoted for 1989 is estimated to increase to 1.2 million tonnes in 1994. The reasons for such a high growth are associated with improved properties, processability and often favourable economics in relation to single polymer systems.

From an industrial point of view, polymer blends fill the deficiency in price/performance of existing single component polymers for a relatively minor capital investment. A shorter period of time and effort are required to develop a new product via blending existing materials in comparison with that needed to develop a new polymer.

Polymer blends may be defined as intimate mixtures of two or more polymers. Depending on their overall phase morphology, they can be divided into three basic groups:

1. Miscible blends:
Miscibility generally prevails when strong exothermic interactions are exerted between the polymer chains of the constituents of the blend. These are usually via hydrogen bonding or charge transfer. They are homogeneous down to molecular level, and yield properties intermediate between those of the constituent polymers. Examples of these systems include Poly(butylene terephthalate)/Phenoxy and Polystyrene/Poly(2,6-dimethyl 1,4-phenylene oxide).

2. Immiscible blends:
These are the largest group of blends due to the thermodynamic incompatibility of the majority of polymers. A heterogeneous, (multiple phase), mixture of the constituent non-interactive polymers arises owing to the very small entropy gained on mixing. They often produce properties inferior to either component due to gross phase segregation of the constituents. Examples of these systems are widespread and include Polyethylene/Poly(methyl methacrylate) and Polystyrene/Poly(methyl methacrylate).
3. **Compatible Blends:**
This group of blends are neither totally immiscible or miscible at molecular level. Instead, they reveal a limited but controlled miscibility with good adhesion between the polymer constituents. They are mechanically processable blends which resist gross phase segregation and give desirable physical properties. This implies either the existence of a thermodynamic miscibility window or physical constraints that are set up to prevent demixing such as grafting, cross-linking, the presence of block copolymers or compatibilisers, formation of an interpenetrating network, (IPN), or quenching the mixed system to a temperature at which demixing is thermodynamically but not kinetically favoured. Examples of these systems include Poly(ethylene oxide)/Polyethersulphone\(^8\) and Phenoxy/Polyethersulphone.\(^9\)

In partially miscible polymer mixtures, mechanical compatibility can be produced and thus a property intermediate between the constituents achieved. Therefore, with a partially miscible polymer blend, a range of price/performance characteristics between the component polymers can lead to a large number of potentially useful products. Blending can also be used to modify the properties of a given polymer so as to extend its range of application or to tailor its properties to fit a specific requirement. This versatility places partially miscible polymer blends into a unique situation with potential commercial importance. However, there are only a few polymers that are intrinsically partially miscible, hence a large number of studies have been carried out into improving the adhesion of the more common immiscible blends.\(^10\) As a result, many new polymer systems have been developed through the addition of compatibilising agents which permit the blending of incompatible polymers to yield compositions with unique physical properties.\(^11\)

1.1 **OBJECTIVES**

The aim of this study is to improve the solvent resistance of both Polysulphones by blending with semi-crystalline Polyesters. Both PES and PSO are high performance engineering thermoplastics that are employed in a number of high temperature applications. They are competitive with many basic thermosetting compounds but possess the important advantage of low cost injection moulding.

Applications particularly suited for Polysulphones include moulded articles and extrusions for which hydrolytic stability and good electrical properties are required. They are therefore employed in applications requiring prolonged exposure to steam and hot water. High heat distortion temperatures combined with excellent hydrolytic
stability and the ability to retain mechanical properties in hot, wet environments, are the keys to their use in medical and food service applications which require repeated cleaning with hot water or sterilisation. Microwave cookware is a significant market for Polysulphones. Electrical and electronic applications constitute a growing market, particularly injection moulded printed circuit boards and connectors. Other applications include hot-water pipes, under-bonnet automobile components, lenses, appliance autoclavable equipment and wiring devices.

However, as a result of their glassy nature, both Polysulphones are soluble in or easily stress cracked by a majority of solvents. It is thought that by successfully blending them with a semi-crystalline polyester it would improve their solvent resistance without deteriorating their high temperature performance. The Polyesters considered include; Poly(ethylene terephthalate), (PET), Poly(butylene terephthalate), (PBT), and a PBT-TMO block copolymer, (Hytrel).

The applications of PET include; fibres, films, bottles and precision mouldings. The uniaxially drawn fibres have high strength and stiffness, and recover well after stretching. They are mainly used for making synthetic fibres for fabrics, curtains, upholstery and fibrefill, and for industrial applications such as sewing threads, tyre cords and filter fabrics. The biaxially orientated film is of sparkling clarity, high tear strength and low water absorption and gas permeability. These properties, together with PET's inherent electrical properties, make biaxially orientated PET sheet/film suitable for photographic film, audio and video magnetic tape material, typewriter ribbons, capacitors and due to its safe toxicology, food container packaging. PET bottles exhibit the high strength essential for carbonated beverage bottles and low carbon dioxide permeation. Extruded preforms that are subsequently reheated and biaxially orientated are used for the blownware due to its inherent barrier performance and total inertness to almost all foodstuffs. Only special grades of high molecular weight PET are injection moulded due to its slow crystallisation rate, Section [3.1:4]. PBT however, is far faster crystallising than PET and so is more generally used for precision injection mouldings, Section [3.1:5].

The merits of the Hytrel block copolymers is that at normal service temperatures they are elastic and behave like a chemically crosslinked elastomer but, at elevated temperatures they flow and become processable like conventional thermoplastics. Good melt-flow properties, melt stability, low mould shrinkage and rapid crystallisation rate enables them to be processed by a wide variety of techniques, including extrusion and both rotational and injection moulding. They exhibit outstanding elasticity, tear strength, abrasion resistance, creep resistance, solvent and oil resistance, outstanding resistance to
flex cracking and good impact strength at both high and low temperatures, low
temperature flexibility and strength at elevated temperatures. Typical applications
include tyres, flexible couplings, seals, valves, gears, gaskets, car body components, ski
shoes, pneumatic tubing and power transmission belts.

This study seeks to extend the research previously undertaken in the Institute of Polymer
Technology and Materials Engineering which suggests that a common polymer,
Poly(hydroxy ether of bisphenol-A), (Phenoxy), can be used as a compatibiliser, by
forming a ternary blend.\textsuperscript{12} The studies also show that the binary PES/Phenoxy mixture
exhibits a Lower Critical Solution Temperature, (LCST), at 185°C and that
PET/Phenoxy blends are partially miscible in the amorphous regions.\textsuperscript{12,210} The
PES/Phenoxy/PET ternary blends however, were found to be immiscible and produced a
matrix/dispersed particle type of morphology.

These blends are examined in more detail in this investigation along with additional
compatibility studies of both PES and PSO with PBT, PET, PBT-TMO block
copolymers, (Hytrel), and Phenoxy compatibiliser. The polymer combinations examined
in this study include: PES/Phenoxy, PSO/Phenoxy, PET/Phenoxy, PBT/Phenoxy, PBT-
TMO/Phenoxy, PSO/PBT, PSO/PBT-TMO, PSO/PET, PES/PBT, PES/PBT-TMO,
PES/PET binary blends, PSO/Phenoxy/PBT, PSO/Phenoxy/PET, PSO/Phenoxy/PBT-
TMO, PES/Phenoxy/PBT, PES/Phenoxy/PET, PES/Phenoxy/PBT-TMO ternary blends
and the PES/Phenoxy/PET/PBT quarternary blend. It is intended to identify the
compositions which form an Interpenetrating Network (IPN) Morphology, Section
[2.8:3], ie:- a co-continuous microstructure which is expected to exhibit overall enhanced
mechanical and solvent resistance properties.

The relative compatibility of the blends are generally established by examining the
thermodynamic transitions using both mechanical and thermal methods. However, infra
red spectroscopy, optical clarity and direct observation of the phase structure using a
scanning electron microscope are also used to analyse the compatibility and phase
behaviour of these systems.
2 LITERATURE REVIEW

2.1 INTRODUCTION

Two polymers may be combined in search of novel properties (ie- beyond the range of the virgin materials). This can be achieved by selecting blend components in such a way that the principal advantages of the first polymer will compensate for deficiencies of the second and vice-versa. For example, the addition of an elastomer to any engineering polymer will improve its impact strength, or the addition of a high modulus material to a lower modulus matrix will increase its rigidity. These improvements only occur if there is good stress transfer between the component interphases.

The most important reason for blending polymers is the cost/performance ratio. An expensive polymer whose property spectrum is much higher than is needed for a new application may be blended with an inexpensive polymer whose property spectrum is such that the resulting blend has a cost/performance ratio that makes it very attractive for the given application. Thus, the standard of performance demanded by the new application is satisfied by a mixture of commercially available polymers without the need to develop a new polymer or to invest heavily in a new plant. Other reasons for blending include, easier processability, toughening, enhanced strength, modulus and heat deflection temperature, flammability and solvent resistance, thermal and dimensional stability, and recycling of plastics scrap.

2.2 DEFINITION OF MISCIBILITY

Polymer blends with behaviour similar to that of a single phase system, are known as miscible. The term miscibility does not imply ideal molecular mixing, but suggests the level of molecular mixing is adequate to yield macroscopic properties expected of a single phase material.

Miscible blends usually owe their miscibility to either segmental structural identity, ie- a solubility parameter difference less than 1 for which the main driving force is the increased entropy, or more commonly, to specific interactions between the components which provide an enthalpic driving force. The latter can either be dipole-dipole, ion-dipole, hydrogen bonding, acid base, or charge transfer interactions.
In miscible blends, miscibility mainly occurs on a molecular level in the amorphous regions. Thus, for semi-crystalline polymers, miscibility mainly refers to the remaining amorphous material. However, there are exceptional situations in which co-crystallisation of two isomorphic polymers is possible, as has been reported for PEK/PEEK binary blends.

The property which is widely used to classify a blend as miscible, is usually the glass transition temperature \((T_g)\). Here, miscibility implies homogeneity of the mixture up to a scale whose dimensions is similar to the segmental size responsible for the major glass transition. However, thermodynamic miscibility implies homogeneity on a scale equivalent to the range of intermolecular forces and thus miscibility is not necessarily satisfied by the \(T_g\) criterion.

Blends that are homogeneous at some temperatures and phase separate in other accessible temperature regions are referred to as partially miscible blends. They exhibit a 'window' of miscibility, i.e. only miscible at some concentrations and temperatures. Many miscible polymer systems show this behaviour as they phase separate at elevated temperatures to reveal lower critical solution temperatures, Section [2.4].

An immiscible blend that reveals good adhesion between the constituents and resists gross phase segregation during processing is referred to as a compatible blend. They may consist of two or more phases but reveal some favourable interfacial interactions to yield a material with desirable properties.

Immiscibility in a polymer blend is rarely well concealed, revealing itself as opacity, delamination, multiple glass transition temperatures, or combinations of those properties. These blends exhibit two or more phases at almost all compositions and temperatures. However, they may be some limited miscibility present at very low concentrations as it is difficult to differentiate between a blend that is miscible at 1% from one that is totally immiscible.

### 2.3 THERMODYNAMIC PRINCIPLES

2.3:1 Thermodynamics of Miscibility

A necessary requirement for miscibility is that the free energy of mixing from the second law of thermodynamics:
\[ \Delta G_m = \Delta H_m - T\Delta S_m \]  

be negative where:

\[ \Delta H_m = \text{enthalpy change during mixing} \]

\[ \Delta S_m = \text{entropy change during mixing} \]

\[ T = \text{absolute temperature (K)} \]

and also satisfy the additional requirement:

\[ \frac{\delta^2 \Delta G_m}{\delta \phi_i^2} > 0 \]  

which ensures stability against phase segregation over the complete composition range.\(^{21-24}\)

Figure [2.1] shows three possible patterns of behaviour of the free energy of mixing for a binary mixture.

Curve B satisfies both miscibility criteria for all compositions while the more common curve A, never satisfies either. A system described by curve C has a miscibility gap in the middle composition region because the second condition is not satisfied here.

Figure [2.2] shows the dependence of the free energy of a mixture on composition at three different temperatures. At T\(_1\), the above two conditions are fully satisfied and a
homogeneous system is obtained for all compositions. At \( T_2 \), the second condition is not satisfied for all compositions and mixtures with initial composition between points \( \phi' \) and \( \phi'' \) separate into two phases as this results in an equilibrium total free energy falling on the dashed line, which is lower than that of the homogeneous phase (solid line). The points of contact define the limiting conditions of composition for a miscible system, i.e.: \( \phi_1 < \phi' \) or \( \phi_1 > \phi'' \)

\[ \text{Figure 2.2: Free energy of mixing versus composition and temperature. (After van de Grampe[12]).} \]

The limiting case of temperature dependence is the critical temperature \( T_c \), for which \( \left( \frac{\delta^2 G}{\delta \phi^2} \right) \) and \( \frac{\delta^2 G}{\delta \phi' \delta \phi''} \) equal zero. If a system becomes unstable, (phase separates), on lowering the temperature, this point, \( (T_c) \), is referred to as the Upper Critical Solution Temperature (UCST). If phase separation occurs when increasing the temperature, this point is referred to as the Lower Critical Solution Temperature (LCST), Section [2.4].

Returning to \( T_2 \), at the inflection points \( \phi'_s \) and \( \phi''_s \), the second derivative is negative and spontaneous phase separation takes place giving rise to spinodal decomposition. However, in the intervals \( \phi' \rightarrow \phi'_s \) and \( \phi'' \rightarrow \phi''_s \), \( \left( \frac{\delta^2 G}{\delta \phi^2} \right) \) is positive, but the molecular heterogeneity present decreases the free energy of the system, thus producing a metastable region where there are small fluctuations in concentration but they are insufficient to cause total phase separation. For the latter to occur much larger concentration
fluctuations called nuclei (nucleation and growth of individual components) are required.\textsuperscript{26}

Figure [2.3] shows a phase diagram for a binary system.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{phase_diagram.png}
\caption{Corresponding binary phase diagram to figure [2.2]. (after van de Grampel\textsuperscript{17}).}
\end{figure}

The boundary between the stable one phase system and the metastable region is called the binodal and defines the equilibrium phase behaviour. The boundary between the metastable and unstable region is called the Spinodal, for which $(\delta^2 G/\delta \phi^2) = 0$. This curve is significant with respect to the mechanisms and kinetics of phase separation processes.\textsuperscript{15/27}

\subsection*{2.3.2 Elaboration of Theory}

Three contributions to the Gibbs free energy of mixing have to be considered when explaining the miscibility of polymer systems.\textsuperscript{29/31} These are: the combinatorial entropy of mixing, the intermolecular interaction and the free volume effect arising from the different thermal expansion coefficients of the two components. According to Scott\textsuperscript{31} who applied the Flory Huggins theory\textsuperscript{32-34} to mixtures of dissimilar polymers, the entropy of mixing polymer A and B is given by:

$$\Delta S_m = -R(V_A + V_B)(\phi_A \ln \phi_A / \phi_A^c + \phi_B \ln \phi_B / \phi_B^c)$$

\textit{equation 2.3}
Where, \( V_i \) is the volume of component \( i \) in the blend, \( \phi_i \) the volume fraction of \( i \), and \( \bar{Q}_i \) is the molar volume of \( i \) which is related to molecular weight and density by:

\[
\bar{Q}_i = \frac{M_i}{\rho_i}
\]  \hspace{1cm} \text{equation 2.4}

The Flory-Huggins treatment also assumes that the heat of mixing follows a Van Laar relationship with blend composition and is given by:

\[
\Delta H_m = (V_A + V_B)B\phi_A\phi_B
\]  \hspace{1cm} \text{equation 2.5}

Where \( V_i \) is the volume of component \( i \) in the blend and \( \phi_i \) is its volume fraction in the binary mixture. The parameter \( B \) is an interaction energy for mixing segments of the two components and can alternatively be expressed as:

\[
\frac{B}{RT} = \chi_A\bar{Q}_A = \chi_B\bar{Q}_B = \chi_{AB}
\]  \hspace{1cm} \text{equation 2.6}

where, \( R \) is the gas constant, \( \bar{Q}_i \) the segmental molar volume and \( \chi_{AB} \), the interaction parameter for the system.

It is clear from these equations that the entropy of mixing is a function of the molecular sizes being mixed and that it decreases rapidly toward zero as the degrees of polymerisation of the component polymers approach the values typically found in commercial materials.\(^{35}\) The enthalpy of mixing however, is primarily dependent on the energy change associated with changes in nearest neighbour contacts during mixing\(^{22,36}\) and is much less dependent on molecular lengths. The net result is that the free energy of mixing is primarily influenced by the sign and magnitude of \( \Delta H_m \) for high molecular weight mixtures. Therefore, in general, for complete polymer miscibility there has to be a negative heat of mixing (ie:- exothermic process) which is obtained by specific interactions (eg:- charge transfer or hydrogen bonding) leading to a negative interaction parameter.\(^{37,39}\)

The third contribution to the Gibbs free energy of mixing is the free volume term.\(^{7,21,30}\) Two liquid components generally have different free volumes or degrees of thermal expansion. A liquid polymer has extremely low free volume because of chain connectivity. The chain segments are linked by strong covalent bonds which decrease the number of expansion-promoting degrees of freedom/segment. Thus, the difference in free volume of a polymer and a solvent will be large. However, two polymeric liquids will have a free volume difference because of differing flexibilities of the chain backbones and/or different pendant groups. According to the Prigogine-Flory
two liquids of differing free volume will experience a net contraction on mixing, thus causing negative contributions to both \( \Delta H_m \) and \( \Delta S_m \). The overall net effect will be a positive \( \Delta G_m \) thus suggesting that the free volume term is unfavourable to mixing.

The free-volume effect arises from the different free volumes of the components and is represented by \( \Gamma \). It is non-combinatorial and so contributes to the interaction parameter \( (\chi) \) along with the segmental interaction \( (\chi_{AB}) \) and the size effect \( (\rho) \) resulting from the differences in the sizes of the segments.\(^\text{41}\)

Figure [2.4] depicts schematically the temperature dependence of the interaction parameter \( (\chi) \) with \( \Gamma \) corresponding to the free volume, \( \chi_{AB} \) to the interactional contribution for dispersion forces and specific interactions, \( \chi_{\text{disp}} \) to the total interaction parameter in the case of dispersion forces and \( \chi_{\text{spec}} \) to the total interaction parameter for specific interactions. With an increase in temperature, the free volume difference between polymers increases as does the corresponding contribution to the interaction parameter. For weak dispersion forces, the sum of the two contributions gives a u-shaped curve bringing about phase separation above a \( \chi_{\text{crit}} \) critical value at both low (UCST) and high (LCST) temperatures. On the other hand, the specific interactions case dominates the unfavourable free volume and size effect terms, especially at low temperatures, and gives rise to a sloping curve from negative to positive \( (\chi) \) allowing only the possibility of an LCST. This again suggests that if miscibility is to occur, strong specific interactions are required between components.

![Figure 2.4: schematic representation of temperature dependent contributions towards the interaction parameter, \( (\chi) \). (after Patterson\(^\text{41}\)).](image)
2.4 PHASE BEHAVIOUR OF POLYMER BLENDS

2.4:1 Binary Phase Behaviour

Phase separation may occur in homogeneous blends by either raising or lowering the temperature, depending on whether the behaviour is LCST or UCST. This gives rise to two general forms of phase diagram as depicted by the cloud point curve in Figure [2.5]. The cloud point curve is used to show phase behaviour in a polymer blend. This can be estimated or measured experimentally for a real system. Theoretically, it lies somewhere in-between the binodal and spinodal curves in the metastable region.

The cloud point curve which is associated with phase separation on heating is referred to as the lower critical solution temperature (LCST) phase diagram; LCST behaviour is common for high molecular weight polymer blend systems which are classed as partially miscible. Flory's equation of state theory successfully interprets LCST behaviour for polymer mixtures leading to negative entropies and heats of mixing (exothermic system). Phase separation occurs due to an increasing unfavourable free volume effect, Section [2.3:1] and a decrease in mutual solubility as the temperature is increased. This suggests that a LCST should generally be anticipated for binary polymer blend systems.

The cloud point curve which is associated with phase separation upon lowering of temperature is referred to as the upper critical solution temperature (UCST) phase diagram; UCST behaviour is usually observed for low-molecular-weight oligomeric mixtures and in mixing of a polymer solvent or two liquids. It is usually characteristic of a system that mixes endothermically but is less common for high-
molecular-weight polymers as many critical points occur below the $T_g$ of the blends and so are not accessible experimentally.

Phase behaviour of polymer blend systems usually depend on molecular weight, thermal expansion coefficient, thermal compression coefficient and interaction parameter. As a result, McMaster$^{29}$ and others$^{51-53/58}$ have simulated spinodals for binary systems by manipulation of the above parameters. These theories predict systems that simultaneously show both LCST and UCST behaviour$^{54}$, figure [2.6] and thus have a "miscibility window".$^{19/20}$ This phase behaviour is possible when the interaction energy assumes small positive values, ie: no strong hydrogen bonding or acid-base interactions occurring between the components. For larger positive values of this parameter, the LCST and UCST merge to yield an "hourglass" shaped diagram, figure [2.7], in which there is no temperature with complete miscibility of the components.

![Figure 2.6: binary phase behaviour.](image)

![Figure 2.7: binary phase behaviour.](image)

Examples of blends revealing LCST behaviour include: ethylene-vinyl acetate copolymer with Poly(vinyl chloride), Polycarbonate with Poly($\varepsilon$-caprolactone),$^{16}$ Polystyrene with Poly(vinyl methyl ether)$^{56}$ and Polycarbonate with Poly ($\alpha$-methylstyrene-co-acrylonitrile).$^{57}$

Blends revealing UCST behaviour are usually concerned with polymers of modest molecular weight and include: Polyisobutene with Poly(dimethyl siloxane),$^{59}$ low molecular weight Polystyrene with Polyisobutene,$^{60}$ and a low molecular weight $\alpha$-methylstyrene-vinyl toluene copolymer with a low molecular weight Polybutene.$^{61}$

13
The existence of both a UCST and LCST has been found in some blends of high molecular weight polymers including: Polybutadiene with Poly(styrene-co-butadiene), Poly(acrylonitrile-co-styrene) with Poly(acrylonitrile-co-butadiene), Poly(methyl methacrylate) with Poly(vinylidene fluoride) and Polystyrene with carboxylated Poly(2,6-dimethyl-1,4-phenylene oxide).

2.4.2 Ternary Phase Behaviour

Phase behaviour of ternary mixtures where one component is a solvent appeared early in literature for the case of symmetric systems ($\chi_{12} = \chi_{13}$) by Scott, using Flory-Huggins lattice theory. More recently, the restriction of symmetry has been relaxed and the importance of polymer-solvent interactions on phase behaviour of ternary solutions has been realised.

Using the Flory-Huggins theory, ternary phase diagrams can be calculated in terms of the $\chi$ parameter for the interaction between the three pairs of components. However, this simple additivity of binary terms does not allow for ternary effects and so an equation-of-state theory developed by Flory, Prigogine and Patterson includes a ternary correction. This term takes into account the dissimilarity in contact surface and in free volume between polymers and liquids, which the Flory-Huggins theory neglects.

The primary requirement for ternary blend miscibility as with the binary systems, is a negative heat of mixing between blend components. Ternary phase diagrams can therefore be constructed by plotting spinodals and critical points calculated for different combinations of the interaction parameter. Optimal conditions for miscibility are obtained when all three interaction parameters are favourable, i.e.: $\chi_{ij} < 0$, and have similar values. Small differences in $\chi_{ij}$ values can result in phase separation, even when all three pairs are separately miscible.

The ternary phase diagram is usually at a single temperature on an equilateral triangle, figure [2.8]. Each corner represents a component, the sides represent the corresponding binary mixture and the interior represents the ternary system. As expected, an enormous variety of phase diagrams can be calculated, complete with binodals, spinodals and critical points. The types of data that have appeared in literature for real mixtures are shown in figures [2.9 and 2.10]; those for calculated mixtures are given in figure [2.11]. Figure [2.9] shows data for a mixture of polymers that is immiscible in the absence of solvent. Figure [2.10] shows data for a mixture of polymers that is miscible in the absence of solvent, and in which each polymer is separately miscible with the solvent in
all proportions, but where separation occurs in some compositions when all three components are mixed. Figure [2.11] shows a hypothetical phase diagram for a ternary system, with spinodals calculated for different interaction parameters producing closed loop miscibility gaps.

Figure 2.8: ternary phase diagram.

Figure 2.9: ternary phase diagram for benzene/butyl rubber/EPDM.

Figure 2.10: ternary phase diagram for benzene/butyl rubber/EPDM.

Figure 2.11: spinodal curves for a symmetric ternary blend of three partially immiscible pairs producing closed loop miscibility gaps. (after Su et al).

2.4.3 Phase Separation Phenomena

Phase separation phenomena in miscible polymer liquids is generally brought about by variations in temperature, pressure and composition of the mixture. The phase separation that occurs is either due to a nucleation and growth mechanism, or a spinodal decomposition.

Nucleation is the process of generating within a metastable mother phase the initial fragments of a new and more stable phase. This initial fragment is called a nucleus and its formation requires an increase in the free energy which is obtained by a finite
undercooling in the binodal region. Nucleation is therefore an activated process which forms unstable intermediate embryos in the metastable region; compositions $\phi^s \rightarrow \phi^s_1$ and $\phi^s \rightarrow \phi^s_2$, figure [2.2]. Once the nuclei are formed, the miscible system decomposes with a decrease in free energy, and the nuclei grow. This growth process as well as the corresponding phase structure is illustrated in figure [2.12].

![Diagram](image)

**Figure 2.12**: phase separation by the nucleation and growth mechanism: (I) one-dimensional evolution of concentration profiles; (II) two-dimensional picture of the resultant phase structure. (After Olabisi	extsuperscript{15}).

Given a homogeneous solution of composition $C_0$, if a nucleus of composition $C'_a$ is formed the composition of the mother phase in the immediate vicinity of that nucleus would be $C_a$. The molecules within the mother phase with the concentration $C_o$ would then diffuse into the lower concentration phase, ($C_d$), producing a chemical potential gradient which helps to feed the young nucleus. The concentration within the nucleus remains constant at $C'_a$ and that of the second phase at $C_a$ during this growth process; but the interfaces between the two phases move with time as illustrated in figure [2.12].

The final droplet sizes and the distances between them depend on the number of nuclei, the time scale of the decomposition and the rate of diffusion. The final morphology obtained by a nucleation and growth phase separation mechanism is therefore a matrix containing inclusions of the minor phase; i.e:- a matrixdispersed particle type of structure.

Spinodal decomposition is the mechanism by which a homogeneous blend starts to phase separate at temperatures inside the unstable spinodal region; compositions $\phi^s \rightarrow \phi^s_1$, figure [2.2]. Unlike the nucleation and growth mechanism, an activation energy is not
required for this process as growth originates from small fluctuations of concentration with time. This is therefore a diffusion process which is free energy driven.

At the early stage of Spinodal decomposition when infinitesimal composition fluctuations start to grow, the phase sizes are very small and interconnected, with decomposition occurring spontaneously. As the components separate by diffusion, the amplitude of concentration fluctuations increase and a growth process occurs as illustrated in figure [2.13] with the corresponding phase structures.

Figure 2.13: phase separation by the spinodal decomposition mechanism: (I) one-dimensional evolution of concentration profiles; (II) two-dimensional picture of the resultant phase structure. (after Olabisi).

Decomposition by this method produces at some point a high level of phase interconnectivity in both the minor and major phases thus producing an interpenetrating network (IPN) structure, Section [2.8:3]. However, as total phase separation becomes complete, the system tends to minimise its interfacial free energy by reducing the amount of interface area, through the formation of spheres, i.e., dispersed particles. This effect usually occurs for low viscosity polymers with higher diffusion rates. If the viscosities are relatively high however, the final structure may remain interconnected.

The overall morphology of the blends that phase separate by this method, can be controlled by chemically pinning the spinodal decomposition. Methods for doing this include: i) quenching below the glass transition temperature, ii) crystallisation, iii) setting up of strong intermolecular interactions and iv) crosslinking.
2.5 PREDICTION OF MISCIBILITY

Early attempts to predict the miscibility of polymer blends concentrated on the use of Hildebrand's solubility parameter (δ) defined by:

\[ \delta = \sqrt{\frac{\Delta E}{V}} \]  

i.e. the square root of the energy of vapourisation per unit volume of material.

The solubility parameter of a species is determined by its chemical structure and is proportional to its cohesive energy. This in turn is defined as the increase in internal energy (ΔU) per mole if all the intermolecular forces are discounted. The solubility parameters are usually calculated by the use of group molar attraction constants for the repeat units of the polymer. This is achieved by referring to tables of molar attraction constants, (F), attributed to both Small and more recently, Hoy and thus, using the relationship:

\[ \delta = \Sigma F/V \]  

Predicting miscibility by this method necessitates looking for closely matched non-hydrogen bonded solubility parameters which would produce a very small exothermic heat of mixing. This approach however, has proved unsuccessful in determining polymer-polymer miscibility and so a more plausible approach is used nowadays which considers intermolecular interactions leading to negative values for both interaction parameter, (χ), and enthalpy of mixing, (ΔH), Section [2.3].

An exothermic heat of mixing may arise as a result of the reaction between a proton donor and a proton acceptor. This may occur due to interactions such as dipole-dipole, charge transfer and hydrogen bonding. It has been found that the greater the relative strength of the intermolecular interactions present between the polymer components of the blend, the greater the probability of miscibility. It is therefore possible to select two polymers which have 'complementary dissimilarity' to yield an exothermic heat of mixing. However, there will still be an endothermic contribution to the overall enthalpy of mixing between the remaining parts of the structure which do not interact specifically. Hence, specific interactions do not guarantee miscibility of polymer pairs.

Polymer-polymer miscibility may also be predicted from the heats of mixing data obtained experimentally for mixtures of low molecular weight compounds which closely
resemble the polymer repeat units. Interaction parameters, obtained from fitting $\Delta H_m$ of low molecular weight liquid analogues to a simple Van Laar heat of mixing model, equation (2.9), agree reasonably well with the parameters obtained from the corresponding miscible polymer blends.\textsuperscript{85/86}

$$\frac{\Delta H_m}{V} = \Sigma_{i,j} B_{ij} \phi_i \phi_j$$ \hspace{1cm} \text{equation 2.9}

The observation that polymers are immiscible when their analogues mix endothermically\textsuperscript{35/87} also justify this method for predicting miscibility as it confirms the importance of nearest neighbour enthalpic interactions to the thermodynamics associated with the phase behaviour of binary polymer blends. However, the use of this technique critically depends on how close the analogues selected actually simulate the interactions of the polymers. For instance, polymeric structural features such as stereoregularity and sequence distribution in copolymers can strongly influence polymer miscibility, but are difficult to simulate in analogue calorimetry measurements. Chain conformation and long hydrocarbon-polymer chains that are unfavourable for mixing are also impossible to simulate from low molecular weight analogues and it is also difficult to find analogues whose structures precisely replicate those of the polymer repeat units.

Recently, several investigators\textsuperscript{88-90} have discovered that the enthalpy of mixing can be calculated from the composition weighted sum of binary interactions between unlike molecular groups, (structural units), within the repeat units of the polymer components. Thus, each repeat unit itself becomes a mixture of structural units and the heat of mixing associated with forming the structural units for each repeat unit must be subtracted from that of forming the mixture directly from the structural units. This approach\textsuperscript{91} properly considers the self interactions between groups on the same molecule to give;

$$\Delta H_m/V = \Sigma_{i,j} B_{ij} \phi_i \phi_j - \Sigma_k \psi_k \Sigma_{i,j} B_{ij} \phi^k_i \phi^k_j$$ \hspace{1cm} \text{equation 2.10}

where, $\psi_k$ = volume fraction of polymer $k$ in the blend.

