

POLYETHERSULPHONE POLYMER BLENDS

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### ABSTRACT

The miscibility of polyethersulphone (PES) with a number of polymers has been investigated. Poly(ethylene oxide) (PEO) and phenoxy resin were found to be miscible with PES. The miscibility of both PES/PEO and PES/phenoxy blends was confirmed by optical clarity and by the observation of a single composition dependent glass transition temperature. Both of the blends were found to phase separate on heating and this was confirmed by optical and electron microscopy. The cloud point curves were constructed by turbidimetry. The PES/PEO cloud point curves were very skewed with a minimum around 10 weight percent PES. The skewness was independent of molecular weight. The PES/phenoxy cloud point curve was symmetrical with a minimum around 50 weight percent.

A thermodynamic interpretation of the miscibility of PES/PEO and PES/phenoxy mixtures was obtained by measurement of negative (favourable) interaction parameters by melting point depression and by water vapour sorption. The interaction energy parameters,  $X_{12}$ , for both the systems were also obtained indirectly from the heats of mixing of low molecular weight analogues. For PES/PEO mixtures  $X_{12}$  was calculated from melting point depression data by modifying the melting point expression in terms of the equation of state theory. This was found to give results similar to those obtained from heat of mixing measurements. The heat of mixing values for PES/PEO analogues were much greater than for the PES/phenoxy analogues, implying stronger specific interactions in the former system. For the PES/PEO blends strong specific inter-

actions are postulated to be of the  $n-\pi$  type, between the free electrons of the ether oxygen of PEO and the  $\pi$  electrons of the aromatic ring of PES. In the case of PEO/phenoxy the miscibility is possibly enhanced by similarity in structure and state parameters. Interactions are possible through the phenoxy hydroxyl group or the aromatic moieties in both the polymers.

Theoretical spinodals for both of the systems gave similar trends to those of the experimental phase diagrams. For the PES/PEO system simulated spinodals were well inside the cloud point curve but for the PES/phenoxy they were very close to the cloud point curve.

Water vapour sorption measurements showed that none of the PES/PEO or PES/phenoxy blends absorbed less water than pure PES, as has been previously stated for PES/PEO mixtures.

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## CHAPTER 1

### INTRODUCTION

The concept of mixing two or more polymers to obtain a new material with desirable properties dates back to as early as the eleventh century<sup>1</sup>. The coatings and rubber industries have long been blending together different polymers to get the required product properties. Over the years, numerous systems based on the chemical combination of different monomers through random, block and graft copolymerisation have been developed to improve on the individual polymer properties. The physical mixing of two or more high molecular weight polymers to form a homogeneous blend in order to improve the properties or obtain new products was considered impossible, mainly because the combinatorial entropy of mixing for two high molecular weight polymers is extremely small, and mixing is difficult due to kinetic reasons (very small diffusion rates). During the last decade interest in polymer blends has greatly increased for the following reasons :-

- (i) the low development costs involved in mixing two polymers,
- (ii) the high cost of developing new monomers and making new polymers,
- (iii) the health and environmental protection legislation which adds to the problems of manufacturing and marketing new materials,
- (iv) the easy processing of polymer blends,
- (v) the advantage of controlling properties and cost at will,
- (vi) the great versatility in producing new and useful products.

In this work, polyethersulphone (PES) polymer blends are studied. The blends of polyethersulphone with poly(ethylene oxide) and with phenoxy resins are investigated in detail.

### 1.1 THERMODYNAMICS OF MIXTURES

In polymer-polymer blends, the term miscibility implies homogeneity on a molecular scale and the blend behaves as a single phase system. A blend showing optical clarity and a single glass transition temperature is considered miscible. From a thermodynamic point of view the state of miscibility of any mixture is governed by the free energy of mixing,  $\Delta G_m$ , which must be negative for mixing to occur.  $\Delta G_m$  is given by :

$$\Delta G_m = \Delta H_m - T \Delta S_m \quad 1.1$$

where  $\Delta H_m$  and  $\Delta S_m$  are the enthalpy and entropy changes on mixing, and  $T$  the absolute temperature. Figure 1.1 shows three possible ways in which the free energy of mixing may vary with the composition of the overall mixture ( $\phi_i$  = volume fraction of component  $i$ ). In case A, where  $\Delta G_m$  is always positive, the two components are not miscible with each other. In case B, where  $\Delta G_m$  is negative, the two components are completely miscible in all proportions. In case C,  $\Delta G_m$  is also negative but the components are only partially miscible. This is because there is a hump in the free energy diagram. In the central region the mixture can develop a lower free energy by partial separation into two phases. Thus a negative free energy of mixing is a necessary, but not a sufficient condition for miscibility of polymer mixtures.

The combinatorial entropy of mixing is usually taken in the form of the classical Flory-Huggins<sup>2</sup> theory as :

$$\Delta S_m = -K (N_1 \ln \phi_1 + N_2 \ln \phi_2) = -R (n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad 1.2$$

where  $N_i$ ,  $n_i$  and  $\phi_i$  are the number of molecules, number of moles and

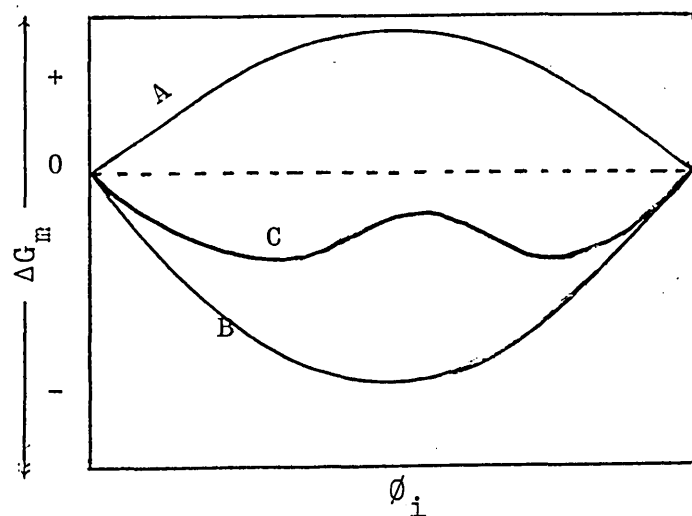


Figure 1.1 Free energy of mixing for binary mixtures which are completely immiscible (A), completely miscible (B), and partially miscible (C).

volume fraction of component  $i$  respectively. Thus as the molecular weights of the two components tend to infinity,  $N_1$  and  $N_2$  tend to zero and the entropy of mixing tends to zero.

The heat of mixing can be thought of as an exchange energy ( $W$ ) of breaking 1/1 and 2/2 contacts and forming 1/2 contacts as :

$$\Delta H_m = VZW \phi_1 \phi_2 / V_s \quad 1.3$$

where  $Z$  is a coordination number,  $V$  the total volume and  $V_s$  a segment volume, or in terms of the Flory-Huggins interaction parameter,  $\chi_{12}$

$$\Delta H_m = RT n_1 \phi_2 \chi_{12} \quad 1.4$$

where  $n_1$  is the number of moles of component 1. Or in the absence of any specific interactions, the enthalpy can be predicted using (Hildebrand's<sup>3</sup>) solubility parameters of the components ( $\delta_1$  and  $\delta_2$ )

$$\Delta H_m = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2 \quad 1.5$$

Equation 1.5 suggests that  $\Delta H_m$  must always be positive and on this basis high polymers should not be miscible (except when  $\delta_1 = \delta_2$ ). This expectancy was borne out by the fact that 90 percent of the 73 polymer

pairs investigated by Dobry and Boyer-Kawenoki<sup>4</sup> were immiscible. This approach is only applicable to mixtures of non-polar molecules with positive enthalpies of mixing.

Due to the shortcomings of the lattice model and its inability to predict experimental results, Flory and co-workers<sup>5, 6, 7</sup> developed an "equation of state" theory. They treated molecules as hard spheres with equal volumes. The hard core properties were introduced which allowed calculation of all the thermodynamic parameters and their corresponding excess values. Possible volume changes on mixing and extra contributions to the free energy of mixing were considered which were assumed to be zero in earlier theories. The theory is discussed in Chapter 2.

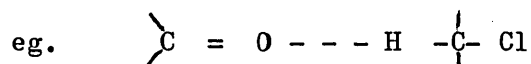
The basic energy equation 1.1 implies that miscibility between two or more polymers is possible under three conditions :

- (a) For low molecular weight polymers the combinatorial entropy of mixing will not be negligible and hence mixing can occur<sup>8</sup>.
- (b) Polymers of similar composition, giving a very small unfavourable heat of mixing could be miscible if this is outweighed by a small favourable entropy of mixing. The commonest example of this is the case of copolymers with differing composition with respect to the two components. Any copolymers must show some variation in composition and yet they are normally considered to be homogeneous. Many commercial copolymers are polymerised to high conversion under far from azeotropic conditions so that large variations must exist. It would not be suprising if phase separation occurred under some circumstances.

Other examples in this category are polymers in two stereoregular forms<sup>9, 10, 11, 12</sup>, polymers which are chemically very similar such as poly(methyl acrylate) and poly(vinyl acetate)<sup>13</sup>, various

chlorinated poly(vinyl chlorides)(PVC) with PVC<sup>14, 15</sup> and chlorinated polyethylenes with PVC<sup>16</sup>.

- (c) Polymers giving a favourable (exothermic) heat of mixing due to specific interactions are in general miscible. For example the miscibility of various polyesters<sup>17, 18</sup>, polyacrylates<sup>19</sup>, and poly(vinyl acetate) copolymers with poly(vinyl chloride)<sup>20</sup> is considered to be due to the postulated weak hydrogen bond between halogen containing polymers and oxygen containing polymers,



Another postulated interaction which has not been well studied is that between ether groups and aromatic rings which may be responsible for the miscibility of polystyrene and poly(vinyl methyl ether). Interactions probably exist between other groups and aromatic moieties.

The majority of miscible high polymers fall in the last category implying that a favourable heat of mixing due to specific interactions is the dominant factor for determining miscibility.

Newton<sup>21</sup> very crudely mixed low molecular weight analogues of approximately 200 polymers. Seven previously unstudied pairs were found to have favourable heats of mixing, and out of these, six polymer pairs were found to be miscible. Earlier Cruz<sup>17</sup> et al concluded that the polymer pairs whose oligomeric analogues have negative heats of mixing, are likely to be miscible and polymer pairs whose oligomeric analogues give positive heat of mixing, are invariably likely to be immiscible.

Many polymers show a variation in miscibility with temperature. Low molecular weight polymers, giving positive heats of mixing, are more

miscible at higher temperatures and may phase separate on cooling, showing upper critical solution temperature behaviour (UCST). A stable homogeneous transparent mixture of miscible high molecular weight polymers often phase separates at a certain temperature on heating showing lower critical solution temperature (LCST) behaviour.

In the case of low molecular weight polymers  $\Delta S_m$  is favourable and the term  $T \Delta S_m$  in equation 1.1 becomes more favourable at high temperatures. If equations 1.2 and 1.4 are substituted into equation 1.1 at a series of temperatures, then the plot of  $\Delta G_m$  against composition  $\phi_2$  may be as given in Figure 1.2. This calculation is based on the simple Flory-Huggins lattice theory and gives :

$$\Delta G_m = RT (n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 \phi_2^{\chi_{12}}) \quad 1.6$$

at  $T_3$  the polymer pair is miscible in all proportions and  $\partial^2(\Delta G_m)/\partial \phi_2^2$  is positive over all compositions. At  $T_1$  compositions between  $\phi_B$  and  $\phi_{B'}$  can phase separate to reduce the overall energy to give two phases at compositions  $\phi_B$  and  $\phi_{B'}$ , where the values :

$$\partial(\Delta G_m)_B/\partial \phi_2 = \partial(\Delta G_m)_{B'}/\partial \phi_2 \quad 1.7$$

At  $T_2$  the two points meet at the critical point and

$$\partial^2(\Delta G_m)/\partial \phi_2^2 = \partial^3(\Delta G_m)/\partial \phi_2^3 = 0 \quad 1.8$$