$\phi^k_i$ = volume fraction of structural unit $i$ in polymer $k$.

$\phi_i$ = volume fraction of structural unit $i$ in the blend.

This equation predicts that miscibility may occur even when all the $B_{ij}$ parameters are positive. This situation can arise when the self-interactions, represented by the second terms in equation (2.10), are more endothermic than the interactions between groups on different polymer molecules in the blend, represented by the first terms. The practical
application of this equation however, is difficult as it requires the evaluation of B parameters from experimental observations of analogue heats of mixing.92

Group contribution methods, in which groups are chosen to closely approximate the multigroup structure of the blend components, offers a comprehensive description of the effect of structure on the heat of mixing and leads to a more accurate prediction of polymer-polymer miscibility. Provided the structural units are chosen to be small enough that they are well represented in a variety of small molecules, it is possible to obtain the B parameters associated with interactions between groups from liquid heats of mixing data for a variety of compounds which are quite different from any particular polymer repeat unit. This method, therefore, avoids the need to have close low molecular weight analogues to the polymer repeat units.

The commonest and most accurate thermodynamic model used to predict polymer-polymer miscibility, based on a group contribution method, is the Modified Guggenheim Quasi-chemical (MGQ) model. This is more flexible than the simple Van Laar model as it assumes local non-randomness. If very high quality heats of mixing data are used it is possible to correlate liquid heats of mixing to within 5% relative error thus yielding group interaction parameters which are sufficiently accurate to permit reasonable prediction of polymer-polymer miscibility.39 However, the MGQ model, like the simpler Flory-Huggins theory, is unable to predict LCST behaviour. Recently, investigators39 have combined this model with 'equation-of-state' theories so as to attempt to provide the additional information required to predict this behaviour.

2.6 METHODS OF POLYMER BLENDING

The three main methods for mixing polymers are:

(i) mechanical mixing in the melt.
(ii) mixing in solution then film casting, freeze or spray drying.
(iii) in situ polymerisation.

The simplest and most economical way of preparing polymer blends is by mechanical melt blending on either a two roll mill, in an internal mixer, or more commonly nowadays, in a compounding extruder. The nature of the resulting blends depend on the temperature and length of mixing, the shear forces exerted by the mixing paddles and the rheological properties of the polymers. Equilibrium mixing by this method can prove difficult to achieve due to the low diffusion coefficient of polymers, even at elevated
temperatures. Mixing times must be kept to a minimum so as to prevent thermal degradation of the polymers and to limit any unwanted transreactions, Section [2.8:5]. Also, it has already been suggested that many polymer blends reveal LCST's, Section [2.4]. Therefore, melt blending of these systems will usually take place above this temperature and will result in multiple phase formation.

The low diffusion coefficients can be overcome by dissolving the two polymers in a common solvent at low concentrations. After mixing in the desired proportions, the solid polymer blend can be recovered by either evaporation or precipitation into a non-solvent. This method can easily be carried out below the LCST of most polymer blends and so, there is a higher probability of forming a homogeneous system. However, solution blending can sometimes fail due to occasions where the solvent strongly interacts with one of the polymer components, thus producing a ternary phase diagram. Secondly, problems may arise from the possible inability to completely remove the solvent from the blend. Excess solvent may become 'trapped' under the polymer skin and thus contribute a plasticising effect to the system. Therefore, mixing in a common solvent does not guarantee homogeneity and would not be industrially viable except in special circumstances.

In situ polymerisation is the polymerisation of one monomer in the presence of another polymer. It has been used extensively in the preparation of two phase blends but, has only recently been applied to the preparation of homogeneous blends. It has many advantages for the preparation of blends where the components are not thermally stable, have high $T_g$'s, or show phase separation on heating which precludes the use of mechanical mixing in the melt. Many systems containing graft copolymers have been successfully prepared by this method but, it does not necessarily guarantee homogeneity as two phase regions can exist within the polymer/polymer/monomer ternary phase diagram.

2.7 METHODS FOR DETERMINING POLYMER BLEND MISCIBILITY

Several techniques are available to determine respectively polymer-polymer compatibility, the nature of the phases and the interaction between the phases of a polymer blend. Optical, mechanical, electrical, morphological and thermodynamic properties are often determined when establishing the extent of miscibility in a system. These are explained in the following sections.
2.7:1 Optical Clarity

A homogeneous polymer blend has a single refractive index which is intermediate between those of the constituents thus, optical clarity usually indicates that the two polymers are miscible. However, transparency is not sufficient proof of homogeneity. A blend may be transparent even when heterogeneous if the refractive indices of the components are similar, the size of the dispersed phase is too small to scatter a significant amount of light, or the sample is a very thin film such that the light only encounters one of the two phases when passing through. Optical clarity is thus, unreliable when characterising polymer blends as both homogeneous and heterogeneous systems can be transparent.95

2.7:2 Morphological Studies

a) Microscopy Methods

Both optical and electron microscopy are widely used in determining the compatibility of a polymer blend.96-99 It is possible to ascertain the multiphase character of a blend by microscopic examination. Staining techniques and phase contrast optics help to differentiate between phases as they allow observation of particles with equivalent refractive indices. Optical microscopy however, can only be employed to examine macroscopically heterogeneous blends. For greater resolution both scanning and transmission electron microscopy techniques are employed. Scanning electron microscopy is used to observe the morphology of surfaces from samples fractured in the glassy state whereas transmission electron microscopy is used to examine the bulk of the material by passing through a microtomed section (≤0.2μm thick).

b) Scattering Techniques

Several scattering techniques can be employed when determining the compatibility of a polymer blend.15 Small angle neutron scattering, (SANS), elucidates the chain conformation100 whereas the local order within a blend is determined by both electron and rayleigh-brillouin scattering.101 The gross morphology of a blend can be studied by both small-angle light scattering, (SALS), and small-angle X-ray scattering, (SAXS), techniques.102 The morphology and hence, compatibility of the blends are ascertained by interpreting the obtained scattering patterns. These methods reveal the overall structure of the polymer system and thus, are also employed to determine spinodal temperatures and to follow both spinodal decomposition and nucleation and growth mechanisms.
2.7:3 Spectroscopic Techniques

a) Nuclear Magnetic Resonance
Molecular level observations of specific interactions between dissimilar blend components can be obtained from high resolution solid-state proton and carbon-13 nuclear magnetic resonance, (NMR). This analytical technique fingerprints the components of a strongly interacting blend as perturbations in the NMR spectra result from conformational changes, hydrogen bonding, electron transfer reactions and packing geometry changes on mixing. The NMR phenomenon of spin diffusion is an especially fruitful source of information when determining the compatibility of a polymer blend. Spin diffusion measurements are sensitive to local structure in polymers as the rate at which spin transfer occurs when the two nuclei interact reflects the degree of contact and hence, compatibility, between the components of the polymer blend.

b) Infra Red
Fourier Transform Infra Red (FTIR) Spectroscopy has been widely used to determine the specific interactions involved in blend miscibility. Observation of bond shifts in the spectra is often used to identify the interacting chemical groups. Many miscible blends involve polymers containing ester groups in the chain which become compatibilised through hydrogen bond formation. The extent of miscibility present is thus determined by significant shifts in the carbonyl stretching frequencies.

2.7:4 Glass Transition Temperature Methods

The most commonly used method for establishing the extent of miscibility in polymer blends is through determination of the glass transition (or transitions) in the blend versus those of the unblended constituents. A miscible polymer blend will exhibit a single and sharp composition dependent glass transition temperature, \( T_g \), in-between those of the constituent polymers, as illustrated by figure [2.14].

![Figure 2.14: dynamic mechanical properties of a miscible polymer blend.](image1)

![Figure 2.15: dynamic mechanical properties of an immiscible polymer blend.](image2)
In cases of borderline miscibility, broadening of the transition will occur, whereas two separate $T_g$'s appear in cases of immiscibility, as illustrated in figure [2.15]. With cases of limited miscibility, two separate transitions between those of the constituents may result, depicting a component A-rich phase and a component B-rich phase, as illustrated in figure [2.16].

![Figure 2.16: dynamic mechanical properties of a partially miscible polymer blend.](image)

The glass transition temperature can be detected using a number of methods but, the most commonly employed are dynamic mechanical measurements. However, various other methods such as dilatometric, dielectric and calorimetric have been used. In general for a miscible blend, it is observed that $T_g$ increases monotonically with changing composition, showing either zero, positive or negative deviation from linearity, figure [2.17].

![Figure 2.17: glass transition temperature behaviour of a miscible polymer blend.](image)
Examples of a linear variation of $T_g$ versus composition include; nitrocellulose/Poly(methylacrylate)$^{119}$ and natural rubber/Polybutadiene.$^{120}$ Examples of negative deviation from linearity are quite common. In many of these cases, data fit theoretical relationships proposed by the simple Fox equation,$^{117}$ equation (2.11) and Gordon-Taylor equation,$^{118}$ equation (2.12).

\[ \frac{1}{T_g} = \frac{W_A}{T_{gA}} + \frac{W_B}{T_{gB}} \]  
\[ T_g = \frac{[W_A T_{gA} + kW_B T_{gB}]}{[W_A + kW_B]} \]

where, $T_{gA}$ and $T_{gB}$ represent the glass transitions of the two undiluted polymer components, $W_A$ and $W_B$ are the weight fractions of the two components, and $k$ is the ratio of thermal expansion coefficients between the rubber and glass states of the component polymers, $(\beta_{RB} - \beta_{GB}) / (\beta_{RA} - \beta_{GA})$.\(^{111}\)

Examples of the successful applications of the linear Fox equation to miscible blends include Poly(vinyl chloride)/butadiene-acrylonitrile copolymers$^{121}$ and Polystyrene/Poly(2,6-dimethyl - 1, 4 - phenylene oxide).$^{122}$ Miscible blends in which the $T_g$-composition data are satisfied by the Gordon Taylor equation include Poly(methyl methacrylate)/Poly(vinyl acetate)$^{123}$ and styrene-butadiene copolymer with Polybutadiene.$^{124}$

Positive deviations of the $T_g$-composition data from linearity imply the existence of strong intermolecular associations between the constituents of the blends. This behaviour has been found for both Poly(acrylic acid)/Poly(ethylene oxide)$^{125}$ and Poly(hydroxy ether) of bisphenol A/Poly(butylene terephthalate)$^{126}$ systems.

There are however limitations in the use of $T_g$ as a criterion for blend miscibility. For example, when the $T_g$'s of the components are close together (<20K) it may not be possible to resolve the transitions. Also, the magnitude of the $T_g$ depends upon the concentration of the component and so, when one component is present in a very small quantity the method used to detect the $T_g$ may not be sufficiently sensitive. Similarly, crystallinity may reduce the baseline shift expected at $T_g$ by thermal analysis, making this transition hard to detect. Finally it is not uncommon to find the $T_g$ of blends to be broader than that of the pure components,$^{127/128}$ owing to composition fluctuations in the mixture. These results may therefore lead to false conclusions concerning the miscibility of the blend.
2.7:5 Melting Point Depression

Melting point depression is the most straightforward way to measure the interaction parameter, \( \chi \), requiring only that at least one of the components be semicrystalline.\(^{129}\) In terms of the Flory-Huggins theory, melting point depression can be determined by the expression:\(^{130}\)

\[
\frac{1}{T_M} - \frac{1}{T_M^0} = \frac{RV_2}{\Delta H_2 V_1} \left[ (1-\phi_2) - \chi_{12}(1-\phi_2)^2 \right]
\]

equation 2.13

where, \( \chi_{12} \) is the interaction parameter, \( T_M \) the experimental melting point, \( T_M^0 \) the equilibrium melting point, \( \Delta H_2 \) the heat of fusion of 100% crystalline polymer per mole of repeat unit, \( V_1 \) the molar volume of the amorphous component, \( V_2 \) the molar volume of polymer repeat unit, and \( \phi_2 \) the volume fraction of crystalline polymer. Therefore, in a miscible blend, the obtained negative interaction parameter, \( \chi_{12} \), will yield a melting point depression.\(^{131}\) This behaviour has been observed for Poly(vinylidene fluoride)/Poly(methyl methacrylate)\(^{111}/^{132}\) systems and is due to the diluent effect of the amorphous component restricting the crystallisation of the semicrystalline polymer. However, there are limitations to this approach as the melting point measured is directly influenced by the perfection and size of the crystals which in turn are influenced by the conditions under which they were grown.

2.7:6 Mutual-Solvent Methods

The mutual-solvent method of determining polymer-polymer miscibility is particularly used in the field of paints, varnishes and lacquers.\(^{14}\) It consists of dissolving a mixture of two polymers at low concentration in a mutual solvent and then allowing it to stand for a few days. The polymers are considered miscible if phase separation does not occur after this time and immiscible if they do.

2.7:7 \( \beta \)-Relaxation Studies

It has been shown that in several miscible polymer blends, the low temperature secondary relaxation transition, \( \beta \)-commonly attributed to rotational movement of groups around the main polymer chain), is significantly reduced in magnitude.\(^{135-137}\) This behaviour, known as antiplasticisation\(^{136}/^{137}\) was also confirmed by Mondragón \textit{et al},\(^{138}\) and has been attributed to the fact that the molecular moiety responsible for the
relaxation is directly involved in the specific interaction responsible for full or partial miscibility. These secondary relaxations are more sensitive to small-scale local environment and as such may be more revealing measures of the intimacy of mixing between different polymer molecules.

The relationship between the $\beta$-relaxation and polymer-polymer miscibility however, is for the moment not completely understood and so future research in this field would be useful.

2.8 METHODS OF ENHANCING MISCIBILITY

Generally, the mixing of two polymers results in a heterogeneous system due to a positive enthalpy of mixing. Compatibilisation is therefore required to overcome this unfavourable condition\textsuperscript{10/11} which, may be achieved by one of the following methods.

2.8:1 Chemical Modification

One of the most direct methods of achieving enhanced miscibility is to modify the structure of one or both components. This is usually achieved by either functionalising the monomer unit itself through incorporation of acid/base groups, hydrogen bonding groups, ionic groups, charge transfer complexes etc., or by copolymerisation.

The most common method of enhancing miscibility is to develop hydrogen bonding between the components.\textsuperscript{129/140} This can be achieved by incorporating electron donor groups, (pyridine, ketones, esters, ethers) and electron acceptor groups, (alcohols, aniline, carboxylic acids, halogenated hydrocarbons), into the polymer chains. Pearce \textit{et al.},\textsuperscript{141} used this technique to produce miscible Polystyrene blends with Polyesters by making the adduct of Polystyrene with hexafluoroacetone. This functionality added a strong hydrogen bonding capability to the polystyrene.

Ionic interactions between polymers constitute the strongest potential for specific interaction short of direct covalent bonding. They are achieved by the introduction of a small amount of bonded salt groups into a relatively non-polar polymer chain, thus producing ionically charged materials, termed ionomers.

Many workers have concentrated on the use of ionomers to enhance miscibility in polymer blends.\textsuperscript{142-146} The improvements in compatibility are generally explained by the
formation of 'ionic crosslinks' or 'ionic clusters'. Immiscibility is overcome by the co­
ordination of both anions and cations, thus forming clusters of ionic species from both
components of the blend. The ionic clusters act as physical crosslinks, forming
aggregates of macromolecules comparable to block or graft copolymers in their
capability to enhance interfacial adhesion. Willis and Favis\textsuperscript{147} employed this technique
to produce a compatible Polyolefin/Nylon 6 blend by incorporating only 5% of surlyn
ionomer.

2.8:2 Block and Graft Copolymer Formation

Block and graft copolymers are often classed as compatibilising agents as they are used
to enhance miscibility in a polymer blend.\textsuperscript{148/149} They function as an organic surfactant
at the interface of two incompatible polymers, where they reduce interfacial tension and
promote adhesion between phases, figure [2.18].

![Figure 2.18: ideal location of block or graft copolymers at the interface
between polymer phases A and B.](image)

The copolymer has to be selected such that the segments are either chemically identical
with those in the respective phases,\textsuperscript{150/151} or miscible with or adhered to one of the
phases.\textsuperscript{152/153} It is found that only a very small concentration of copolymer is required to
compatibilise an immiscible system.\textsuperscript{154} A sharp reduction in interfacial tension is
observed with the addition of a small amount of copolymer followed by a levelling off
indicative of saturation of the interface. Further addition of compatibiliser beyond this
level does not produce additional improvements in properties of the blend, owing to the
copolymer precipitating as a third phase.

Numerous block copolymers have been developed as compatibilising agents with the
consensus that miscibility enhancement varies in the sequence, di-block>tri-block>four-
arm star. Graft copolymers are generally believed to be less effective as interfacial agents than the corresponding block copolymers\textsuperscript{155} but, they are widely used as compatibilisers\textsuperscript{156-158} due to their easier preparation.

### 2.8.3 Interpenetrating Network Formation

Interpenetrating Polymer Networks, (IPN's), are a unique type of polymer blend which are more or less an intimate mixture of two or more distinct crosslinked polymers in network form, of at least one of which is synthesised or crosslinked in the immediate presence of the other.\textsuperscript{159-161} IPN's can therefore be described as combinations of chemically dissimilar polymers in which the chains of one are completely entangled with those of the other thus, producing a co-continuous system as shown in figure [2.19].

![Figure 2.19: schematic of an interpenetrating network structure. (after Paul).](image)

The major advantage of IPN's over other blends is that they represent a way of blending two or more polymers to produce a mixture in which phase separation is restricted by highly interconnected chemical networks. The co-continuity produced in the blend can often enhance the transport properties of the system\textsuperscript{162} as each polymer phase can form a more effective barrier to the diffusion of gases or liquids. Thermoplastic systems can form physical crosslinks instead of covalent or chemical crosslinks in the production of an IPN type morphology. They are usually prepared by either chemical blending through \textit{in situ} polymerisation, or by mechanical blending in the melt state. Co-continuous IPN phases obtained by the latter method usually occur through spinodal decomposition,\textsuperscript{163} Section [2.4:3].

There have been many immiscible systems successfully compatibilised by IPN formation. Walsh \textit{et al},\textsuperscript{164} produced an IPN by polymerising vinyl chloride, (VC), in the presence of Poly(ethyl acrylate), (PEA). This produced a homogeneous system, whereas
the physical blending of PVC and PEA produced immiscible blends. Similarly, Huelck et al.,\textsuperscript{165} produced a compatible PEA/Polystyrene-co-methyl methacrylate) IPN, whereas physical blending of the components produced an immiscible system.\textsuperscript{166}

2.8:4 Crosslinking

Controlled crosslinking is a technique that can be used to enhance polymer-polymer miscibility.\textsuperscript{167} Rizzo et al.,\textsuperscript{168} used irradiation to successfully compatibilise Polyethylene/Polypropylene blends. The resulting system had improved mechanical strength.

Straight blending, followed by crosslinking, has also led to increased miscibility in both Natural rubber/Polypotadiene rubber\textsuperscript{169} and Poly(ethylene terephthalate)/Ethylene-methacrylic acid copolymer blends.\textsuperscript{170} In the latter system, enhanced barrier properties were obtained by crosslinking with epoxides, peroxides and irradiation techniques, thus suggesting the formation of some phase co-continuity.

2.8:5 Co-Reactions

Co-reactions between blend components have enhanced the miscibility of many polymer systems.\textsuperscript{171-173} The potential for interchange reactions between components of a blend relies on chemically dissimilar functional groups to be present on the polymer backbones. In principle, therefore, numerous interchange reactions are possible between condensation polymers.\textsuperscript{174} Devaux et al.,\textsuperscript{175} stated that there are three likely mechanisms taking place in Poly(butylene terephthalate)/Bisphenol-A Polycarbonate blends:

(i) alcoholysis by -OH terminated PBT; (ii) acidolysis by -COOH terminated PBT and the main, (iii) direct transesterification reaction.

i) Alcoholysis:

\[
R-C\equiv O \quad \text{OR'} + R''-OH \quad \rightleftharpoons \quad R-C\equiv O \quad \text{OR''} + R'-OH
\]

ii) Acidolysis:

\[
R-C\equiv O \quad \text{OR'} + R''-C\equiv O \quad \rightleftharpoons \quad R-C\equiv O \quad \text{OH} + R''-C\equiv O \quad \text{OR'}
\]
iii) Transesterification:

\[ R-\overset{\equiv}{C}=O_{\text{'OR'}} + R''-\overset{\equiv}{C}=O_{\text{'OR''}} \rightleftharpoons R-\overset{\equiv}{C}=O_{\text{'OR'}} + R''-\overset{\equiv}{C}=O_{\text{'OR''}} \]

The ester-exchange, (transesterification), reaction however, is the most common mechanism for converting immiscible blends of polyesters to single phase materials as the concentration of ester groups is profoundly greater than those of the end groups for a polyester. Owing to these interchange reactions, block copolymers formed at the first stage of melt blending undergo randomisation as transesterification proceeds, thus producing random copolymers which may not be crystallisable and may exhibit a single \( T_g \) intermediate between those of the constituents.

Further examples of blends that are homogenised by transesterification are; Bisphenol-A and tere/isophthalate based Polyarylate/Poly(ethylene terephthlate) and PC/PET. The interchange reactions of the latter system are slow, but can be accelerated by esterification catalysis. In fact, the ester-exchange reaction itself is found to be initiated by the residual polymerisation catalyst found in commercial polyesters.

Randomisation however, is not always desirable as it leads to a reduction in crystallisation which in turn lowers the solvent resistance properties of the system. Transesterification in polyester blends can also lead to materials with poor mechanical properties and so, both the temperature and residence time of melt blending must be controlled so as to limit the extent of randomisation depending on the desired properties required. Chemical strategies have also been devised to retard the ester-exchange reaction. Organophosphorus compounds, such as phosphites, phosphonates and phosphates have been successfully employed to control the transesterification process. This is especially useful for polyesters that rapidly crosslink by ester-exchange reactions with the hydroxyl functionality of Poly(hydroxy ether) of bisphenol-A, [Phenoxy].

### 2.8.6 High Stress Shearing

By applying high shear forces whilst melt mixing a polymer blend it is possible to enhance the compatibility of the system. Intensive mixing breaks down the large dispersed spheres of the minor component in an immiscible blend which then become dispersed in the matrix. There is therefore a subsequent reduction in the fractional volume of the former and so, with increased shearing, the system becomes homogenised.
This homogeneity is retained if the mixture is immediately quenched but, in annealing, phase separation will occur through spinodal decomposition. These effects were also observed by Lyngaae-Jorgensen et al., for high shear mixing of the immiscible Styrene-acrylonitrile, [SAN]/Poly(methyl methacrylate), [PMMA] blend. They found that by applying a homogeneous shear field to the system the phase boundary, (binodal), is shifted up the temperature scale (a→b), see figure [2.20]. The homogenisation that occurs is therefore a result of moving the stress dependent binodal and spinodal above the temperature of the measurements.

![Figure 2.20: the effect of the shear of mixing on the SAN/PMMA binodal](image)

Takahashi et al., also investigated the effect of shear rate on the incompatible SAN/Polycarbonate (30/70) blends. They found that the size distribution of the SAN particles in the PC matrix became wider with increasing shear rate and thus concluded that the compatibility of SAN with PC is enhanced in extremely high shear rate processing.

2.8:7 Addition of a Common Solvent

A co-solvent is often used to generate compatible blends. Frequently two immiscible polymers will form a true solution in a common solvent. After its removal (eg:- by sublimation, evaporation or freeze-drying), the interfacial area is so large that even weak polymer-polymer interactions will stabilise the system. Using the system Poly(vinyl acetate) and Poly(methyl methacrylate), Ichihara et al., showed that freeze drying from benzene produced metastable miscible systems with intermediate glass transition
temperatures. However, heating the samples above this $T_g$ resulted in phase separation demonstrating the metastable nature of freeze-dried mixtures.

Further applications of the co-solvent principle is the addition of a co-miscible oligomeric plasticiser or a polymer with functional groups which are able to crosslink one or both phases. The latter method has been successfully employed by Remiro et al.\textsuperscript{188} He found that by adding Poly(butylene terephthalate), [PBT], to the immiscible Phenoxy/Polycarbonate blend he could compatibilise the system due to the fact that PBT is miscible with both components.

\section*{2.9 \textbf{MECHANICAL PROPERTIES OF POLYMER BLENDS}}

The mechanical properties of a polymer blend are influenced by both blend composition and morphology. Often the adhesion between polymer phases is weak and therefore gives rise to poor mechanical properties\textsuperscript{189} A significant part of this problem is due to poor stress transfer between the component phases\textsuperscript{190}

On the other hand, blends comprised of polymers that adhere well to each other reveal good mechanical properties\textsuperscript{191} In many cases\textsuperscript{192-194} the mechanical properties exhibit a maximum, i.e.: greater than those observed for either pure component. This behaviour is thought to arise from the suppression of secondary $\beta$ relaxations, indicative of strong polymer-polymer interactions, resulting from negative volumes and heats of mixing observed\textsuperscript{191/192} Kleiner \textit{et al.}\textsuperscript{193} found that the miscible Poly(phenylene oxide), [PPO]/Polystyrene, [PS], blend exhibited a maximum for both modulus and tensile strength. A similar synergism for tensile and flexural strength was also observed by Olabisi \textit{et al.}\textsuperscript{194} for miscible blends of Poly(methyl methacrylate), [PMMA], and a terpolymer formed from $\alpha$-methyl styrene, methyl methacrylate and acrylonitrile.

Interpenetrating polymer network formation also leads to improved mechanical properties. This is because the continuous nature of the phases allows direct load sharing of the components without the need for stress transfer across phase boundaries.
2.10 POLYSULPHONES/PHENOXY/POLYESTER BLENDS

2.10:1 Polyethersulphone/Phenoxy Binary Blends

PES has been shown to be miscible with phenoxy over the entire composition range at room temperature.\textsuperscript{195/196} Singh \textit{et al},\textsuperscript{9} confirmed miscibility by the presence of a single composition dependent glass transition temperature, ($T_g$), measured by Dynamic Mechanical Analysis on blends produced from Dimethylsulphoxide, [DMSO], solution. However, application of the Gordon-Taylor equation, equation (2.12), suggested that the polymer-polymer interaction of the PES/Phenoxy blend is not strong due to the low calculated value of $K$. The heat of mixing of low molecular weight analogues was found to be small and negative, thus suggesting a favourable interaction between the blend components. Phase diagrams for this binary system obtained by the cloud point method reveal a lower critical solution temperature, (LCST), at ca. 185°C. This is well below the temperature suitable for processing such blends in the melt state and thus melt blending is expected to produce a heterogeneous system.

Saito \textit{et al},\textsuperscript{195} also produced homogeneous PES/Phenoxy blends prepared from Dimethyl Formamide, [DMF]. They observed a concave nature in the free volume term with temperature and suggested that this could lead to the co-existence of both LCST and UCST behaviour in mixtures of these polymers at high molecular weights.\textsuperscript{54/64}

2.10:2 Polysulphone/Phenoxy Binary Blends

From the limited studies of PSO/Phenoxy blends it has been suggested that the system is immiscible over the entire composition range. Swinyard \textit{et al},\textsuperscript{197} found the blend to be visually heterogeneous over the entire composition range for films produced from DMF solution, and observed two $T_g$ values at 97°C and 179°C corresponding to Phenoxy and PSO components respectively.

Block copolymers of PSO and Phenoxy (block $M_n \approx 5000$) however, have been found to be miscible as a single $T_g$ is observed intermediate of the components.\textsuperscript{198}

2.10:3 Poly(butylene terephthalate)/Phenoxy Binary Blends

PBT has been shown to be miscible with phenoxy in the amorphous regions over the entire composition range.\textsuperscript{199/200} Robeson \textit{et al},\textsuperscript{126} observed a single $T_g$ for the melt
mixed blend thus suggesting the system to be homogeneous. Quenched specimens obeyed the linear $T_g$ relationship predicted by the Fox equation, equation (2.11).

The annealed samples however, display positive deviations from linearity due to the resultant effect of PBT crystallisation. With the crystallisation of the lower $T_g$ PBT component out of solution, the PBT concentration in the amorphous phase of the blend is depleted thus leaving the $T_g$ dependent amorphous phase richer in the higher $T_g$ component.

Differential thermal analysis showed that increased Phenoxy content in the blend depressed the crystallisation rate of PBT due to dilution and viscosity effects. However, the degree of crystallinity of PBT was found to increase with Phenoxy content when mixing times were kept short. A slight melting point depression also occurred, ($\pm$1-2°C), which is indicative of a small negative interaction parameter that is favourable to homogeneity.

The basis of miscibility in this system is due to interchange reactions between the components. These reactions probably take place through an alcoholysis between hydroxyl groups in Phenoxy and ester groups in PBT, giving rise to the formation of grafted and crosslinked copolymers with reduced crystallisation and melt temperatures and lower crystallinity, as a consequence of the decrease in the length of PBT crystallisable segments as reactions occur. It is therefore imperative to control both the time and temperature of mixing in these studies, so that a totally amorphous random copolymer of the components is prevented.

2.10.4 Poly(ethylene terephthalate)/Phenoxy Binary Blends

PET has been found to be incompatible with Phenoxy over the entire composition range.\textsuperscript{199-201} Eguiazabol \textit{et al},\textsuperscript{201} observed two $T_g$'s for the melt blend, identical to those of the pure components, therefore suggesting immiscibility in the system. Recently however, Bellhadeb\textsuperscript{202} and others,\textsuperscript{203} found PET to be compatible with Phenoxy over a limited range of compositions, (<25% Phenoxy), and processing conditions. This behaviour would be expected as the potential for the proposed hydroxyl-carbonyl reaction exists for both PBT and PET systems.

The miscibility of PET with Phenoxy is much lower than the corresponding PBT system as the interchange reaction of the former is far slower. This is due to the density of interacting points and flexibility of the polymeric chains. PBT has a longer alkane chain
between the benzene rings and thus is more flexible and susceptible to stereospecific transreactions with Phenoxy. There must therefore be an optimum density of ester groups in the Polyester chain for achieving maximum interaction with Phenoxy.

2.10:5 Polyethersulphone/Poly(ethylene terephthlate) Binary Blends

Debrabendere used Transmission Electron Microscopy to investigate the morphology present in the PES/PET blend. He suggests the blend is primarily incompatible due to an observed matrix/dispersed particle type of morphology. However, for the (60/40) combination, a co-continuous interpenetrating network was seen.

Differential thermal analysis reveals two $T_g$'s corresponding to the pure components. However, a reduction in the PES component $T_g$ (±5°C) for the (60/40) combination is most probably due to the partial compatibility and the type of morphology observed for this composition.

2.10:6 Polysulphone/Poly(butylene terephthlate) Binary Blends

Deng et al. investigated the compatibility of the PSO/PBT blend prepared from a solution of Phenol/Carbon tetrachloride. He first discovered that by annealing PBT at 200°C for four hours, multiple melt behaviour would occur at 230°C and 237°C for the pure PBT crystals. This phenomena was revealed by differential thermal analysis and attributed to the fact that annealing makes PBT crystals more perfect. Yeh et al. also observed multiple melt behaviour for PBT and produced a high temperature shoulder on the main melt endotherm by annealing just below the melting temperature of the polymer.

Deng et al. found an increase in PBT's melting point by blending it with PSO. This phenomena is unusual as it is generally recognised that the mixing of amorphous and crystalline polymers reduces the melting point of the latter. However, Runt et al. recognised that in a semi-miscible blend system, the melting point of the crystalline component is related to the free surface energy of the lamellar and the lamellar thickness. Therefore, the melting point will increase with the increase in the thickness of the lamella which, in a blend, can be thicker and more perfect than that of the pure component.
PSO was found to decrease the rate of crystallisation of PBT only marginally due to both dilution and viscosity effects but, had no effect on the degree of crystallinity. Viscoelastomeric measurements revealed a medium level of compatibility between the components due to a broad $T_g$ peak observed at 107°C intermediate between those of the individual components for the (50/50) composition. This partial compatibility of the system must therefore instigate more perfect PBT crystals and thus, the addition of PSO appears to have the same effect on PBT as annealing a pure sample.

Block copolymers of PSO with PBT have been obtained in a totally amorphous state, exhibiting single phase behaviour.198 Annealing above the intermediate $T_g$ of the blend resulted in an increase in the $T_g$ of the block copolymer with a modulus-temperature behaviour suggesting the onset of PBT crystallisation.

2.10:7 Poly(ethylene terephthalate)/Poly(butylene terephthalate) Binary Blends

Compatibility studies of the PET/PBT blend have been reviewed in literature.207-209 Escala et al.,207 observed a single $T_g$ intermediate between those of the pure components for a quenched film, suggesting miscibility in the amorphous phase. This may be due, however, to the occurrence of ester interchange reactions between the components. A sharp drop in intrinsic viscosities was observed after three minutes in the melt which suggests the occurrence of transesterification or degradation of the components through polycondensation.210

Samples cooled slowly from the melt produced two separate $T_g$'s and melt endotherms on reheating, which suggests incompatibility between crystalline forms. A small depression in the melting point of each component was observed with increasing concentration of the second one which can again be attributed to miscibility in the amorphous phases.

Misra et al.,211 produced a block copolymer of this blend by using the minor component as PBT to successfully increase the crystallisation rate of PET. The blocks of faster crystallising PBT are expected to crystallise first, thus providing nucleation sites for the crystallisation of PET. This results in an increase in the overall crystallisation rate of the block copolymer compared to that of the pure PET component. However, it was found that random copolymers did not produce this phenomenon and behaved more like the PET homopolymer. The melting temperature decreased continuously with increasing PBT content which was as expected due to the lower melt temperature of PBT.
2.10:8 Polysulphones/Phenoxy/Polyester Ternary Blends

Debrabandere has investigated the compatibility of the PES/Phenoxy/PET blend. He found this system to be almost completely incompatible by transmission electron microscopy studies since, when adding a small amount of Phenoxy to the PES/PET (60/40) blend, the morphology changed from a co-continuous to a matrix-dispersed particle type. Separate $T_g$'s of both PES and PET were also observed, thus suggesting the inadequacy of Phenoxy as a compatibiliser for the system.
3.1 RAW MATERIALS

3.1:1 Polyethersulphone

The condensation reaction of diphenyl ether with 4,4' - diphenyl ether disulphenylchloride yields Polyethersulphone, (PES).

reaction:

\[
\begin{align*}
\text{n} & \text{-} \text{phenyl ether} + \text{disulphenylchloride} \\
& \xrightarrow{\text{Friedel-Crafts Catalyst}} \\
& \text{o} + \text{HCl}
\end{align*}
\]

Alternatively, self-condensation of 1-4', diphenylether sulphenylchloride will produce the same polymer with a higher molecular weight.

reaction:

\[
\begin{align*}
\text{n} & \text{-} \text{phenyl ether sulphenylchloride} \\
& \xrightarrow{} \\
& \text{polymer} + \text{n HCl}
\end{align*}
\]
PES is a high glass transition engineering polymer with good mechanical and electrical properties.\textsuperscript{212} It is a high performance engineering thermoplastic possessing all the strengths and weaknesses of glassy amorphous polymers.\textsuperscript{221} At room temperature it is tough, strong and rigid but it is best distinguished by its excellent high temperature performance, low smoke emission and intrinsic fire retardancy.

The phenyl groups are linked by thermally stable ether and sulphone groups. The extensively delocalized structure provides good resistance to oxidative degradation and retention of mechanical properties at high temperatures. The presence of ether linkages impart some flexibility to the polymer chain which gives inherent toughness to the material.\textsuperscript{214} The origin of this toughness is a second-order, (\(\beta\)), transition at approximately -100°C, which is believed to be due to two mechanisms, The first involves 180° flips about the aryl ether bond;\textsuperscript{215} while for the second, a concerted motion involving the sulphone group and complexed water has been proposed.\textsuperscript{216}

The Polyethersulphone was kindly supplied by ICI (Victrex 200P). This grade has a number average molecular weight of 17 600g/mol, a density of 1.37g/cm\(^3\), a refractive index of 1.65 and a glass transition temperature of 226°C.

3.1:2 Polysulphone

Polysulphone, (PSO), is produced by the reaction between the sodium salt of 2,2- bis (4-hydroxyphenyl) propane (bisphenol A), and 4,4'-dichlorodiphenyl sulphone.

\[
\begin{align*}
\text{n Cl-} & \text{S} \text{-Cl} + \text{n NaO-} \text{-} & \text{ONa} \\
\text{n} & \text{O} \text{-} & \text{SO} \text{-} & \text{O} \text{-} & \text{O} \text{-} & \text{ONa} \\
\text{[} & \text{O} \text{-} & \text{SO} \text{-} & \text{O} \text{-} & \text{O} \text{-} & \text{O} \text{-} & \text{ONa} \\
\text{]} & \text{n} \\
& + 2\text{NaCl}
\end{align*}
\]
Aqueous Caustic is added after heating the mixture to 60°C and produces a two phase system consisting of predominately chlorobenzene and aqueous dimethyl sulfoxide containing the disodium salt. The solution is heated under reflux to 150-160°C and then the 4,4'-dichlorodiphenylsulphone is added and reacted. Methyl Chloride is added to control polymerisation, which causes the product to take on a pale yellow colour.

Structurally, the comments made for Polyethersulphone apply to Polysulphone except that the replacement of the isopropylidene linkage for the ether linkage causes the glass transition temperature to decrease. The unique feature of the chemical structure of Polysulphones is the diarylsulphone grouping. This is a highly resonating structure, which is enhanced by having oxygen atoms in the para position with respect to the sulphone group.

![Chemical structures](image)

As well as imparting excellent oxidation resistance to the Polysulphones, the high degree of resonance has two additional effects:

1. it increases the strength of the bonds involved, and
2. it fixes the grouping spatially into a planar configuration.

This provides excellent thermal stability and rigidity to the polymer chain, which is retained at high temperatures. Due to this, the Polysulphones have a high glass transition temperature and the resulting melts have a high viscosity.

The high temperature performance of Polysulphones makes them one of the outstanding thermoplastics for use as load bearing, structural materials for long term use at temperatures up to 150°C for PSO and 180°C for PES. Polysulphones are therefore
competitive with many basic thermosetting compounds but possess the important advantage of low cost injection moulding.\textsuperscript{212}

The Polysulphone, (PSO), was kindly supplied by Amoco (Udel P1700). This powder grade has a number average molecular weight of 25-29 000g/mol, a density of 1.24g/cm\textsuperscript{3}, a refractive index of 1.63 and a glass transition temperature of 185\textdegree C.

3.1:3 \textit{Poly(hydroxy ether of bisphenol-A)} \textit{[Phenoxy]}

Phenoxy resins are commercially important thermoplastic polymers derived from bisphenols and epichlorohydrin.

reaction:

\[
\text{HO-Ph} \quad \text{OH} + 2 \text{ClCH}_2-\text{HC-CH}_2 \quad \overset{\text{[HO-R-OH]}}{\text{[Catalyst]}} \quad \text{H}_2\text{C-CH-CH}_2-\text{O-R-O-CH}_2-\text{HC-CH}_2 \quad + 2 \text{HCl} \quad + \text{HOROH}.
\]

Their molecular weights are considerably higher, ie: ca. 45000 than those of conventional Epoxy resins, ie: 8000 maximum.\textsuperscript{217} They lack terminal functionality and so have good thermal stability to match that of the Polysulphones. They are amorphous,
relatively tough and only soluble in a few solvents. They are known to act as compatibilisers by interacting through the formation of a hydrogen bond with its pendant hydroxyl group and proton acceptors.

\[
\begin{align*}
& \text{O} - \text{C} - \text{O} - \text{CH} = \text{CH} - \text{CH}_2 \\
& \text{R} - \text{C} = \text{O} - \text{C} - \text{O} - \text{CH} = \text{CH} - \text{CH}_2
\end{align*}
\]

The Phenoxy was kindly supplied by Union Carbide, (PKHH grade). This grade has a number average molecular weight of approximately 30 000g/mol, a glass transition temperature of 90°C, a density of 1.17g/cm³ and refractive index of 1.598.

3.1.4 Poly(ethylene terephthalate)

Poly(ethylene terephthalate), [PET], is produced by either of the following methods:²¹⁸²¹⁹

1. By the direct esterification of ethylene glycol with Terephthalic acid,

reaction:

\[
n \text{HO(CH}_2\text{)}_2\text{OH} + n \text{HO-C—C—OH} \rightarrow n \text{HO(O—C—C—O—CH} = \text{CH}_2\text{—CH}_2\text{—O—C—C—O—CH} = \text{CH}_2\text{—CH}_2\text{]} + 2n \text{H}_2\text{O}
\]
In recent years, the direct transesterification of ethylene glycol with terephthalic acid has replaced the ester-exchange process. This is because apart from requiring a first stage catalyst, the initial esterification product is a low molecular weight mixture of PET oligomers. The merits of PET is its relatively high melting and glass transition temperature, insensitivity to moisture and common solvents, and the wide range of mechanical properties attainable by variations of molecular weight, orientation and crystallinity. This enables PET to be used for four different large-scale applications: fibres, films, bottles and precision mouldings.

Polymers for use as fibres and films have a number average molecular weight of about 20 000, whereas moulding materials have higher molecular weights. Extruded material is usually quenched from the melt to produce a largely amorphous fibre and sheet. This produces mechanically weak products, so orientation and crystallisation are induced by drawing the polymer, above the $T_g$ value, uniaxially in the case of fibre and biaxally in the case of film, followed by annealing at about 200°C.220
Only special grades of high molecular weight PET, containing crystallisation nucleating agents, are injection moulded for electrical and electronic devices. This is due to its slow crystallisation rate. More commonly, PET is reinforced with glass fibre or compounded with PTFE, silicones, graphite or flame retardants to produce engineering grades.221

The PET was kindly supplied by ICI Melinar, (laser grade). This is a standard, non-reinforced, bottle grade polymer of high viscosity. It has a melt temperature of 253°C, density of 1.37g/cm³, an intrinsic viscosity of 0.82 and a glass transition temperature of 72°C.

3.1:5 Poly(butylene terephthalate)

Poly(butylene terephthalate), (PBT), is produced in a similar manner to Poly(ethylene terephthalate), Section [3.1:4], ie:- either by:

1. the ester interchange reaction between butan-1,4-diol and dimethyl terephthalate

\[
\begin{align*}
\text{n HO(CH}_2\text{)}_4\text{OH} + \text{n CH}_3\text{O-C-}\text{O(CH}_2\text{)}_4\text{C-CH}_3 \\
\text{\hspace{1cm}} \downarrow \\
\text{\hspace{1cm}} \text{O-C-}\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-C-O(CH}_2\text{)}_4\text{C-CH}_3 \quad + \text{2n CH}_3\text{OH}
\end{align*}
\]
2. by the now more common direct esterification of butan-1,4- diol with terephthalic acid.

reaction:

\[
\text{HO(CH}_2\text{)}_4\text{OH} + n\text{HO-C-}\text{C-OH} \downarrow \quad \text{[O-C-}\text{C-O-(CH}_2\text{)}_4\text{]}
\]

PBT products are highly chemical resistant with good dimensional stability. It has a lower \(T_g\) value than PET and so crystallises much more readily on moulding to produce a thermoplastic with high strength and rigidity coupled with good surface hardness and gloss. It is used widely as an engineering plastic moulding material in electronic devices, domestic and office appliances and automotive parts.\(^{21}\)

The PBT was kindly supplied by Ciba Geigy, (Crastin S600), and Bayer, (Pocan 1501). Crastin S600 is a standard non-reinforced, semi-crystalline polymer of medium viscosity. It has a melt temperature of 225°C, density of 1.31g/cm\(^3\) and a \(T_g\) of 54°C. This grade was used for initial blending studies on the Brabender Plastograph, Section [3.2:1]. Pocan 1501 is a standard non-reinforced, semi-crystalline polymer of high viscosity. It has a melt temperature of 225°C, density of 1.3g/cm\(^3\) and a glass transition temperature of 53°C. This grade was used for twin screw compounding and sheet extrusion.

3.1:6 **PBT-TMO Block Copolymer [Hytrel]**
Hytrel is a thermoplastic polyester elastomer supplied by Du Pont de Nemours and Co.\textsuperscript{222} It is a copolymer consisting of two types of blocks, one of which is an amorphous chain segment with a relatively low glass transition temperature. These amorphous blocks are commonly referred to as the 'soft' segments since they impart elastomeric character to the polymer. The second component, the 'hard' block, is an aromatic chain segment which is capable of undergoing intermolecular association to form a thermally reversible network structure.\textsuperscript{223} The hard segments are composed of multiple short chain tetramethylene terephthalate, (4GT), units and the soft segments are composed of amorphous Poly(tetramethylene ether) glycol terephthalate, (PTMEGT), units.\textsuperscript{224}

These block copolymers are prepared by the melt transesterification of dimethyl terephthalate, (DMT), butan-1,4-diol, (4G), and Poly(tetramethylene ether) glycol, (PTMEG).

\[
\begin{align*}
\text{CH}_3\text{O} &-\text{C} &-\text{C} &-\text{OCH}_3 &+ \text{HO(CH}_2\text{)}_4\text{OH} &+ \text{HO[(CH}_2\text{)}_4\text{O}_x\text{]H} \\
\text{DMT} & & & & \downarrow & \\
\text{4G} & & & & \text{PTMEG} \\
\end{align*}
\]

\[
\begin{align*}
4\text{GT "HARD" SEGMENT MW}=220 \\
\text{PTMEG "SOFT" SEGMENT MW=1120}
\end{align*}
\]

Hytrel is produced by randomly joining, head to tail, both PTMEGT and 4GT units which result in a number average molecular weight, \((M_n)\), of approximately 25-30 000. The overall stoichiometry is chosen so that there is a preponderance of 4GT blocks in the mixture on a mole basis. However, by varying the ratio of hard to soft segments, Polyesters ranging from soft elastomers to relatively hard elastoplastics can be obtained.
Hytrel was kindly supplied by Du Pont, (7246 grade). This grade contains approximately 84% by mole of hard segments and has a number average molecular weight of 25-30 000. It has a melt temperature of 217°C, density of 1.25g/cm³ and a broad glass transition temperature at ±0°C.

3.2 BLENDING TECHNIQUES

Before blending, all polymer components were dried to manufacturer’s recommendations, thus preventing degradation during processing. This is particularly important for polyesters as they are susceptible to hydrolytic degradation in their molten state.

3.2:1 Brabender Plastograph

Exploratory studies of the polymer blends were carried out in a Brabender Plastograph. This instrument subjects a polymer melt to shear forces and measures the torque as a function of rotor speed and temperature. Qualitative indications of melt viscosity, viscosity-temperature dependence, degradation and crosslinking may also be obtained.

A mixing chamber of 30cm³ was used which contained counter-rotating rotors with a speed ratio of 3:2. After drying, the components of the polymer blends were charged separately to the heated mixing chamber in percentage mass combinations.

Various processing conditions were then employed to see what effect they had on blend morphology. These variants were shear rate, (analogous to RPM of mixing), temperature and time of mixing. The temperatures recorded on the Brabender Plastograph were that of the mixing chamber and not of the melt. In fact, the latter would be greater due to the high shearing forces and internal friction within the polymer components. Overall, the time of mixing was kept relatively short so that the components had long enough to mix randomly, (constant torque obtained), but not so long as for transesterification and degradation to occur to an appreciable extent.

Details of the blends prepared by this method and their corresponding processing conditions, are listed below:

1. PBT/Phenoxy: [90/10]...[10/90] in 10% wt step combinations.
   Mixed at 250°C for 3 minutes with a rotor speed of 100 rpm.
2. PBT-TMO/Phenoxy: [90/10]...[10/90] in 10% wt step combinations. Mixed at 250°C for 3 minutes with a rotor speed of 100 rpm.

3. PES/Phenoxy: [80/20]...[20/80] in 20% wt step combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

4. PSO/Phenoxy: [90/10], [80/20], [70/30] combinations. Mixed at 260°C for 3 minutes with a rotor speed of 100 rpm.

5. PSO/PBT: [90/10]...[10/90] in 20% wt step combinations. Mixed at 280°C for 3 mins with a rotor speed of 100 rpm.

6. PES/PBT: [70/30] and [50/50] combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

7. PSO/PBT-TMO: [70/30] and [50/50] combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

8. PES/PBT-TMO: [70/30] and [50/50] combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

9. PSO/PET: [70/30], [50/50] and [30/70] combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

10. PES/PET: [80/20]...[20/80] in 10% wt combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

11. PET/PBT: [80/20]...[20/80] in 20% wt combinations. Mixed at 280°C for 3 minutes with a rotor speed of 100 rpm.

12. PSO/Phenoxy/PBT: [60/15/25], [55/5/40] and [45/10/45] combinations. Mixed at 280°C for 4 minutes with a rotor speed of 100 rpm.

13. PSO/Phenoxy/PBT-TMO: [60/15/25], [55/5/40] and [45/10/45] combinations. Mixed at 280°C for 4 minutes with a rotor speed of 100 rpm.

14. PSO/Phenoxy/PET: [60/15/25], [55/5/40] and [45/10/45] combinations. Mixed at 280°C for 4 minutes with a rotor speed of 100 rpm.
15. PES/Phenoxy/PBT: [60/15/25] combination. Mixed at 280°C for 4 minutes with a rotor speed of 100 rpm.

16. PES/Phenoxy/PBT-TMO: [60/15/25] combination. Mixed at 280°C for 4 minutes with a rotor speed of 100 rpm.

17. PES/Phenoxy/PET: [80/5/15], [75/5/20], [55/5/40], [45/10/45], [45/10/45], [40/5/55] and [20/5/75] combinations. Mixed at 280°C for 4 minutes with a rotor speed of 100 rpm.

18. PES/Phenoxy/PET/PBT: [40/10/40/10], [40/10/30/20] and [30/20/20/30] combinations. The PET/PBT combinations are mixed first at 280°C, 100 rpm for two minutes. Mixing then continues for a further 3 minutes with the remaining polymers added.

NB. The processing conditions above list the general method used in producing the polymer blends. However, in addition several variations of shear, time and temperature of mixing were undertaken.

3.2:2 Compression Moulding

The Brabender prepared blends were compression moulded into plaques for analysis by DSC, DMTA, FTIR and SEM. A steel mould was constructed to produce samples 40x15x3mm for analysis by DMTA. Various loads, temperatures and time of pressing were employed to see the effect on the phase behaviour of the samples.

To induce maximum crystallisation, samples were placed between plates, (after pressing), and left to cool to room temperature at a rate of approximately 10°C/min, under a 20 tonne load. To produce amorphous samples, the mixtures where pressed between aluminium foil and then quenched immediately in iced water. Transparent films were obtained by this method.

The PET based blends were compression moulded at 280°C with 2 minutes pre-heating followed by 2 minutes under a 20 tonne load. A similar procedure was used with the PBT and PBT-TMO based blends at a moulding temperature of 250°C.

The sheet extruded samples, Section [3.2:4b], were pressed between steel plates at their cooling cycle crystallisation temperature (Tc2). After preheating for 5 minutes a load of
20 tonnes was applied. Five minutes later the load was doubled and pressing continued for a further 5 minutes. The samples were then cooled slowly under pressure, (20 tonnes), to allow for maximum crystallisation and to prevent deformation of the sheet. This method was employed to try and encourage maximum crystallisation in the blends and thus, increasing the solvent resistance properties.

3.2:3 Tumble Blending

For large scale experiments, the separate polymer components were first dry blended by mixing the granules in a tumble blender before compounding. The following combinations were prepared by mixing at a constant speed for ten minutes to produce 5 kg batches.

<table>
<thead>
<tr>
<th>BLEND</th>
<th>COMBINATION</th>
<th>MASS (k g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES/Phenoxy</td>
<td>80/20</td>
<td>4/1</td>
</tr>
<tr>
<td>PES/PET</td>
<td>70/30</td>
<td>3.5/1.5</td>
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<tr>
<td>PES/PBT</td>
<td>70/30</td>
<td>3.5/1.5</td>
</tr>
<tr>
<td>PSO/PBT</td>
<td>70/30</td>
<td>3.5/1.5</td>
</tr>
<tr>
<td>PET/PBT</td>
<td>75/25</td>
<td>3.75/1.25</td>
</tr>
<tr>
<td>PES/Phenoxy/PET</td>
<td>60/15/25</td>
<td>3/0.75/1.25</td>
</tr>
<tr>
<td>PES/Phenoxy/PBT</td>
<td>60/15/25</td>
<td>3/0.75/1.25</td>
</tr>
<tr>
<td>PSO/Phenoxy/PBT</td>
<td>60/15/25</td>
<td>3/0.75/1.25</td>
</tr>
<tr>
<td>PSO/Phenoxy/PBT-TMO</td>
<td>60/15/25</td>
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</tr>
<tr>
<td>PES/Phenoxy/PET/PBT</td>
<td>60/5/25/10</td>
<td>3/0.25/1.25/0.5</td>
</tr>
</tbody>
</table>

3.2:4 Compound Extrusion

Materials are extruded when forced through a die in their molten state. The polymer is fed into the extruder in the solid state and as the material is compressed and melted, it is conveyed under shear by the extruded screw from feed port to the die; this process is generally called plasticising extrusion. Compounding occurs when two or more polymers are added to the reaction chamber. These are then mixed in their molten state and the resulting polymer blend is discharged through the die. Two different types of extruder are used in these studies. First a twin screw extruder is used to compound the polymer blends. The resulting material is then fed to a single screw extruder where the blend is melted again and discharged through a sheet die.
a) Compounding Twin Screw Extruder

The premixed polymer blends were compounded on an APV MP2030 twin screw extruder which contained intermeshing co-rotating screws. The co-rotating twin screw extruder provides excellent homogenisation and somewhat greater intermeshing volume than the corresponding counter-rotating screws. The latter tend to provide greater shear stress due to the direction of the screws, but they have trouble providing longer residence times because of their very positive conveyance.

1. Co-rotating; in which the two screws rotate in the same direction.

2. Counter-rotating; in which the two screws rotate in opposite directions.

The most common intermeshing extruder employed for compounding is the co-rotating twin screw. The flexibility of these compounders is epitomised by the modular construction of the screws which, facilitates different screw profiles for different compounding operations. Unlike counter-rotating screws, these machines can accommodate large reaction volumes by utilising deep screw flights. Different screw configurations and kneading elements can also be used depending on the requirements of the polymers/additives that are to be mixed.

Figure [3.1] shows a detailed diagram of a compounding twin screw extruder.
Feed Mechanism: This section consists of two primary control variables; feed rate and main screw speed. The former is controlled by a volumetric screw feeder and the rotational speed of the extruder screws is a separate control variable. These are adjusted to starve feed the twin screw compounders so as to avoid excessive torque. In these studies the controls were varied so as to obtain a torque value of 70%.

Conveying: The twin feed screws pick up the polymer material at the feed throat and transport it forwards along the barrel. The intermeshing prevents the material from rotating with the screw and so conveys it to the mixing section.

Mixing: At this stage the material has absorbed heat and become compressed at the intermeshing point. The mixing paddles then induce high shear conditions causing melting and dispersive mixing of the polymers. The extent of the distributive mixing depends on the total imposed strain/deformation, (shear). This in turn depends on the position of the paddles as they are the primary working components of the agitator assembly. The transport of the molten polymer material continues as the intermeshing and self cleaning action of the screws ensures no particle remains prone to degradation by excessively high residence times.

Orifice plugs: These are attached to the ends of the mixing paddles and are used to hold and restrict the flow of the melt in the mixing section. These maintain the shear forces in the mixing section and so improve the distributive mixing of the blend.

Discharge: The intermeshing co-rotating screws take up the molten material after mixing and transport it along the barrel towards the die. Here, a restriction to flow occurs as the die provides a resistance to the forward conveying efficiency. To relieve this pressure build up in the discharge zone, a camelback discharge screw is attached to the end of the helical screw shaft. The unique shape of these screws, figure [3.2], is because of the multiple functions of their part. In addition to conveying the final product from the extruder, camel-back discharge screws function as the downstream bearing of the agitator assembly. The unique shape maintains the self wiping action while exposing fresh polymer surface for devolatisation. The wide flight hand also acts as a journal to support the shaft assembly.

![Diagram of discharge plug and screw](image-url)
a) (i) experimental variables
An APV MP2030 compounding twin screw extruder was employed in these studies.

Specifications:  
**APV MP2030**
- L/D ratio 15/1
- Screw diameter 30mm
- Screw speed up to 500 rpm
- Direction of screws co-rotating
- Single strand die diameter 5mm

This compounder has a wide range of operating variables such as:

- Specific energy input
- Residence time
- Screw configuration
- Melt temperature
- Melt pressure
- Screw speed
- Torque
- L/D
- Feed rate/output rate

a) (ii) screw configuration
The screw configuration for mixing Polyesters with Polysulphones was proposed in conjunction with both the machinery manufacturers and studies previously carried out by Robinson, figure [3.3].

*Figure 3.3: screw configuration. (after Robinson)*

54
The mixing paddle pairs must always be orientated 90° to each other, figure [3.4], and the first two paddles on the same shaft are set at 30° to each other so as to ease the polymer into the mixing section, figure [3.5].

![Figure 3.4: Paddle pairs set at 90°. (courtesy of APV).](image1)

![Figure 3.5: Mixing paddles set at 30°. (courtesy of APV).](image2)

The feed screws are a normal helix and have a double lead with a pitch of 1 diameter, figure [3.6].

A pair of orifice plugs were used immediately beneath the barrel valve vane. The barrel valve allows for external adjustment of the mixing section filled length. This adjustment is continuously variable for fine tuning, whereas the orifice plug size is a stepwise, more coarse adjustment, figure [3.7].

![Figure 3.6: Feed screws. (courtesy of APV).](image3)

![Figure 3.7: Orifice plug assembly. (courtesy of APV).](image4)
a) (iii) method of operation

After making sure both the screws and chamber were clean, the six temperature zones were set, figure [3.8].

![Diagram of Twin Screw Compounder Barrel Temperature Zones]

Figure 3.8: Twin Screw Compounder Barrel Temperature Zones

1. Die  
2. Discharge zone  
3. Mixing zone  
4. Mixing zone  
5. Feed zone  
6. Feed throat

The temperature of the feed throat was kept low, (well below the melt temperature), so that the polymer material would not soften in the throat and cause a blockage.

The compounder was used as a one stage mixer as the polymers were preblended beforehand in a tumble mixer. They were then left to dry in an oven at 100°C before placing in a Conair Churchill dehumidifying hopper dryer at 130°C for three hours, prior to processing. The polymer passed from the hopper dryer into the metered volumetric feed hopper and feed screws conveyed the granules to the mixing zones.

Low feed rate and screw speed were first used so that the molten polymer could lubricate the system. These were then increased until a torque of 40NM was recorded in the mixing zone. The machinery manufacturers suggest that this amount of torque, (70%), is most favourable for mixing with the screw configuration selected. Barrel, (water), cooling was also employed in the mixing zone so as to restrict the amount of temperature rise due to shear heating.
The camelback discharge screws provided an even delivery to a single strand die. The polymer strand was then drawn into the water bath and out through the hot air dryer into the pelletizer where the blended granules were collected. The pelletizer haul off speed was varied until a continuous thin polymer strand was obtained from the die.

Between processing runs, the system was purged with HDPE due to its high viscosity and hence, purging ability.

a) (iv) blend composition
The blend compositions selected for compounding are shown overleaf. They were chosen because of the results and morphology displayed by the samples prepared in the Brabender.

No problems were encountered when processing at the conditions shown. Apart from the PET/PBT blend, the strands obtained were even and had a high melt strength and therefore, were easily pelletised. The very low viscosity and melt strength of the PET/PBT blends did not permit the use of the pelletiser and so the strand had to be first hauled off by hand and then subsequently pelletised. Examination of the pellets by optical microscopy suggested that all the blends were thoroughly mixed.

b) Single Screw Extruder
Single screw extruders are not widely used for compounding as only a small degree of mixing occurs. They are, however, useful for mixing low molecular weight polymers and for shaping molten material into a desired product.\textsuperscript{228/233} A single screw extruder is used in this study to shape the polymer blends into sheet material.

b) (i) experimental variables
A Betol BK32 single screw extruder was employed in these studies.

\textbf{Specifications:}  
\begin{itemize}
  \item \textit{screw diameter} \hspace{1cm} 32mm
  \item \textit{L/D ratio} \hspace{1cm} 30:1
  \item \textit{Screw compression ration} \hspace{1cm} 3:1
  \item \textit{Screw speed} \hspace{1cm} 17-100 RPM
  \item \textit{Die heating zones} \hspace{1cm} 2
  \item \textit{Barrel heating zones} \hspace{1cm} 4
  \item \textit{Sheet Die thickness} \hspace{1cm} 0-10mm
\end{itemize}

A Betol three roll stack machine, (Model 1013), was used in conjunction with the extruder and sheet die. The machine consists of three highly polished chrome plated
<table>
<thead>
<tr>
<th>Blend</th>
<th>Combination</th>
<th>Temperature Parameters</th>
<th>Zone 1 (°C)</th>
<th>Zone 2 (°C)</th>
<th>Zone 3 (°C)</th>
<th>Zone 4 (°C)</th>
<th>Zone 5 (°C)</th>
<th>Zone 6 (%)</th>
<th>Torque (Nm)</th>
<th>Screw Speed (rpm)</th>
<th>Pellitiser Speed (rpm)</th>
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</table>
water cooled rolls, positioned one above the other, the centre roll being in a fixed position with the upper and lower rolls raised and lowered by means of pneumatic cylinders, the precise gap required between the rolls being set by the means of wedge shaped stops. All three rolls are driven by a common drive which also drives a set of rubber covered nip rolls through a manually adjusted slipping clutch. This section containing the rolls may be moved towards or away from the die along guide rails by turning a handwheel, figure [3.9].

![Diagram](image)

*Figure 3.9: sheet line extrusion process, using a three cooling roll stand. (after Rosato et al)*

b) (ii) method of operation

After making sure the extruder, die and polishing rolls were clean, the six temperature zones were set, figure [3.10].

![Diagram](image)

*Figure 3.10: Single Screw Extruder Barrel Temperature Zones*

1. Die
2. Die
3. Metering zone
4. Compression zone
5. Feed zone
6. Feed Throat
The die gap was set to 0.45mm with the aid of a feeler gauge. The gap between the polishing rolls was then set to 0.5mm to allow for the die swell of the material. The polishing rolls were also heated to 120°C so that the extrudate would not cool to below its glass transition temperature immediately on contact with them. This then allowed the sheet to be easily wound around the rolls and so produced a more even and polished sheet.