Between  $\phi_B$  and  $\phi_S$  and between  $\phi_{B'}$  and  $\phi_{S'}$ , a region of metastability occurs. This arises because any small fluctuations which occur in the composition, produce an increase in energy which acts as a barrier to phase separation. If composition X (Figure 1.2) phase separates to a mixture of Y and Z, the average energy is higher. The phase separation in this area can only occur by nucleation and growth. Between  $\phi_S$  and  $\phi_{S'}$ , concentration fluctuations are stable and phase separation can take place by spinodal decomposition. The spinodal curve is given by :

$$\partial^2(\Delta G_m)/\partial \phi_2^2 = 0 \quad 1.9$$

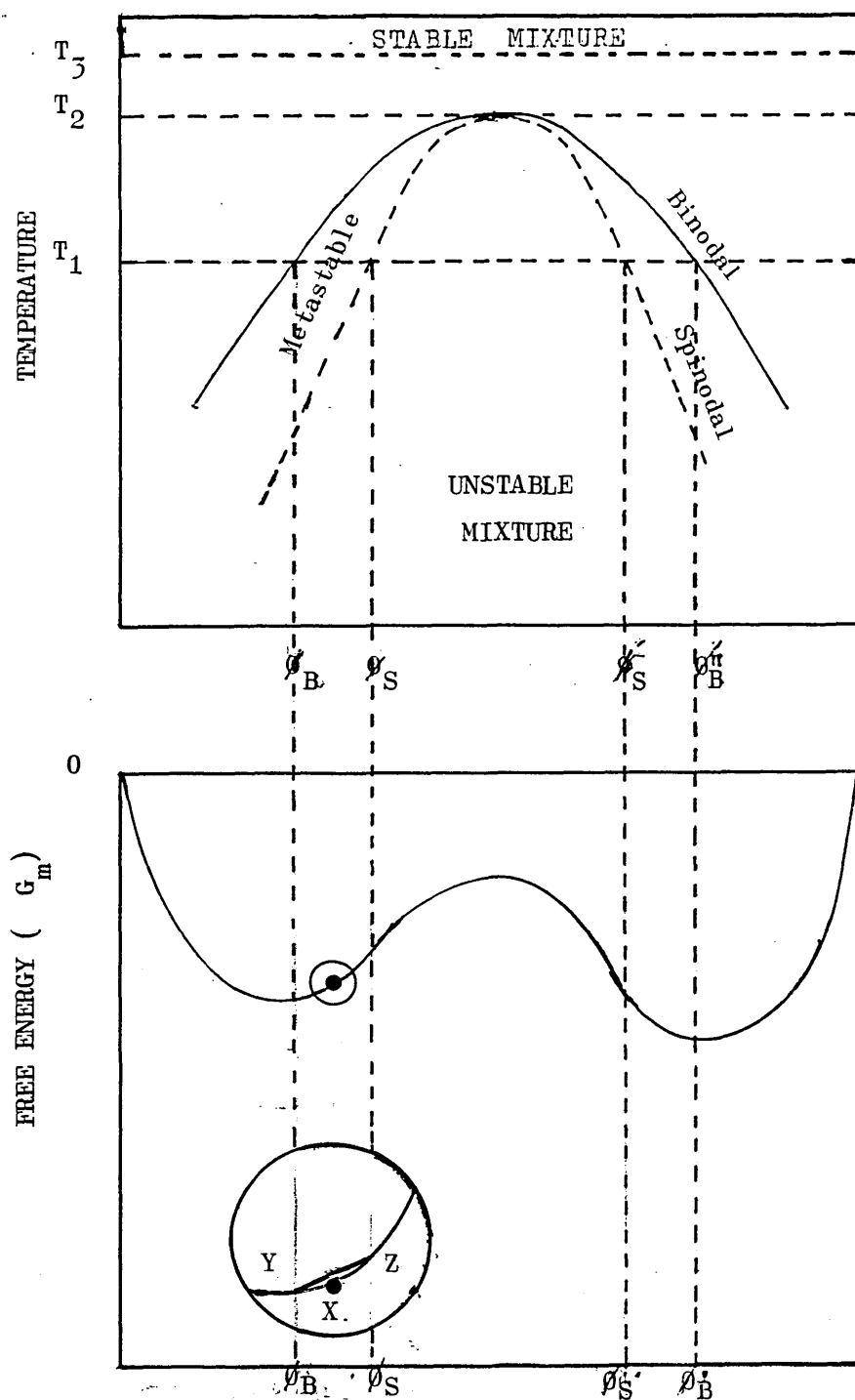


Figure 1.2 The phase diagram for a system showing upper critical behaviour. At temperature  $T_3$  mixtures are stable at all compositions whereas at  $T_1$  phase separation can occur. The origins of this phase separation are shown in the lower diagram which shows the plot of free energy against composition at  $T_1$ . A metastable region exists between the binodal and the spinodal points ( $\phi_B$ ,  $\phi'_B$  and  $\phi_S$ ,  $\phi'_S$  respectively). The inset in the lower diagram shows that if composition X partially phase separates into Y and Z the average free energy is higher even though complete phase separation to  $\phi_B$  and  $\phi'_B$  produces a lower energy.

The resultant phase diagram is shown in Figure 1.2. The line connecting points which satisfy equation 1.7, on the temperature composition diagram, is called the binodal curve.

In the case of high molecular weight polymers, a similar phase diagram is obtained but upside down, phase separation occurs on heating and the critical point is called the lower critical solution temperature. The origins of this phase separation are more complex but can be due to the following possible causes.

- (a) The equation of state terms as calculated by Flory and co-workers<sup>5, 6</sup>, which take into account the volume changes on mixing become more unfavourable at higher temperature. The effect of the polymer properties and the resultant phase diagrams using this theory have been reported by McMaster<sup>22</sup>.
- (b) Specific interactions within the system infer ordering of the system resulting in a larger negative entropic contribution to the free energy equation.
- (c) The heat of mixing could be temperature dependent. Although favourable at low temperatures it may become less so at higher temperatures as specific interactions dissociate. This may be an important factor but as yet no theory describes it.

The problem of specific interactions has been recently discussed by Walsh et al<sup>23</sup> who concluded that they play a major part in polymer-polymer miscibility. Moskala et al<sup>24</sup> studied the changes in infra-red spectra on heating of blends of chlorinated polyethylene with ethylene-vinyl acetate (EVA) copolymers. The gradual reduction in infra-red shift, with increasing chlorinated polyethylene content, was attributed to a dissociation of this specific interaction on heating. Studies of blends of PVC with polycaprolactone showed shifts of  $4 - 6 \text{ cm}^{-1}$  in the carbonyl band of polycaprolactone

relative to pure polymer<sup>25, 26</sup>, but this figure should be treated with caution as the peak probably consists of the sum of shifted and unshifted peaks and it is difficult to say what the frequency of shifted peaks would be and what fraction of carbonyl groups are involved in the interaction.

Olabisi<sup>26</sup> measured a negative interaction parameter for PVC with poly ( $\epsilon$ -caprolactone) by inverse gas chromatography (IGC). He concluded that miscibility was due to a charge transfer interaction which became weaker at higher temperature giving rise to phase separation and LCST behaviour.

Nishi and Wang<sup>27</sup> found a negative interaction parameter for the poly(vinyl fluoride)(PVF<sub>2</sub>) and poly(methyl methacrylate) (PMMA) system by melting point depression measurements. Paul and Barlow<sup>28</sup> also found a negative interaction parameter for PVF<sub>2</sub>-poly(ethyl methacrylate), PVF<sub>2</sub>-poly(methylacrylate), PVF<sub>2</sub>-poly (ethyl acrylate) and PVF<sub>2</sub>-poly(vinyl methyl ether). The LCST behaviour of polycarbonate-poly( $\epsilon$ -caprolactone) and mixtures of PVF<sub>2</sub> with poly(methyl acrylate), poly(ethyl acrylate), poly(methyl methacrylate), and poly (ethyl methacrylate) is described by Bernstein et al<sup>29</sup>. Inaki Mondragon<sup>30</sup> reported a negative interaction parameter determined from melting point measurements for the polycarbonate-polyacrylate blend system. Nishi and Kwei<sup>31</sup> studied the LCST behaviour of monodisperse polystyrene and poly(vinyl methyl ether) mixtures. Detailed studies of this system were carried out by Davies and Kwei<sup>32</sup> and Cowie and Sæki<sup>33</sup> who found both LCST and UCST behaviour when polystyrene had appropriate molecular weights.

## 1.2 METHODS FOR THE PREPARATION OF HOMOGENEOUS BLENDS

There are three main methods for the preparation of homogeneous blends, mixing in the melt (mechanical mixing), mixing in solution (using

a common solvent) followed by evaporation or precipitation, and in-situ polymerisation.

#### 1.21 Melt Mixing

Melt mixing has the advantage that no solvents are needed and is a very common process for compounding and mixing polymers in industry. The low diffusion rates of high polymers means that very long periods would be required to produce complete homogeneity. The low thermal stability of many polymers means that such prolonged mixing may not be possible. Also, many polymer blends exhibit phase separation on heating which may mean that they are not miscible at the temperature of mixing. Problems may also arise due to large differences in melt viscosity of the two polymers.

In practice, however, complete homogeneity may not be necessary or even desirable and many commercial blends are prepared in this way. Mechanical mixing is used, for example, to blend poly(phenylene oxide) with polystyrene<sup>34</sup> (Noryl R) and poly(vinyl chloride) with butadiene/acrylonitrile copolymer<sup>35</sup> (NBR). Many polymeric plasticisers, impact modifiers, and processing aids for PVC are incorporated into PVC by mechanical mixing<sup>20</sup>. Many of these materials, including butadiene-acrylonitrile copolymers<sup>36</sup>, ethylene-vinylacetate copolymers<sup>37, 38</sup>, chlorinated polyethylene<sup>39</sup> and various polyacrylates and copolymers<sup>19</sup> are known to be miscible or partially miscible with PVC. In the case of polymeric plasticisers, homogeneity may be desirable but optimum impact modification is often achieved by a heterogeneous structure.

#### 1.22 In Situ-polymerisation

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, for example, high impact polystyrene<sup>40</sup> and recently to prepare homogeneous blends<sup>39, 41, 42</sup>.

It is possible to prepare blends where the base polymers tend to be thermally unstable and have a high Tg, or phase separate on heating which precludes the use of mechanical mixing. In this process monomers act as solvents for the polymer during polymerisation and can interfere with miscibility. In situ polymerisation, therefore does not guarantee homogeneous blends as two phase regions can exist within the polymer/polymer/monomer three component phase diagram. This two phase region can be avoided by step polymerisation.

#### 1.23 Mixing in a common solvent followed by evaporation or precipitation.

This is the commonest laboratory method used in the preparation of homogeneous blends. The method has a number of advantages, for example, low energy costs, no polymer degradation and no cross-linking or decomposition of polymer components due to heat. However, solvents are sometimes difficult to remove and can interact with the polymer causing two phase structures to be formed when blends of miscible polymers are prepared in this way<sup>42, 43</sup>. It is, therefore, not surprising to see conflicting evidence of miscibility when blends are prepared using different solvents. A two phase region can exist within the polymer/polymer/solvent three component phase diagram as shown in Figure 1.3. When a dilute solution at composition A is evaporated, phase separation takes place at B. When this system leaves the two phase region, at overall composition C, the phases have grown too large and the rate of diffusion in the mixture is too low for the polymers to remix and therefore the resultant polymer blend, of overall composition D, is two phase.

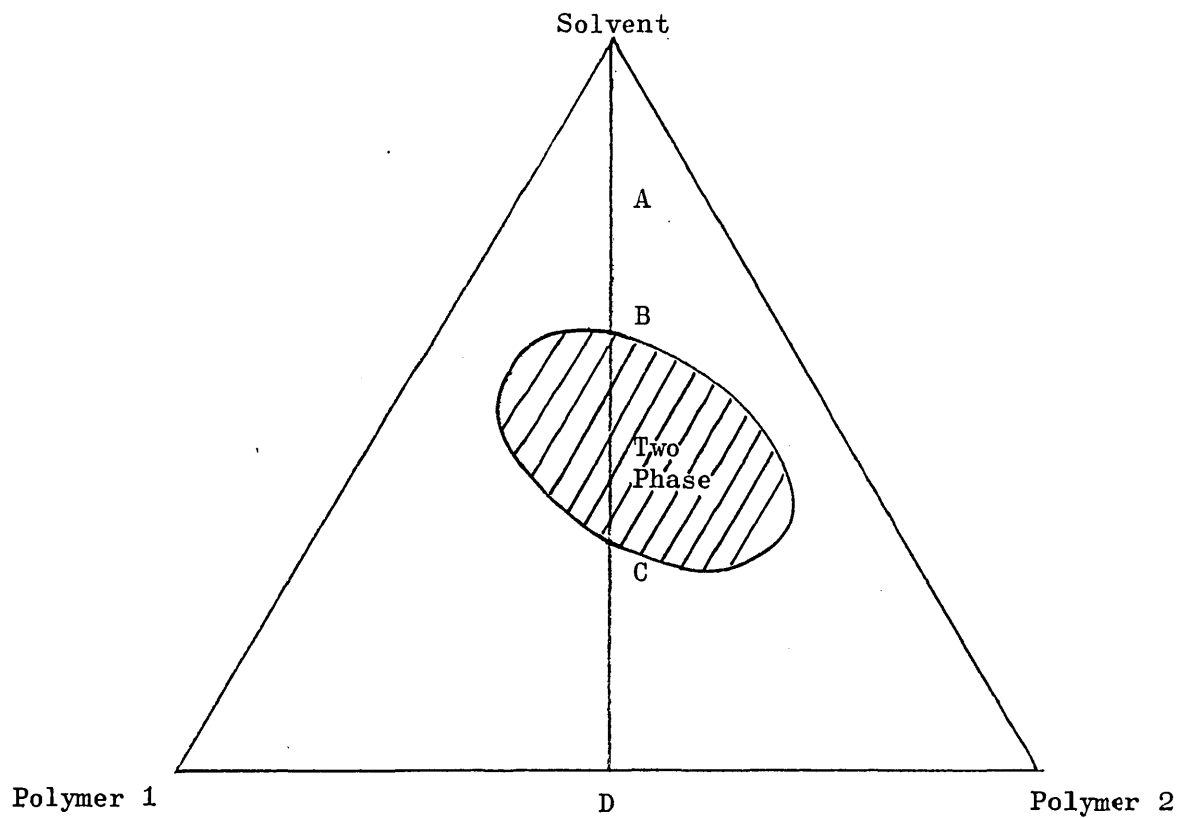


Figure 1.3 A hypothetical phase diagram for two polymers with a common solvent showing a two phase region.