The polymer blends prepared on the APV compounding were processed into sheet using the Betol sheet extrusion line. After drying in an oven at 100°C, the blends were placed into a Conair Churchill hopper dryer at 130°C for three hours before processing. In the initial stage, a low screw speed was used to convey the polymer material up the screw channel towards the die. The die head pressure was constantly monitored to make sure that the machine did not overload. By varying the screw speed and temperature of the barrel, it was possible to produce a constant thickness of sheet. This extrudate was then threaded through the 3-roll stack machine with the roll gaps set to maximum. The rubber nip rolls were then closed and the rolls rotated at a speed where the haul-off and extrusion rate were equivalent. The polishing rolls were then closed to their set gap and rotated at a speed where a slight "bank" of polymer material was formed at the entry to the first polishing roll. This bank was maintained at a minimum throughout processing.

Between runs, the system was purged with HDPE and therefore, the first and last parts of the collected sheet were disregarded so as to minimise contamination.

b) (iii) processing conditions
As well as the blends prepared by the APV compounding, it was decided to sheet extrude virgin PSO and PES so that comparative solvent resistance measurements could be made. It was also decided to disregard the PET/PBT (75/25) binary blend in these studies as its very low viscosity made it impossible to extrude even sheets.

No problems were encountered when processing at the conditions shown overleaf and a consistent polished sheet was produced. Blends containing Phenoxy, however, tended to stick to the rollers. This problem was alleviated by reducing the temperature of the rollers to 80°C which, is lower than the glass transition temperature of Phenoxy.

The only other problem encountered was the inability to extrude PES/Phenoxy/PBT through the sheet die. The initial compounded pellets suggest that this blend is fairly incompatible and the system completely phase separates on leaving the die to produce a conglomerate mass.
<table>
<thead>
<tr>
<th>Blend</th>
<th>Combination</th>
<th>Temp Zone 1 (°C)</th>
<th>Temp Zone 2 (°C)</th>
<th>Temp Zone 3 (°C)</th>
<th>Temp Zone 4 (°C)</th>
<th>Temp Zone 5 (°C)</th>
<th>Temp Zone 6 (°C)</th>
<th>Screw Speed (rpm)</th>
<th>Roller Speed (rpm)</th>
<th>Roller Temperature (°C)</th>
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<tr>
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<td>120</td>
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<td>300</td>
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</tbody>
</table>
3.2:5 Solution Blends

a) Polyethersulphone/Phenoxy Binary Blends
PES and Phenoxy were dissolved separately in Dimethyl Formamide, (DMF), at room temperature to form 20% wt solutions. These two solutions were mixed in the desired proportions, then subsequently cast onto microscope slides and left at 70°C in a vacuum oven until all of the solvent was removed, (usually 1 week). The transparent films produced were examined by Fourier Transform Infra Red (FTIR), Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA) and Scanning Electron Microscopy (SEM). Annealing experiments were also carried out, in conjunction with SEM so that the phase behaviour of the blend could be studied.

There were, however, problems associated with casting of films onto microscope slides. The blends containing a higher proportion of Phenoxy tended to stick to the slide and so were impossible to remove cleanly. Different techniques, such as using a mould release agent and casting onto both Aluminium foil and Polytetrafluoroethylene (PTFE), were therefore employed, to try and overcome this problem. The former method eased the removal of the film whereas the blends adhered strongly to the foil. Casting onto PTFE proved to be the most successful method and so was adopted later in these studies.

Other problems associated with solvent casting include the formation of an uneven film and the ease of moisture uptake which produces an opaque sample. The latter is overcome by placing the samples into the vacuum oven quickly after casting. The uneven film that occurs on drying is trimmed around the thick edges to leave a more regular and smoother specimen, approximately 30µm thick. Thin films were also prepared from 5% wt solutions and cast on both Aluminium foil and NaCl plates for analysis by DSC and FTIR respectively.

Blends of PES/Phenoxy with composition [90/10], [80/20], [70/30], [60/40], [50/50], [40/60], [30/70], [20/80] and [10/90] were prepared by the above methods.

b) Polysulphone/Phenoxy Binary Blends
PSO and Phenoxy became opaque when mixing in DMF and so were subsequently produced as 20% wt solutions in 1-Methyl 2-Pyrrolidinone. The same procedure was then repeated, as with the PES/Phenoxy blends, to produce films 30µm thick. After drying these films were found to be slightly opaque.

Various annealing experiments were carried out to study the phase behaviour of the blend. Films were also analysed by DSC, DMTA, SEM and FTIR to again assess the
removal of solvent and to investigate the degree of miscibility. Blends of PSO/Phenoxy with composition [90/10], [80/20], [70/30], [60/40], [50/50], [40/60], [30/70], [20/80], and [10/90] were prepared.

3.3 MECHANICAL TESTS

3.3:1 Dynamic Mechanical Analysis

Dynamic mechanical analysis involves imposing a small oscillatory mechanical strain on a solid or viscoelastic liquid and resolving the resulting stresses and strains. Measurements are usually made in the linear viscoelastic region of the material where the dynamic moduli are a function of only the temperature and frequency. Testing can be made using free oscillations at the resonant frequency of the sample or by using a sinusoidal oscillation at a forced frequency. The latter method is used in these studies where the changes in the state of molecular motion, as temperature is scanned, are detected.

a) Principle

Elastic materials obey Hooke's Law, that is the applied stress is proportional to the resultant strain but is independent of the rate of strain. Viscous liquids follow Newton's law of viscosity, that is the applied stress is proportional to the rate of strain and not the strain itself. Polymeric materials have properties which lie between these two and are classified as viscoelastic. In a dynamic mechanical test the clamped sample is subjected to a sinusoidally varying stress of angular frequency, $\omega$, for a viscoelastic polymer material, the resulting strain will also be sinusoidal, but will be out of phase with the applied stress owing to energy dissipation as heat, or damping, in the sample, figure (3.11).

Figure 3.11: dynamic mechanical analysis in fixed frequency operating mode. (after Robinson).
This phase lag, defined as phase angle, (δ), is used with known sample geometry and driver energy to calculate the viscoelastic properties of the sample. The stress, σ, and strain, ε, can be expressed as follows:

\[ \sigma = \sigma_0 \sin(\omega t + \delta) \]
\[ \varepsilon = \varepsilon_0 \sin \omega t \]

Thus,

\[ \sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \]

The stress can be considered to consist of two components, one in phase with strain, (σ₀cosδ), and the other 90° out of phase, (σ₀sinδ). When these are divided by strain, the modulus can be separated into in-phase, (real), and out-of-phase, (imaginary), components. The relationships are:

\[ \sigma = \varepsilon_0 \varepsilon' \sin \omega t + \varepsilon_0 \varepsilon'' \cos \omega t \]

Where the storage modulus ε' is equal to (σ₀/ε₀)cosδ that is, the component of stress in phase with the strain divided by the strain amplitude, and the loss modulus ε'' is equal to (σ₀/ε₀)sinδ, that is the component of stress out of phase with strain divided by the strain amplitude. Dividing the loss modulus by the storage modulus leads to the loss tangent, (tanδ), ie:-

\[ \frac{\varepsilon''}{\varepsilon'} = \frac{(\sigma_0/\varepsilon_0) \sin \delta}{(\sigma_0/\varepsilon_0) \cos \delta} = \tan \delta \]

This equation shows that tanδ is the ratio of the energy lost as dissipation energy to the energy stored as potential energy during a cycle. Therefore, at the glass to rubber transition temperature, (T_g), ε' exhibits a drop in magnitude while both ε'' and tanδ display a maxima, figure (3.12). A plot of ε'' against temperature will thus give a value of the glass transition temperature for the system.

\[ Figure \ 3.12: \ variation \ of \ storage \ modulus, \ loss \ modulus \ and \ tan \delta \ with \ temperature. \]
b) Dynamic Mechanical Analysis (DMA)

A Dupont 983 DMA was employed for the initial analysis of both compression moulded and solution blends, figure [3.13]. Samples were heated at a rate of 10°C/min from room temperature to 250°C so that the glass transition temperature of the blend could be measured. PBT-TMO containing blends were analysed from -40°C to 220°C due to its low glass transition temperature. Low temperature secondary relaxation transitions, (β transitions - commonly attributed to rotational modes), were measured for selected samples. In this instance, a heating rate of 10°C/min was used from -160°C to room temperature.

![Figure 3.13: Du Pont 983 dynamic mechanical analyser. (courtesy of Du Pont analytical instruments).](image)

The sample is clamped between the ends of two parallel arms, which are mounted on low force flexure pivots, allowing motion in the horizontal plane. An electromagnetic motor attached to one arm drives the arm/sample to a strain, (amplitude), of 0.5-2mm, (selected). As the arm is displaced, the sample undergoes a flexural deformation as depicted in figure [3.14]. A Linear Variable Differential Transformer (LVDT) mounted on the motorised arm measures the sample's response, (strain and frequency), to the amplitude stress. These measurements are then interpreted to provide values of $\varepsilon'$, $\varepsilon''$ and $\tan\delta$ with respect to temperature.

![Figure 3.14: sample deformation in the DMA. (courtesy of Du Pont analytical instruments).](image)
The results obtained for PSO/Phenoxy and PES/Phenoxy solution blends were not too accurate due to a very low force signal obtained with these rather pliable amorphous films. This signal fell to zero above the Tg of phenoxy (≈120°C) as the apparatus is not sensitive enough to measure the low force signals obtained with armophous blends having a difference in glass transition temperatures of ≈100°C. Dynamic Mechanical Thermal Analysis was therefore employed for thin film studies.

c) Dynamic Mechanical Thermal Analysis (DMTA)

The dynamic mechanical behaviour of both the solution and brabender prepared blends were analysed with a Polymer Laboratories Dynamic Mechanical Thermal Analyser, (DMTA). This consisted of a DMTA head, figure [3.15], with a cooling coil, a microprocessor controlled temperature programmer and a computer accessory. The DMTA head required a rectangular sample clamped onto a fixed frame with bars at both ends, figure [3.16]. The sample was oscillated at its centre by a central clamp attached to a drive shaft linked to a mechanical oscillator. The frequency and amplitude, (strain), of oscillation were pre-set, (1Hz and 4mm respectively), along with the temperature range, (variable), and heating rate, (10°C/min). The resistance to the applied deformation is recorded as a function of the magnitude and phase of the sample displacement. The signals are automatically converted to yield the dynamic storage modulus, (ε’), and the loss tangent, (tanδ), which were plotted as a function of temperature.

![Figure 3.15: Polymer Laboratories dynamic mechanical thermal analyser. (courtesy of Polymer Laboratories).](image)

![Figure 3.16: dual cantilever clamping arrangement.](image)

3.3:2 Tensile Testing

A Hounsfield tensometer was employed to measure both the tensile strength and "solvent resistance" of the blends. This apparatus was used as it enables the samples to be clamped into a horizontal position, thus allowing for the application of solvent. Test
pieces were cut from the compression moulded sheet extrudate parallel to the directional flow, figure [3.17].

![Schematic of a dumbbell test specimen.](image)

It was impossible to produce a dumbbell test specimen for all samples due to their brittleness. Therefore, a hole punch was used to produce a semi-circle waste in the sample so as to reduce the cross-sectional test area. The thickness, \( t \) and width, \( w \), of this section were measured in millimetres.

Measurements were carried out in ambient conditions and the test pieces clamped at both ends with vice chucks. A cross-head speed of 1 cm/min was applied and the corresponding force measured on a 300N mercury spring beam scale.

The obtained load/extension plots were analysed and the maximum tensile strength for each material calculated from the following equation:

\[
\sigma = \frac{F}{A}
\]

where, 
\[
\sigma = \text{the maximum tensile stress at yield (N/mm}^2\text{)}
\]
\[
F = \text{the force at yield (N)}
\]
\[
A = \text{the initial cross-sectional area (mm}^2\text{)}
\]

A mean value of the tensile strength for each material was calculated from 3 separate tests and used for the solvent resistance measurements.

### 3.3.3 Solvent Resistance Measurements

Semi-circular wasted samples, figure [3.17], of both the polymer controls and blends were prepared and their force at 50% of the tensile strength calculated, i.e.-

\[
F_{50\%} = \frac{\sigma A}{2}
\]
This force was applied to the corresponding test piece and 0.025ml of Methyl Ethyl Ketone, (MEK), was placed on the sample in the waste region. The stress relaxation was observed and time to fracture recorded for five separate runs. The mean fracture time was calculated for each blend material and their respective solvent resistance was compared on the basis of "time to fracture at 50% tensile stress".

Measurements were also carried out at 30% of the tensile strength and with 0.01ml of MEK since some of the blends fractured instantly at 50% of their tensile strength.

3.4 CHARACTERISATION

3.4.1 Differential Thermal Analysis (DTA)

A Du Pont Instruments 910 Differential Thermal Analyser fitted with a Differential Scanning Calorimeter cell, (DSC), was employed to examine the thermal behaviour of the polymer blends. This instrument enables the measurement of specific heat, glass transition temperature, melting and crystallisation characteristics, and the thermal stability for polymer systems. The DSC cell consists of a sample holder and an identical reference holder, both having a built in heating element and temperature sensor, figure [3.18]. The sample, which may vary in weight from (0.1 to 25mg), is placed in a small Aluminium pan; a similar empty pan is normally used as a control. A large variety of samples can be analysed such as solids, (granules, films or powders) and liquid resins. Both sample holders can be cooled or heated at various fixed rates (from 0.5 - 50°C/min) in a controlled Nitrogen atmosphere. Isothermal measurements can also be carried out by holding the sample accurately at a programmed temperature.

![Differential scanning calorimeter cell](courtesy of Du Pont analytical instruments).
During an experiment the temperature of both sample holders is kept the same. Therefore, when a thermal transition takes place in the sample, the heat flow to it has to be changed to keep it at the same temperature as the reference holder. The differential heat is measured and the difference in heat flow per unit of time is recorded as a function of both the temperature and time.\textsuperscript{239}

A typical DTA thermogram of a polymer exhibiting various thermal phenomena is shown in figure [3.19].

The glass to rubber transition is visible as a base line shift due to the step-like increase in heat capacity ($C_p$) at the glass transition temperature ($T_g$). The breadth of the transition region reveals the extent of compatibility in mixed systems.\textsuperscript{1} A single glass transition temperature intermediate to the characteristic $T_g$'s of the individual homopolymers suggests that the system is miscible.\textsuperscript{2} The crystallisation and melting of the sample, ($T_c$ and $T_m$, respectively), is visible as peaks superimposed upon the thermogram baseline. A cold crystallisation peak, ($T_{c1}$), occurs when an amorphous polymer crystallises on heating. A further crystallisation peak, ($T_{c2}$), occurs when the polymer recrystallises on cooling. The crystallisation shows up as an exothermic change on the DTA thermogram whereas the melting peak reveals an endothermic change. The position of both transitions depends on intrinsic polymer variables such as molecular weight, degree of stereospecificity, mechanical and thermal history, number of crystallite imperfections and the presence of nucleating agents.
a) Method of Operation
Each sample was weighed, (5-15mg), and placed into the standard Aluminium pan. The solution prepared blends, PSO/Phenoxy and PES/Phenoxy, were heated at a rate of 20°C/min to establish glass transition temperatures and hence compatibility of the systems. The programmed DTA cycles used for both the PET and PBT containing blends are shown below:

\[
\begin{align*}
A: \text{PET containing blends} & & B: \text{PBT containing blends (inc. PBT-TMQ)} \\
i. \text{RT} & \rightarrow 300^\circ C \text{ (heat)} & i. \text{RT} & \rightarrow 350^\circ C \text{ (heat)} \\
\text{ii. isothermal for 1 min} & & \text{ii. isothermal for 1 min} \\
\text{iii. 300^\circ C} & \rightarrow 120^\circ C \text{ (cool)} & \text{iii. 250^\circ C} & \rightarrow 120^\circ C \text{ (cool)} \\
\text{iv. isothermal for 1 min} & & \text{iv. isothermal for 1 min} \\
\text{v. 120^\circ C} & \rightarrow 300^\circ C \text{ (heat)} & \text{v. 120^\circ C} & \rightarrow 250^\circ C \text{ (heat)}
\end{align*}
\]

The shape and position of the T_g's were analysed to determine the extent of compatibility in the polymer systems. A more accurate estimate of the T_g was obtained by using 1st derivative values with respect to temperature. This method produced a peak in the position of the maximum slope of the onset point and therefore was more easily measured.

The position and shape of the melting peaks indicated the extent of randomness in the polymer blends and revealed any imperfections in crystal dimensions and structure. They also revealed the presence of co-polymerisation in the blends.

Generally, non-isothermal crystallisation studies were measured by DTA. The heat of crystallisation, \(\Delta H_c\), recorded on the heating cycles, \(T_c\), revealed the percentage crystallinity of the blend material. Crystallisation of the molten material on cooling gave information about the onset and peak temperatures, peak height, half width crystallisation time and the heat of crystallisation, \(\Delta H_{c,239/241}\). These data however are only of relative value and so were used in comparative studies for my polymer systems. In other words: does the addition of one polymer to another enhance or reduce both the crystallisation rate or extent of crystallisation?

3.4.2 Infra Red Analysis (IR)
The infra red spectrum of the solvent cast films were obtained by a Pye Unicam SP3-200 spectrophotometer. This method was used to observe whether all of the solvent was removed from the "dried" film. Solutions, (20%), of both PSO/Phenoxy and PES/Phenoxy blends were cast onto microscope slides and dried at 70°C, under vacuum, for one week. The samples obtained by this method however were too thick, (≈0.4mm), for the absorption peaks to be resolved. It was therefore impossible to confirm the complete removal of solvent.

3.4:3 Fourier Transform Infra Red Analysis (FTIR)

This method of infra red analysis was employed to accurately determine the removal of solvent from the solution mixed blends and to investigate the occurrence of specific interactions involved in blend miscibility. Hydrogen bond formation and the observation of band shifts help to identify the interacting chemical groups.²⁴²

A Pye Unicam Mattson 3000 FTIR spectrophotometer was employed with 4cm⁻¹ resolution to obtain the FTIR spectra for the solution blends. Cast films and KBr disc methods of analysis proved to be unsuccessful. Therefore, low concentrations, (5%), of the blends were cast onto NaCl plates and dried under an infra red lamp. Their absorption spectrum in the middle infra red region, (600-4000cm⁻¹), was then measured in 64 scans. A detailed spectra was obtained and analysed for both the removal of solvent and chemical group interaction.

3.4:4 Scanning Electron Microscopy (SEM)

A Cambridge Stereoscan 360 scanning electron microscope was employed to study the morphology of the polymer blends. This is a technique used for viewing specimen detail at a resolution well exceeding that of the light microscope.²⁴³ It is essentially a closed circuit television system of some complexity in which the subject of the picture is illuminated by a flying spot of electrons.²⁴⁴ The electron beam originates at a highly negative tungsten cathode heated by Current I_p, figure [3.20]. The emitted electrons are accelerated from the cathode through a grid and then through an anode that is at ground potential. This system of electrodes is called the electron gun. A system of magnetic lenses then demagnifies the electron beam. An adjustable Current I_cd, is applied to the deflection yoke to move the beam across the sample in a raster pattern. The ratio of this current to the current I_d in the deflection yoke of the cathode ray tube determines the magnification of the microscope.
When the primary electron beam strikes the sample, it gives rise to secondary electrons whose number varies with the geometry and other properties of the specimen. The secondary electrons, collected by a detector (a), are normally used to produce a scanning electron micrograph, but backscattered electrons and photons emitted by the sample under bombardment can also be used to produce an image. Other kinds of images can be produced by transmitted electrons (b) and by currents induced in the sample (c). The obtained micrograph images vividly display the three dimensional characteristics of the polymer surface under investigation.

Specimens for testing were first fractured in liquid nitrogen so that they would reveal the internal three dimensional morphology on analysis. The non-conductive polymer samples were then surface coated in gold so that a constant electric potential could be produced. Images of the fracture surface were then taken and the average particle diameter of the dispersed phases were determined by measurements from the SEM micrograph. In some cases the fractured specimens were immersed in MEK for 20 minutes to dissolve the Polysulphone phase, thereby attempting to improve the contrast in relation to the PET or PBT phases.
4 RESULTS

4.1 SOLUTION BLENDS

4.1:1 Polyethersulphone/Phenoxy Binary Blends

A full range of compositions for this blend was prepared from dimethylformamide (DMF). 20% polymer solutions were mixed and left to dry on microscope slides at 70°C for one week. This method produced pliable, transparent films, (±20μm thick), therefore suggesting the system to be miscible.

a) Morphological Studies

Six lots of samples were prepared for analysis by scanning electron microscopy, (SEM). They were annealed at various temperatures as shown in table [4.1] chosen according to theoretical $T_g$ values calculated from the Fox equation and LCST values reported from literature\(^1\).

Micrographs of the morphology for selected samples are shown in SEM figures [4.1 to 4.8] inclusive. Two general trends are apparent. Firstly, demixing becomes more pronounced on annealing as the PES content in the blend increases. Secondly, demixing again becomes more apparent as the annealing time increases. SEM figure [4.7] displays the morphology of the PES/Phenoxy (40/60) composition annealed at 163°C, (20°C below the reported LCST), for one day. This shows that demixing is just beginning to occur via the formation of an Interpenetrating Network by spinodal decomposition. A single homogenous phase was observed for all compositions that were not annealed, thus suggesting the binary PES/Phenoxy solution blend to be miscible at room temperature.

b) Dynamic Mechanical Analysis Data

Dynamic mechanical measurements were made on 20% solution cast films using the DMA in low mass mode. The variation of loss modulus ($\varepsilon''$) with temperature is plotted in figure [4.1]. The occurrence of single peaks suggest the system to be miscible although the $T_g$ values are somewhat lower than expected. A plot of the loss modulus values, (at the peak of the curve), against composition, figure [4.2], reveals both positive and negative deviation from linearity, thus suggesting that the interactive strength between components varies with composition.
c) Infra Red Analysis
Infra red analysis of the cast films proved unsuccessful in determining the complete removal of solvent as the samples were too thick to resolve the absorption peaks accurately.

Fourier Transform Infra Red analysis was carried out on 5% blend solutions dried on NaCl plates. The absorption spectrum, shown in table [4.2], was measured for all compositions and revealed shifts in both peak absorption maxima and peak height for specific interacting groups, figure [4.3].

4.1:2 Polysulphone/Phenoxy Binary Blends

A full range of compositions for this blend were prepared from 1-methyl 2-pyrrolidinone, (1-MP). 20% solutions were mixed and left to dry on microscope slides at 70°C for one week. This method produced slightly opaque films, (~20μm thick), therefore suggesting an immiscible system.

a) Morphological Studies
Scanning electron microscope was used to investigate the morphology of the PSO/Phenoxy solution blends before and after annealing at 120°C for one week. Micrographs of the obtained structures are shown in SEM figures [4.9 to 4.12] inclusive. This system is shown to be marginally miscible at room temperature whilst phase separating further with physical ageing. As with the PES/Phenoxy system, demixing becomes more profound as the PSO content in the blend increases.

b) Dynamic Mechanical Analysis Data
Dynamic mechanical measurements were made on 20% solution cast films using the DMA in low mass mode. Generally, measurements proved unresolvable due to the very low force signal obtained with the pliable films. The PSO/Phenoxy (90/10) specimen however displayed three tanδ peaks as shown in figure [4.4]. This suggests the blend is partially compatible, with peaks corresponding to the PSO, Phenoxy and compatibilised phases respectively.

Further dynamic mechanical measurements were made on 20% solution cast films using the more sensitive DMTA. The results obtained are shown in table [4.3] and reveal single tanδ peaks for all compositions tested. The temperature of these transitions were substantially lower than those predicted by the Fox equation. However, by increasing
annealing time and employing solvent extraction techniques with the more volatile methanol, the temperature of the tan δ transitions was increased.

c) Differential Thermal Analysis Data
Differential thermal analysis measurements were made on 10% solution cast films. The glass transition temperatures were more accurately measured by plotting 1st derivative values with respect to temperature, as shown in figure [4.5]. The single, intermediate glass transition temperatures were somewhat lower than those predicted by the Fox equation but nonetheless suggest that the PSO/Phenoxy blend is miscible. An almost linear relationship was obtained for a plot of glass transition temperature against PSO composition, figure [4.6]. This behaviour is analogous to that predicted by the Fox equation and thus, by manipulating the latter it was possible to calculate the % solvent remaining in the blend. As figure [4.7] shows, the error between the experimental data and PSO control sample is minimal. The % solvent remaining was therefore calculated at this composition by using the following equation:

\[
\frac{1}{T_{gc}} = \frac{W_a}{T_{ga}} + \frac{W_b}{T_{gb}}
\]

where,
- \( T_{ga} \) = \( T_g \) of Udel PSO standard (458K).
- \( T_{gb} \) = \( T_g \) of 1-methyl, 2-pyrrolidinone (249K).
- \( T_{gc} \) = \( T_g \) of PSO control sample from solution (439K).
- \( W_a \) = Weight fraction of PSO (1-x).
- \( W_b \) = Weight fraction of solvent remaining (x).

A value of 5.4% solvent remaining in the "dried" sample was calculated, thus suggesting the system behaves as a ternary blend with the solvent acting as compatibiliser.

d) Infra Red Analysis
Infra red analysis of the cast films proved unsuccessful in determining the complete removal of solvent as the samples were too thick to resolve the absorption peaks accurately.

Fourier Transform Infra Red analysis was carried out on 5% blend solutions dried on NaCl plates. The absorption spectrum shown in table [4.4] was measured for all compositions after drying at 70, 105 and 160°C. Two trends were generally observed. Firstly, shifts in both peak absorption maxima and peak height were obtained for specific interacting groups, figure [4.8], thus suggesting the blend to be compatible. Secondly, the extent of shift in peak maxima reduces as the drying temperature increases.
4.2 BRABENDER PREPARED MELT BLENDS

4.2:1 Polyethersulphone/Phenoxy Binary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PES/Phenoxy melt blends. The micrographs shown in SEM figures [4.13 to 4.15] indicate that the compatibility of the system increases with PES concentration from a matrix/dispersed type of morphology (40/60), to an almost co-continuous structure for the (80/20) combination.

b) Dynamic Mechanical Analysis Data
Dynamic mechanical measurements were made using Polymer Laboratories DMTA. Two tan \( \delta \) peaks were obtained for all compositions, thus suggesting the system to be immiscible, figure [4.9]. However, a third peak, intermediate to that corresponding to the pure components, was obtained for the PES/Phenoxy (90/10) and (80/20) combinations, suggesting that a third miscibilised phase was present.

4.2:2 Polysulphone/Phenoxy Binary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PSO/Phenoxy melt blends. The micrographs shown in SEM figures [4.16 to 4.18] generally reveal that the blends are partially miscible and that the miscibility increases marginally with increasing Phenoxy content. The PSO/Phenoxy (90/10) composition, SEM figure [4.16], reveals some small, \((\approx 1 \mu m)\) diameter, Phenoxy particles dispersed in the PSO matrix. The PSO/Phenoxy (80/20) composition, SEM figure [4.17], reveals fewer and more finely dispersed Phenoxy particles whereas the (70/30) composition reveals a degree of co-continuity with no dispersed particles.

b) Differential Thermal Analysis Data
Differential thermal analysis measurements were made to ascertain the level of compatibility in the amorphous PSO/Phenoxy system. The variation of heat flow (1st derivative w.r.t temperature) with temperature is plotted in figure [4.10]. The two separate \( T_g \)'s recorded for all compositions are broader and closer together than those of the pure polymers indicating that the components are partially miscible.
4.2:3 Poly(butylene terephthalate)/Phenoxy Binary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of both quenched, (amorphous), and slow cooled, (annealed), PBT/Phenoxy blends. The micrographs reveal a single homogeneous phase for all compositions, SEM figures [4.19 and 4.20]. However, the annealed (80/20) composition reveals heterogeneities in the phase structure, possibly due to the crystallinity of the PBT component.

b) Dynamic Mechanical Analysis Data
Dynamic mechanical measurements were made on both amorphous and slow cooled samples using the DMA in the low mass mode. The variation of loss modulus with temperature is plotted in figures [4.11 and 4.12] for both amorphous and annealed samples respectively. The single peaks obtained suggest that the PBT/Phenoxy blend is miscible at all compositions in both amorphous and annealed states. The variation of \( T_g \) with %Phenoxy, figure [4.13], reveals positive deviation from linearity for the slow cooled sample due to the crystallisation of the PBT component.

c) Differential Thermal Analysis Data
Differential thermal analysis measurements were made on both amorphous, table [4.5] and slow cooled, table [4.6], PBT/Phenoxy blends. The amorphous samples reveal an almost linear relationship for the cold crystallisation temperature \( (T_{c,}\)\) with the %Phenoxy in the blend, figure [4.14]. The values for the cold crystallisation enthalphy \( (\Delta H_{c,}\)\) were, however, somewhat lower than the corresponding values for the heat of fusion \( (\Delta H_r)\), thus implying that the quenched samples were not totally amorphous. Figure [4.15] shows the relationship between the crystallisation temperature on cooling and the %Phenoxy in the blend. This reveals that the greater the concentration of Phenoxy in the blend, the lower the crystallisation temperature \( (T_{c,}\)\) and corresponding heat of crystallisation from the melt \( (\Delta H_{c,}\)\).

The differential thermal analysis results also indicate a slight reduction in the peak melting temperature of PBT in the blended samples compared to that of the pure polymer. This depression in \( T_m \) was enhanced on the second heating cycle as the melting point was reduced further by 5-9°C with a corresponding reduction in the heat of fusion \( (\Delta H_f)\). To highlight this phenomena, a continuous DTA heating and cooling cycle was carried out on the PBT/Phenoxy (50/50) composition, table [4.7]. It can be clearly seen that each heating cycle brings about a reduction in both the crystallisation temperature, melting temperature and the respective height of the enthalpy peaks.
4.2:4 PBT-TMO/Phenoxy Binary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of both quenched, (amorphous), and slow cooled, (annealed), PBT-TMO/Phenoxy blends. The micrographs reveal a single homogeneous phase for all compositions, SEM figures [4.21 and 4.22], however, the slow cooled (80/20) composition reveals minor heterogeneities in the phase structure, which is possibly due to the crystallisation of the PBT-TMO component.

b) Dynamic Mechanical Analysis Data
Dynamic mechanical measurements were made on the annealed samples using the DMA in low mass mode. The variation of loss modulus with temperature is plotted in figure [4.16] for slow cooled samples. The single peaks obtained in all cases suggest that the PBT-TMO/Phenoxy blend is miscible at all compositions. The variation of Tg with %Phenoxy, figure [4.17], reveals positive deviation from linearity due to the crystallisation of the PBT-TMO component.

c) Differential Thermal Analysis Data
Differential thermal analysis measurements were made on both amorphous, table [4.8] and slow cooled, table [4.9], PBT-TMO/Phenoxy blends. It can be clearly seen that the trends in results are analogous to the PBT/Phenoxy binary system. The samples reveal an almost linear relationship for the cold crystallisation temperature (Tc) with the %Phenoxy in the blend, figure [4.18]. As expected, the quenched blends were found not to be totally amorphous since the cold crystallisation exotherms (ΔHc) were somewhat lower than their corresponding melt heat of fusion (ΔHf). Figure [4.19] shows the relationship between the crystallisation temperature on cooling and the %Phenoxy in the blend. Like the PBT/Phenoxy system, this again shows that the greater the Phenoxy content in the blend, the lower the crystallisation temperature (Tc) and corresponding heat of crystallisation from the melt (ΔHc).

The differential thermal analysis results also indicate a slight reduction in the peak melting temperature of PBT-TMO in the blended samples compared to that of the pure copolymer. This depression was enhanced on the second heating cycle as the melting was reduced further by 2-13°C with a corresponding reduction in the heat of fusion (ΔHf). To highlight this phenomena, a constantly repeated DTA heating and cooling cycle was carried out on the PBT-TMO/Phenoxy (50/50) composition, table [4.10]. Like the PBT/Phenoxy system, it can be clearly seen that each heating cycle brings about a
reduction in both the crystallisation temperature, melting temperature and the respective height of the enthalpy peaks.