Computer simulations of the binodal in the phase diagram of polymer/polymer/solvent mixtures have been carried out and show the effect of the various interaction parameters on the shape of the phase diagram<sup>44</sup>.

In the case of polystyrene blends with poly(vinyl methyl ether) two phase behaviour was found for blends from various chlorinated solvents,<sup>32, 43</sup> whereas single phase behaviour was found from toluene. The phase separation of these blends in various solvents has been studied and the interaction parameter of the two polymers measured by inverse gas chromatography. It was found that those solvents which induced phase separation were those for which a large difference existed between the two separate polymer-

solvent interaction parameters. This has been called the  $\Delta \chi$  effect<sup>44</sup> (where  $\Delta \chi = \chi_{12} - \chi_{13}$  and component one is solvent). Similar solvent effects have been noticed in a phenoxy resin and copolyester solution in tetrachloroethane<sup>45</sup> and in mixtures of PVC with various acrylates in tetrahydrofuran<sup>19</sup>.

Coprecipitation of polymers from a common solvent into a non-solvent is an alternative way of making blends. This method is useful when a common solvent has a very high boiling point. It however produces finely divided or coarse particulate samples which must be pressed before testing by many techniques. The hot pressing could result in phase separation.

#### 1.24 Other Methods of Mixing

Blends can also be prepared by freeze drying where polymers are dissolved in a common solvent, and the mixture quickly frozen. On freezing, the blend will be thrown out. Very good mixing is obtained using this method, but it has certain drawbacks. It is somewhat complex, gives inconvenient products, and its use is restricted to only a few solvents.

Another method of blending two polymers is by emulsion mixing. In this process two separate polymer emulsions are mixed together and coagulated. This is an easy, inexpensive and convenient method but emulsions of many polymers of interest are not available.

#### 1.3 WAYS OF CONFIRMING MISCIBILITY AND STUDYING PHASE SEPARATION PHENOMENA

The optical, mechanical, electrical, morphological and thermodynamic properties of various polymer mixtures are often used as evidence

for establishing miscibility. The above criterias have been extensively reviewed by MacKnight et al<sup>46</sup> and Olabisi<sup>47</sup>.

### 1.31 Optical Clarity

Films or molded objects made from two miscible polymers are optically clear and have good mechanical integrity. These are the first signs that two polymers are miscible. These criterion can, however, be deceptive if the refractive indices of the blend components happen to be close to each other, if the blend has phase separated into two separate layers, or if a two phase structure exists with domains much smaller than the wave length of light<sup>48, 49</sup>. Bank et al<sup>43</sup> have reported the effect of domain size on film clarity for the LCST of polystyrene poly(vinyl methyl ether). As the two polymers phase separated and the domain size of the dispersed phase enlarged the film changed from showing complete clarity to a bluish appearance. Bohn<sup>50</sup> has indicated that for transparency the critical difference between refractive indices can be no greater than 0.01. Incompatible blends of polystyrene and bisphenol A polycarbonate with refractive indices 1.585 and 1.590, yield films that are clear<sup>51</sup>. A powerful Transmission Electron Microscope was employed in this study to give good resolution of the domains present.

### 1.32 Glass Transition Temperature Methods

One of the most sensitive methods of determining polymer-polymer compatibility is the detection of a single Tg, usually intermediate between two polymers. If polymers are incompatible, two separate Tg's relevant to the individual polymers are obtained. In cases of borderline miscibility, slight displacement of the Tg's of the components towards each other may be expected. MacKnight, Karasz and Fried<sup>46</sup> have discussed the above possibilities. Another case of partial miscibility,

represented by a broadening of the transitions has also been observed<sup>52</sup>. In cases where strong specific interactions occur, the Tg of the blend is higher than the expected average<sup>53</sup>. In this case the blend requires a higher activation energy than its additivity value in the form of heat to allow chain movements. A review of this subject and of the relations between Tg and chemical structure of blends has been given by Cowie<sup>54</sup>.

For miscible blends, many attempts have been made to correlate the Tg with the blend composition as is frequently done with random copolymers. Several miscible blends studied by Hammer<sup>37</sup>, Hichman and Ikeda<sup>55</sup> and Zabrzewski<sup>56</sup> exhibit a composition dependence of Tg which can be predicted by the simple Fox<sup>57</sup> relationship.

$$\frac{1}{T_{g_b}} = \frac{W_1}{T_{g_1}} + \frac{W_2}{T_{g_2}} \quad 1.10$$

where  $W_i$  is the weight fraction of polymer  $i$  with  $T_{g_i}$ . Other miscible blends have been reported to follow The Kelley-Bueche<sup>58</sup> expression, the Gordon-Taylor<sup>59</sup> equation and the Dimarzio Gibbs<sup>60</sup> and Couchman<sup>61</sup> expressions.

In order to get meaningful results from this method the component Tg's must be at least 20°C apart. If one component is present in small quantity, its Tg may not be detectable. In cases where one of the blend component is crystalline, the detection of Tg by calorimetric means will be difficult, unless the boundaries between the amorphous and crystalline regions are sharp and distinct. Tg results also vary with the method of measurement.

There are several methods available for measuring glass transition temperatures as given below.

(a) Dynamic mechanical analysis (DMA) involves the determination

of the dynamic properties of the polymers and their mixtures, usually by applying a mechanical sinusoidal stress. For linear viscoelastic behaviour the strain will alternate sinusoidally but will be out of phase with the stress. The phase lag results from the time necessary for molecular rearrangements and this is associated with relaxation phenomena. The energy loss per cycle, or damping in the system, can be measured from the loss tangent ( $\tan \delta$ )

$$\tan \delta = \frac{E''}{E'} \quad 1.11$$

where  $E'$  is the storage modulus and  $E''$  is loss modulus.

A peak in the value of  $\tan \delta$  occurs around  $T_g$ . Because of the limited number of frequencies available on the usual instruments, it is common to keep the frequency constant while lowering or raising the temperature to match the molecular motion of the blend. This method has been used in studying blends of poly(vinyl chloride) with polyacrylates or polymethacrylate<sup>19, 42</sup> and poly(vinylidene fluoride) with poly(methyl methacrylate<sup>62</sup>).

DMA can be used to estimate the position of the phase boundary. This is done by heating the blends to a given temperature, quickly cooling the sample and then determining  $T_g$ . By repeating this procedure for several temperatures until two peaks appear, an approximate phase separation temperature can be obtained. This method is especially useful for blends with small differences in the refractive indices of the two components or for blends which degrade on prolonged heating.

(b) Differential Scanning Colorimetry (DSC) and Differential Thermal Analyser (DTA)

DSC measures the amount of heat required to increase the sample temperature over that required to heat up a reference material, normally an empty pan, to the same temperature. The variation in power necessary to maintain this level during a transition is monitored. DTA measures the difference in temperature between the sample and reference material when both are heated at the same rate. A detailed description of these methods is given by Manche et al<sup>63</sup> and Ke<sup>64</sup>.

Both these methods are rapid and need only 5 - 30 mg samples and have sophisticated controlled rates of heating and cooling. Rapid temperature scanning permits the study of heat sensitive polymers such as poly(vinyl chloride) without the addition of stabilisers. Co-precipitated blends in powder form can be studied. It is possible to determine the composition of the blend from the measured T<sub>g</sub> and the change in specific heat of the glass transition<sup>65</sup>.

The use of DSC in the study of polymer thermodynamics has been described by Flynn<sup>66</sup>. DSC has been used to study the miscibility of PPO - polystyrene<sup>67</sup>, nitrile rubber - PVC<sup>56</sup>, polystyrene - poly(vinyl methyl ether)<sup>43</sup>, PVF<sub>2</sub> - poly(methyl methacrylate)<sup>68</sup>, PVC - (ethylene/vinyl acetate/sulphur dioxide) terpolymer<sup>55</sup>, PPO - poly(styrene-co-chlorostyrene)<sup>69</sup> phenoxy-poly(N-vinyl-2-pyrrolidone)<sup>70</sup> and poly(vinyl butyral) - poly(N-vinyl-2-pyrrolidone)<sup>70</sup>. DSC and DTA can in principle also be used to study the phase boundary of a blend by the same heating and quenching procedure

as described earlier for dynamic mechanical measurements. The phase boundary of poly(methyl methacrylate)-chlorinated polyethylene (52% w/w cl.) has been obtained in this way by using DTA<sup>71</sup>.

- (c) Dielectric Relaxation Measurements are similar to dynamic mechanical measurements, except that they exploit the dipole electrical properties of the blend. They are therefore, not applicable to blends of polymers without dipole moments. The advantage of dielectric over dynamic relaxation measurements, is the range of frequencies available. This permits the dynamic dielectric constants or  $\tan \delta$  to be determined either as a function of temperature (temperature-plane measurements) over a range of frequencies or as a function of frequency (frequency-plane measurements) at selected temperatures. The use of dielectric relaxation in studying blends has been described by Wetton et al<sup>72</sup>.

The dielectric constant increases as molecular motion in a polymer increases; thus large secondary relaxations and the glass transition will yield increasing values.

The use of thermodielectric loss measurements in which dielectric loss is measured under a definite temperature programme, has recently been used to study polymer-polymer miscibility<sup>73</sup>.

- (d) Dilatometry measures the specific volume as a function of temperature. In the glass transition region a discontinuity is observed. Dilatometry requires large samples, long measurement times and great care in sample preparation and measurement.

### 1.33 Optical and Electron Microscopy

Both optical and electron microscopy are widely used in studies of polymer blends. Both transmitted-light and phase contrast microscopy require a difference in refractive index between the phases for contrast. With transmission, contrast is best obtained with opaque or coloured samples. However, with phase-contrast optics, good contrast is often obtained with transparent material and this is therefore often the preferred method for polymer polymer blends. In phase contrast microscopy, the beam from the interference diffraction maxima of light passing through a specimen is split into two parts by a beam splitting prism. Each part contains the full object information. These beams recombine in an interferometer and by shearing one beam vertically against the other the two waves hit each other sheared, and interference will occur depending on the phase differences of the components. This method produces coloured pictures of the specimen, with homogeneous blends having one colour over the observed field, and two phase samples showing two different colours. This technique avoids the effects of artefacts due to staining which is a problem in electron microscopy. However, it has a limited resolution depending on the polymer mixture and the microscope used. This method has been successfully used to study miscibility and phase transition of several blends<sup>74</sup>.

The resolving power of a light microscope is limited by the nature of the light. The minimum spacing which can be resolved by a good microscope is of the order of the wavelength of the radiation source. For better resolution, a larger angle of acceptance of the lens and a shorter wavelength radiation are required.

A transmission microscope fitted with a hot stage can be used to study the phase behaviour on heating or cooling a thin film sample

of a blend.

Transmission Electron microscopy (TEM) with a resolution of 10 - 20 Å has been very useful for studying polymer-polymer miscibility and phase separation. The electron wavelength is associated with the electron beam through the application of de Broglie's principle of wave-particle duality of electrons. Electrostatic or electromagnetic lenses replace the glass lenses of an optical microscope. The primary source of image contrast is produced by electron density variations in the specimen. The image can often be enhanced by techniques of shadowing or staining. The specimen thickness is limited to 1 µm or less. A reasonable contrast is produced with polymers containing heavier atoms, such as chlorine or sulphur, without staining. Miscible blends can be phase separated and quenched and then observed under an electron microscope to see the microstructure. This technique has been used for blends of PVC with poly(butylacrylate)<sup>41</sup> and for ethylene vinyl acetate copolymers with chlorinated polyethylene.

Scanning electron microscopy (SEM) has also been used to study phase morphology. A fine beam of electrons is scanned across the surface of an specimen to which a conducting film has been applied by evaporation. Secondary or back scattered electrons, or (in the electron microprobe) x-ray photons are emitted when the beam hits the specimen they are collected to provide a signal used to modulate the electron beam in a television tube, scanning in synchronism with the microscope beam. Because the latter maintains its small size over the large distance relative to the specimen, the resulting images have great depth of field and a remarkable three dimensional appearance. Contrast depends on differences in surface topography or texture.

### 1.34 The Observation of Cloud Point Temperatures

A clear homogeneous blend of two polymers may phase separate and become cloudy on heating. The temperature at which the blend changes from a transparent to a turbid state is called the cloud point. For many systems this process reverses itself on cooling. Such behaviour gives a good indication that the original clear blend consisted of a single phase. The observation of the cloud point thus confirms miscibility. An experimental phase diagram can be constructed by observing the phase separation temperatures for a range of compositions. The cloud point may be difficult to observe if the mobility of the two polymers is not sufficiently high.

### 1.35 Other Methods

Other methods, such as small angle x-ray scattering (SAXS), small angle neutron scattering (SANS) and pulse induced critical scattering (PICS) are not much used for polymer blends mainly because of the instrumental limitations. SAXS is sensitive to differences in electron density and hence usually requires a heavy atom in the blend to give a larger scattering cross section for x-rays after phase separation. Stein et al.<sup>76</sup> have used this method for blends of poly( $\epsilon$ -caprolactone) with PVC. SANS measures the difference in the neutron scattering cross-section, for example, of a deuterated chain dispersed in a matrix of protonated blends or vice versa. SANS has been used for deuterated poly(2, 6-dimethyl 1, 4 diphenylene oxide)-polystyrene blends<sup>77</sup>.

The use of pulse induced critical scattering (PICS) is very limited by the slow diffusion rate of high molecular weight polymers. It is mainly used for polymer-solvent mixtures and only recently been applied to low molecular weight polymer-polymer mixtures showing UCST<sup>66, 78</sup>.

#### 1.4 WAYS OF STUDYING THE THERMODYNAMICS OF MIXTURES

The previous section describes empirical ways of confirming miscibility. This section gives the methods of studying the thermodynamic interaction in polymer-polymer mixtures. The favourable interaction parameter ( $\chi$ ) infers miscibility and therefore this is also related to the previous section. There are many different ways of measuring the interaction parameters between two polymers. These include heat of mixing measurements, inverse gas chromatography, solvent vapour sorption, various scattering techniques and viscosity measurements. For crystalline materials measurement of melting point depression by techniques such as DSC or turbidimetry can also be used.

##### 1.41 Heat of Mixing Measurements

The direct measurement of the heats of mixing of two high molecular weight polymers is not possible because of the low diffusion rates, and thermal stability of some polymers. Several authors have tried to measure the heats of mixing in the presence of a solvent, using Hess's law to extract the heat of mixing of the polymers<sup>79</sup>. This has not been successful, possibly due to accumulation of errors in the series of experiments involved. Other workers have used the heat of mixing measurements of low molecular weight analogues of the polymers to calculate the polymer-polymer interaction parameter<sup>80, 81</sup>. This method may not always give reliable results due to differences between the high polymers and the analogues used. These differences could arise from chain end effects, steric differences or dissimilarity in densities. Low molecular weight materials often have a lower density. The cohesive energy density is strongly dependent on the density so that in a system where the dispersive forces are important

the use of low molecular weight analogues may be less reliable. When dispersive forces are small and specific interactions strong, the low molecular weight materials may be more representative of the polymers themselves. Heats of mixing of analogue materials are measured in a specially designed microcalorimeter<sup>82</sup>.

#### 1.42 Inverse Gas Chromatography (IGC)

Conventional gas liquid chromatography determines the retention of an unknown sample in the moving phase with a known stationary phase. The inverse method, however, determines the property of the stationary phase using a known volatile solute in the moving phase. The volatile molecules are referred to as probe molecules. The calculated interaction parameter when using different probes, tends to vary more than can be explained by experimental error. The effects of both surface adsorption and diffusion limitation in the stationary phase are difficult to overcome. This technique is limited for use at temperatures at least 50°C above the Tg's of the homogeneous systems to reduce the effects of surface adsorption and diffusion limitations<sup>16, 83</sup>. From measurements on two polymers and blend, one can calculate polymer-polymer interaction. This method measures the total free energy of the interaction which includes combinatorial and residual interaction parameters as well as any residual entropy contributions.

#### 1.43 Solvent Vapour Sorption

Measurement of the sorption of solvent vapour by films of two polymers and the polymer blends can be used to obtain information about the interactions within mixtures. In theory the technique is similar to IGC but, being a static rather than dynamic method it is easier to reduce the effects of surface adsorption and diffusion limitations

inherent in IGC. The technique is however, not so fast as IGC.

Kwei et al<sup>84</sup> applied polymer solution theory to a ternary system consisting of one solvent and two polymers and calculated the polymer-polymer interaction parameter. The activity of the solvent in the ternary mixture is given by :-

$$\ln a_1 = \ln \phi_1 + (1-\phi_1) + (X_{12}\phi_2 + X_{13}\phi_3)(1-\phi_1) - X'_{23}\phi_2\phi_3 \quad 1.12$$

where  $a$  is the activity of the solvent vapour, subscript 1 refers to solvent and subscripts 2 and 3 refer to the two polymers.  $\phi$  is the volume fraction and  $X_{12}$  and  $X_{13}$  are the solvent-polymer interaction parameters and  $X'_{23}$  is the polymer-polymer interaction parameter expressed per segment of polymer 2. The solvent polymer interaction parameters  $X_{12}$  and  $X_{13}$  can be calculated using the binary solution equation.

$$\ln a_1 = \ln \phi_1 + \phi_2 + X_{12}\phi_2^2 \quad 1.13$$

Cates and White<sup>85, 86</sup>, reported water sorption in blends of poly(acrylonitrile) (PAN) and cellulose, silk, and cellulose acetate respectively. They showed that the sorption of water varied linearly for PAN/cellulose and PAN/cellulose acetate blends implying homogeneity. The sorption for PAN/silk blends was complicated, suggesting a two phase structure. The results of vapour sorption have been compared with IGC for PVC, polystyrene, and poly(methyl methacrylate) with various solvents and the interaction parameters have been found to agree within experimental error<sup>87</sup>.

There are a number of difficulties in sorption measurements due to the long time required to establish equilibrium condition. Accurate temperature control is essential and is difficult to achieve

over long periods, especially at higher temperatures. Experimental errors are high in the regions of low and high solvent concentrations. At low concentration, the pressure measurements are inaccurate because of the small changes and at high concentration the solvent condensation causes problems.

#### 1.44 Melting Point Depression

The depression of the melting point of a crystalline polymer in polymer blends can be used to measure the Flory-Huggins interaction parameter of the blend. The melting point on heating, or crystallisation point on cooling, can be measured using techniques such as differential scanning calorimetry or by turbidity measurement.

For very high molecular weight polymers the interaction parameter  $\chi_{12}$  (segmental) can be obtained using a simplified version of that derived by Flory<sup>2</sup> as used by Nishi and Wang<sup>27</sup>.

$$1/T_m - 1/T_m^0 = R \chi'_{12} \phi_1^2 / \Delta H_u \quad 1.14$$

where  $T_m^0$  is the melting point of the pure crystallisable polymer and  $T_m$  its value in the blend,  $\Delta H_u$  is the heat of fusion, and  $\phi_1$  the volume fraction of the amorphous component. A plot of  $1/\phi_1 (1/T_m - 1/T_m^0)$  against  $\phi_1$  should give a straight line from the slope of which the interaction parameter can be found. In practice, the plot does not go through the origin as expected, and this has been attributed to the effect of morphological changes on the melting point depression. A generalised form of the above equation for non-infinite molecular weights including corrections for morphological effects, has been given by Kwei et al.<sup>88</sup>.

$$\frac{\Delta H_u (T_m^0 - T_m)}{\phi_1 R T_m^0} - \frac{T_m}{m_1} - \frac{\phi_1 T_m}{m_2} = \frac{C}{R} - b \phi_1 \quad 1.15$$

This assumes that the morphological contribution is solely proportional to  $\phi_1$  with a proportionality constant C. The left-hand side of the above expression is plotted against  $\phi_1$  and the slope, b, is related to the interaction parameter.

This method has been used to study the interaction between poly(vinylidene fluoride) and polymethacrylate<sup>27</sup> and between poly(ethylene oxide) and the polyhydroxyether of bisphenol A<sup>89</sup>.

### 1.5 MISCIBLE POLYMER BLENDS

During the last twenty years a host of new miscible polymer pairs have been reported. A thorough listing of known miscible blends up to 1980 has been given by Krause<sup>90</sup>, Olabisi et al<sup>91</sup> and Paul et al<sup>92</sup>. Here the literature concerning some polymer pairs related to high performance engineering plastics and to PEO blends and phenoxy blends with polymers other than PES are briefly reviewed.

In the engineering plastics field, the first homogeneous polymer blend of commercial importance was probably that of poly(2,6 dimethyl-1, 4 phenylene oxide) (PPO) and polystyrene available under the trade name of 'Noryl'. PPO has a Tg of 210°C and polystyrene 100°C. The blends have a single Tg and other properties intermediate between the two. Shultz<sup>93, 34</sup> studied PPO/polystyrene blends and confirmed their miscibility. PPO/poly( $\alpha$ -methyl styrene)-polystyrene AB block copolymers have been reported to be miscible<sup>94</sup>. It has been found that homopolymers of p-chlorostyrene and o-chlorostyrene both, are not miscible with PPO but their copolymers in the range of 23-64 percent p-chlorostyrene are miscible<sup>95</sup>.

Crutz et al<sup>96</sup> have reported homogeneous blends of polycarbonate with a number of polyesters. Blends of the polycarbonate of bisphenol A with poly(ethylene terephthalate) (PET)<sup>97</sup> exhibited single Tg's up to

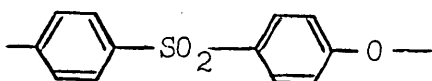
50% polycarbonate. Poly(1, 4 cyclohexylene dimethylene tere/isophthalate)<sup>97</sup> blends with polycarbonate were shown to be miscible over the entire composition range. Poly(butylene terephthalate)<sup>98</sup> has been found to show only limited miscibility with the polycarbonate. Polycarbonate has been found to be completely miscible with poly-( $\epsilon$ -caprolactone)<sup>96, 98</sup>(PCL). Using heat of mixing of low molecular weight analogues Cruz et al<sup>97</sup> suggested that miscibility of polycarbonates with polyesters is due to specific interaction resulting from n- $\pi$  complex formation between the electrons of the ester carbonyl and the aromatic ring of the carbonate molecule.

The polyhydroxyether of bisphenol A, (Phenoxy), has been found to exhibit miscibility with poly( $\epsilon$ -caprolactone<sup>99</sup>), poly(butylene terephthalate<sup>100</sup>), a cyclohexane dimethanol based polyester<sup>100</sup>, a polyester based polyurethane<sup>101</sup>, polyethylene adipate, polybutylene adipate<sup>100</sup>, poly(N-vinyl-2-pyrrolidone<sup>70</sup>), poly(ethylene oxide) and poly(vinyl methyl ether)<sup>102</sup>. It is postulated that miscibility is achieved via hydrogen bonding.

Poly(ethylene oxide), a water soluble polymer, forms complexes with poly(acrylic acid)<sup>103</sup>, poly(methacrylic acid)<sup>104</sup>, a vinyl methyl ether/maleic anhydride copolymer<sup>105</sup>, and carboxymethyl dextran<sup>105</sup>. It has been found to be miscible with phenolic resins<sup>106</sup>. In most of these mixtures PEO is assumed to act as an electron donor and other polymer as an electron acceptor. PEO has been reported to be miscible with poly(vinyl acetate)<sup>107</sup> because of the similarity in solubility parameters.

#### 1.6 POLYETHERSULPHONE (PES) POLYMER BLENDS

PES is a high temperature engineering plastic with a repeatunit:



Because of its aromatic character and the presence of the sulphone group which increases the stiffness of the chain, the polymer has very good mechanical and electrical properties even at high temperatures (up to 200°C). PES is used in the electrical, mechanical, automobile and aircraft industries. It is also used for ultrafiltration membranes, medical appliances and food processing industries.

PES is insoluble in water and dissolves only in a few solvents such as N-methyl pyrrolidone, methylene chloride, dimethylformamide, dimethyl sulfoxide, 1,1,2 trichloroethane and cyclohexanone (above 70°C).

It has been suggested<sup>108</sup> that PES is miscible with poly(ethylene oxide) (PEO). At some compositions the two polymers form clear films when cast from a common solvent (N-methyl-2-pyrrolidone/methylene chloride). It was impossible to leach out PEO from the blend and the wettability of the films was considerably increased. At other compositions the mixtures were cloudy. The clear compositions became cloudy on heating which suggests that it has an LCST. No explanation was offered for this behaviour.

In another patent<sup>109</sup> two phase blends of low molecular weight PEO with PES and polysulphones were described which had been prepared by casting from dimethylformamide at 50°C. The PEO could be extracted from these blends.

There are several reasons for wanting to blend other polymers with PES. Firstly, in spite of its excellent properties it absorbs a small percentage of moisture (around 2.2%) which causes problems in the soldering of printed circuits. It is possible that miscible blends with other polymeric materials with strong specific interactions, may reduce moisture absorption. Secondly, PES is a new

high performance plastic and therefore blends with other polymers may open new application areas yet undiscovered. Uses in areas of high temperature membranes, ultrafiltration, reverse osmosis, medical dose release and hollow filaments etc could be envisaged. And thirdly, understanding the thermodynamics of the miscibility of PES polymer blends may open new areas of research in other high performance plastic fields yet undiscovered.

In the two patents mentioned earlier, no explanation was offered for the miscibility of PES with PEO. It could be postulated that miscibility may be due to the specific interaction between ether groups and aromatic rings for example  $n-\pi$  interactions. Therefore in this work, blends of PES with a number of other polymers which can provide this type of interaction, including PEO were studied. The miscibility of PES/PEO blends, the effect of solvent used in preparing the mixture on the phase structure and the temperature composition phase diagram, are described. The phase diagram is explained in terms of the thermodynamics of the system. It was suggested in the literature that some compositions of PES/PEO absorb less water than PES, therefore, the sorption of water vapour in blend compositions was studied and this was also used to obtain information about the thermodynamic interaction parameters.

Similar work was done with PES/phenoxy mixtures which were also found to be miscible.