Differential thermal analysis measurements were also made at low temperatures to determine the glass transition temperatures of the blends. Single, intermediate \( T_g \) values were obtained for all compositions with results analogous to the recorded dynamic storage modulus \( (\varepsilon') \), table [4.11]. An almost linear relationship is produced for the \( T_g \) versus composition plot, suggesting complete miscibility for all combinations and confirming that Phenoxy is miscible with both TMO and PBT segments.

4.2.5 Poly(ethylene terephthalate)/Phenoxy Binary Blends

(90/10), (70/30) and (50/50) compositions of this blend were prepared in a Brabender mixer and then quenched, (amorphous), or slow cooled, (annealed), from the melt. The amorphous (90/10) composition was transparent and the slow cooled sample displayed a hazy grey appearance. However, on increasing Phenoxy content the samples became opaque, (whiter), indicating an immiscible system.

a) Morphological Studies

Scanning electron microscopy was used to investigate the morphology of both the quenched and slow cooled PET/Phenoxy blends. SEM figure [4.23] reveals an almost miscible system for the amorphous (90/10) composition although there are a few minute inclusions (\( \approx 0.2 \mu m \) diameter) observed in the matrix. SEM figure [4.24] reveals a less compatible system for the slow cooled sample although the morphology is not an immiscible matrix/dispersed particle type. The amorphous (70/30) composition, SEM figure [4.25], reveals a very finely dispersed co-continuous structure. Similarly, so does the slow cooled sample, SEM figure [4.26], although the dispersed domains are larger by a factor of five. The amorphous (50/50) composition reveals again a much coarser co-continuous structure, SEM figure (4.27), whereas the slow cooled sample reveals an incompatible matrix/dispersed particle type of morphology, SEM figure [4.28].

b) Differential Thermal Analysis Data

Differential thermal analysis measurements were made on both amorphous and slow cooled samples, table [4.12]. It can be clearly seen that the trends in results are completely different to the equivalent PBT and PBT-TMO/Phenoxy blends. The Phenoxy has little effect on the cold crystallisation temperature (\( T_c )\), and there is no reduction in the melting point of the blend. Significantly, a continuous heating and
cooling cycle for both the (90/10) and (50/50) compositions reveals an almost identical trace which indicates that the system is at its equilibrium state of immiscibility.

However, similarly to the PBT and PBT-TMO/Phenoxy systems, the greater the concentration of Phenoxy in the blend, the lower the rate of crystallisation and crystallisation temperature. It is interesting to note that all the blends exhibit a higher crystallisation temperature and a higher rate of crystallisation than pure PET implying that Phenoxy has a nucleating effect on the crystallisation of PET when present at low concentrations.

4.2.6 Polysulphone/Poly(butylene terephthalate) Binary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PSO/PBT blends. Micrographs of the obtained morphology are shown in SEM figures [4.24 to 4.39] inclusive. The (70/30) composition reveals an interpenetrating network (IPN) type of morphology, whereas the absence of gross phase separation in the (50/50) and (30/70) compositions suggests partial miscibility between component phases.

Although the micrographs reveal only relatively small changes in morphology with variations in processing temperature, they do indicate that miscibility improves with increasing shear rate and time of mixing. Furthermore, the micrographs show that the miscibility improves with increasing annealing time and temperature to the extent that an almost miscible blend is obtained for the (50/50) composition annealed at 195°C for 65 hours, SEM figure [4.39].

b) Dynamic Mechanical Analysis Data
Dynamic mechanical analysis measurements were made on both (50/50) and (70/30) compositions. The variation of loss modulus with temperature is plotted in figure [4.20] and reveals two peaks for both compositions, however, the peaks are considerably closer together and broader than those of the pure components, indicating that the system is partially miscible.

c) Differential Thermal Analysis Data
Differential thermal analysis measurements were made on the PSO/PBT blends, table [4.13]. A second high temperature melting endotherm was observed for the (70/30) composition which remained on further reheating of the sample. The traces for other
compositions are similar to pure PBT but have slightly increased crystallisation temperatures, thus suggesting a nucleating effect by the high Tg PSO component.

Differential thermal analysis measurements on the (50/50) blend mixed under different shear rates, table [4.14] reveals a linear relationship between the latent heat of fusion and mixing shear rate. Other processing variables, however, tables [4.15 and 4.16] for time and temperature of mixing respectively, fail to reveal any significant differences between the blends. The higher temperature melting peaks were not observed this time but a low temperature shoulder of the PBT melting endotherm occurred on the second heating cycle which increased in intensity at higher processing temperatures.

Table [4.17] shows the differential thermal analysis measurements of both the (50/50) and (70/30) compositions after annealing at 235°C for 4 hours. The higher melt endotherm is erased and a more sharp peak at the melting temperature of the PBT phase is produced. Noticeably however, the temperature of the crystallisation exotherm is increased considerably with annealing. Annealing at 185°C for 48 hours, table [4.18], produces a double melting endotherm with a low temperature shoulder of the main melting peak which remains after the thermal history of the sample is destroyed.

Finally, to study the effect of heat treatment more thoroughly, the (50/50) composition was annealed at 280°C for various time intervals, table [4.19]. It can be seen that the difference between the two melting endotherms increases with annealing time and the low temperature shoulder becomes more pronounced.

4.2.7 Polyethersulphone/Poly(butylene terephthalate) Binary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PES/PBT blends. SEM figure [4.40] reveals a semi compatible structure for the (70/30) composition. It is not a full immiscible matrix/dispersed particle type of morphology as there are signs of adhesion between the two phases. Unlike the equivalent PSO/PBT composition, the PES/PBT (70/30) blend does not become more compatible after annealing at 195°C for 65 hours, SEM figure [4.41].

b) Dynamic Mechanical Analysis Data
Dynamic Mechanical analysis measurements were made on both (70/30) and (50/50) compositions. The variation of loss modulus with temperature is plotted in figure [4.21] and reveals two peaks for both compositions, which are slightly closer together than
those of the pure components indicating the occurrence of limited miscibility between phases, but to a lesser extent than the PSO/PBT system.

c) Differential Thermal Analysis Data
Differential thermal analysis measurements were made on the PES/PBT blends, table [4.17]. A second high temperature melting endotherm was obtained for the (70/30) composition which remained on reheating the sample. A reduction in the temperature of both melting and crystallisation enthalpy peaks occurred also for this composition but, the (50/50) blend behaved like pure PBT, thus suggesting an immiscible system.

Table [4.17] shows the differential thermal analysis measurements after annealing at 235°C for 4 hours. The higher melting endotherm is erased and a more sharp peak at the melting temperature of pure PBT is produced. Annealing at 185°C for 48 hours and at 195°C for 65 hours, table [4.18], produces a higher crystallisation temperature exotherm for the (50/50) composition, thus suggesting PES to have a nucleating effect. Noticeably, both a low temperature and high temperature shoulder of the main melting endotherm is produced by annealing. However, on reheating, the high temperature shoulder is removed with the thermal history.

4.2:8 Polysulphone/PBT-TMO Binary Blends

a) Morphological Studies
Scanning electron microscopy reveals a semi-compatible matrix-dispersed particle morphology for the PSO/PBT-TMO (70/30) combination, SEM figure [4.42]. Adhesion between phases can be seen even though the level of compatibility is low.

b) Differential Thermal Analysis Data
Differential thermal analysis measurements reveal a second high temperature melting endotherm for both the (50/50) and (70/30) compositions, table [4.20], at approximately 25°C above the melt temperature of the pure PBT-TMO copolymer and is about half the size of the main melting peak, figure [4.22]. A slight decrease in both the main melting and crystallisation temperatures also occurs, thus suggesting that a limited level of compatibility exists for this system.

4.2:9 Polyethersulphone/PBT-TMO Binary Blends
a) Morphological Studies
Scanning electron microscopy reveals a matrix/dispersed particle morphology for the PES/PBT-TMO (70/30) composition, SEM figure [4.43]. Noticeably, this blend has much larger dispersed particles than the equivalent PSO/PBT-TMO system and therefore it is less compatible. However, some adhesion between the two components does occur and suggests that this system exhibits a low level of compatibility.

b) Differential Thermal Analysis Data
Differential thermal analysis measurements reveal a second high temperature melting endotherm for both the (50/50) and (70/30) compositions, table [4.20]. This occurs at approximately 25°C above the melt temperature of the pure PBT-TMO copolymer but, it is only about 20% of its size. No significant reduction in the melt and crystallisation temperatures occurs and thus suggests an immiscible system.

4.2:10 Polysulphone/Poly(ethylene terephthalate) Binary Blends

a) Morphological Studies
Scanning electron microscopy reveals a co-continuous interpenetrating network for the (70/30) composition, SEM figure (4.44). The (50/50) composition, SEM figure [4.45], reveals a matrix/dispersed particle morphology containing large areas of pure polymer with limited interactions at the interphases. The (30/70) composition, SEM figure [4.46], reveals a much less coarse matrix/dispersed particle morphology than the [50/50] composition.

b) Dynamic Mechanical Analysis Data
Dynamic mechanical analysis measurements, figure [4.23], reveal two definite loss modulus peaks. These are however, both broader and closer together than those of the pure components, therefore suggesting a degree of compatibility. Noticeably, the $T_g$ of the PET rich component in the (50/50) composition is 30°C higher than that of the pure component.

c) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements for the PSO/PET blends are shown in table [4.21]. Noticeably, the melt temperatures on the second heating cycle are approximately 5°C lower and the corresponding heats of fusion are also reduced. However, a continuous heating and cooling cycle produces a mirror image trace after the thermal history of the sample is destroyed, therefore suggesting no further interactions with physical ageing.
4.2:11 Polyethersulphone/Poly(ethylene terephthalate) Binary Blends

a) Morphological Studies
Scanning electron microscopy reveals a highly dispersed close knit co-continuous structure for the (20/80) composition, SEM figures [4.47 and 4.48]. The (80/20) composition, SEM figure [4.49] also reveals this type of morphology, although the network formation is less well dispersed. The morphology of the (50/50) composition is difficult to establish, SEM figure [4.50]. However, it seems to be analogous to the PSO/PET (50/50) composition with large areas of dispersed polymers.

b) Dynamic Mechanical Analysis Data
Both dynamic mechanical analysis and dynamic mechanical thermal analysis measurements reveal two separate loss modulus peaks corresponding to the pure components, figures [4.26 and 4.27] respectively. These are broadened slightly and therefore, suggest a low level of compatibility. However, this may be due to a concentration effect as the peaks have moved slightly closer to each other. Noticeably, although the peak positions have moved, the difference in temperature between them remains fairly constant, therefore implying a limited level of compatibility.

c) Differential Thermal Analysis Data
Differential thermal analysis measurements reveal a reduction in temperature of the second heat melting endotherms analogous to the equivalent PSO/PET blends, table [4.22]. However, again a continuous heating and cooling cycle produces a mirror image trace after the thermal history is destroyed, therefore suggesting no further interactions with physical ageing. A reduction in the first heat melting temperature also occurs for all compositions, implying a level of compatibility at the component interphases. Noticeably, except for the (80/20) composition, no cold crystallisation exotherms are observed and so unlike PSO, PES does not suppress the crystallisation of PET. This behaviour is also noticeable on the cooling cycle as both the temperature and rate of crystallisation of the blends are somewhat higher than that of pure PET, thus suggesting a nucleation effect by the PES phase.

4.2:12 Poly(ethylene terephthalate)/Poly(butylene terephthalate) Binary Blends

a) Optical Studies
The white crystalline sample removed from the mixing chamber tends to turn into a clearer grey/brown colour with increasing mixing time and is probably the result of
further randomisation reactions with time at elevated temperatures. Quenched samples are transparent and so imply that they are miscible in the amorphous regions.

b) Morphological Studies
Scanning electron microscopy reveals a homogeneous system for all amorphous compositions, SEM figures [4.51] and [4.52] for (60/40) and (40/60) respectively. The slow cooled samples have been allowed to crystallise and reveal a co-continuous microstructure, SEM figures [4.53] and [4.54] for [40/60] and [60/40] respectively.

c) Dynamic Mechanical Thermal Analysis Data
Dynamic mechanical measurements reveal a single composition dependent glass transition temperature for all amorphous compositions, figure [4.28], therefore suggesting a miscible system.

d) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements, table [4.23], reveal two melting endotherms for the PET/PBT blends, the ratio of the enthalpy peaks being composition dependent. The two melting peaks reduce considerably in size on the second heat which is attributed to randomisation caused by transesterification reactions. Analysis of the rate of crystallisation, (gradient of $T_c$ exotherm), suggests the addition of PBT to PET lowers the latters crystallisation temperature but increases its rate of crystallisation significantly. A continuous heating and cooling cycle, table [4.24], eventually produces a single melt endotherm and crystallisation exotherm at a much lower temperature than the two pure polyesters. This suggests the blend becomes more compatible with physical ageing as increased randomisation occurs through transesterification, and eventually a random copolymer is produced, which is, however, crystalline.

4.2:13 Polysulphone/Phenoxy/Poly(butylene terephthalate) Ternary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PSO/Phenoxy/PBT blends. SEM figure [4.55] reveals a homogeneous structure for the (60/15/25) composition. The (55/5/40) composition however, SEM figure [4.56], displays a matrix-dispersed particle type of morphology, whereas the (45/10/45) blend, SEM figure [4.57], reveals a semi-miscible co-continuous network.
b) Dynamic Mechanical Thermal Analysis Data
Dynamic mechanical measurements reveal two separate glass transition temperatures for all compositions, figure [4.29]. The low temperature tanδ peak is analogous to the PBT/Phenoxy binary system but the value for the (60/15/25) composition is approximately 13°C higher than that of the equivalent binary blend and so suggests compatibility with the PSO phase. This is further confirmed by a reduction in the glass transition temperature of the PSO component.

c) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements are shown in table [4.25]. The (60/15/25) composition displays highly depressed melting and crystallisation temperatures. These are, in fact, much lower than the equivalent PBT/Phenoxy blend and so it suggests a higher compatibility for the PSO/Phenoxy/PBT ternary system than the PSO/PBT binary blend.

Both the (45/10/45) and (55/5/40) compositions show little difference from the equivalent binary system, although a reduction in melting temperature occurs on the second heat due to further randomisation reactions between the PBT/Phenoxy components.

4.2:14 Polysulphone/Phenoxy/PBT-TMO Ternary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PSO/Phenoxy/PBT-TMO blends. It is noticeable that the system becomes more solubilised with increasing Phenoxy content. SEM figure [4.58] reveals a partially miscible matrix/dispersed particle morphology for the [55/5/40] composition which becomes further compatibilised with an increase in Phenoxy content. Accordingly, the (45/10/45) composition, SEM figure [4.51], displays a much finer dispersed phase structure, and the (60/15/25) system, SEM figure [4.60], reveals an almost homogeneous system.

b) Dynamic Mechanical Thermal Analysis Data
The data for the dynamic mechanical measurements are again similar to the equivalent PSO/Phenoxy/PBT blends, figure [4.70]. Two separate Tg's are obtained which are somewhat broader and closer together than those of the pure components and therefore, suggest that the system is semi-miscible.
c) Differential Thermal Analysis Data
Differential thermal analysis measurements, table [4.26], again reveal an identical behaviour to the ternary PSO/Phenoxy/PBT system. Highly depressed melting and crystallisation temperatures are obtained for the (60/15/25) composition, which again suggests a much higher compatibility in the ternary system than that of the equivalent PSO/PBT-TMO binary blend. However, unlike the ternary PSO/Phenoxy/PBT system, no further reduction in melting temperature occurs on the second heating cycle.

4.2:15 Polysulphone/Phenoxy/Poly(ethylene terephthalate) Ternary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PSO/Phenoxy/PET blends. SEM figure [4.61] reveals a partially solubilised matrix/dispersed particle type structure for the (55/5/40) composition which becomes further solubilised with an increase in Phenoxy content. The (45/10/45) composition, SEM figure [4.62], reveals an almost homogeneous system, while the (60/15/25) composition, SEM figure [4.63], reveals a semi-miscible co-continuous network.

b) Dynamic Mechanical Thermal Analysis Data
Dynamic mechanical measurements reveal two separate $T_g$'s for all compositions, figure [4.31], but the broad low temperature $T_g$ is due to both PET and Phenoxy components as they have similar $T_g$ values. The two tan$\delta$ peaks for the (45/10/45) composition are somewhat closer together than those of the pure components and therefore, imply that the system is semi-miscible.

c) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements are shown in table [4.27]. A high crystallisation temperature is obtained for the (60/15/25) composition, which suggests that the amorphous PSO/Phenoxy phase nucleates the crystallisation of PET. The (55/5/40) and (45/10/45) compositions however, gave a similar trace to pure PET and displayed cold crystallisation exotherms. This behaviour implies that the amorphous PSO/Phenoxy phase does not nucleate the crystallisation of PET in these compositions, but in fact, hinders it.

4.2:16 Polyethersulphone/Phenoxy/Poly(butylene terephthalate) Ternary Blends
a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PES/Phenoxy/PBT (60/15/25) blend. A slow cooled sample reveals an almost homogeneous system, SEM figure [4.64], whereas a quenched sample, SEM figure [4.65] displays a less solubilised, semi-miscible matrixdispersed particle type of morphology.

b) Dynamic Mechanical Analysis Data
Dynamic mechanical measurements reveal two separate T_g's for the (60/15/25) blend, figure [4.32], with the low temperature tanδ peak corresponding to the PBT/Phenoxy phase. A correspondingly large reduction in the T_g of the PES rich phase implies that the ternary system is semi-miscible.

c) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements for both slow cooled and quenched samples are shown in table [4.28]. The quenched samples reveal much depressed crystallisation and melting temperatures, therfore suggesting compatibility, but to a lesser extent than the equivalent PSO/Phenoxy/PBT blend. The slow cooled sample, in fact, reveals only a slight reduction in melting and crystallisation temperatures and therefore, it indicates to be less compatible than the more amorphous quenched sample.

4.2:17 Polyethersulphone/Phenoxy/PBT-TMO Ternary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PES/Phenoxy/PBT-TMO blends. SEM figures [4.66 and 4.67] reveal an almost homogeneous system for both the quenched and slow cooled samples respectively and therefore, confirms that Phenoxy has solubilised the system since the morphology is generally monophase with only small inclusions of the crystalline PBT-TMO component.

b) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements for both quenched and slow cooled samples are shown in table [4.28]. Both sets of samples display much depressed melting and crystallisation temperatures although to a slightly lesser extent than the equivalent PSO system. For this blend, however, the slow cooled sample
unexpectedly reveals more depressed melting and crystallisation temperatures than for the quenched sample.

4.2.18 Polyethersulphone/Phenoxy/Poly(ethylene terephthlate) Ternary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PES/Phenoxy/PET blends. SEM figure [4.68], reveals a co-continuous structure for the (80/5/15) composition, which is similar to its equivalent PES/PET (80/20) blend but with less coarsening and no dispersed particles present. The (75/5/20) composition, SEM figure [4.69], reveals a similar morphology again but contains some tiny dispersed (0.2µm), Phenoxy, PET or crosslinked PET/Phenoxy particles. The (55/5/40) composition, SEM figure [4.70], displays a near monophase morphology and shows that Phenoxy solubilises the system. As this blend contains an almost (50/50) mix of PES/PET, there is less tendency to produce an IPN and a greater tendency for the two major constituents to “fuse” together by the solubilisation of the Phenoxy. The (45/10/45) composition, SEM figure [4.71], reveals again a similar nearly monophase morphology, except for the presence of some dispersed phenoxy particles (0.5-1µm) not used in the solubilisation. The (40/5/55) composition, SEM figure [4.72], again reveals a near monophase morphology but with less dispersed particles than the previous sample. The (20/5/75) composition, SEM figure [4.73], displays a crystalline PET matrix containing large dispersed PES particles.

b) Dynamic Mechanical Thermal Analysis Data
Dynamic mechanical measurements were made on the PES/Phenoxy/PET blends, figure [4.33]. Two separate glass transition temperatures corresponding to both major components were obtained for all compositions, but the peaks are slightly broader and closer together than those of the pure components indicating that there is some miscibility. Except for the (45/10/45) composition, the difference in temperature between the tanδ peaks is only marginally less (≈5°C) than that of the equivalent PES/PET binary blends. The glass transition temperatures of the (45/10/45) composition are somewhat closer together due to the higher amount of Phenoxy solubilising the system. Finally, it is noted that a high temperature shoulder of the tanδ occurs, which is associated with the PET component in the (20/5/75) composition. It may correspond to a miscibilised PET/Phenoxy component, since this binary system has been found to be miscible at high concentrations of PET.
c) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements are shown in table [4.29]. The crystallisation temperature on cooling is approximately 5°C higher than that of pure PET and therefore, suggests that the amorphous PES/Phenoxy phase nucleates the crystallisation of PET. This behaviour is analogous to the equivalent PES/PET binary systems. As expected, however, the amorphous PES/Phenoxy component suppresses the crystallisation rate of PET to the extent that the low concentration PET blends are partially amorphous, as indicated by a cold crystallisation exotherm, \( T_c \). Finally, there is little reduction in the melting temperature on the first heat, thus suggesting only a low level of compatibility. The melting temperature of the second heating cycle however, is somewhat reduced, especially for those compositions with a large PET/Phenoxy ratio, as these are expected to be more miscible.

### 4.2:19 Polyethersulphone/Phenoxy/Poly(ethylene terephthalate)/Poly(butylene terephthalate) Quarternary Blends

a) Morphological Studies
Scanning electron microscopy was used to investigate the morphology of the PES/Phenoxy/PET/PBT blends. SEM figure [4.74], reveals a well dispersed co-continuous structure containing very small (≈0.5 μm) dispersed particles, for the (40/10/40/10) composition. SEM figure [4.75] reveals a more solubilised amorphous type structure for the (40/10/30/20) system whereas the (30/20/20/30) composition, SEM figure [4.76], displays a nearly monophase morphology.

b) Differential Thermal Analysis Data
The data from the differential thermal analysis measurements are shown in table [4.30]. Two melting endotherms are obtained for both Polyester components but, these merge in the second heating cycle to produce a single PET/PBT randomised melting endotherm. Both the second heat melting and crystallisation enthalpy peaks occur at somewhat lower temperatures, suggesting an increased level of compatibilisation with a greater extent of Polyester randomisation.

### 4.3 COMPOUNDING EXTRUSION BLENDS

Both the blends and Polysulphone controls were prepared according to the guidelines shown in the experimental section. The blends produced on the twin screw extruder
were: PES/Phenoxy (80/20), PSO/PBT (70/30), PES/PBT (70/30), PES/PET (70/30),
PSO/Phenoxy/PBT (60/15/25), PSO/Phenoxy/PBT-TMO (60/15/25), PES/Phenoxy/PBT
(60/15/25), PES/Phenoxy/PET (60/15/25) and PES/Phenoxy/PET/PBT (60/5/25/10).
Samples were extruded into sheets and then press-annealed at their maximum
crystallisation temperature (Tc) for ten minutes before testing.

4.3:1 Morphological Studies

Scanning electron microscopy was used to investigate the morphology of the sheet
extruded blends, produced according to the procedure described in section [3.2:4b]. SEM
figure [4.77] reveals a semi-miscible co-continuous structure for the sheet extruded
PES/Phenoxy (80/20) blend.

SEM figure [4.78] reveals a matrix/dispersed particle type of morphology for the sheet
extruded and pressed PSO/PBT (70/30) blend. However, gross phase separation is not
apparent as the interphases are not well defined. By immersing the fracture surface of
the specimen in methyl ethyl ketone, (MEK), for twenty minutes a polished,
homogeneous system is seen, SEM figure [4.79].

The PES/PBT (70/30) blend reveals a semi-miscible co-continuous network for the sheet
extruded sample, SEM figure [4.80]. On press-annealing at Tc, for ten minutes the
morphology becomes more coarse due to the further separation of crystalline PBT, SEM
figure [4.81]. However, there is definite interactions, (tearing), between component
phases and the co-continuity of phases remains. On immersing in MEK, SEM figure
[4.82], this sample reveals a highly polished amorphous phase containing small (≥1μm)
dispersed PBT particles.

Figures [4.83 and 4.84] reveal a partially solubilised matrix/dispersed particle
morphology for both the PES/PET (70/30) sheet extruded and press-annealed samples
respectively. On immersing in MEK, SEM figure [4.85], this sample reveals a highly
polished amorphous phase containing dispersed PET particles.

SEM figure [4.86] reveals a finely dispersed co-continuous morphology for the sheet
extruded PSO/Phenoxy/PBT (60/15/25) blend. This morphology remains after press-
annealing, SEM figure [4.87], and is more finely dispersed than the equivalent PSO/PBT
binary blend. On immersing in MEK, a highly polished monophase morphology is
observed, SEM figure [4.88].
The sheet extruded PSO/Phenoxy/PBT-TMO (60/15/25) blend reveals a highly interlocked co-continuous morphology, SEM figure [4.89]. On immersing in MEK, SEM figure [4.90], this sample reveals a polished co-continuous network containing areas of highly interlocked PBT-TMO/Phenoxy component.

The PES/Phenoxy/PBT (60/15/25) blend proved extremely difficult to sheet extrude but analysis of a fracture surface reveals a partially solubilised co-continuous morphology, SEM figure [4.91].

The sheet extruded and press-annealed PES/Phenoxy/PET (60/15/25) blend, SEM figure [4.92], reveals a near monophase amorphous structure. On immersing in MEK, SEM figure [4.93], this sample reveals a well defined matrix/dispersed particle morphology containing many voids.

SEM figure [4.94] reveals a partially solubilised matrix/dispersed particle morphology for the sheet extruded PES/Phenoxy/PET/PBT blend. On immersing in MEK, SEM figure [4.95], this sample again reveals a partially solubilised amorphous system, but with distinct areas preferentially removed by the solvent. Gross phase separation, however, is not apparent and so the blend is considered to be semi-miscible.

### 4.3:2 Differential Thermal Analysis Data

The data from the differential thermal analysis measurements for both sheet extrudates and the samples press-annealed at Tc, are shown in table [4.31]. Both PSO/PBT and PES/PBT blends reveal crystallisation exotherms at considerably higher temperatures (±15°C) than those mixed in the Brabender. However, unlike the internal mixer prepared blends, a high temperature melting endotherm was not observed for the sheet extrudate. A (50/50) split of the melting peak occurs though on the second heat, thus suggesting the presence of two types of PBT crystallites. Similarly, the PES/PET blend also reveals a much higher crystallisation temperature, (±7°C). This again is considerably higher (±15°C) than that of the pure PET and thus suggests a nucleating effect by the PES component. Interestingly, a reduction in temperature (±5°C) of the melting endotherm also occurs compared to that of the internally mixed system.

Both the PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO systems reveal different DSC traces for the sheet extrudate and the press-annealed samples. A reduction in temperature of both the melting and crystallisation enthalpy peaks occurs with press-annealing as more of the co-reacted PBT/Phenoxy component is produced. Interestingly,
no crystallisation of the PBT-TMO component occurs on cooling for the press-annealed sample which suggests the complete randomisation of the PBT-TMO/Phenoxy reaction products. The sheet extrudate samples however, reveal much higher crystallisation and melting temperatures, (≥25°C), than the equivalent blends prepared by the internal mixer. This difference implies that the extent of reaction of the components in the sheet extruded samples is much less due to the shorter residence time.

The PES/Phenoxy/PET blend reveals a DSC trace similar to that of the Brabender mixed sample. However, even though identical cooling rates were used, a much lower temperature (≥10°C) melting endotherm was revealed in the sheet extrudate sample on the second heat. The cold crystallisation exotherm (T_c) displayed by the sheet extrudate sample is completely removed on press-annealing above the T_g of PET.

The removal of the cold crystallisation exotherm by press-annealing, also occurs in the PES/Phenoxy/PET/PBT blend. This system also displays a higher crystallisation temperature (T_c) than the corresponding internally mixed sample and produces an already randomised single melting endotherm, which occurs at a lower temperature in the second heating cycle.

4.3:3 Solvent Resistance Measurements

500μm thick sheet extruded samples for tensile testing were prepared as described in the experimental section [3.3:2]. Table [4.32] shows the mean ultimate tensile strength calculated for each sample. It is noticeable that the blends displaying a finely dispersed interpenetrating network type of morphology, have higher tensile strengths, approaching the values recorded for pure Polysulphone.

Conversely, the PET based blends possess poor tensile strength properties, which can be related to their matrix-dispersed particle morphology.

Table [4.33] reports the data for the solvent resistance of the blends obtained by measuring the time to failure on the dropping of 0.025ml of MEK on the surface of the specimen subjected to a stress equal to 50% of the tensile strength and also with the use of 0.01ml of MEK at a stress of 30% of the tensile strength. It is noted that the time to failure decreased with applied stress and the solvent resistance improves when the two phases are co-continuous.
Figure 4.1: PES/Phenoxy (50/50) solution blend.

Figure 4.2: PES/Phenoxy (50/50) solution blend. Annealed at 117°C for 1 week. (30°C below T_g).

Figure 4.3: PES/Phenoxy (50/50) solution blend. Annealed at 225°C for 1 hour. (30°C above LCST).

Figure 4.4: PES/Phenoxy (80/20) solution blend. Annealed at 161°C for 1 week. (30°C below T_g).

Figure 4.5: PES/Phenoxy (80/20) solution blend. Annealed at 250°C for 1 hour. (30°C above LCST).

Figure 4.6: PES/Phenoxy (70/30) solution blend.

Figure 4.7: PES/Phenoxy (40/60) solution blend. Annealed at 163°C for 1 day. (20°C below LCST).

Figure 4.8: PES/Phenoxy (20/80) solution blend. Annealed at 240°C for 1 hour. (30°C above LCST).
Figure 4.9: PSO/Phenoxy (90/10) solution blend.

Figure 4.10: PSO/Phenoxy (90/10) solution blend. Annealed at 120°C for 1 week.

Figure 4.11: PSO/Phenoxy (80/20) solution blend.

Figure 4.12: PSO/Phenoxy (80/20) solution blend.

Figure 4.13: PES/Phenoxy (80/20) melt blend.

Figure 4.14: PES/Phenoxy (60/40) melt blend.

Figure 4.15: PES/Phenoxy (40/60) melt blend.

Figure 4.16: PSO/Phenoxy (90/10) melt blend.
Figure 4.25: PET/Phenoxy (70/30) quenched melt blend.

Figure 4.26: PET/Phenoxy (70/30) slow cooled melt blend.

Figure 4.27: PET/Phenoxy (50/50) quenched melt blend.

Figure 4.28: PET/Phenoxy (50/50) slow cooled melt blend.

Figure 4.29: PSO/PBT (9/10) melt blend.

Figure 4.30: PSO/PBT (70/30) melt blend.

Figure 4.31: PSO/PBT (30/70) melt blend.

Figure 4.32: PSO/PBT (50/50) melt blend. Processed at 250°C, 100rpm for 3mins.
Figure 4.33: PSO/PBT (50/50) melt blend. Processed at 270°C, 100rpm for 3mins.

Figure 4.34: PSO/PBT (50/50) melt blend. Processed at 250°C, 100rpm for 16mins.

Figure 4.35: PSO/PBT (50/50) melt blend. Processed at 250°C, 100rpm for 28mins.

Figure 4.36: PSO/PBT (50/50) melt blend. Processed at 250°C, 75rpm for 3mins.

Figure 4.37: PSO/PBT (50/50) melt blend. Processed at 250°C, 125rpm for 3mins.

Figure 4.38: PSO/PBT (50/50) melt blend. Annealed at 185°C for 48hrs.

Figure 4.39: PSO/PBT (50/50) melt blend. Annealed at 195°C for 68hrs after melting.

Figure 4.40: PES/PBT (70/30) melt blend.
Figure 4.41: PES/PBT (70/30) melt blend. Annealed at 195°C for 65hrs after melting.

Figure 4.42: PSO/PBT-TMO (70/30) melt blend.

Figure 4.43: PES/PBT-TMO (70/30) melt blend.

Figure 4.44: PSO/PET (70/30) melt blend.

Figure 4.45: PSO/PET (50/50) melt blend.

Figure 4.46: PSO/PET (30/70) melt blend.

Figure 4.47: PES/PET (20/80) melt blend.

Figure 4.48: PES/PET (20/80) melt blend.
Figure 4.57: PSO/Phenoxy/PBT (45/10/45) melt blend.

Figure 4.58: PSO/Phenoxy/PBT-TMO (55/5/40) melt blend.

Figure 4.59: PSO/Phenoxy/PBT-TMO (45/10/45) melt blend.

Figure 4.60: PSO/Phenoxy/PBT-TMO (60/15/25) melt blend.

Figure 4.61: PSO/Phenoxy/PET (55/5/40) melt blend.

Figure 4.62: PSO/Phenoxy/PET (45/10/45) melt blend.

Figure 4.63: PSO/Phenoxy/PET (60/15/25) melt blend.

Figure 4.64: PES/Phenoxy/PBT (60/15/25) slow cooled melt blend.
Figure 4.65: PES/Phenoxy/PBT (60/15/25) quenched melt blend.

Figure 4.66: PES/Phenoxy/PBT-TMO (60/15/25) quenched melt blend.

Figure 4.67: PES/Phenoxy/PBT-TMO (60/15/25) slow cooled melt blend.

Figure 4.68: PES/Phenoxy/PET (80/5/15) melt blend.

Figure 4.69: PES/Phenoxy/PET (75/5/20) melt blend.

Figure 4.70: PES/Phenoxy/PET (55/5/40) melt blend.

Figure 4.71: PES/Phenoxy/PET (45/10/45) melt blend.

Figure 4.72: PES/Phenoxy/PET (40/5/55) melt blend.
Figure 4.75: PES/Phenoxy/PET (20/5/75) melt blend.

Figure 4.77: PES/Phenoxy (80/20) sheet extruded.

Figure 4.79: PSO/PBT (70/30) sheet extruded and pressed at Tc, for 10mins.

Figure 4.80: PES/PBT (70/30) sheet extruded.
Figure 4.84: PES/PET (70/30) sheet extruded and pressed at Tc for 10mins.

Figure 4.85: PES/PET (70/30) sheet extruded, pressed and etched in MEK.

Figure 4.87: PSO/Phenoxy/PBT (60/15/25) sheet extruded and pressed at Tc for 10mins.

Figure 4.88: PSO/Phenoxy/PBT (60/15/25) sheet extruded, pressed and etched in MEK.
Figure 4.89: PSO/Phenoxy/PBT-TMO (60/15/25) sheet extruded and pressed at Tc2 for 10mins.

Figure 4.90: PSO/Phenoxy/PBT-TMO (60/15/25) sheet extruded, pressed and etched in MEK.

Figure 4.91: PES/Phenoxy/PBT (60/15/25) sheet extruded.

Figure 4.92: PES/Phenoxy/PBT (60/15/25) sheet extruded and pressed at Tc2 for 10mins.

Figure 4.93: PES/Phenoxy/PET (60/15/25) sheet extruded, pressed and etched in MEK.

Figure 4.94: PES/Phenoxy/PET/PET (60/5/25/10) sheet extruded and pressed at Tc2 for 10mins.

Figure 4.95: PES/Phenoxy/PET/PBT (60/5/25/10) sheet extruded, pressed and etched in MEK.
NB: Both the DMTA and DMA figures were digitised from the original traces and imported into the computer program. Only one measurement was made for each formulation and therefore, the degree of accuracy cannot be calculated.

**Figure 4.1: DMA Measurements of PES/Phenoxy Solution Blends**

![DMA Measurements of PES/Phenoxy Solution Blends](image)

**Figure 4.2: Glass Transition Temperatures of PES/Phenoxy Solution Blends**

![Glass Transition Temperatures of PES/Phenoxy Solution Blends](image)
Figure 4.3: FTIR (-OH) Group Absorption Peaks for PES/Phenoxy Solution Blends

![FTIR (-OH) Group Absorption Peaks](image)

Figure 4.4: DMA Measurements of PSO/Phenoxy Solution Blends

![DMA Measurements of PSO/Phenoxy Solution Blends](image)
Figure 4.5: DTA Measurements of the Glass Transition Temperature of PSO/Phenoxy Solution Blends

Figure 4.6: Glass Transition Temperatures of PSO/Phenoxy Solution Blends
Figure 4.7: Calculated and Experimentally Obtained Glass Transition Temperatures for PSO/Phenoxy Solution Blends

Figure 4.8: FTIR (-OH) Group Absorption Peaks for PSO/Phenoxy Solution Blends
Figure 4.9: DMTA Measurements of PES/Phenoxy Blends

Figure 4.10: DTA Measurements of the Glass Transition Temperature of PSO/Phenoxy Blends
Figure 4.11: DMA Measurements of Amorphous PBT/Phenoxy Blends

Temperature (°C)

Loss Modulus (MPa)

- PBT
- PBT/Phenoxy (90/10)
- PBT/Phenoxy (70/30)
- PBT/Phenoxy (50/50)
- PBT/Phenoxy (30/70)
- PBT/Phenoxy (10/90)
- Phenoxy

Figure 4.12: DMA Measurements of Slow Cooled PBT/Phenoxy Blends

Temperature (°C)

Loss Modulus (MPa)

- PBT
- PBT/Phenoxy (90/10)
- PBT/Phenoxy (70/30)
- PBT/Phenoxy (50/50)
- PBT/Phenoxy (30/70)
- PBT/Phenoxy (10/90)
- Phenoxy
Figure 4.13: Glass Transition Temperatures for Both Slow Cooled and Quenched PBT/Phenoxy Blends

Figure 4.14: Cool Crystallisation Temperatures of Amorphous PBT/Phenoxy Blends
Figure 4.15: Crystallisation Temperature on Cooling for PBT/Phenoxy Blends

![Graph showing crystallisation temperature on cooling for PBT/Phenoxy blends.](image)

- Amorphous
- Slow cooled

Figure 4.16: DMA Measurements of Slow Cooled PBT-TMO/Phenoxy Blends

![Graph showing DMA measurements of slow cooled PBT-TMO/Phenoxy blends.](image)

- PBT-TMO
- PBT-TMO Phenoxy (80:20)
- PHT-TMO Phenoxy (60:40)
- PHT-TMO Phenoxy (40:60)
- PHT-TMO Phenoxy (20:80)
- Phenoxy
Figure 4.17: Glass Transition Temperatures for Both Slow Cooled and Quenched PBT-TMO/Phenoxy Blends

Figure 4.18: Cool Crystallisation Temperatures of PBT-TMO/Phenoxy Blends
Figure 4.19: Crystallisation Temperature on Cooling for PBT-TMO/Phenoxy Blends

Figure 4.20: DMA Measurements of PSO/PBT Blends
Figure 4.21: DMA Measurements of PES/PBT Blends

Figure 4.22: DTA Trace of a PSO/PBT-TMO (70/30) Blend
Figure 4.23: DMA Measurements of PSO/PET Blends

Figure 4.24: DMA Measurements of PES/PET Blends
Figure 4.25: DMTA Measurements of PES/PET Blends

![Graph showing DMTA Measurements of PES/PET Blends](image)

Figure 4.26: DMTA Measurements of PET/PBT Blends

![Graph showing DMTA Measurements of PET/PBT Blends](image)
Figure 4.27: DMTA Measurements of PSO/Phenoxy/PBT Blends

![Graph showing DMTA measurements of PSO/Phenoxy/PBT blends.](image)

- PBT
- PSO/Phenoxy/PBT (60:15:25)
- PSO/Phenoxy/PBT (55:5:40)
- PSO/Phenoxy/PBT (45:10:45)
- PSO

Figure 4.28: DMTA Measurements of PSO/Phenoxy/PBT-TMO Blends

![Graph showing DMTA measurements of PSO/Phenoxy/PBT-TMO blends.](image)

- PBT-TMO
- PSO/Phenoxy/PBT-TMO (60:15:25)
- PSO/Phenoxy/PBT-TMO (55:5:40)
- PSO/Phenoxy/PBT-TMO (45:10:45)
- PSO
Figure 4.29: DMTA Measurements of PSO/Phenoxy/PET Blends

Figure 4.30: DMA Measurements of PES/Phenoxy/PBT Blends
Figure 4.31: DMTA Measurements of PES/Phenoxy/PET Blends
### Table 4.1: Annealing Times and Temperatures for PES/Phenoxy Solution Blends

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<th>PES/PHEN</th>
<th>Tg(°C)</th>
<th>LCST (°C)</th>
<th>30°C below Tg</th>
<th>30°C below LCST</th>
<th>20°C below Tg</th>
<th>20°C below LCST</th>
<th>30°C above LCST</th>
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### Table 4.2: FTIR Absorption Spectra of PES/Phenoxy Solution Blends

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### Table 4.3: DMTA Measurements for PSO/Phenoxy Solution Blends

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<td>[90/10] aged 115°C (72hrs)</td>
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<tr>
<td>[100/0] aged 70°C (1 week)</td>
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<tr>
<td>[100/0] methanol inversion</td>
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<tr>
<td>[100/0] melt</td>
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Table 4.4: FTIR Absorption Spectra of PSO/Phenoxy Solution Blends

**i) Normal drying**

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**ii) 18 hrs at 105°C**

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**iii) 1 hr at 160°C**

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<td>1888</td>
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### DTA Nomenclature

- $T_c_1$ = cold crystallisation temperature on heating.
- $\Delta H_{C_1}$ = heat of crystallisation on heating.
- $T_c_2$ = crystallisation temperature on cooling.
- $\Delta H_{C_2}$ = heat of crystallisation on cooling.
- $T_m_1$ = melt temperature on first heating cycle.
- $\Delta H_{f_1}$ = heat of fusion of first heat melt endotherm.
- $T_m_2$ = melt temperature on second heating cycle.
- $\Delta H_{f_2}$ = heat of fusion of second heat melt endotherm.
- NB: Significant peak shoulders in brackets.

### Table 4.5: DTA Measurements of Amorphous PBT/Phenoxy blends

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<th>$T_c_2$ (°C)</th>
<th>$\Delta H_{C_2}$ (J/g)</th>
<th>$T_m_1$ (°C)</th>
<th>$\Delta H_{f_1}$ (J/g)</th>
<th>$T_m_2$ (°C)</th>
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### Table 4.6: DTA Measurements of Slow Cooled PBT/Phenoxy blends

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<tr>
<th>PBT/Phenoxy</th>
<th>$T_c_1$ (°C)</th>
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<th>$T_c_2$ (°C)</th>
<th>$\Delta H_{C_2}$ (J/g)</th>
<th>$T_m_1$ (°C)</th>
<th>$\Delta H_{f_1}$ (J/g)</th>
<th>$T_m_2$ (°C)</th>
<th>$\Delta H_{f_2}$ (J/g)</th>
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### Table 4.7: Continuous DTA Measurements of a PBT/Phenoxy [50/50] blend

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<th>Melt Temperatures (°C)</th>
<th>Heats of Fusion (J/g)</th>
<th>Crystallisation Temperatures (°C)</th>
<th>Heats of Crystallisation (J/g)</th>
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<tr>
<td>Tm₁ = 222.02</td>
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<td>Tc₁ = 172.59</td>
<td>ΔHc₁ = 26.32 J/g</td>
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<tr>
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<td>Tc₂ = 167.86</td>
<td>ΔHc₂ = 23.34 J/g</td>
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<tr>
<td>Tm₃ = 212.31</td>
<td>ΔHf₃ = 23.73 J/g</td>
<td>Tc₃ = 163.17</td>
<td>ΔHc₃ = 19.96 J/g</td>
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<td>Tm₄ = 209.01</td>
<td>ΔHf₄ = 19.53 J/g</td>
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- Tm₁: Melt temperature on first heat
- Tm₂: Melt temperature on second heat
- Tm₃: Melt temperature on third heat
- Tm₄: Melt temperature on fourth heat
- Tc₁: Crystallisation temperature on first cool
- Tc₂: Crystallisation temperature on second cool
- Tc₃: Crystallisation temperature on third cool

ΔHf = Heat of fusion
ΔHc = Heat of crystallisation

### Table 4.8: DTA Measurements of Quenched PBT-TMO/Phenoxy blends

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<th>Tc₂ (°C)</th>
<th>ΔHc₂ (J/g)</th>
<th>Tm₁ (°C)</th>
<th>ΔHf₁ (J/g)</th>
<th>Tm₂ (°C)</th>
<th>ΔHf₂ (J/g)</th>
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<td>17.72</td>
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### Table 4.9: DTA Measurements of Slow Cooled PBT-TMO/Phenoxy blends

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<th>Tc₁ (°C)</th>
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<th>Tc₂ (°C)</th>
<th>ΔHc₂ (J/g)</th>
<th>Tm₁ (°C)</th>
<th>ΔHf₁ (J/g)</th>
<th>Tm₂ (°C)</th>
<th>ΔHf₂ (J/g)</th>
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### Table 4.10: Continuous DTA Measurements of a PBT-TMO/Phenoxy [50/50] blend

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<th>Melt Temperatures (°C)</th>
<th>Heats of Fusion (J/g)</th>
<th>Crystallisation Temperatures (°C)</th>
<th>Heats of Crystallisation (J/g)</th>
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<tbody>
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<tr>
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<td>Tc₃ = 146.66</td>
<td>ΔHc₃ = 21.01</td>
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<td>Tm₄ = 191.11</td>
<td>ΔHf₄ = 24.59</td>
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<td></td>
</tr>
</tbody>
</table>

- Tm₁ = Melt temperature on first heat
- ΔHf₁ = Heat of fusion of first melt
- Tm₂ = Melt temperature on second heat
- ΔHf₂ = Heat of fusion of second melt
- Tm₃ = Melt temperature on third heat
- ΔHf₃ = Heat of fusion of third melt
- Tm₄ = Melt temperature on fourth heat
- ΔHf₄ = Heat of fusion of fourth melt
- Tc₁ = Crystallisation temperature on first cool
- ΔHc₁ = Heat of crystallisation on first cool
- Tc₂ = Crystallisation temperature on second cool
- ΔHc₂ = Heat of crystallisation on second cool
- Tc₃ = Crystallisation temperature on third cool
- ΔHc₃ = Heat of crystallisation on third cool

### Table 4.11: DTA and DMA Measurements of PBT-TMO/Phenoxy blends, Tg Analysis

<table>
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<th>PBT-TMO/Phenoxy</th>
<th>Tg (°C)</th>
<th>E₁ onset (°C)</th>
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### Table 4.12: DTA Measurements of PET/Phenoxy blends

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<th>PET/Phenoxy</th>
<th>Tc₁ (°C)</th>
<th>ΔHc₁ (J/g)</th>
<th>Tc₂ (°C)</th>
<th>ΔHc₂ (J/g)</th>
<th>Tm₁ (°C)</th>
<th>ΔHf₁ (J/g)</th>
<th>Tm₂ (°C)</th>
<th>ΔHf₂ (J/g)</th>
</tr>
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<tbody>
<tr>
<td>[100/0]</td>
<td>190.92</td>
<td>201.99</td>
<td>143.02</td>
<td>141.05</td>
<td>140.85</td>
<td>193.34</td>
<td>140.85</td>
<td>20.77</td>
</tr>
<tr>
<td>[90/10] amor</td>
<td>23.05</td>
<td>31.79</td>
<td>25.87</td>
<td>19.81</td>
<td>17.34</td>
<td>17.99</td>
<td>18.44</td>
<td>10.96</td>
</tr>
<tr>
<td>[80/20] amor</td>
<td>245.89</td>
<td>245.11</td>
<td>245.87</td>
<td>245.35</td>
<td>247.69</td>
<td>19.99</td>
<td>16.08</td>
<td>62.36</td>
</tr>
<tr>
<td>[70/30] amor</td>
<td>251.02</td>
<td>251.06</td>
<td>251.06</td>
<td>251.06</td>
<td>251.06</td>
<td>251.06</td>
<td>251.06</td>
<td>251.06</td>
</tr>
<tr>
<td>[60/40] amor</td>
<td>244.46</td>
<td>244.46</td>
<td>244.46</td>
<td>244.46</td>
<td>244.46</td>
<td>244.46</td>
<td>244.46</td>
<td>244.46</td>
</tr>
</tbody>
</table>
Table 4.13: DTA Measurements of PSO/PBT blends

<table>
<thead>
<tr>
<th>PSO/PBT</th>
<th>Tc (°C)</th>
<th>ΔHc1 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(90/10)</td>
<td>223.76</td>
<td>4.97</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(70/30)</td>
<td>184.91</td>
<td>10.21</td>
<td>220.49(245.73)</td>
<td>14.84(2.73)</td>
<td>219.88(245.23)</td>
<td>11.92(1.24)</td>
</tr>
<tr>
<td>(50/50)</td>
<td>184.86</td>
<td>28.05</td>
<td>222.76</td>
<td>23.77</td>
<td>221.44</td>
<td>1.24</td>
</tr>
<tr>
<td>(30/70)</td>
<td>193.44</td>
<td>38.44</td>
<td>229.15</td>
<td>34.52</td>
<td>224.53</td>
<td>35.13</td>
</tr>
<tr>
<td>(10/90)</td>
<td>193.57</td>
<td>38.13</td>
<td>230.59</td>
<td>30.96</td>
<td>225.84</td>
<td>32.1</td>
</tr>
<tr>
<td>(0/100)</td>
<td>182.01</td>
<td>46.16</td>
<td>227.92</td>
<td>42.98</td>
<td>223.51</td>
<td>52.81</td>
</tr>
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</table>

Table 4.14: DTA Measurements of PSO/PBT [50/50] blend with variable Shear Rate

<table>
<thead>
<tr>
<th>shear rate (rpm)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>ΔHc1 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>184.5</td>
<td>192.79</td>
<td>23.22</td>
<td>226.63</td>
<td>21.69</td>
<td>224.57</td>
<td>21.62</td>
</tr>
<tr>
<td>75</td>
<td>185.3</td>
<td>193.34</td>
<td>18.58</td>
<td>227.07</td>
<td>15.43</td>
<td>224.84(219.07)</td>
<td>16.07</td>
</tr>
<tr>
<td>100</td>
<td>184.5</td>
<td>193.61</td>
<td>22.65</td>
<td>227.41</td>
<td>18.54</td>
<td>225.49(219.84)</td>
<td>20.71</td>
</tr>
<tr>
<td>150</td>
<td>185.9</td>
<td>194.41</td>
<td>37.11</td>
<td>227.38</td>
<td>32.66</td>
<td>225.15(218.87)</td>
<td>33.67</td>
</tr>
</tbody>
</table>

Table 4.15: DTA Measurements of PSO/PBT [50/50] blend with variable Processing Time

<table>
<thead>
<tr>
<th>process time (mins)</th>
<th>Tc (°C)</th>
<th>ΔHc1 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>194.99</td>
<td>23.17</td>
<td>225.61</td>
<td>21.95</td>
<td>223.55(218.41)</td>
<td>21.71</td>
</tr>
<tr>
<td>16</td>
<td>195.74</td>
<td>21.23</td>
<td>226.71</td>
<td>18.21</td>
<td>224.32(219.22)</td>
<td>19.22</td>
</tr>
<tr>
<td>28</td>
<td>196.32</td>
<td>23.74</td>
<td>226.68</td>
<td>22.06</td>
<td>224.38(218.51)</td>
<td>22.36</td>
</tr>
</tbody>
</table>

Table 4.16: DTA Measurements of PSO/PBT [50/50] blend with variable Processing Temperature

<table>
<thead>
<tr>
<th>process temp (°C)</th>
<th>Tg (°C)</th>
<th>Tc (°C)</th>
<th>ΔHc1 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>230</td>
<td>185.5</td>
<td>193.53</td>
<td>28.81</td>
<td>227.44</td>
<td>25.37</td>
<td>224.85</td>
<td>23.66</td>
</tr>
<tr>
<td>250</td>
<td>184.5</td>
<td>193.61</td>
<td>22.65</td>
<td>227.41</td>
<td>18.54</td>
<td>225.49(219.84)</td>
<td>20.71</td>
</tr>
<tr>
<td>270</td>
<td>185.2</td>
<td>193.63</td>
<td>19.71</td>
<td>230.65</td>
<td>19.71</td>
<td>226.77(219.79)</td>
<td>18.81</td>
</tr>
<tr>
<td>290</td>
<td>182.9/-71.4</td>
<td>194.96</td>
<td>23.44</td>
<td>227.61</td>
<td>23.44</td>
<td>225.85(218.37)</td>
<td>22.58</td>
</tr>
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</table>
Table 4.17: DTA Measurements of PSO/PBT and PES/PBT blends before(i) and after annealing at 235°C for 4hours(ii)

<table>
<thead>
<tr>
<th>BLEND</th>
<th>Tc (°C)</th>
<th>ΔHc (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSO/PBT [70/30]</td>
<td>184.91</td>
<td>10.21</td>
<td>220.49(245.73)</td>
<td>14.84(2.73)</td>
<td>219.88(245.23)</td>
<td>11.92(1.24)</td>
</tr>
<tr>
<td>PSO/PBT [50/50]</td>
<td>184.86</td>
<td>28.05</td>
<td>222.76</td>
<td>23.77</td>
<td>221.44</td>
<td>20.81</td>
</tr>
<tr>
<td>PES/PBT [70/30]</td>
<td>185.21</td>
<td>13.63</td>
<td>221.45(244.49)</td>
<td>14.26(2.91)</td>
<td>244.49(243.82)</td>
<td>2.91(2.48)</td>
</tr>
<tr>
<td>PES/PBT [50/50]</td>
<td>191.16</td>
<td>23.17</td>
<td>224.52</td>
<td>19.18</td>
<td>223.28</td>
<td>21.41</td>
</tr>
</tbody>
</table>

Table 4.18: DTA Measurements of PSO/PBT and PES/PBT blends after annealing at 185°C for 48hours

<table>
<thead>
<tr>
<th>BLEND</th>
<th>Tc (°C)</th>
<th>ΔHc (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES/PBT [50/50]</td>
<td>193.21</td>
<td>25.71</td>
<td>225.21(214.97)</td>
<td>32.49</td>
<td>224.11(216.02)</td>
<td>25.57</td>
</tr>
<tr>
<td>PES/PBT [50/50]</td>
<td>195.74</td>
<td>22.05</td>
<td>226.22(216/235)</td>
<td>26.11</td>
<td>224.03(218.53)</td>
<td>20.61</td>
</tr>
</tbody>
</table>

Table 4.19: DTA Measurements of PSO/PBT [50/50] Blend with elevated ageing temperatures

<table>
<thead>
<tr>
<th>Time at 280°C (mins)</th>
<th>Tc (°C)</th>
<th>ΔHc (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>194.21</td>
<td>22.74</td>
<td>226.16</td>
<td>21.21</td>
<td>223.49(215.56)</td>
<td>18.45</td>
</tr>
<tr>
<td>120</td>
<td>195.14</td>
<td>30.94</td>
<td>225.29</td>
<td>23.54</td>
<td>221.46(211.13)</td>
<td>29.74</td>
</tr>
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</table>

Table 4.20: DTA Measurements of PSO/PBT-TMO and PES/PBT-TMO blends

<table>
<thead>
<tr>
<th>BLEND</th>
<th>Tc (°C)</th>
<th>ΔHc (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSO/HYT [70/30]</td>
<td>178.78</td>
<td>12.01</td>
<td>214.75(245.52)</td>
<td>13.17(5.96)</td>
<td>212.67(243.93)</td>
<td>12.83(6.34)</td>
</tr>
<tr>
<td>PES/HYT [70/30]</td>
<td>178.72</td>
<td>12.57</td>
<td>217.56(244.93)</td>
<td>6.46(3.69)</td>
<td>217.61(244.18)</td>
<td>9.99(1.24)</td>
</tr>
<tr>
<td>PSO/HYT [50/50]</td>
<td>177.67</td>
<td>22.55</td>
<td>216.88(245.48)</td>
<td>15.78(1.99)</td>
<td>215.22(244.69)</td>
<td>16.54(1.28)</td>
</tr>
<tr>
<td>PES/HYT [50/50]</td>
<td>178.55</td>
<td>22.78</td>
<td>218.15(244.78)</td>
<td>14.85(1.65)</td>
<td>214.77(243.45)</td>
<td>16.55(1.64)</td>
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</tbody>
</table>
### Table 4.21: DTA Measurements of PSO/PET blends

<table>
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<tr>
<th>PSO/PET</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_2$ (J/g)</th>
<th>$T_m_1$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_m_2$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[30/70]</td>
<td>167.1</td>
<td>90.62</td>
<td>1.02</td>
<td>201.92</td>
<td>26.93</td>
<td>256.98</td>
<td>28.06</td>
<td>250.61</td>
<td>22.42</td>
</tr>
<tr>
<td>[50/50]</td>
<td>183.0</td>
<td>138.6</td>
<td>2.21</td>
<td>202.36</td>
<td>18.31</td>
<td>253.84</td>
<td>18.86</td>
<td>247.39</td>
<td>15.47</td>
</tr>
<tr>
<td>[70/30]</td>
<td>181.1</td>
<td>143.1</td>
<td>5.69</td>
<td>197.68</td>
<td>3.25</td>
<td>254.19</td>
<td>10.08</td>
<td>251.05</td>
<td>6.02</td>
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### Table 4.22: DTA Measurements of PES/PET blends

<table>
<thead>
<tr>
<th>PES/PET</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_2$ (J/g)</th>
<th>$T_m_1$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_m_2$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[0/100]</td>
<td>72</td>
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<td></td>
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<tr>
<td>[20/80]</td>
<td>76.9</td>
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<td>[40/60]</td>
<td>77.3</td>
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<td>[60/40]</td>
<td>72.2</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>[80/20]</td>
<td>73.4</td>
<td>127.59</td>
<td>5.63</td>
<td>209.63</td>
<td>3.12</td>
<td>256.6(228.4/242.8)</td>
<td>8.59</td>
<td>252.15(231.82)</td>
<td>9.26</td>
</tr>
</tbody>
</table>

### Table 4.23: DTA Measurements of Amorphous and Slow Cooled PET/PBT Blends

#### i) Slow Cooled

<table>
<thead>
<tr>
<th>PET/PBT</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_2$ (J/g)</th>
<th>$T_m_1$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_m_2$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[80/20]</td>
<td>186.51</td>
<td>30.74</td>
<td>(218.56/252.56)</td>
<td>(0.57/26.66)</td>
<td>(192.55/247.91)</td>
<td>(0.93/28.61)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[60/40]</td>
<td>187.41</td>
<td>29.97</td>
<td>(220.82/252.11)</td>
<td>(7.23/25.03)</td>
<td>(208.97/244.44)</td>
<td>(7.04/21.31)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[40/60]</td>
<td>180.63</td>
<td>32.91</td>
<td>(223.31/252.19)</td>
<td>(15.27/15.14)</td>
<td>(215.22/237.57)</td>
<td>(14.46/6.11)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[20/80]</td>
<td>187.43</td>
<td>36.06</td>
<td>(226.51/253.01)</td>
<td>(22.13/5.23)</td>
<td>222.58</td>
<td>29.53</td>
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<td></td>
</tr>
</tbody>
</table>

#### ii) Amorphous

<table>
<thead>
<tr>
<th>PET/PBT</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_2$ (J/g)</th>
<th>$T_m_1$ ($^\circ$C)</th>
<th>$\Delta H_1$ (J/g)</th>
<th>$T_m_2$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[80/20]</td>
<td>122.33</td>
<td>26.61</td>
<td>194.38</td>
<td>33.28</td>
<td>251.91</td>
<td>41.31</td>
<td>(198.21/248.52)</td>
<td>(1.064/31.66)</td>
</tr>
<tr>
<td>[60/40]</td>
<td>94.92</td>
<td>26.98</td>
<td>195.77</td>
<td>31.61</td>
<td>(216.21/252.52)</td>
<td>(7.113/33.15)</td>
<td>(209.81/243.48)</td>
<td>(7.233/24.81)</td>
</tr>
<tr>
<td>[40/60]</td>
<td>71.05</td>
<td>15.11</td>
<td>186.67</td>
<td>39.18</td>
<td>(218.84/251.21)</td>
<td>(15.95/18.84)</td>
<td>(216.99/236.71)</td>
<td>(13.06/7.088)</td>
</tr>
</tbody>
</table>

### Table 4.24: Continuous DTA Measurements of a PET/PBT [40/60] blend

<table>
<thead>
<tr>
<th>CYCLE</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
<th>$T_c$ ($^\circ$C)</th>
<th>$\Delta H_f$ (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st heat &amp; cool</td>
<td>[224.47/252.77]</td>
<td>[14.85/14.73]</td>
<td>179.83</td>
<td>35.88</td>
</tr>
<tr>
<td>2nd heat &amp; cool</td>
<td>[214.61/237.15]</td>
<td>[14.22/3.29]</td>
<td>175.01(186.92)</td>
<td>34.93</td>
</tr>
<tr>
<td>3rd heat &amp; cool</td>
<td>211.38(227.98)</td>
<td>30.43</td>
<td>172.45(185.54)</td>
<td>35.26</td>
</tr>
<tr>
<td>4th heat</td>
<td>209.32</td>
<td>29.55</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[ ] = individual peaks

( ) = shoulder of main melt peak
Table 4.25: DTA Measurements of PSO/Phenoxy/PBT blends

<table>
<thead>
<tr>
<th>PSO/PHEN/PBT</th>
<th>Tg's (°C)</th>
<th>Tc1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tc2 (°C)</th>
<th>ΔHf2 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[60/15/25]</td>
<td>154.6</td>
<td>6.62</td>
<td>209.85</td>
<td>14.93</td>
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<tr>
<td>[55/5/40]</td>
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<td>18.52</td>
<td>225.21</td>
<td>19.72</td>
<td>221.88</td>
<td>15.96</td>
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</tr>
<tr>
<td>[45/10/45]</td>
<td>188.62</td>
<td>22.78</td>
<td>225.94</td>
<td>22.94</td>
<td>220.18</td>
<td>19.28</td>
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Table 4.26: DTA Measurements of PSO/Phenoxy/PBT-TMO blends

<table>
<thead>
<tr>
<th>PSO/PHEN/PBT-TMO</th>
<th>Tc1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tc2 (°C)</th>
<th>ΔHf2 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
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<tbody>
<tr>
<td>[60/15/25]</td>
<td>149.14</td>
<td>6.93</td>
<td>197.11</td>
<td>12.21</td>
<td>191.41</td>
<td>11.64</td>
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<td></td>
</tr>
<tr>
<td>[55/5/40]</td>
<td>185.32</td>
<td>15.38</td>
<td>218.08</td>
<td>14.96</td>
<td>213.84</td>
<td>11.38</td>
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<td></td>
</tr>
<tr>
<td>[45/10/45]</td>
<td>180.52</td>
<td>18.31</td>
<td>217.91</td>
<td>17.21</td>
<td>212.17</td>
<td>12.72</td>
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Table 4.27: DTA Measurements of PSO/Phenoxy/PET blends