## CHAPTER 2

### THEORY

#### 2.1 FLORY-HUGGINS LATTICE THEORY

A polymer blend can be envisaged as a solution of a polymeric solute, (the component with the larger chain length) dissolved in a polymeric solvent (the component with the smaller chain length). The mixing of two polymers is therefore treated as an extension of polymer solution theory, which in turn, is an extension of the liquid lattice model which was developed for mixtures of molecules with weak interactions and approximately similar sizes. Early polymer solution thermodynamics, considered only two aspects of mixing ie. the interaction energy between segments of different types and the combinatorial entropy of mixing (the possible arrangement of chain molecules within the lattice). In the lattice model a polymer chain is conceptually divided into segments of the same size as the lattice sites, and the size is set equal to that of the solvent molecule. The most important features of regular solution theory, namely, maximum random mixing and no volume change on mixing were used by Flory<sup>110, 5</sup> and Huggins<sup>111, 112</sup>.

#### 2.11 The Entropy of Mixing

The combinatorial entropy of mixing can be obtained from computations of the number of ways of arranging a flexible chain on the points of a lattice. Consider first a solution involving small solute and solvent molecules of the same size occupying the points of a regular lattice. The number of ways, in which the molecules can be arranged on the lattice can be related to the change in thermodynamic probability,  $\Delta\Omega$  on mixing and this, in turn, can be

related to the corresponding entropy change  $\Delta S_m$  by:

$$\Delta S_m = K \ln \Omega \quad 2.1$$

where  $K$  is Boltzmann constant. If solute and solvent molecules can replace each other indiscriminately on the points of the lattice, that is, if mixing is random, then:

$$\Delta S_m = -R(n_1 \ln x_1 + n_2 \ln x_2) \quad 2.2$$

where  $n_1$  and  $n_2$  are the number of moles and  $x_1$  and  $x_2$  are the mole fraction in the solution of solvent and solute, respectively, and  $R$  is a gas constant.

If a polymer solution is now considered, each polymer molecule can be regarded as composed of a large number  $x$  of chain segments of equal length. Flory and Huggins assumed that each point on the lattice of coordination number  $z$  could be occupied by a solvent molecule or by a polymer segment. They counted the number of ways of placing  $N_1$  solvent molecules and  $N_2$  polymer molecules, each composed of  $x$  segments, on  $N_1 + xN_2$  sites of the lattice. It was assumed that the polymer chains were flexible, so that  $(i + 1)$ th segment was free to occupy any of the  $z$  sites surrounding that occupied by the  $i$ th segment, the site occupied by the  $(i - 1)$ th segment being excluded. The calculation leads to the evaluation of  $\Delta\Omega$  from which, by use of equation 2.2, Flory obtained.:

$$\Delta S_m = -R\left(n_1 \ln \frac{N_1}{N_1 + xN_2} + n_2 \ln \frac{xN_2}{N_1 + xN_2}\right) \quad 2.3$$

Replacing  $\frac{N_1}{N_1 + xN_2}$  and  $\frac{xN_2}{N_1 + xN_2}$  by  $\phi_1$  and  $\phi_2$ ,

respectively, the volume fractions of solvent and polymer, then:

$$\Delta S_m = -R(n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad 2.4$$

The combinatorial entropy of mixing of two monodisperse polymers with an arbitrary segmental volume  $V^0$  and each consisting of  $N_1$  molecules with  $x_1$  segments, can be obtained by assuming that the segments are occupying  $(N_1x_1 + N_2x_2)$  sites of a three dimensional lattice. The total volume of the mixture is  $(N_1x_1 + N_2x_2) V^0$ . If  $n_1$  and  $n_2$  are the number of moles of polymer 1 and polymer 2 respectively and  $N_A$  is Avagadro's number, then :

$$n_1 N_A = N_1 \quad \text{and} \quad n_2 N_A = N_2 \quad 2.5$$

therefore :

$$\phi_1 = \frac{n_1 x_1}{n_1 x_1 + n_2 x_2} \quad \text{and} \quad \phi_2 = \frac{n_2 x_2}{n_1 x_1 + n_2 x_2} \quad 2.6$$

where  $\phi_1$  is the volume fraction of polymer 1. Assuming that  $i_2$  molecules of polymer 2 are already in the lattice, the fraction of occupied sites is :

$$f_{i_2} = \frac{i_2 x_2}{N_1 x_1 + N_2 x_2} \quad 2.7$$

$$\text{and the fraction of unoccupied sites} = 1 - f_{i_2} \quad 2.8$$

Following the same argument as for polymer solutions, the number of distinguishable ways of placing the  $(i_2 + 1)^{\text{th}}$  segment on the lattice is the product of the following series:

$$v_{i_2} + 1 = \frac{1}{2} (1 - f_{i_2})^{x_2} z(z-1)^{x_2-2} (N_1 x_1 + N_2 x_2) \quad 2.9$$

The factor  $\frac{1}{2}$  being introduced since the two chain ends are indistinguishable. Therefore, the number of ways,  $\Omega_2$ , of adding  $N_2$  polymer molecules in the lattice is :

$$\Omega_2 = \frac{1}{N_2!} \prod_{i_2=0}^{N_2-1} v_{i_2} + 1 \quad 2.10$$

By an analogous procedure the segments of polymer one are introduced into the remaining vacant sites, and one obtains:

$$\Omega_1 = \frac{1}{N_1!} \prod_{i_1=0}^{N_1-1} v_{i_1} + 1 \quad 2.11$$

$$\text{where } v_{i_1} + 1 = \frac{1}{2} (1 - J_{i_1})^{x_1} z(z-1)^{x_1-2} (N_1 x_1 + N_2 x_2) \quad 2.12$$

$$\text{and } J_{i_1} = (N_2 x_2 + i_1 x_1) / (N_1 x_1 + N_2 x_2) \quad 2.13$$

The total number of ways of introducing  $N_1 x_1$  and  $N_2 x_2$  segments into the lattice is :

$$\Omega = \Omega_1 \Omega_2 \quad 2.14$$

From Boltzmann's Law the entropy of mixing is given by :

$$\frac{S_m}{K} = \ln \Omega_1 \Omega_2 = \ln \Omega_1 + \ln \Omega_2 \quad 2.15$$

Where  $K = \frac{R}{N_A}$  Boltzmann Constant and  $N_A$  is Avagadro's number.

Applying Stirling's approximation for the logarithmic factorial gives :

$$\begin{aligned} S_m/K = & -N_2 \ln N_2 + N_2 - N_2 \ln 2 + N_2 \ln z (z-1)^{x_1-2} + N_2 \ln (N_1 x_1 + N_2 x_2) \\ & -N_2 x_2 - N_1 \ln N_1 + N_1 - N_1 \ln 2 + N_1 \ln z (z-1)^{x_1-2} + N_1 \ln (N_1 x_1 + \\ & N_2 x_2) - N_1 x_1 \end{aligned} \quad 2.16$$

The entropy  $S_2$  of polymer 2 in a lattice of  $N_2 x_2$  sites and the entropy

$S_1$  of polymer 1 in a lattice of  $N_1 x_1$  sites can be obtained easily by using  $N_1 = 0$  for the former and  $N_2 = 0$  for the latter, then in order to obtain the change in the entropy of mixing of the mixture the following relation must hold :

$$\frac{\Delta S_m}{K} = \frac{1}{K} (S_m - S_1 - S_2) \quad 2.17$$

therefore,

$$\begin{aligned} \frac{\Delta S_m}{K} &= N_1 \ln (N_1 x_1 + N_2 x_2) + N_2 \ln (N_1 x_1 + N_2 x_2) - N_1 \ln N_1 x_1 \\ &\quad - N_2 \ln N_2 x_2 \end{aligned} \quad 2.18$$

By replacing the number of molecules by the practical unit of mole, the total volume of the mixture by  $(n_1 x_1 + n_2 x_2) V^0$  and the volume fraction of each component from equation 2.6, then as a first approximation for the combinatorial entropy of mixing per mole of mixture equation 2.18 gives :

$$\Delta S_{m, \text{comb.}} = -R (n_1 \ln \phi_1 + n_2 \ln \phi_2) \quad 2.19$$

## 2.12 The Enthalpy Change on Mixing

The enthalpy change on mixing results from the replacement of some of the contacts between like species in the pure components with contacts between unlike species in the mixture. Assuming  $\epsilon_{11}$ ,  $\epsilon_{22}$  and  $\epsilon_{12}$  are the energies associated with these respective pair contacts,  $\Delta \epsilon_{12}$ , the energy change for the formation of an unlike contact pair is given by :

$$\Delta \epsilon_{12} = \frac{1}{2} (\epsilon_{11} + \epsilon_{22}) - \epsilon_{12} \quad 2.20$$

In a polymer-polymer mixture on average, surrounding each segment of polymer 1 in the mixture are  $\frac{(z N_1 x_1)}{(N_1 x_1 + N_2 x_2)}$  segments of polymer 1 and

$(z N_2 x_2 / (N_1 x_1 + N_2 x_2))$  segments of polymer 2. The total energy of pure component before mixing are :

$$H_{\text{pure}} = -\frac{1}{2} \left\{ (N_1 x_1 \epsilon_{11}) + (N_2 x_2 \epsilon_{22}) \right\} \quad 2.21$$

and the total energy of the mixture is :

$$H_m = -\frac{1}{2} \left\{ (z N_1^2 x_1^2 \epsilon_{11}) / (N_1 x_1 + N_2 x_2) \right\} - \left\{ (z N_1 x_1 N_2 x_2 \epsilon_{12}) / (N_1 x_1 + N_2 x_2) \right\} - \frac{1}{2} \left\{ (z N_2^2 x_2^2 \epsilon_{22}) / (N_1 x_1 + N_2 x_2) \right\} \quad 2.22$$

Hence, the enthalpy of mixing is :

$$\Delta H_m = H_m - H_{\text{pure}} \quad 2.23$$

From eq. 2.21, 2.22, 2.23 one gets :

$$\Delta H_m = n_1 x_1 \phi_2 \Delta \epsilon \quad 2.24$$

$$\text{where } \Delta \epsilon = z N_A \left\{ (\epsilon_{11} + \epsilon_{22}) / 2 - \epsilon_{12} \right\} = \chi_{12} RT \quad 2.25$$

$$\text{and } \Delta H_m = RT n_1 x_1 \phi_2 \chi_{12} \quad 2.26$$

where  $\chi_{12}$  is the "interaction parameter".

### 2.13 The Free Energy Change on Mixing

The Gibbs free energy change on mixing is given by equation

$$1.1 \quad (\Delta G_m = \Delta H_m - T \Delta S_m). \quad \text{Substituting the values of } \Delta H_m \text{ and } \Delta S_m$$

from equations 2.26 and 2.19

$$\Delta G_m = RT (n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_1 x_1 \phi_2 \chi_{12}) \quad 2.27$$

In general, for a multicomponent system of monodisperse polymers

$$\Delta G_m = RT \left\{ \left( \sum \phi_i / x_i \right) \ln \phi_i + \sum \phi_i \phi_j \chi_{ij} \right\} \quad 2.28$$

Thus for a three component system,

$$\Delta G_m = RT (n_1 \ln \phi_1 + n_2 \ln \phi_2 + n_3 \ln \phi_3 + n_1 \phi_2 \chi_{12} + n_1 \phi_3 \chi_{13} + n_2 \phi_3 \chi_{23}) \quad 2.29$$

The above equations are not absolutely correct because the contact energy associated with  $\Delta H_m$  may change the non-interacting combinatorial entropy change on mixing. It was shown by Hildebrand<sup>113</sup> that the entropy of mixing expression can be derived without resort to a liquid lattice model assuming similar free volumes for both components. Starting from free-energy of mixing, Longuet-Higgins<sup>114</sup> using classical statistical approach derived the same expression as Flory. The Flory-Huggins lattice theory makes a number of assumptions which are inherent in the above equations.

- (i) A single lattice structure is used for the individual pure components as well as for the mixtures. This is not true for the mixtures because of the stereochemistry of the individual polymers.
- (ii) The volume change on mixing is ignored.
- (iii) Only immediate neighbour interactions are considered by the theory.
- (iv) Only combinatorial entropy contributions are taken into account.
- (v) Contributions due to specific interactions are ignored.

## 2.2 FLORY'S EQUATION OF STATE THEORY

Due to the shortcomings of the classical Flory-Huggins lattice model, Flory and co-workers<sup>5, 6</sup> abandoned the whole concept of a lattice, and characterised each pure component by three equation of state parameters,  $v^*$ ,  $T^*$  and  $P^*$  which may be evaluated from the pure

component data, density, thermal expansion coefficient and thermal pressure coefficient. In addition an interaction term,  $X_{12}$ , associated with a difference in chemical nature between the components was introduced in order to calculate the properties of the mixture. The residual quantities arising from the volume effect on mixing are derived in this theory while the combinatorial parts are borrowed from the lattice model. This theory like other new theories of Patterson and Delmas<sup>115</sup> and Sanchez and Lacombe<sup>116</sup> benefits from the essential assumption of Prigogine et al<sup>117</sup> who divided a chain into "r-segments" and specified the number of external degrees of freedom. Flory's theory uses a partition function which requires a separation of internal and external degrees of freedom. The external degrees of freedom,  $c$ , attributable to a chain of "r-segments" are less than those for a similar small molecule. Thus a segment in a polymer molecule consisting of "r-segments" will only have  $3c$  ( $c < 1$ ) instead of three degrees of freedom. External degrees of freedom are assumed to depend only on intermolecular forces, whereas internal degrees of freedom are associated with intramolecular chemical bond forces.