<table>
<thead>
<tr>
<th>PSO/PHEN/PET</th>
<th>Tg's (°C)</th>
<th>Tc1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tc2 (°C)</th>
<th>ΔHf2 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
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</thead>
<tbody>
<tr>
<td>[60/15/25]</td>
<td>79.5</td>
<td>172.7</td>
<td>206.63</td>
<td>4.07</td>
<td>252.95</td>
<td>11.27</td>
<td>250.45</td>
<td>6.52</td>
<td></td>
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<tr>
<td>[55/5/40]</td>
<td>73.4</td>
<td>178.9</td>
<td>144.39</td>
<td>10.58</td>
<td>198.62</td>
<td>15.37</td>
<td>213.84</td>
<td>11.38</td>
<td></td>
</tr>
<tr>
<td>[45/10/45]</td>
<td>76.5</td>
<td>173.2</td>
<td>129.78</td>
<td>6.98</td>
<td>199.12</td>
<td>17.31</td>
<td>212.17</td>
<td>12.72</td>
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Table 4.28: DTA Measurements of PES/Phenoxy/PBT and PES/Phenoxy/PBT-TMO blends

<table>
<thead>
<tr>
<th>Quenched</th>
<th>Tc1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tc2 (°C)</th>
<th>ΔHf2 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PES/Phenoxy/PBT</td>
<td>164.16</td>
<td>9.09</td>
<td>199.09</td>
<td>8.24</td>
<td>198.46</td>
<td>7.08</td>
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<tr>
<td>PES/Phenoxy/PBT-TMO</td>
<td>168.06</td>
<td>10.98</td>
<td>212.83</td>
<td>16.42</td>
<td>204.29</td>
<td>7.01</td>
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Table 4.29: DTA Measurements of PES/Phenoxy/PET blends

<table>
<thead>
<tr>
<th>PES/Phenoxy/PET</th>
<th>Tg's (°C)</th>
<th>Tc1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tc2 (°C)</th>
<th>ΔHf2 (J/g)</th>
<th>Tm1 (°C)</th>
<th>ΔHf1 (J/g)</th>
<th>Tm2 (°C)</th>
<th>ΔHf2 (J/g)</th>
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<tbody>
<tr>
<td>[20/5/75]</td>
<td>74.7</td>
<td>202.89</td>
<td>26.4</td>
<td>256.29</td>
<td>35.42</td>
<td>251.24</td>
<td>23.13</td>
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<td></td>
</tr>
<tr>
<td>[40/5/55]</td>
<td>74.7</td>
<td>206.25</td>
<td>22.77</td>
<td>256.58</td>
<td>29.91</td>
<td>248.53</td>
<td>21.44</td>
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<td></td>
</tr>
<tr>
<td>[45/10/45]</td>
<td>75.0</td>
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<td>18.65</td>
<td>256.87</td>
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<td>259.94</td>
<td>17.83</td>
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<td></td>
</tr>
<tr>
<td>[55/5/40]</td>
<td>75.2</td>
<td>206.72</td>
<td>15.57</td>
<td>255.56</td>
<td>22.46</td>
<td>248.85</td>
<td>17.23</td>
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</tr>
<tr>
<td>[75/5/20]</td>
<td>65.7</td>
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<td>0.71</td>
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<td>14.04</td>
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</tr>
<tr>
<td>[80/5/15]</td>
<td>68.4</td>
<td>131.68</td>
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<td>6.51</td>
<td>250.48</td>
<td>6.55</td>
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Table 4.30: DTA Measurements of PES/Phenoxy/PET/PBT blends

<table>
<thead>
<tr>
<th>PES/Phenoxy/PET/PBT</th>
<th>Tc₂ (°C)</th>
<th>ΔHc₂ (J/g)</th>
<th>Tm₁ (°C)</th>
<th>ΔHf₁ (J/g)</th>
<th>Tm₂ (°C)</th>
<th>ΔHf₂ (J/g)</th>
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</thead>
<tbody>
<tr>
<td>[40/10/40/10]</td>
<td>198.79</td>
<td>10.91</td>
<td>[217.76/256.02]</td>
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<td>11.55</td>
</tr>
<tr>
<td>[40/10/30/20]</td>
<td>166.77</td>
<td>7.07</td>
<td>[220.49/254.01]</td>
<td>4.88/15.94</td>
<td>219.25</td>
<td>8.22</td>
</tr>
<tr>
<td>[30/20/20/30]</td>
<td>138.16</td>
<td>2.78</td>
<td>[225.07/253.63]</td>
<td>8.13/5.88</td>
<td>181.78</td>
<td>6.46</td>
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</table>

Table 4.31: DTA Measurements of Compounded Extrusion blends before(a) and after(b) annealing at Tc₂ for 10minutes
Table 4.32: Mechanical Properties of the Compounded Extrusion blends

<table>
<thead>
<tr>
<th>Blend</th>
<th>width (mm)</th>
<th>thickness (mm)</th>
<th>maximum force (N)</th>
<th>ultimate tensile strength (N/mm²)</th>
<th>mean U.T.S. (N/mm²)</th>
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</thead>
<tbody>
<tr>
<td>PES</td>
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<td>0.29</td>
<td>182</td>
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<tr>
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<td>9.8</td>
<td>0.25</td>
<td>195</td>
<td>79.6</td>
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</tr>
<tr>
<td></td>
<td>7.9</td>
<td>0.19</td>
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<td>69.3</td>
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<tr>
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<td>0.39</td>
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<td>6.3</td>
<td>0.39</td>
<td>104</td>
<td>66.8</td>
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<tr>
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<td>57</td>
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<td>0.5</td>
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<tr>
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<tr>
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<td>0.54</td>
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<td>66.7</td>
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</tr>
<tr>
<td></td>
<td>3.9</td>
<td>0.54</td>
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<td>66.8</td>
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<td>32.3</td>
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</tr>
<tr>
<td>PES/PET [70/30]</td>
<td>9.3</td>
<td>0.36</td>
<td>96</td>
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<td>7.1</td>
<td>0.33</td>
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<td>35.4</td>
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<tr>
<td>PSO/Phenoxy/PBT [60/15/25]</td>
<td>5.0</td>
<td>0.69</td>
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<td>78</td>
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<td>5.0</td>
<td>0.68</td>
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<td>78</td>
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<td>5.0</td>
<td>0.67</td>
<td>260</td>
<td>77.5</td>
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<tr>
<td>PSO/Phenoxy/PBT-TMO [60/15/25]</td>
<td>7.8</td>
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<td>51.1</td>
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<td>46.4</td>
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<tr>
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<td>10.0</td>
<td>0.46</td>
<td>170</td>
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<td>35</td>
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<tr>
<td></td>
<td>9.7</td>
<td>0.46</td>
<td>144</td>
<td>32.3</td>
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<tr>
<td></td>
<td>10.0</td>
<td>0.46</td>
<td>170</td>
<td>36.9</td>
<td></td>
</tr>
<tr>
<td>PES/Phenoxy/PET/PBT [60/5/25/10]</td>
<td>8.7</td>
<td>0.59</td>
<td>170</td>
<td>33.1</td>
<td>30</td>
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<tr>
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<td>6.0</td>
<td>0.45</td>
<td>73</td>
<td>26.5</td>
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</tr>
<tr>
<td></td>
<td>8.1</td>
<td>0.58</td>
<td>138</td>
<td>29.4</td>
<td></td>
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Table 4.33: Solvent Resistance Measurements for the Compounded Extrusion blends

<table>
<thead>
<tr>
<th>Blend</th>
<th>Ultimate Tensile Strength (N/mm²)</th>
<th>Time to Failure (secs) 50% force</th>
<th>Time to Failure (secs) 30% force</th>
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<tbody>
<tr>
<td>PSO</td>
<td>78</td>
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<td>0</td>
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<tr>
<td>PES</td>
<td>67.5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PES/Phenoxy [80/20]</td>
<td>57.5</td>
<td>2.5</td>
<td>5.5</td>
</tr>
<tr>
<td>PSO/PBT [70/30]</td>
<td>66.5</td>
<td>20</td>
<td>50</td>
</tr>
<tr>
<td>PES/PBT [70/30]</td>
<td>31</td>
<td>2.5</td>
<td>5.8</td>
</tr>
<tr>
<td>PES/PET [70/30]</td>
<td>32</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PSO/Phenoxy/PBT [60/15/25]</td>
<td>78</td>
<td>no break</td>
<td>no break</td>
</tr>
<tr>
<td>PSO/Phenoxy/PBT-TMO [60/15/25]</td>
<td>51</td>
<td>no break</td>
<td>no break</td>
</tr>
<tr>
<td>PES/Phenoxy/PET [60/15/25]</td>
<td>35</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>PES/Phenoxy/PET/PBT [60/5/25/10]</td>
<td>30</td>
<td>9.5</td>
<td>23.5</td>
</tr>
</tbody>
</table>
5 DISCUSSION

5.1 SOLUTION BLENDS

The influence of the solvent on the overall miscibility of a polymer blend, prepared by dissolution, is often neglected. A number of cases have been cited in the literature in which a change of solvent has caused a blend which was previously a two-phase system to become miscible. For example, Polystyrene/Poly(vinyl methyl ether) blends have been found to be miscible when cast from toluene, benzene and tetrachloroethylene but produced two phase mixtures when cast from both chloroform and methylene chloride. Gashgari and Frank have also discussed the influence of casting temperature on the morphology of a polymer blend prepared by dissolution. When the casting temperature is greater than that of the blend glass transition temperature, there should be sufficient molecular mobility after removal of all the solvent for the blend to achieve thermodynamic equilibrium and thus, the obtained morphology is characteristic of the binary polymer blend. However, if the casting temperature is below the glass transition temperature of the ternary mixture, (polymer/polymer/solvent), the solvent will evaporate slowly from the blend but, there will be insufficient mobility of the polymer chains and so the overall morphology is characteristic of the ternary mixture and not the binary polymer blend. Also, when casting a film below the glass transition temperature of the blend, the solvent will evaporate from the surface first to leave a glassy polymer skin encapsulating the remaining solvent. As the molecular mobility of the polymer chains is frozen, the remaining solvent may become trapped in the film and thus the morphology will again be characteristic of the ternary mixture. i.e:- the solvent could form a third phase containing both polymers but in different concentrations.

5.1:1 Polyethersulphone/Phenoxy Binary Blends

Both scanning electron microscopy and dynamic mechanical analysis measurements show that this system is fully miscible at room temperature. However, as the casting temperature was below the T_g of the blends, the overall morphology is related to the ternary system and therefore the solvent most probably acts as a compatibiliser for the polymer blend. There may have also been a small amount of solvent remaining in the films as the casting temperature of the blends was considerably lower (≤100°C) than the boiling point of DMF. This would then explain the much lower than expected T_g values
obtained for both the solution blends and controls, as the remaining solvent would act as a plasticiser. The occurrence of both positive and negative deviation of the \( T_g \) values from linearity, figure [4.10], could actually be due to the difference in affinity of the solvent for the two respective polymers. Compositions containing a higher percentage of Phenoxy tend to exhibit lower \( T_g \) values than those predicted by the Fox equation, using the \( T_g \) values of the pure components obtained from solution. This may be due to Phenoxy having a greater affinity for the solvent than PES and thus, by forming stronger associations with it, the system becomes more highly plasticised to give lower \( T_g \) values. The interactions likely to occur will be between the hydroxyl group of Phenoxy, (\(-\text{OH}\)) and the positively charged Carbonyl group of DMF, (\(C^{\delta+}=0\)).

The solvent cast films used for DMA measurements were too thick to examine the removal of solvent by infra red analysis and so extremely thin films dried on NaCl plates were used. No solvent was detected in the absorption spectrum albeit the casting temperature was again below the \( T_g \) of the blends. The significant shifts observed for the blends in the \(-\text{OH}\) stretching frequency region reveals the occurrence of intermolecular hydrogen bonding and suggests that this blend may be miscible in the absence of solvent. The miscibility could be due to hydrogen bonding between the sulphonate group of PES, (\(S=0\)), and the hydroxyl group of Phenoxy, (\(-\text{OH}\)).

Annealing experiments reveal that phase separation can occur below the reported lower critical solution temperatures (LCST) for all but the PES/Phenoxy (20/80) blend. The SEM micrographs suggest that as the PES content in the blend increases the ease with which Phenoxy is being excluded out of the matrix increases thus giving rise to a greater extent of phase separation at the same temperature distance from the calculated \( T_g \) of the blend. This composition related extent of demixing is possibly due to the difference in \( T_g \) of the blend components. i.e.- in the PES/Phenoxy (20/80) mix there is a greater percentage of the Phenoxy component, but the \( T_g \) of Phenoxy is only \((\approx100^\circ\text{C})\) and consequently it is very hard for the Phenoxy to provide the driving force to exclude the high \( T_g \) PES component \((T_g=226^\circ\text{C})\) out of the matrix. Similarly, it is possible to envisage that the high \( T_g \) component does not have sufficient internal energy to diffuse out of the Phenoxy matrix to produce a separate glassy phase. Therefore, the blend tends to be miscible at temperatures higher than the calculated \( T_g \) of the blend.

On the other hand, as the %PES in the blend increases, it becomes easier for the mixture to demix since the higher \( T_g \) component finds it far easier to displace the Phenoxy out of the matrix. Also, it is possible that Phenoxy has a greater affinity for the solvent.
compatibiliser and therefore, the blends containing a higher proportion of Phenoxy are expected to be more compatible.

Figure [4.4] reveals the onset of phase separation for the PES/Phenoxy (80/20) composition, even though annealing was carried out below the calculated \( T_g \) of the blend and at 60°C below the reported LCST. This is unexpected as there should only be a low molecular mobility below the \( T_g \) of the blend. This observation implies the presence of residual solvent in the cast film which has a plasticising effect and lowers the \( T_g \) of the system. During the one week annealing period, which causes this phase separation, the solvent is expected to continually evaporate from the film. While the annealing temperature is above the \( T_g \) of the ternary PES/Phenoxy/DMF system there will be sufficient molecular mobility for the blend to achieve its thermodynamic equilibrium state at this temperature. There will be therefore, a critical temperature for the ternary composition at which this system starts to phase separate and which appears to be below the LCST’s reported in literature. In fact, with increased annealing time, demixing became more pronounced and suggests that phase separation can occur in the absence of solvent at temperatures below the reported LCST’s.

5.1:2 Polysulphone/Phenoxy Binary Blends

SEM micrographs reveal that this system is less miscible than the equivalent PES/Phenoxy blend and that it is not fully miscible at room temperature over the entire range of compositions. A semi-IPN type morphology is displayed by the PSO/Phenoxy (90/10) composition which phase separates further on annealing at 120°C for one week to produce a matrix/dispersed particle type of morphology. The dispersed Phenoxy particles are very smooth and spherical and thus suggests that the blend must have been compatibilised initially by the solvent as the casting temperature is again below the \( T_g \) of the blend. On annealing however, there is further removal of the solvent compatibiliser and densification of the PSO phase occurs, forcing the Phenoxy to form small dispersed particles.

Similarly to the PES/Phenoxy system, demixing becomes more pronounced as the PSO content in the blend increases. This again may be attributed to the difference in \( T_g \) of the blend components as discussed in the preceding section.

DMTA measurements reveal single \( T_g \) values for the blends at temperatures much lower than expected from the Fox equation. The solution cast controls also reveal much lower \( T_g \)’s than those expected and so, these results appear to suggest that there is some solvent
remaining in the film after casting which acts as a plasticiser, producing large reductions in $T_g$. However, by annealing at 115°C for 72 hours and by methanol extractions it was possible to increase the $T_g$ of this blend to 113°C, which is still lower than expected. It is possible that the remaining solvent acts as a compatibiliser for this polymer blend, as a single $T_g$ intermediate between those of the constituents is also revealed by DTA for all compositions. By the application of the Fox equation, the %solvent remaining in the films after casting was calculated to be approximately 5%, section [4.1:2c]. Therefore, this result implies that the two polymer components in the cast films are actually part of a ternary mixture in which the remaining solvent is contained in both phases. This would again be expected as the casting temperature of the films is below the $T_g$ of the blend and so the overall behaviour and morphology is typical of the ternary system.

To observe whether this blend is miscible in the absence of solvent, extremely thin films were cast on NaCl plates and analysed by FTIR. No solvent was detected in the absorption spectrum although the casting temperature was again below the $T_g$ of the blend. The shifts observed in peak absorption maxima suggest strong interactions between the two components. This can be clearly seen in the -OH stretching region where there is considerable shift in the -OH absorption peak and a higher wave number shoulder indicating specific intermolecular hydrogen bonding interactions. This high temperature shoulder is particularly prevalent in compositions containing a greater concentration of Phenoxy and so, in agreement with the SEM micrographs, this blend is more miscible at higher concentrations of Phenoxy.

These results are in disagreement with those observed by Swinyard et al[91], as these authors suggested the blend is immiscible when cast from DMF solution. In this study opaque films were also obtained when casting from DMF solutions. However, when they were cast from 1-methyl, 2-pyrrolidinone (1-MP), only slightly opaque films were produced. This again proves that when casting solution blends at temperatures below the $T_g$ of the system, the morphology of the blend is characteristic of a ternary system and so the solvent affects the overall compatibility. Therefore, in this instance, PSO was found to have a higher level of solubility with 1-MP than DMF.

5.2 BRABENDER PREPARED MELT BLENDS

5.2:1 Polyethersulphone/Phenoxy Binary Blends

Unlike the compositions prepared from solution, this type of blend was found to be immiscible when mixed in the melt state. This could be expected as mixing occurs
above the reported LCST for the system. However, on cooling from the melt, the compositions with a higher concentration of PES tended to change appearance from that of a white two-phase material to a light grey/brown. This is probably the result of the decrease in temperature causing some solubilisation as the blend tends towards its more thermodynamically stable state. However, to allow for this change in morphology, the blend requires sufficient kinetic energy to go from two separate phases to an interconnected homogeneous system. This kinetic energy is very restricted below the glass transition temperature and so, when the blend reaches the $T_g$ of PES, the morphology is frozen in and complete solubilisation is prevented. As the $T_g$ of PES is above the LCST of the system only limited solubilisation occurs. Also, as the phase boundary is concave in nature with phase separation occurring at higher temperatures for blends with a majority component, a lower level of miscibility is found at these high ratio compositions. In other words the PES/Phenoxy (80/20) composition reveals a light grey/brown colour as a degree of solubilisation is expected.

This phenomenon is confirmed by both DMTA measurements and SEM. Immiscible matrix/dispersed particle type structures are displayed by the white coloured compositions. These also display two separate $T_g$'s with a temperature difference similar to those of the pure polymers and thus, these systems can be classed as immiscible.

The PES/Phenoxy (90/10) and (80/20) compositions however, reveal a high level of co-continuity and so the system exhibits a degree of compatibility. This is confirmed by DMTA as a third tan$\delta$ peak occurs for both compositions, intermediate of the two corresponding to the pure polymers. This intermediate $T_g$ corresponds to a third miscibilised phase which increases the compatibility of the system.

5.2:2 Polysulphone/Phenoxy Binary Blends

Unlike the equivalent PES/Phenoxy melt blends, all PSO/Phenoxy compositions display a semi-transparent light grey/brown colour. This suggests that this system exhibits a greater level of miscibility than the PES/Phenoxy blend, which is confirmed by both DTA measurements and SEM.

The two $T_g$ values obtained by DTA are considerably closer than those of the pure polymers and therefore, a level of compatibility between the components is attained. Significantly, as the concentration of Phenoxy in the blend increases, the difference in temperature between the two $T_g$'s is reduced and so the compatibility increases.
The SEM micrographs confirm the deductions made from the DTA results as the miscibility can be clearly seen to increase with Phenoxy concentration. In fact, SEM suggests that the melt blends display higher levels of compatibility than those prepared by solution methods, even though a single $T_g$ is exhibited by the latter technique. This is possibly due to the solvent however, since annealing below the $T_g$ of PSO causes demixing and immiscibility. The only assumption that can be made therefore is that unlike the PES/Phenoxy blend, this ‘binary’ system exhibits a greater level of miscibility at this higher mixing temperature. Therefore, if the blend exhibits a LCST, it will be above the $T_g$ of PSO and so on cooling from the melt the blend will solubilise to its thermodynamically stable state. It can also be assumed that the phase diagram is more complicated than the ideal LCST behaviour, as the miscibility was found to be greater at higher temperatures and the blend has been found to be immiscible at lower temperatures when cast from other solvents. There is a possibility therefore, that these high molecular weight polymers display both a UCST and LCST, to produce a hourglass type phase diagram. Similar behaviour has been found by other combinations of high molecular weight polymers, section [2.4:1], with the “miscibility window” attributed to the lack of any strong interactions between the components. The lack of any carbonyl group in PSO would suggest the omission of any strong interactions in this blend, and so, this explanation may be the reason for the observed behaviour. The only deduction that may be made from these results is that the blends mixed in the melt state are further away from the critical temperature on the phase diagram than those cast from solution.

5.2:3 Poly(butylene terephthalate)/Phenoxy Binary Blends

Both the quenched and slow cooled samples are found to be fully miscible at all compositions as a single composition dependent $T_g$ is obtained and a homogeneous morphology observed by SEM. The quenched specimens obey the linear $T_g$ relationship predicted by the Fox equation, whereas the slow cooled samples display positive deviation from linearity. This positive deviation is due to the effect of PBT crystallisation. With the crystallisation of the lower $T_g$ PBT component out of solution, the PBT concentration in the amorphous phase of the blend is depleted, thus leaving the $T_g$ dependent amorphous phase richer in the higher $T_g$ component.

DTA measurements also suggest this blend to be miscible as a melting point depression occurs which is indicative of a negative interaction parameter, $(\chi_{12})$, which is favourable to homogeneity. Also, on the second heating cycle, the melting point decreases further with a corresponding reduction in the heat of fusion. This suggests that reactions between the two polymers causes the formation of more imperfect PBT crystals.
The basis for miscibility in this system and the reason for reduced crystallinity with heating is due to interchange reactions between the components. These reactions probably take place through an alcoholysis between hydroxyl groups in Phenoxy and ester groups in PBT. This will give rise to the formation of grafted and crosslinked copolymers with reduced crystallisation and melt temperatures and lower crystallinity, as a consequence of the decrease in length of PBT crystallisable segments as reactions occur. This behaviour is confirmed by the continuous heating and cooling cycle which brings about a reduction in both the crystallisation and melting temperature due to the increasing larger extent of reaction between the two polymers. Eventually, it would be expected that total randomisation would occur and an amorphous copolymer produced.

DTA measurements also showed that the increased Phenoxy content in the blend depressed the crystallisation rate of PBT due to the dilution and viscosity effects. This is confirmed by the occurrence of a cold crystallisation peak for the slow cooled samples on heating which indicates the presence of amorphous PBT not crystallised on cooling due to the dilution and viscosity effect of Phenoxy.

Finally, it is observed that a considerable drop in both melting and crystallisation temperature occurs for compositions of 30% PBT and less. It is therefore possible that at around this composition the crystal structure of PBT may change in a different manner to that at higher concentrations in the blend.

5.2:4 PBT-TMO/Phenoxy Binary Blends

PBT-TMO, (Hytrel 7246), contains a high proportion of PBT blocks and so as expected, this blend displayed the same behaviour as the analogous PBT/Phenoxy system. Again, a single \( T_g \) was recorded by DMA and a homogeneous morphology observed by SEM.

DTA measurements also displayed identical behaviour to the PBT/Phenoxy system with the same explanation of results as already discussed in the previous section. Therefore, the low concentration of TMO blocks in the block copolymer has little effect on the miscibility of PBT with Phenoxy. In fact, DTA measurements revealed a single composition dependent \( T_g \) showing positive deviation from linearity identical to the PBT/Phenoxy system. This result suggests that Phenoxy is miscible with the TMO segment as well as the PBT chains. If Phenoxy was incompatible with the TMO segment, (20-30%), the positive deviation would be 20-30% lower than the corresponding PBT/Phenoxy composition due to the lower number of miscible PBT
blocks. This is not the case and so therefore, Phenoxy is completely miscible with the PBT-TMO block copolymer.

5.2:5 Poly(ethylene terephthalate)/Phenoxy Binary Blends

The miscibility of this blend could not be ascertained by $T_g$ analysis due to the closeness of the two transitions. SEM however, revealed two trends in the morphology of the system:

(i) the amorphous blends exhibit a higher level of miscibility than the equivalent slow cooled samples.

(ii) the lower the concentration of Phenoxy in the blend, the greater the level of miscibility.

The former phenomena can be expected as the greater the amorphous material, the higher the compatibility. These findings are also in line with the optical properties of the blends as they become "whiter" with increasing Phenoxy concentration.

The SEM micrograph of the (90/10) composition reveals an almost miscible system although the DTA measurements contradict this. Unlike the PBT and PBT-TMO/Phenoxy systems there is no apparent reduction in either the melting or crystallisation temperatures and so this blend is expected to be immiscible. In fact, the Phenoxy nucleates the crystallisation of PET as both the crystallisation temperature and rate of crystallisation increase, which again suggests that the blend is immiscible. The homogeneity displayed by SEM therefore must be due to the closeness of the $T_g$'s of the components such that on cooling from the melt they vitrify at the same time and therefore restrict one phase becoming excluded from the other. This could therefore explain the highly interconnected structure displayed by the (70/30) composition.

The much lower miscibility of PET with Phenoxy compared to that of PBT and PBT-TMO is most unusual as the potential for the alcoholysis reaction exists for all the Polyesters. The extent of miscibility must therefore be analogous to the rate of crystallisation of the Poly (alkylene terephthalates); ie:- the miscibility is related to the density of interacting points and the flexibility of the alkyl part of the polymeric chain. PET has a shorter alkane chain between the benzene rings and thus is more rigid and less susceptible to stereospecific interchange reactions with Phenoxy. This would therefore explain the incompatibility observed in this system.
5.2:6 Polysulphone/Poly(butylene terephthlate) Binary Blends

This blend exhibits a low level of miscibility as indicated by the broadening of the glass transition temperatures and the lack of gross phase segregation. The compatibility is found to increase with annealing time and temperature as the morphology becomes more monophase and a lower temperature melting endotherm is produced. This depression in melting temperature is indicative of a compatible system and so this result implies the formation of the more imperfect PBT crystals with heat treatment which are more soluble in the PSO matrix. This behaviour is also confirmed by the lower level of crystallinity obtained and the increase in miscibility with mixing time.

It may be that a limited amount of copolymerisation occurs with increasing annealing and time of mixing. It is unsure how reactions would proceed as PSO is very stable to both hydrolysis and alcoholysis. The only possibility is that there may be reactions between the end groups of the polymers. These would form block copolymers of PSO/PBT which could then act as a surfactant at the interface of the pure polymers and solubilise the system. In fact, on annealing at 185°C for 48 hours, almost complete randomisation occurs as there is no melt peak on the second heat.

Both DTA and SEM micrographs reveal similar results for the blends mixed at different temperatures but, by increasing the shear rate the miscibility seems to improve as the microstructure becomes less distinct. A linear relationship between the latent heat of fusion and mixing shear rate is also found for this system. This is because at higher shear rates a larger number of nucleation sites are probably produced and so the overall crystallinity of the blend increases. However, this behaviour should produce a less miscible system as there is more of the incompatible crystalline PBT present.

The most interesting facet of this blend is the formation of an IPN by the (70/30) composition removed straight from the Brabender mixer. A second high temperature melting endotherm also occurs above the melt temperature of the virgin PBT homopolymer which may be attributed to the high \( T_g \) component restricting the motion of the PBT chains due to the “locked in” ribbon like morphology of the IPN. The net effect will be a reduction in PBT’s entropy in the blend which will give rise to a higher melt temperature as:

\[
T_m \approx \frac{\Delta H_m}{\Delta S_m}
\]
The semi-miscible IPN morphology obtained is the result of spinodal decomposition on cooling from the melt state. The fact that there is an effect of shear rate must imply that we are near the critical solution conditions. At only certain parameters of composition, shear rate, temperature, pressure and rate of cooling will spinodal decomposition occur leading to the formation of an IPN for this system. With annealing this high temperature endotherm is removed as the internal energy of the polymer chains is increased. A depression in melting temperature then occurs, similarly to the other compositions, which can then again be attributed to a low level of copolymer formation increasing the miscibility of the system.

The copolymerisation, (randomisation), occurring in this system is at a much slower rate than that in the equivalent Polyester/Phenoxy blends. This is confirmed by a continuous heating and cooling DTA cycle which produces an almost mirror image. The interactions are far fewer due to the steric hinderance of the aromatic rings attached to the sulphonate group and its stability to both hydrolysis and alcoholysis. The interaction is more likely to be between the end groups of the polymers or between the lone pair on the sulphonate oxygen and the positively charged carbonyl carbon of the PBT.

5.2:7 Polyethersulphone/Poly(butylene terephthalate) Binary Blends

DMA measurements suggest this system to be less miscible than the PSO/PBT blend as there is a lesser effect on the \( T_g \) of the pure polymers. A semi-miscible structure is again displayed by the (70/30) composition although it is a less ordered IPN than the equivalent PSO/PBT blend. However, a second high temperature melting endotherm occurred which can be attributed to the locked in PBT chains, as discussed in the previous section. The high \( T_g \) (226°C) PES component will lock in some of the PBT chains and therefore the latter will only be able to melt at a temperature above the \( T_g \) of the PES component. A higher temperature melting endotherm is therefore obtained.

This high temperature peak is also removed on annealing but, unlike the equivalent PSO/PBT blend, the miscibility is not enhanced further. There is therefore a lesser tendency for interaction between the two components and thus, a lower level of randomisation and miscibility. This is proved by DTA measurements as there is little difference between the traces for the PBT in the blend and pure PBT. Also, on annealing at 195°C for 65 hours, there is a lower depression of melting temperature relating to randomisation and an increased temperature of crystallisation, suggesting a nucleating
effect of PES instead. This is understandable as the PES would solidify first from the melt and so could nucleate the subsequent PBT crystallisation.

5.2:8 Polysulphone/PBT-TMO Binary Blends

As expected, this system displays similar results to the PSO/PBT blend. A semi-miscible IPN type morphology is obtained again with a corresponding second higher temperature melting endotherm. A slight depression of both the main melting and crystallisation temperatures also implies a certain level of compatibility which is expected to increase with annealing, as the potential for copolymerisation is the same as the PSO/PBT system.

5.2:9 Polyethersulphone/PBT-TMO Binary Blends

Likewise, again with the analogous PBT systems, PES/PBT-TMO blends are less compatible than their equivalent PSO systems. There is a lower level of interconnection in the IPN type structure and so therefore, there is a lower latent heat of fusion for the higher melting endotherm. Like the PES/PBT system, there is no significant reduction in the melting and crystallisation temperatures and so the blend can be considered immiscible.

Generally, the SEM micrographs imply a greater level of compatibility in the Polyethersulphones/PBT blends than the equivalent Polyethersulphones/PBT-TMO.

5.2:10 Polysulphone/Poly(ethylene terephthlate) Binary Blends

This system is shown to become less compatible with an increase in concentration of the PET component. A slight reduction in melt temperature suggests a low level of compatibility for both the PSO/PET (70/30) and (50/50) compositions. A further reduction in both melting temperature and corresponding heat of fusion occurs on the second heat. This phenomena is interesting as the cooling cycle in the DTA run is considerably slower and therefore more of the PET would be expected to crystallise out if the blend is incompatible. However, there are no further interactions occurring between the components with further heating as a continuous heating and cooling DTA cycle produces an identical trace. Therefore, the decrease in temperature of the second
heat melting endotherm implies more imperfect PET crystals forming with the reduced cooling rate as these would then have a lower heat of fusion and melting temperature.

A cold crystallisation exotherm, \((T_c)\), is obtained for all compositions, therefore implying the suppression of PET crystallisation by PSO. This cold crystallisation exotherm increases in temperature with PSO concentration and therefore suggests a degree of miscibility between the components. Both SEM and DMA measurements also suggest this system to be more compatible with an increase in concentration of the PSO content. The blend is not miscible as two definite loss modulus peaks are obtained. However, the (50/50) composition reveals an increase in temperature of 30°C for the PET component and a reduction of 20°C for the PSO component is observed in the PSO/PET (70/30) blend. Interestingly, the (50/50) composition reveals a large scale co-continuous system containing large areas of pure polymers. This could explain the high increase in \(T_g\) of the PET component as the chains of this polymer would be interlocked with the chains of the PSO. Softening of the PET will therefore be hindered by the PSO component and thus, a higher \(T_g\) for PET will be recorded.

The PSO/PET (70/30) composition reveals an IPN on a much finer scale which suggests a higher level of compatibility due to the greater surface area obtained at the interface. The PSO/PET (30/70) composition, however, reveals a matrix/dispersed particle type of morphology and so implies immiscibility.

**5.2:11 Polyethersulphone/Poly(ethylene terephthalate) Binary Blends**

DMA measurements suggest this system to be less compatible than the equivalent PSO/PET blend as there is little difference in temperature between the loss modulus peaks of the pure polymers and those of the components in the blend. DTA measurements confirm this deduction as there is only a slight reduction in melting temperature and a cold crystallisation peak is obtained only at a high PES concentration. This suggests little compatibility between components as the crystallisation rate of PET is not suppressed. In fact, at low concentrations of PES, PET crystallisation is nucleated.

Interestingly, the crystallisation temperatures for the PES/PET blends are considerably higher (\(\geq 3-10°C\)) than would be expected for the pure PET polymer. Even at high PES concentrations this phenomena occurs which is unexpected as the overwhelming presence of amorphous PES should suppress the PET crystallisation. This phenomena can only be attributed to PES nucleation effects as there is little compatibility between the components. On cooling from the melt the PES component will vitrify first at
(≈230°C) and then act as a nucleating agent for the PET. Due to the lack of any interactions, the PET will therefore crystallise at a higher temperature to form dispersed areas of PET polymer.

Apart from the (50/50) composition, SEM micrographs suggest this system to be compatible. The PES/PET (20/80) composition reveals a very fine detail IPN morphology while the PES/PET (80/20) composition reveals a more coarse semi-IPN type morphology. These findings are in disagreement with the results obtained by both DMA and DTA measurements, but no explanation can be given at this time.

5.2:12 Poly(ethylene terephthalate)/Poly(butylene terephthalate) Binary Blends

The transparent samples obtained by quenching from the melt suggest this system to be fully miscible in the amorphous regions. This is confirmed by SEM and DMA as both a homogeneous system and a single composition dependent $T_g$ are obtained for all compositions. The slow cooled samples on the other hand, are opaque, and so imply immiscibility between the crystalline forms. However, as the time of mixing is increased, the slow cooled samples become a clearer grey/brown colour, thus suggesting increased compatibility in the system with longer residence times.

This phenomena is confirmed by SEM as the slow cooled samples reveal a highly interconnected co-continuous morphology which becomes finer with increased residence time. This suggests the occurrence of ester interchange reactions between the components which progress with the melt residence time. The occurrence of transesterification reactions is also confirmed by DTA measurements as a reduction in temperature and heat of fusion of the melting endotherms arises on the second heating cycle. Furthermore, a continuous heating and cooling cycle eventually produces an single melting endotherm at a lower temperature than the pure Polyesters. This suggests that the PET/PBT blend becomes more compatible with heating as transesterification reactions occur leading to randomisation of the system. This phenomena is analogous to the PBT/Phenoxy blend as both the melt and crystallisation temperature reduces each cycle with increased transesterification reactions producing non-crystallisable random copolymers. The decrease in melting temperature with increasing amount of transesterified copolymer is in good agreement with the theory of equilibrium melting of random copolymers. This theory predicts a depression in melting temperature caused by the non-crystallising units according to Flory, equation [2.13].
The non-crystallisable units also impose restraints on the crystallisation of PET such that the majority of PET units could not crystallise out. As a result there is a large decrease in melt temperature because the random copolymer is less ordered and therefore thermodynamically easier to melt.

5.2:13 Polysulphone/Phenoxy/Poly(butylene terephthalate) Ternary Blends

This blend is found to exhibit a higher level of miscibility than the equivalent PSO/PBT binary blend due to the addition of Phenoxy compatibiliser. The SEM micrographs reveal a higher level of miscibility with an increasing amount of Phenoxy such that the (60/15/25) composition displays an almost miscible blend.

This phenomenon is confirmed by DTA measurements as it is clearly evident that the crystallisation is suppressed considerably more so than the equivalent PBT/Phenoxy blend. There is also a much larger reduction in melting point which is indicative of a negative interaction parameter, \( \chi_{12} \), that is favourable to homogeneity. The blends containing less of the Phenoxy, however, have little effect on the thermoanalysis data although, as with the PBT/Phenoxy blend, the crystallisation temperature of PBT is suppressed with increasing Phenoxy content. The significant change in results for the (60/15/25) composition must therefore indicate that the ratio of components is such that a high level of miscibility is exhibited. These results therefore imply an interactive presence of PSO with the randomised PBT/Phenoxy binary component, as miscibility increases with heating.

This increased compatibility in the (60/15/25) system is possibly due to an approximate (1/1) mix of PBT/Phenoxy which leads to a greater extent of the randomised copolymer via interchange reactions. This new bicomponent is then obviously more compatible with PSO due to the further depressed nature of both the crystalline and melting temperatures. However, the increased compatibility may also be due to the more amorphous nature of the co-reacted PBT/Phenoxy system having greater compatibility with the amorphous PSO. This could be expected as there are fewer incompatible crystalline PBT segments in the randomised PBT/Phenoxy system.

DMTA measurements also indicate an increase in miscibility of the PSO/PBT blend by the addition of Phenoxy. Two \( T_g \)'s are obtained and so the system is not fully miscible but the transitions are closer together than those of the binary system and so Phenoxy enhances the miscibility. Again, it can be seen that the difference in temperature of the
two transitions decreases with an increasing amount of Phenoxy and it therefore follows that Phenoxy compatibilises the system.

The two transitions obtained correspond to the PSO polymer and the miscible PBT/Phenoxy binary system. As indicated in the results section however, the \( T_g \) of the binary system is somewhat higher than that expected for the pure binary blend and it would therefore seem that the PSO interacts with the PBT/Phenoxy to produce a compatible system. This behaviour could be expected though as Phenoxy is fully miscible with PBT and exhibits a reasonable level of miscibility with PSO. Likewise with the ternary system, PSO/Phenoxy exhibits a higher level of miscibility with increasing Phenoxy content.

5.2:14 Polysulphone/Phenoxy/PBT-TMO Ternary Blends

This blend displays identical behaviour to the ternary PBT system. This could be expected as PBT-TMO primarily consists of PBT blocks and exhibits similar blend morphology as PBT with both Phenoxy and PSO. Likewise with the Polysulphone/Polyester binary system though, the blends containing PBT-TMO seem to be slightly less compatible than those with PBT and so therefore, from SEM analysis, it would seem that PSO is incompatible with the TMO segments.

Corresponding thermoanalysis data to the PBT system is obtained with significant increases in compatibility displayed by the (60/15/25) composition. The reasons behind this enhanced miscibility have been covered in detail in the previous section and as analogous behaviour occurs here, the reasons for this behaviour will not be discussed again.

5.2:15 Polysulphone/Phenoxy/Poly(ethylene terephthlate) Ternary Blends

As for the case of the binary Polysulphone/Polyester system, the PSO/Phenoxy/PET ternary blend is found to be less compatible than the equivalent PBT and PBT-TMO systems. SEM reveals a more miscible system for the (45/10/45) composition than the (55/5/40) system. Again, this could be due to the additional Phenoxy in the system increasing the solubilisation, since the compatibility of the PSO/Phenoxy binary blend is found to increase with Phenoxy concentration. However, unlike the equivalent PBT and PBT-TMO ternary blends, the (60/15/25) composition is less compatible than the others and displays a semi-miscible IPN type morphology. Therefore, similarly to the binary
PSO/PET system, it can be seen that as the binary ratio tends to 1, the miscibility increases and the morphology becomes more monophase. The enhanced miscibility seen in the ternary system though is due to the additional Phenoxy which, unlike the PBT and PBT-TMO systems, interacts mainly with the PSO component. The miscibility in the PET system is lower therefore because of the lack of any strong interactions between PET and Phenoxy components.

This hypothesis is consistent with both DTA and DMA measurements. A continuous heating and cooling DTA cycle produces an almost mirror image trace and so there are limited transreactions between the PET and Phenoxy components. The blends displaying the higher degree of miscibility, notably the (45/10/45) and (55/5/40) compositions, have little effect on the melting point and crystallisation temperature of the PET compared to that of the pure polymer. There is, however, a cold crystallisation exotherm produced, \( T_c \), which indicates suppression of the PET crystallisation and thus infers a level of compatibility in the system. As the (60/15/25) composition contains even less of the crystalline PET component it is expected that an even greater effect on crystallisation will occur. Interestingly, however, the opposite phenomenon arises as an increased rate of crystallisation and crystallisation temperature occurs along with the suppression of any cold crystallisation temperature. This therefore suggests an immiscible system which, is consistent somewhat with the morphology observed by SEM, as the amorphous PSO/Phenoxy combination nucleates the crystallisation of PET.

DMA measurements again confirm this behaviour as the two transitions for the (45/10/45) composition are considerably closer together than those of the standards and the (60/15/25) composition. This therefore implies a higher level of miscibility in the (45/10/45) composition and thus suggests that the compatibility of the blend is more dependent on the ratio and interaction of both the PSO/PET and PSO/Phenoxy components than the interaction of the Polyester/Phenoxy system as was found with the other ternary blends.

5.2.16 Ternary Blends of Polyethersulphone/Phenoxy with PBT-TMO and Poly(butylene terephthalate)

The (60/15/25) compositions of these blends are found to be less compatible than their PSO counterparts but exhibit higher miscibility than the equivalent PES/Polyester binary blends. SEM micrographs reveal an almost monophase system for the slow cooled samples whereas the quenched PBT blend displays a less solubilised matrix/dispersed particle type of morphology.
This behaviour could be expected as the opaque quenched sample indicates a matrix/dispersed particle type of morphology in the melt state. Therefore, at this temperature the binary PES/Phenoxy component in the ternary blend will be above the recorded LCST and so a less solubilised system would occur. On the other hand, the slow cooled sample would be allowed to solubilise to its more thermodynamically stable state on cooling, particularly if the T_g of the PES component is reduced to below the critical temperature of the phase diagram due to the enhanced miscibility. DMA measurements reinforce this deduction as there is a considerable reduction in the T_g of the PES component and therefore, the PES exhibits a higher level of miscibility with the randomised PBT/Phenoxy component than either of the pure polymers.

Interestingly, there is little difference in the morphology of the quenched and slow cooled PBT-TMO blends, although they are both less compatible than the slow cooled PBT system. This result is therefore analogous to the PSO ternary systems and so suggests immiscibility between the PES and the TMO segment in the PBT-TMO copolymer. Near homogeneity displayed for both quenched and slow cooled samples though are different to the morphology revealed by the quenched PBT blend. The occurrence of solubilisation in the quenched PBT-TMO blend must therefore be due to the ineffective freezing of the morphology. This can possibly be explained by considering that the temperature of the water used for quenching is higher than the T_g of the PBT-TMO component. There will therefore be relaxation of the PBT-TMO chains with time and so further solubilisation may be possible.

DTA measurements also suggest these blends to be miscible, as there is a large reduction in both crystallisation and melting temperatures. These are again slightly less reduced than those of the PSO blends and so it can be concluded that the PSO/Phenoxy/PBT ternary blend is more compatible than the corresponding PES/Phenoxy/PBT system. This phenomenon is consistent with the cold crystallisation exotherms displayed by the PBT ternary systems. The PSO/Phenoxy/PBT blend exhibits a cold crystallisation exotherm at a temperature 13°C above that of the PES/Phenoxy/PBT system and so suggests that the PSO ternary system is more miscible due to the greater effect on crystallisation rate.

The PES/Phenoxy/Polyester blends do exhibit a high level of compatibility since both the crystallisation and melting temperatures are depressed more than the equivalent PBT/Phenoxy (60/40) composition. This therefore implies further interaction between the PES and PBT/Phenoxy or PBT-TMO/Phenoxy systems, although to a lesser extent than the equivalent PSO blends.
The reasons for the greater miscibility in the PSO system are not clear, but may be due to the fact that when mixed in the melt, the PES/Phenoxy system is less miscible than the equivalent PSO blend as the former is being mixed above the LCST. This critical temperature is below the $T_g$ of PES and so, solubilisation is limited on cooling. The phase diagram for the PSO/Phenoxy system though is not clear but it exhibits a higher level of miscibility in the melt than the PES blend and has a lower $T_g$, therefore allowing for further solubilisation.

5.2:17 Polyethersulphone/Phenoxy/Poly(ethylene terephthalate) Ternary Blends

Similarly to the PSO/Phenoxy/PET blend, this ternary system tends to become more miscible as the binary PES/PET ratio approaches 1. This same effect is displayed by the PES/PET blend and like the binary systems, the PES/Phenoxy/PET blend is found to be less compatible than that of the equivalent PSO.

Many factors confirm this lower miscibility. SEM micrographs generally display a less solubilised system for the equivalent PES/Phenoxy/PET blend. For instance, the (45/10/45) composition reveals the presence of excess dispersed Phenoxy particles not used in the solubilisation, as both the PES/Phenoxy and PET/Phenoxy systems are far less compatible than their equivalent PSO and PBT blends respectively. DMTA measurements confirm this conjecture as there is a far lesser effect on the positions of the $T_g$ in the PES blend than compared to that of the PSO. Also, unlike the PSO system, Phenoxy has little effect on the position of the $T_g$'s and hence miscibility of the PES/PET system, as similar values are obtained by both binary and ternary systems. Finally, DTA measurements confirm this lower miscibility as a cold crystallisation exotherm, indicating an interactive presence of the amorphous Polysulphones, occurs for the PSO blends, but does not arise for the equivalent PES/Phenoxy/PET compositions.

Other combinations of this blend however, reveal an interesting interconnected morphology. The (80/5/15) composition displays a co-continuous structure similar to its equivalent PES/PET (80/20) blend but with less coarsening and dispersed particles evident. The role of the Phenoxy in this instance is that it has appeared to solubilise the semi-IPN structure, found with PES/PET (80/20), into a clearly defined co-continuous system. However, DTA measurements indicate a substantial suppression of PET crystallisation at this low concentration due to dilution and viscosity effects. The observed morphology may therefore be due to a totally amorphous mix of the components as these would appear to be more compatible than the system containing unreacted crystalline PET.
Both SEM and DMTA measurements indicate enhanced miscibility as the ratio of PES/PET approaches 1. The SEM micrographs reveal a nearer homogeneous system and the difference between the T_g's of the major components decreases. There is a further reduction in the temperature difference of the T_g's as a greater amount of Phenoxy compatibiliser is added. This therefore suggests that Phenoxy does enhance the miscibility, even if only on a marginal level. Apart from the (80/5/15) composition however, the DTA measurements imply the nucleation of PET crystallisation by the amorphous PSO/Phenoxy components. This is analogous to the PES/PET system, although to a lesser extent and therefore, the PES/Phenoxy/PET system would appear to be incompatible.

5.2:18 Polyethersulphone/Phenoxy/Poly(ethylene terephthalate)/Poly(butylene terephthalate) Quarternary Blends

These blends were prepared as it was thought that PBT would enhance the miscibility of the ternary PES/Phenoxy/PET system. SEM micrographs confirm this phenomenon as solubilisation of the blend increases with increasing PBT concentration.

DTA measurements are also consistent with this behaviour as the crystallisation is suppressed further with an increasing amount of PBT present. On the first heating cycle, two melting endotherms are produced suggesting incomplete randomisation of the PET/PBT system. It is noticeable that the melting point of the PBT component is reduced considerably more than that of the PET component, particularly when at lower concentrations to Phenoxy, as the PBT reacts with the Phenoxy to a greater extent than the PET component. However, with increasing PBT concentration, the melting point of the PET component is depressed, indicating a favourable interaction. This then implies a higher level of miscibility, which is confirmed by SEM.

On the second heating cycle, the two melting endotherms merge due to transesterification reactions and reveal a melting point at a temperature proportional to the PET/PBT composition. For the (40/10/40/10) composition, this melting point is at a temperature expected for the PET/PBT (80/20) blend and there is no apparent suppression of the crystallisation temperature. This therefore suggests an immiscible system, as confirmed by SEM which is because the PET/PBT components are in a 8/2 ratio and so there will be a lesser extent of randomisation, leaving more of the pure incompatible PET to crystallise out.
A lower crystallisation temperature of 166°C and a slightly depressed melting point from that expected on the second heating cycle suggests increased solubilisation for the (40/10/30/20) composition. This is because the PET/PBT composition is nearer to a (50/50) mix where maximum randomisation and hence, solubilisation of the semi-crystalline components takes place.

The greatest suppression of both crystallisation temperature and melting point from that expected on the second heat, occurs for the (30/20/20/30) composition. This is again due to the almost maximum randomisation of the PET/PBT (≈50/50) composition. However, there is also a higher concentration of Phenoxy present which is miscible with PBT and so, a random ternary transesterified system is produced with a lower crystallinity. Therefore, an almost homogeneous system occurs as the crystallinity is decreased and is due to the fact that polymer mixes exhibit a higher level of miscibility in their amorphous regions.

These DTA measurements suggest that the random PET/PBT copolymer is more compatible with both PES and Phenoxy than the equivalent homopolymesters as there is a greater suppression of melt and crystallisation temperature. In fact, a highly solubilised system is obtained for the (30/20/20/30) composition with the miscibility increasing with processing time. This is due to the additional transesterification reactions that occur leading to greater randomisation and hence, miscible amorphous material. Phenoxy has a greater effect on the random copolymer than the pure Polyester as the former is less ordered and so is more open to transesterification with Phenoxy. However, this increased solubility produces a more amorphous product which, in turn, would be expected to exhibit a lower solvent resistance. Therefore, the processing time and hence, randomisation, must be tailored to a specific miscibility/solvent resistance requirement.

5.3 COMPOUNDING EXTRUSION BLENDS

5.3:1 Morphological Studies

At a glance the morphology of these extruded blends appears to be similar to that of the blends prepared in the internal mixer. However, except for the PSO/PBT and PES/PBT blends, those prepared by compound extrusion generally display a more finely dispersed co-continuous or matrix-dispersed particle system, which is possibly due to the additional shear and thus, degree of mixing, generated by the twin screw compounder. What is also noticeable is that the compatible systems containing Phenoxy exhibit a
higher level of miscibility on press-annealing at $T_a$ due to the increasing number of interchange reactions occurring. Conversely, the less compatible PES/PBT blend phase separates further on annealing due to the additional immiscible crystalline PBT produced. Likewise, with the blends prepared in the internal mixer, the ternary systems containing Phenoxy also display a higher level of miscibility than the Polysulphones/Polyester binary blends and therefore again confirm the usefulness of Phenoxy as a compatibiliser for these systems.

The samples etched in MEK show improved phase contrast and therefore, the morphology of the blends can be more readily investigated. It is evident that the blends exhibiting a high level of miscibility and highest solvent resistance properties display an almost monophase system. For instance, the PSO/PBT, PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO blends reveal a co-continuous structure which, on etching, becomes a highly "polished" monophase system as the excess PSO at the surface is removed; ie:- the solvent first dissolves the amorphous PSO at the surface and then diffuses through the sample until it encounters the crystalline Polyester phase. When the sample contains a co-continuous IPN structure, the solvent will not be able to diffuse further through the blend due to the highly organised and interlocked Polyester phases. If the sample is incompatible and displays a matrix/dispersed particle morphology however, the solvent will continue to diffuse through the blend until it has evaporated. Clearer phase separation may therefore be seen in these blends, as has been found here for the matrix/dispersed particle PES/PBT, PES/PET and PES/Phenoxy/PET systems.

The highly polished structures obtained by etching the co-continuous systems could actually be the result of the following scenario. The solvent dissolves the PSO and diffuses through the sample to the interconnected PBT phase. At this point it cannot diffuse any further and so, on evaporation, it leaves a thin film of PSO covering the PBT phase and thus, a highly polished monophase structure is observed.

5.3:2 Differential Thermal Analysis Data

The DTA measurements generally reveal different results for the extruded blends compared to the blends prepared in the internal mixer. For instance, the PSO/PBT and PES/PBT blends reveal considerably higher temperature crystallisation exotherms and do not display the high temperature melting endotherm of the blends prepared in the internal mixer. This can possibly be explained by the morphology as these systems exhibit a lower level of interconnection and thus, miscibility, when sheet extruded. Crystallisation may therefore be nucleated by the dispersed high temperature $T_g$
Polysulphones and the crystalline PBT chains may melt as they are not restricted by the highly interlocked IPN. Similarly, the PES/PET blend displays a higher temperature for the crystallisation exotherm than that of the blend prepared in the internal mixer which again suggests PES nucleation and hence, immiscibility.

The morphology can also explain the difference in DTA results obtained for the PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO blends compared to those prepared in the internal mixer. Much higher crystallisation and melting temperatures are displayed by the sheet extrudate samples, thus suggesting a lower level of miscibility. In fact, a highly interlocked semi-miscible IPN is revealed by the sheet extrudate sample, whereas an almost homogeneous system is displayed by the blend prepared in the internal mixer. This latter blend will therefore exhibit lower crystallisation and melting temperatures due to the greater randomisation and enhanced miscibility present.

5.3.3 Solvent Resistance Measurements

The mechanical properties of the sheet extruded blends are also related to the morphology of the systems. It is clearly evident that the blends exhibiting IPN structures and a single polished monophase system on etching, exhibit tensile strength values similar to the homogeneous PSO component. The blends that show this behaviour include PSO/PBT, PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO systems. Conversely, those blends displaying a matrix/dispersed particle type of morphology, namely the PES/PET, PES/PBT and PES/Phenoxy/PET systems, display much lower tensile strengths compared to those of the pure Polysulphones.

The solvent resistance measurements were found to be related to the morphology of the blends. The systems that display both a high degree of co-continuity and tensile strength reveal much improved solvent resistance properties. This is first evident for the PSO/PBT (70/30) blend as there is a significant improvement in the solvent resistance of the PSO by blending with only 30% of semi-crystalline PBT. This improvement is due to the observed co-continuity which reduces the diffusion of the solvent. With the addition of only 15% of Phenoxy however, (PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO 60/15/25 blends), the solvent resistance increased considerably and failure was prevented when stressed at 30% of the ultimate tensile strength of the material. The samples also displayed very little stress relaxation, (ie:-10% for PSO/Phenoxy/PBT and 5% for PSO/Phenoxy/PBT-TMO), indicating that solvent diffusion is highly reduced. This further improvement in solvent resistance properties compared to that of the PSO/PBT binary blend, can be attributed to the role of the Phenoxy compatibiliser, ie:- it
produces a more finely dispersed IPN structure and so the ternary blends exhibit a higher degree of co-continuity. In fact, the greater the compatibility between blend components, the greater the degree of interpenetration of the networks and hence better mechanical properties achieved. For example, the lower stress relaxation and hence, greater solvent resistance shown by the PSO/Phenoxy/PBT-TMO blend can be explained by the more ordered and finely dispersed IPN displayed.

As expected the blends displaying a matrix/dispersed particle type of morphology display poor solvent resistance properties due to the lack of co-continuity in the semi-crystalline phase. Likewise with the blends prepared in the internal mixer, this behaviour usually occurs for the less compatible PES and PET component systems. The addition of Phenoxy to these systems only marginally improves the miscibility as it exhibits only a low level of compatibility with either component. However, the binary components in the PSO/Phenoxy/PBT and PSO/Phenoxy/PBT-TMO blends have a higher affinity with each other and so produce a useful compatible ternary system. It may be possible to vary the compositions of these systems in order to produce different levels of interpenetration and hence, tailor the mechanical properties for a required application.
The main conclusions that can be drawn from this work are as follows:

1) The presumed thermodynamic miscibility of PES/Phenoxy blends produced from solution, reported in the literature, is due to the presence of small amounts of residual solvent which remains even after prolonged extraction's at temperatures below the $T_g$ of the mixture. Although such a mixture exhibits a single glass transition temperature, subsequent annealing treatments at temperatures just above the $T_g$ of the mixture causes phase separation. It is still not certain however, as to whether this occurs as a result of the removal of the residual solvent or it simply reaches its thermodynamic equilibrium.

2) The PSO/Phenoxy solution blends were also found to be reliant on both the solvent used and the casting temperature. While a totally immiscible system was obtained from DMF solution, a miscible ternary mixture was formed when cast from 1-Methyl, 2-Pyrrolidinone. The miscibility was due to the compatibilising nature of the residual solvent, as demixing occurred with annealing.

3) Both Polysulphones/Phenoxy binary blends are immiscible when mixed in the melt state. This is expected for the case of the PES/Phenoxy system as the blending temperature was above the reported LCST. The PSO/Phenoxy melt blend however, revealed a degree of miscibility which increased with Phenoxy concentration. This blend was found to be more compatible at these higher temperatures but, unlike the equivalent PSO/Phenoxy mixture produced from solution, it did not produce a miscible system. It can be concluded therefore, that a complicated phase diagram was displayed by this binary system and that the blends mixed in the melt state were further away from the critical temperature on the phase diagram than those cast from solution, owing to the presence of residual solvent in the latter.

4) Both the PBT/Phenoxy and PBT-TMO/Phenoxy melt blends are totally miscible at all compositions. This is believed to be due to a reaction between the hydroxyl groups in Phenoxy and the ester groups in PBT that eventually lead to the formation of a copolymer exhibiting reduced crystallinity. Phenoxy was also found to be compatible with the TMO segment in the PBT-TMO block copolymer as a linear change in $T_g$ was obtained, thereby confirming that part of the Phenoxy resides in the TMO phase.

5) Conversely, the PET/Phenoxy system was found to be immiscible although a degree of compatibility was observed in the amorphous blends containing a high concentration
of PET. This lower miscibility is probably due to the lower density of interacting points of PET, as it is less susceptible to stereospecific alcoholysis reactions with Phenoxy.

6) The Polysulphones/PBT and Polysulphones/PBT-TMO binary blends exhibit some intriguing characteristics. Some degree of miscibility was displayed by all the blends, particularly for compositions containing PSO. Miscibility was found to increase with annealing and time of mixing therefore implying that slow reactions occurred between the components. A highly interlocked “Interpenetrating Network” occurred in conjunction with a second high temperature melting endotherm for the (70/30) compositions. This phenomena has been previously discovered before by Deng et al., but the melting peaks were lower than the values obtained in this work. As explained in the discussion, this behaviour may be due to the solubilised high T\text{g}\ component forming strong associations with the PBT chains, thereby delaying the melting process. Since the high temperature melt endotherm was removed by annealing this implies that the processing conditions used in this study were near to the critical solution conditions for these binary systems. The PSO/PBT blend produced by twin screw extrusion was found to be more compatible than the equivalent blend produced on the Brabender as a more finely dispersed IPN was formed. The PES/PBT twin screw compounded blend on the other hand was found to be less compatible than its equivalent blend mixed in the internal mixer. As a result of these morphologies, the PSO/PBT blends displayed good mechanical and solvent resistance properties whereas the matrix/dispersed particle PES/PBT blends displayed poor properties.

7) The PSO/PET blends are immiscible although a small degree of compatibility was obtained at high PSO concentrations. The suppression of the PET crystallisation and a large increase of its T\text{g}\ were both indicative of the occurrence of interactions between the components. The PES/PET blends were also found to be totally immiscible and no interactions occurred between the components. Infact, the high T\text{g}\ PES component was found to nucleate the crystallisation of the PET phase, such that the crystallisation temperature occurred up to 10°C higher than that of the pure polymer. As a consequence of this behaviour, a matrix/dispersed particle morphology was obtained with poor mechanical and solvent resistance properties.

8) The PET/PBT blends are totally miscible in the amorphous regions. With annealing and increased mixing times, transesterification reactions occurred which lead to the formation of a non-crystallisable random copolymer.

9) The addition of Phenoxy to the PSO/PBT and PSO/PBT-TMO systems increases their compatibility considerably. The crystallisation of PBT infact, became greatly
suppressed and miscibility increased with increasing Phenoxy concentration and annealing time and temperature. This could be expected as the PBT/Phenoxy and PBT-TMO/Phenoxy blends are totally miscible, and the PSO/Phenoxy exhibits a degree of compatibility in the melt state. It can be concluded therefore, that the Phenoxy component acts as a useful compatibiliser for this system as the very fine IPN morphology displayed gave rise to excellent mechanical and solvent resistance properties.

10) With the exception of the (45/10/45) composition, the PSO/Phenoxy/PET blends are totally immiscible. This is to be expected as unlike the PBT/Phenoxy system, the PET/Phenoxy blend was found to be immiscible in the melt state. Similarly, the PES/Phenoxy/PET blends are totally immiscible as unlike the equivalent ternary system, no miscibility window exists. Although some of the brabender mixed blends revealed a semi-IPN type structure, the twin screw compounded PES/Phenoxy/PET blend displayed a matrix-dispersed particle type of morphology, which gave rise to poor mechanical and solvent resistance properties. However, similarly to the PSO/Phenoxy/PBT and PBT-TMO blends, the PES ternary systems were more compatible than their binary Polysulphone/Polyester counterparts. The miscibility in the PES/Phenoxy/PBT and PBT-TMO blends however, was lower than the equivalent PSO systems. The highly suppressed crystallisation temperatures displayed by the PBT component are greater than in the equivalent PBT/Phenoxy binary system, thus indicating that the PES component is more compatible with the binary PBT/Phenoxy mixture than with the pure components.

11) The miscibility of quaternary PES/Phenoxy/PET/PBT blends increases with both Phenoxy and PBT concentration. This is because a more randomised amorphous PBT/Phenoxy component is produced which, similarly to the equivalent ternary system, is more compatible with the amorphous PES. Furthermore, transesterification reactions between the Polyester components gave rise to a non-crystallisable PET/PBT/Phenoxy system that was more compatible with the amorphous PES than either the pure Polyesters. By restricting the extent of randomisation, a semi-miscible system was produced by twin screw compounding and improved solvent resistance properties were obtained.

Finally, this work has shown that the overall miscibility of both the PES and PET systems is lower than their PSO and PBT based counterparts. As explained, this may be due to the increased steric hindrance of the PET component. Steric hindrance may also explain the lower miscibility found in the PES systems. Both ether and isopropylidene
linkages in the PSO allow for a greater flexibility of the polymeric chain and thus, the sulphone group is more inclined to exhibit stereospecific interactions with Polyesters than in the PES. The greater distance between the rigid sulphone groups and thus, the greater flexibility in the former, enables the polar groups to interact more readily with the carbonyl groups of the Polyesters. This chain flexibility can also be observed by comparing densities. The density of PES is somewhat higher than PSO as it is a more planar molecule and therefore, it is again less susceptible to stereospecific interactions. It is possible therefore, that the lower miscibility and higher $T_g$ of PES are a reflection of the higher chain rigidity. Hence, in support of the first conclusion, it can be presumed that the presence of residual solvent induces miscibility with Phenoxy through a plasticisation effect.
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