For a pure liquid, Flory obtained the free energy of mixing ( $\Delta G_m$ ) in terms of an appropriate partition function  $Z$ , because

$$\Delta G_m = kT \ln Z \quad 2.30$$

Thus  $Z$  for pure liquid is given by

$$Z = \Omega e^{-E_0/kT} \quad 2.31$$

where  $\Omega$  is Tonk's partition function for  $N$  non-interacting molecules in a volume  $V$  and  $E_0$  is the mean intermolecular energy of a system per molecule. To obtain  $\Omega$ , Tonk considered a one dimensional system of  $N$  impenetrable, non-interacting particles on a line of length  $L$ .

If  $l^*$  is the hard core length of a particle and  $l = \frac{L}{N}$  then  $l - l^*$  is the free length available to each particle and  $\Omega$  is given by:

$$\Omega = \{ (l - l^*) e \}^N \quad 2.32$$

Flory extended Tonk's partition function in a notation appropriate to three dimensions and this becomes :

$$\Omega = \left[ \gamma^{1/3} \left( v^{1/3} - v^{*1/3} \right) e \right]^{3N} \quad 2.33$$

where  $\gamma = l^{*3}/V$  is a purely geometric factor

$v = \frac{V}{N}$  is the volume per molecule

$V =$  is the total volume

and  $v^* =$  hard-core volume of the molecule.

Equation 2.33 can be transformed into a form suitable for chain molecules by dividing a chain into  $r$ -segments.  $v^*$  then becomes the hard core volume per segment and  $v$  is the volume per segment given by:

$$v = (V/rN) \quad 2.34$$

For chain molecules of  $r$ -segments equation 2.33 becomes:

$$\Omega = \left[ \gamma^{1/3} \left( v^{1/3} - v^{*1/3} \right) e \right]^{3Nr} \quad 2.35$$

substituting (2.35) into (2.31) gives :

$$Z = \Omega_c \left[ \gamma^{1/3} \left( v^{1/3} - v^{*1/3} \right) \right]^{3Nr} e^{-E_0/kT} \quad 2.36$$

where  $\Omega_c$  is a combinatorial factor which connects the number of ways of mixing  $Nr$  segments with each other, as in Flory-Huggins lattice theory. Provided that only nearest-neighbour interactions are important, the mean intermolecular interaction energy :

$$E_0 = (\text{no. of contacts}) \eta/v = - (NrS\eta/2v) \quad 2.37$$

where  $S$  is the number of intermolecular contact sites per segment,  $-\eta/v$  is the average interaction energy per contact and  $N$  is the number of molecules.

The partition function is therefore given by .

$$Z = \Omega_c \left[ \gamma^{1/3} (v^{1/3} - v^{*1/3}) \right]^{3Nrc} e^{NrS\eta / 2vkT} \quad 2.38$$

eq. 2.37 can be expressed in terms of temperature by introducing the reduced volume, temperature and pressure as :

$$\tilde{v} = v/v^*, \quad \tilde{T} = T/T^*, \quad \tilde{P} = P/P^* \quad 2.39$$

where the characteristic hard core parameters  $P^*$ ,  $v^*$  and  $T^*$  satisfy the equation

$$P^* v^* = ckT^* \quad 2.40$$

and

$$\tilde{T} = 2v^*ckT/S\eta \quad 2.41$$

therefore equation 2.40 gives

$$P^* = S\eta / 2v^{*2} \quad 2.42$$

The partition function now becomes :

$$\begin{aligned} Z &= \Omega_c \gamma^{Nrc} \left[ (\tilde{v}/\tilde{v}^*)^{1/3} - \tilde{v}^{*1/3} \right]^{3Nrc} e^{(Nrc/\tilde{v} \tilde{T})} \\ &= \text{constant} \times (\tilde{v}^{1/3} - 1)^{3Nrc} e^{(Nrc/\tilde{v} \tilde{T})} \end{aligned} \quad 2.43$$

the constant being independent of  $v$  and  $T$ .

The pure component equation of state can be derived by differentiating equation 2.43 with respect to the pressure of the system,

$$P = (kT/Nr) \left( \partial \ln z / \partial v \right)_{T, N} \quad 2.44$$

substituting equation 2.39 and 2.40 and solving equation 2.44 gives

$$\tilde{P} = (\tilde{T}/Nrc) \left( \partial \ln Z / \partial \tilde{v} \right)_{\tilde{T}, N} \quad 2.45$$

The resulting equation of state is :

$$\tilde{P}\tilde{v}/\tilde{T} = \tilde{v}^{1/3} / (\tilde{v}^{1/3} - 1) - (1/\tilde{v} \tilde{T}) \quad 2.46$$

At atmospheric pressure  $\bar{P} \approx 0$  therefore

$$\bar{T} = (\bar{v}^{1/3} - 1) \bar{v}^{4/3} \quad 2.47$$

This is the effective equation of state for the pure components and is connected to two easily measureable quantities, the coefficient of thermal expansion  $\alpha$  and thermal pressure  $\gamma$ , defined as

$$\alpha = (1/\bar{v}) (\partial \bar{v} / \partial T)_{P, N} = (\partial \ln \bar{v} / \partial T)_{P, N} \quad 2.48$$

$$\gamma = (\partial P / \partial T)_{\bar{v}, N} \quad 2.49$$

from which it follows

$$\bar{v} = (1 + \alpha T / 3 (1 + \alpha T))^3 \quad 2.50$$

Thus if  $\alpha$  is known, equation 2.50 gives  $\bar{v}$  and equation 2.47 will give  $\bar{T}$ . Differentiation of equation 2.45 followed by substitution from equation 2.39 and 2.47 gives

$$P^* = \gamma \bar{T} \bar{v}^2 \quad 2.51$$

Evaluation of the equation of state parameters in this way enables one to obtain the other parameters such as  $c$  and  $(s\eta/2v)$  (intermolecular energy per segment) etc.

#### The Equation of State for Mixture

The theory can be adapted to binary mixtures by a set of combining rules.

- 1 The core volumes of the pure components are additive; and specification of a segment for each component remains arbitrary. Hence, it is convenient to use segments of the equal size so that  $v_1^* = v_2^* = v^*$ . The segment here means monomer repeat unit.
- 2 The intermolecular energy depends on the surface area of contacts between molecules and/or segments. These assumptions give :

$$N = N_1 + N_2 \quad 2.52$$

$$\bar{r} = (\phi_1/r_1 + \phi_2/r_2)^{-1} \quad 2.53$$

$$S = \phi_1 S_1 + \phi_2 S_2 = (r_1 N_1 S_1 + r_2 N_2 S_2) / \bar{r} N \quad 2.54$$

$$\bar{c} = \phi_1 c_1 + \phi_2 c_2 = (r_1 N_1 c_1 + r_2 N_2 c_2) / \bar{r} N \quad 2.55$$

$\phi_1$  and  $\phi_2$  are redefined as segment fractions instead of the volume fractions which are used in the lattice model, ie.

$$\phi_2 = 1 - \phi_1 = (r_2 N_2 / \bar{r} N) \quad 2.56$$

The molar hard core volume is given by  $V_i^* = r v_i^*$ , thus  $(r_2/r_1) = (V_2^*/V_1^*)$  and we may write segment fractions as

$$\phi_2 = N_2 V_2^* / (N_2 V_2^* + N_1 V_1^*) \quad 2.57$$

$$\text{or} \quad \phi_2 = M_2 v_{Sp,2}^* / (M_2 v_{Sp,2}^* + M_1 v_{Sp,1}^*) \quad 2.58$$

Where  $M_i$  is the mass of component  $i$  and  $v_{Sp,i}^*$  is the hard core volume per gram. From these we get the partition function

$$Z = Z_{comb.} (\gamma v^*)^{\bar{r} N c} (\bar{v}^{1/3} - 1)^{3 \bar{r} N \bar{c}} \frac{e^{E_{0m}/kT}}{e} \quad 2.59$$

where  $Z_{comb.}$  is the combinatorial factor for intermixing the two components.

Provided that only the nearest neighbour contacts are assumed, the energy  $E_0$  of the mixture takes the form of that for a pure component.

$$E_{0m} = (A_{11} \eta_{11} + A_{22} \eta_{22} + A_{12} \eta_{12}) / v \quad 2.60$$

where  $A_{ij}$  is the number of nearest neighbour contents of energy  $\eta_{ij}/v$ .

Assuming random mixing, it follows from eq. 2.37.

$$A_{12} = S_1 r_1 N_1 \Theta_2 = S_2 r_2 N_2 \Theta_1 \quad 2.61$$

$$2 A_{11} + A_{12} = S_1 r_1 N_1 \quad 2.62$$

$$2 A_{22} + A_{12} = S_2 r_2 N_2 \quad 2.63$$

$$\Delta \eta = \eta_{11} + \eta_{22} - 2 \eta_{12} \quad 2.64$$

$\theta_2$  and  $\theta_1$  are site fractions and defined by :

$$\begin{aligned} \theta_2 &= 1 - \theta_1 = S_2 r_2 N_2 / (S_2 r_2 N_2 + S_1 r_1 N_1) \\ &= (S_2/S_1) \phi_2 / \{ \phi_1 + (S_2/S_1) \phi_2 \} \\ &= S \phi_2 / (S \phi_2 + \phi_1) \\ &= S_2 \phi_2 / (S_1 \phi_1 + S_2 \phi_2) \end{aligned} \quad 2.65$$

substitution of these equations into equation 2.60.

$$E_{Om} = -(\bar{S}rN/2v) (\theta_1 \eta_{11} + \theta_2 \eta_{22} - \theta_1 \theta_2 \Delta \eta) \quad 2.66$$

By analogy with equation 2.37 and 2.42, the energy for the pure component mixture can be defined as :

$$- E_{Om}/\bar{r} N = P^* v^* / \bar{v} \quad 2.67$$

Comparison of this equation with 2.66 and 2.42 gives the first characteristic parameter for a mixture :

$$P^* = P_1^* \phi_1 + P_2^* \phi_2 - \phi_1 \theta_2 X_{12} \quad 2.68$$

$$\text{where } X_{12} = \frac{S_1 \Delta \eta}{2 v^{*2}} \quad 2.69$$

and is the interaction term, with dimensions of energy per unit volume and arises from the chemical nature of the components.

Since equation 2.40 is also applicable to the mixture, it follows that the second parameter  $T^*$  is obtained.

$$P^* v^* = \bar{c} k T^* \quad 2.70$$

$$\text{and } T^* = P^* / (\phi_1 P_1^* T_1^{*-1} + \phi_2 P_2^* T_2^{*-1}) \quad 2.71$$

Equations 2.68 and 2.71 show that the reduced parameters,  $\bar{P}$  and  $\bar{T}$ ,

for the mixture are composition dependent. Knowing  $\bar{v}$  for the mixture, equation 2.47 provides  $\bar{v}$ , which is essential in order to specify the binary mixture quantitatively.

### The Enthalpy Change on Mixing

The enthalpy change on mixing is equal to the energy change on mixing at low pressure :

$$\Delta H_m = E_{o_{1,2}} - (E_{o_1} + E_{o_2}) \quad 2.72$$

Where (1, 2) refers to cross terms ( $o_{1,2}$ ) and ( $o_1$ ) and ( $o_2$ ) refer to pure components. Equation 2.72 could be expressed in terms of a subscripted version of equation 2.67 as :

$$\Delta H_m = \bar{r}N\bar{v}^*\{\phi_1 P_1^*/\bar{v}_1 + \phi_2 P_2^*/\bar{v}_2 - P^*/\bar{v}\} \quad 2.73$$

Introducing  $P^*$  from equation 2.68 gives :

$$\begin{aligned} \Delta H_m = \bar{r}N\bar{v}^*\{ & \phi_1 P_1^*(\bar{v}_1^{-1} - \bar{v}^{-1}) + \phi_2 P_2^*(\bar{v}_2^{-1} - \bar{v}^{-1}) \\ & + \phi_1 \phi_2 X_{12}/\bar{v} \} \end{aligned} \quad 2.74$$

Since  $\phi_i \bar{r}N = r_i N_i$  and  $r_i \bar{v}^* = V_i^*$ , Equation 2.74 can be written as :

$$\begin{aligned} \Delta H_m = N_1 P_1^* V_1^* (\bar{v}_1^{-1} - \bar{v}^{-1}) & + N_2 P_2^* V_2^* (\bar{v}_2^{-1} - \bar{v}^{-1}) \\ & + N_1 V_1^* \phi_2 X_{12}/\bar{v} \end{aligned} \quad 2.75$$

The last term in equations 2.74 and 2.75 represent the contributions from contact interactions attributable to a difference between 1, 2 pairs and the mean of 1, 1 and 2, 2 contact pairs. The terms preceding it are the equation of state terms. Their contribution to the enthalpy change on mixing depends on the reduced volume of the mixture. The conventional expression for the heat of mixing is :

$$\Delta H_m = BN_1 \phi_2 \quad 2.76$$

where B is assumed to be constant and independent of concentration.

B is determined from the measured heat of mixing of one polymer with the large excess of the other. The parameter B can be obtained in the limit of infinite dilution by a series of expansion of equation 2.74 in powers of  $\phi_2$ ,

$$B = \lim_{\phi_2 \rightarrow 0} (\Delta H_m / N_1 \phi_2) = \lim_{N_2 \rightarrow 0} (\Delta H_m / N_2) (V_1^* / V_2^*)$$

$$= (V_1^* / \tilde{v}_1) \{ P_2^* [ \tilde{v}_1 / \tilde{v}_2 - 1 - \alpha_1 T (1 - \tilde{T}_2 / \tilde{T}_1) ] + (1 + \alpha_1 T) (S_2 / S_1) X_{12} \}$$
2.77

If  $\tilde{T}_1 > \tilde{T}_2$  the equation of state contribution within the square bracket is negative, and enthalpy change on mixing for a large excess of solvent will be negative unless  $X_{12}$  is large enough to dominate the terms in the brackets. The negative change on mixing will ensure a negative excess volume change on mixing defined as :

$$\frac{\tilde{v}^E}{\tilde{v}} = \frac{\tilde{v} - \tilde{v}^0}{\tilde{v}}, \quad \tilde{v}^0 = \phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2$$
2.78

or

$$\frac{\tilde{v}^E}{\tilde{v}} / \tilde{v}^0 = \frac{\tilde{v}}{\phi_1 \tilde{v}_1 + \phi_2 \tilde{v}_2} - 1$$
2.79

equation 2.79 is related to the composition through  $\tilde{T}$  or  $T^*$ .

Measurement of the volume change on mixing  $\Delta V_m$  and the unmixed  $V^0$  gives  $\tilde{v}^E / \tilde{v}^0 = \Delta V_m / V^0$  directly.

Differentiating the enthalpy equation 2.75 with respect to  $N_i$  will give the partial molar heat of mixing of component i, which in turn is related to the enthalpy interaction parameter  $\chi_H$  :

$$\Delta \bar{H}_1 = \bar{H}_1 - H_1^0 = \left( \partial \Delta H_m / \partial N_1 \right)_{\tilde{T}, \tilde{P}, \tilde{N}_2}$$
2.80

$$= \left( \partial H_m / \partial N_1 \right)_{N_2, \tilde{T}, \tilde{v}} + \left( \partial \Delta H_m / \partial \tilde{v} \right)_{N_2, \tilde{T}, N_1}$$

$$\left( \partial \tilde{v} / \partial N_1 \right)_{N_2, \tilde{T}, \tilde{v}}$$
2.81

The final result is:

$$\Delta \bar{H}_1 = P_1^* V_1^* \left\{ \left( \frac{\tilde{v}_1^{-1}}{\tilde{v}_1} - \frac{\tilde{v}^{-1}}{\tilde{v}} \right) + \left( \alpha T / \tilde{v} \right) \left( \frac{\tilde{T}_1}{T} - \frac{\tilde{T}}{T} \right) / \tilde{T} \right\} + (V_1^* X_{12} / \tilde{v})$$

$$(1 + \alpha T) \theta_2^2 = RT \chi_H \phi_2^2 \quad 2.82$$

Applying similar procedure, the entropy equation gives  $TS_1^{-R}$ , which is similarly related to the entropy interaction parameter,  $\chi_s$ :

$$TS_1^{-R} = -P_1^* V_1^* \left\{ 3T_1 \ln \left( \frac{\tilde{v}_1^{1/3}}{\tilde{v}^{1/3}} - 1 \right) / \left( \frac{\tilde{v}_1^{1/3}}{\tilde{v}^{1/3}} - 1 \right) - \left( \alpha T / \tilde{v} \right) \left( \frac{\tilde{T}_1}{T} - \frac{\tilde{T}}{T} \right) \right\} +$$

$$(V_1^* \theta_2^2 / \tilde{v}) \left( \alpha T X_{12} + T \tilde{v} Q_{12} \right) = -RT \chi_s \phi_2^2 \quad 2.83$$

Where  $Q_{12}$  is the entropy correction parameter.

The partial molar residual chemical potential of component one is therefore :

$$\mu_1^R = P_1^* V_1^* \left\{ 3 \tilde{T}_1 \ln \left( \frac{\tilde{v}_1^{1/3}}{\tilde{v}^{1/3}} - 1 \right) / \left( \frac{\tilde{v}_1^{1/3}}{\tilde{v}^{1/3}} - 1 \right) + \left( \frac{\tilde{v}_1^{-1}}{\tilde{v}^{-1}} - \frac{\tilde{v}^{-1}}{\tilde{v}^{-1}} \right) \right\} +$$

$$V_1^* \theta_2^2 / \tilde{v} (X_{12} - T \tilde{v} Q_{12}) = RT \chi_t \phi_2^2 \quad 2.84$$

Where  $\chi_t$  is the total interaction parameter, ie.  $\chi_t = \chi_H + \chi_S$  2.85

The equations 2.82, 2.83 and 2.84 serve as definitions of  $\chi_H, \chi_S$  and  $\chi_t$  respectively. The value of  $X_{12}$  and  $Q_{12}$  are supposed to be composition independent, whereas the composition dependence of  $\chi_t, \chi_H$  and  $\chi_S$  are given as :

$$\chi_t = \chi_{t,1} + \chi_{t,2} \phi_2 + \chi_{t,3} \phi_2^2 + \dots \quad 2.86$$

$$\chi_H = \chi_{H,1} + \chi_{H,2} \phi_2 + \chi_{H,3} \phi_2^2 + \dots \quad 2.87$$

$$\chi_S = \chi_{S,1} + \chi_{S,2} \phi_2 + \chi_{S,3} \phi_2^2 + \dots \quad 2.88$$

The chemical potential of component one in the mixture is composed of a combinatorial and residual part. The combinatorial part is given by the Flory-Huggins lattice theory. Therefore :

$$(\mu - \mu_1^0) = (\mu_1 - \mu_1^0)_{\text{comb}} + (\mu_1 - \mu_1^0)^R \quad 2.89$$

$$(\mu - \mu_1^0)_{\text{comb}} = RT \{ \ln \phi_1 + (1 - r_1/r_2) \phi_2 \} \quad 2.90$$

On this basis, the chemical potential of component one in the mixture may be written as :

$$(\mu - \mu_1^0)/RT = \ln(1 - \phi_2) + (1 - r_1/r_2) \phi_2 + \{ (\mu - \mu_1^0)^R / RT \} \phi_2^2 \quad 2.91$$

By equating the chemical potential from the two theories one gets a relation between  $X_{12}$  and  $\chi_{12}$  (the Flory-Huggins) interaction parameter.

$$\chi_{12} = \frac{P_1^* V_1^*}{RT \phi_2^2} \left\{ 3 \frac{1}{\phi_1} \ln \left( \frac{\phi_1^{1/3}}{v_1} - 1 \right) / \left( \frac{\phi_1^{1/3}}{v_1} - 1 \right) + \left( \frac{\phi_1^{-1}}{v_1} - \frac{\phi_1^{-1}}{v_1} \right) + X_{12} \phi_2^2 / P_1^* v_1 \right\} \quad 2.92$$

#### The Free Energy Change on Mixing

The free energy of mixing is obtained from the partition function equation 2.43 with the appropriate renotation for the pure components and the solution,

$$Z^J = \Omega_c^J (\gamma v^*)^N \prod_j r_j c_j^{1/3} \left( \frac{\phi_j}{v_j} - 1 \right)^{3 N_j r_j c_j} e^{N_j r_j c_j / v_j T_j} \quad 2.93$$

where  $j = \{1, 2, (1.2)\}$

Thus:

$$\Delta G_m = kT \ln (Z^{(1.2)} / Z^1 Z^2) \quad 2.94$$

The actual mathematical manipulation is not difficult but the subsequent substitutions are complicated, therefore the result is given here :

$$\begin{aligned}
\Delta G_m = & kT (n_1 \ln \phi_1 + n_2 \ln \phi_2) + 3\bar{r} \cdot N v^* \{ (\phi_1 P_1^* \ln (\bar{v}_1^{1/3} - 1) / (\bar{v}^{1/3} - 1)) \\
& + \phi_2 P_2^* \ln (\bar{v}_2^{1/3} - 1) / (\bar{v}^{1/3} - 1) \} + \bar{r} N v^* \{ (\phi_1 P_1^* (1/\bar{v}_1 - 1/\bar{v}) + \phi_2 P_2^* \\
& (1/\bar{v}_1 - 1/\bar{v})) \} + (\phi_1 \theta_2 X_{12} / \bar{v})
\end{aligned} \tag{2.95}$$

Etchinger and Flory<sup>7</sup> derived the above equation for the free energy of mixing. The first term is the combinatorial entropy term just as in equation 2.19 in the Flory Huggins lattice theory. The second term reflects the equation of state contributions and the third represents the enthalpy which contains interaction contributions ( $X_{ij}$ ). The reduced volume  $\bar{v}$  of the mixture contains both the equation of state and interaction contributions. Varying the value of  $\bar{v}$  can cause  $\Delta G_m$  to change from negative to positive and hence influence the state of miscibility under conditions when the interaction term is small.

The "equation of state" theory successfully predicts lower and upper critical solution phase boundaries for polymer mixtures. It can also predict negative heats of mixing, interaction parameters and excess volumes of mixing. Chalal<sup>118</sup> found that the theoretical prediction of the interaction parameter,  $\chi$ , by the equation of state theory was not matched by the experimental findings. The theory assumed that only contact interactions between nearest neighbour segments contribute to  $X_{12}$  and treated  $X_{12}$  as an enthalpy parameter. However, the interactions between the nearest neighbour also affect the entropy. Such an entropy contribution involving contacts of end and midchain segments must depend on the composition of the mixture in the same manner as the interactional energy term. Due to this, discrepancies between the theoretical and experimental values of the interaction parameter  $X_{12}$  were noticed by

Abe and Flory<sup>119</sup>. Flory overcame these by introducing an entropy correction parameter,  $Q_{12}$ , which is represented by its contribution,  $\bar{v}TQ_{12}$ , to the total exchange interaction parameter  $X_{12}$ . The enthalpy interaction parameter is defined as :

$$\bar{X}_{12} = X_{12} - \bar{v}TQ_{12} \quad 2.96$$

To test the equation of state theory McMaster<sup>22</sup> carried out an extensive numerical analysis for polymer blends. The effect of polymer chain length, thermal expansion coefficient, thermal pressure coefficient, exchange energy parameter,  $X_{12}$ , and polydispersity were studied. He found negative or very small positive values of  $X_{12}$ , low molecular weight of one or both polymers and similar thermal expansion coefficients favour compatibility. For non-polar polymers  $X_{12}$  is expected to be positive, therefore in this case miscibility is enhanced by low molecular weights and similar characteristic temperatures. Polymer-polymer mixtures with acceptable component parameters were found to show LCST behaviour. These predictions were found to be true for polystyrene-poly(vinyl methyl ether) and styrene/acrylonitrile-poly(methyl methacrylate) and styrene/acrylonitrile copolymer - polycaprolactone blends<sup>120</sup>. Patterson's<sup>121</sup> simplified treatment of Flory's equation of state theory, however, showed that the specific interactions dominate miscibility and not free volume as pointed out by McMaster.

ten Brinke et al<sup>122</sup> studied the effect of binary parameters on the asymmetrical shape of the spinodal curves and found good agreement between experimental cloud point curves and the calculated spinodals for the PVF<sub>2</sub>/isotactic PEMA system.

## 2.5 OTHER THEORIES

The corresponding equation of state theory.

This theory considers the effect of volume change on mixing on the excess thermodynamic functions. The concept of a division of the degrees of freedom of the chain molecules into external and internal degrees of freedom has been used. Prigogine used the lattice model to calculate  $X_{12}$  while Flory's approach considers the actual molecular structure. In corresponding state theory the pressure effects on  $\chi$  are better represented than Flory's state theory.

Patterson and Delmas<sup>123</sup> by comparing  $\Delta H_m$ ,  $T\Delta S_m$  and  $\Delta V_m$  pointed out that the predictions from Flory's theory were superior to the corresponding state theory. In general this theory does not offer any advantage over Flory's equation of state theory.

Renuncio and Prausnitz<sup>124</sup> introduced a partition function by modifying the energy of interaction to take into account the non-random mixing of two components. Canovas<sup>125</sup> et al have derived the following equation of state by using the non-randomness concept of mixing

$$\frac{\tilde{P}\tilde{V}}{\tilde{T}} = \left( \frac{\tilde{V}^{1/3}}{\tilde{V}} - 1 \right) - \left( \frac{1}{\tilde{T}\tilde{V}} + \frac{A}{\tilde{T}^2\tilde{V}^2} + \frac{c}{\tilde{T}\tilde{V}} \right) \quad 2.97$$

For  $A = c = 0$  this equation reduces to Flory's equation of state.

The third term of above equation is due to the volume dependence of local compositions and the fourth due to the volume dependence of the combinatorial contribution. By using a new partition function it has considered the entropy in the interaction term, and hence removed the  $Q_{12}$ . It, however, assumes  $v_1^* = v_2^* = v^*$  and neglects the effect of internal degrees of freedom. This model<sup>126</sup> has been found

to show good agreement between predicted and experimental values of  $\chi$ , but gave a theoretical prediction of positive volume changes of mixing for

mixtures of PDMS with some solvents compared to experimentally found negative values. This theory is more complicated than Flory's.

Sanchez and Lacombe<sup>116, 127, 128</sup> developed a Lattice-Fluid (LF) theory by allowing the lattice to have some vacant sites and to be compressible. Thus the compressible lattice theory is capable of describing volume changes on mixing as well as LCST and UCST behaviour.  $X_{12}$  is obtained from heat of mixing similar to Flory's theory. This theory shows that miscibility for high molecular weight polymers can only be predicted when the heat of mixing of two components is negative. The main disadvantages of the (LF) theory is the prediction of  $\Delta V^m$  from the close packed densities. Most of the hard core densities,  $\rho^*$ , predicted by the (LF) theory are about 10 percent smaller than their known crystalline densities, most probably due to the packing factor of the lattice. The (LF) theory is basically intended to describe the fluid (disordered) and not crystalline (ordered) state, even though a lattice is used in the formation of the theory.

#### 2.4 APPLICATION OF "EQUATION OF STATE" THEORY TO PHASE SEPARATION

The theoretical phase diagram consists of a binodal curve which is the line connecting the equilibrium compositions of phase separated mixtures and is given by :

$$(\Delta\mu_1)_A = (\Delta\mu_1)_B \quad 2.98$$

$$(\Delta\mu_2)_A = (\Delta\mu_2)_B \quad 2.99$$

where  $(\Delta\mu_i)_A$  and  $(\Delta\mu_i)_B$  are the chemical potentials of component  $i$  at A and B, two compositions on the binodal at a given temperature.

The spinodal curve lies inside the binodal, represents the limits of

metastable compositions, and is given by equation 1.9 ( $\frac{\partial^2(\Delta G)}{\partial \phi^2} = 0$ )

The spinodal and binodal meet at the critical point where equation 1.8

( $\frac{\partial^3(\Delta G)}{\partial \phi^3} = \frac{\partial^2(\Delta G)}{\partial \phi^2} = 0$ ) is satisfied. Polymer composition between

the binodal and the spinodal can separate by nucleation and growth, whereas within the spinodal fluctuations in concentration are stable and phase separation may occur spontaneously by the spinodal decomposition. The observed cloud points curve therefore should lie between the binodal and the spinodal.

#### 2.41 Application of "Equation of State" Theory to Cloud Point

The chemical potential of component one in the mixture is given by<sup>80, 81</sup>

$$\begin{aligned} \Delta \mu_1/RT = & \ln \phi_1 + (1-r_1/r_2) \phi_2 + P_1^* V_1^*/RT \left\{ \frac{\bar{v}_1}{3T_1} \ln (\bar{v}_1^{1/3} - 1) / \right. \\ & \left. (\bar{v}^{1/3} - 1) + 1/\bar{v}_1 - 1/\bar{v} \right\} + P_1^* (\bar{v} - \bar{v}_1) + V_1^* X_{12} \theta_2^2 / RT \bar{v} \\ & - V_1^* Q_{12} \theta_2^2 / R \end{aligned} \quad 2.100$$

Applying the spinodal condition,  $\frac{\partial(\mu_1/RT)}{\partial \phi_2} = 0$ , to this equation yields the equation used in the simulation of the spinodals<sup>80, 81</sup>.

$$\begin{aligned} \frac{\partial(\mu_1/RT)}{\partial \phi_2} = & -1/\phi_1 + (1 - r_1/r_2) + (P_1^* V_1^*/RT_1^*) \left( -D/(\bar{v} - \bar{v}^{2/3}) \right) \\ & + P_1^* V_1^* D/(RT \bar{v}^2) + P V_1^* D/(RT) \\ & + V_1^* X_{12} 2 \theta_2^2 / (RT \bar{v} \phi_1 \phi_2) - V_1^* X_{12} D \theta_2^2 / (RT \bar{v}^2) \\ & - V_1^* Q_{12} 2 \theta_2^2 \phi_1 / (R \phi_1 \phi_2) \end{aligned} \quad 2.101$$

$$\text{where } \frac{\partial \bar{v}}{\partial \phi_2} = D \quad 2.102$$

$$\text{and } \theta_1 = 1 - \theta_2$$

In order to solve this equation, one needs to know the following state parameters of the pure components.

(a) The specific volume,  $v_{sp} = 1/d$

- (b) The thermal expansion coefficient,  $\alpha = 1/v \left( \frac{\partial v}{\partial T} \right)_P$
- (c) The thermal pressure coefficient,  $\gamma = \left( -\frac{\partial P}{\partial T} \right)_v$
- (d) The surface per unit of core volume ratio  $\frac{S_2}{S_1} = S$
- (e) The interaction terms,  $X_{12}$ ,  $Q_{12}$ ,  $\bar{X}_{12}$ .

There are two methods of calculating the parameters in equation 2.101.

Firstly one could calculate the values of  $v_{sp}$ ,  $\alpha$ ,  $\gamma$  at each temperature  $T$  from

$$v_{sp} = v_{sp}^0 e^{c\Delta T} \quad 2.103$$

$$\alpha = \alpha_0 + \alpha_0^2 (7 + \alpha_0 T) \Delta T/3 \quad 2.104$$

$$\gamma = \gamma_0 - \gamma_0 (1 + 2 \alpha_0 T) \Delta T/T \quad 2.105$$

Values of  $\tilde{v}$ ,  $P^*$  and  $\tilde{T}$  can then be found for each component from 2.50, 2.51 and 2.47 and for the mixtures  $P^*$  from 2.68,  $\tilde{v}$  for the mixture is then found from

$$\tilde{v}^{1/3} = 1/(1 - \tilde{T}\tilde{v}) \quad 2.47$$

The alternative procedure is to use equation 2.50, 2.51 and 2.47 to calculate  $\tilde{v}_i$  and  $P_i^*$  at the single temperature, where both  $\alpha$  and  $\gamma$  are known and hence  $\tilde{T}_i$ . One can then calculate  $P^*$  and  $T^*$  for the mixture.  $\tilde{T}$  for any component or the mixture can be found from equation 2.39 at any temperature and hence  $\tilde{v}$ . Both the procedures give the same result except where the ratio of the two components is very large or small and the equations become very sensitive to small errors in  $\tilde{v}$ .

Since normally  $X_{12}$  is found from the heat of mixing,  $Q_{12}$  would have to be used as an adjustable parameter. If  $\bar{X}_{12}$  is known no adjustable parameter is needed.

## 2.42 Application of "Equation of State Theory" to Melting Point Depression

The equation 1.15 used for calculating the interaction parameter  $\chi_{21}$ , from melting point depression data which include a correction for morphological effects has been given by Kwei<sup>88</sup>, and is reproduced here again :

$$\frac{\Delta H_{2u} (T_m^0 - T_m)}{\phi_1 R T_m^0} - \frac{T_m}{m_2} - \frac{\phi_1 T_m}{2m_2} = \frac{C}{R} - \frac{\chi_{12}}{T_m \phi_1} \quad 1.15$$

When the melting point equation 1.15 is reformulated in terms of the equation of state theory Walsh and Rostami<sup>129</sup> wrote equation 2.100 for component 2 ignoring the pressure term and using  $\bar{\chi}_{12}$  as defined in equation 2.96 as :

$$\begin{aligned} \frac{\Delta \mu_2}{RT} = & \ln \phi_2 + \left(1 - \frac{r_2}{r_1}\right) \phi_1 + \frac{P_2^* V_2^*}{RT} \left\{ \tilde{v}_2 \ln \frac{(\tilde{v}_2^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \right. \\ & \left. \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right\} + \frac{V_2^* \bar{\chi}_{12} \phi_1^2 S}{RT \tilde{v}} \end{aligned} \quad 2.106$$

Equation 1.15 would then become

$$\begin{aligned} \frac{H_{2u} (T_m^0 - T_m)}{\phi_1 R T_m^0} - \frac{T}{m_2} \left( \frac{\ln \phi_2}{\phi_1} - \left(1 - \frac{r_2}{r_1}\right) \right) - \frac{P_2^* V_2^*}{R \phi_1 m_2} \left\{ \tilde{v}_2 \ln \frac{(\tilde{v}_2^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \right. \\ \left. \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right\} = \frac{V_2^* \bar{\chi}_{12} \phi_1^2 S}{\phi_1 R \tilde{v} m_2} + \frac{C}{R} \end{aligned} \quad 2.107$$

Where C is the adjustment for morphological contributions identical to that used in equation 1.15. Thus, if, as in the previous case, a plot of the left handside of equation 2.107 is made against  $\phi_1$  one obtains a slope

$$\frac{V_2^* S \bar{X}_{12}}{m_2 R \tilde{v}} \left( \frac{\theta_1}{\phi_1} \right)^2 \approx \frac{V_2^* \bar{X}_{12}}{m_2 R \tilde{v}_2 S} \quad 2.108$$

the approximation being made as  $\phi_1$  tends to zero.

An alternative equation is:

$$\frac{\Delta H_{2u} (T_m^c - T_m)}{\theta_1 R T_m^o} - \frac{T}{m_2} \left\{ \frac{\ln \phi_2}{\theta_1} - \left( 1 - \frac{r_2}{r_1} \right) \frac{\phi_1}{\theta_1} \right\} - \frac{P_2^* V_2^*}{r \phi_1 m_2}$$

$$\left\{ 3T_2 \ln \left( \frac{\tilde{v}_2^{1/3} - 1}{(\tilde{v}^{1/3} - 1)} \right) + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right\} = \frac{V_2^* S \bar{X}_{12}}{R \tilde{v} m_2} \theta_1 + \frac{C'}{R} \quad 2.109$$

Where  $C' = C \left( \frac{\phi_1}{\theta_1} \right)$  can be used which assume morphological contributions contribute as  $\theta_1$  instead of  $\phi_1$  which is an attractive assumption.

Then the slope of a plot against  $\theta_1$  gives

$$\frac{V_2^* S \bar{X}_{12}}{R \tilde{v} m_2} \approx \frac{V_2^* S \bar{X}_{12}}{R \tilde{v}_2 m_2} \quad 2.110$$

which is a closer approximation.

In order to calculate  $\tilde{v}$ , a value of  $X_{12}$  is required for equation 2.68. If  $Q_{12}$  is zero then  $\bar{X}_{12} = X_{12}$  and the equations can be solved iteratively, but if  $Q_{12} \neq 0$  then an exact solution is not possible. Fortunately the value of  $X_{12}$  chosen for equation 2.68 does not have a very large effect on the value of  $\bar{X}_{12}$  calculated. In the systems examined any reasonable value of  $X_{12}$  has an effect on  $\bar{X}_{12}$  which is well within the estimated effects of experimental error.

## CHAPTER 3

### EXPERIMENTAL

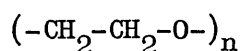
#### 3.1 POLYMERIC MATERIALS

##### Polyethersulphone

Polyethersulphone was kindly supplied by ICI. (Victrex 200P), formula  $(-\text{C}_6\text{H}_4-\text{SO}_2-\text{C}_6\text{H}_4-\text{O})_n$ . It has a quoted reduced viscosity of  $0.41 \text{ cm}^3 \text{ g}^{-1}$  as a 1% solution in dimethylformamide (DMF) at  $25^\circ\text{C}$ , a density of  $1.37 \text{ g cm}^{-3}$  at  $25^\circ\text{C}$ , a refractive index of 1.65 and a  $T_g$  of  $226^\circ\text{C}$ . The quoted number average molecular weight was  $17651 \text{ g mole}^{-1}$  and thus the degree of polymerisation was approximately 76. It was dried in an oven at  $150^\circ\text{C}$  for 5 hours before use.

##### Poly(ethylene oxide) (PEO)

Poly(ethylene oxide) is a liquid or wax at low molecular weight and a crystalline low-melting point solid at higher molecular weight. It is soluble in water and many other solvents. PEO has a repeat unit

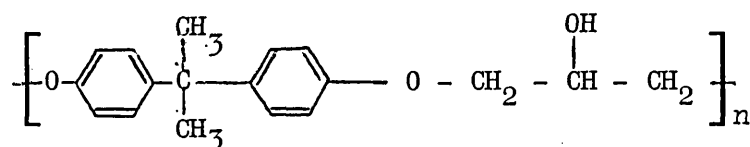


Low molecular weight PEO used in this work, Breox 4000, was obtained from BP Chemicals. It has a quoted molecular weight range of 3500 to  $4500 \text{ g. mole}^{-1}$  a density of  $1.072 \text{ g. cm}^{-3}$  at  $80^\circ\text{C}$  and a refractive index of 1.46 (of a low molecular weight liquid analogue).

Other grades of PEO used were Carbowax M20 (BP Chemicals) with a quoted molecular weight of 15,000 to 20,000  $\text{g. mole}^{-1}$  and a density of  $1.065 \text{ g. cm}^{-3}$ , and Polyox WSRN 80 (Union Carbide) with a quoted molecular weight of 200,000  $\text{g. mole}^{-1}$ .

### Phenoxy Resin (Polyhydroxyether of Bisphenol A)

Phenoxy resins (alternatively referred to as the polyhydroxyethers of bisphenol A) are the condensation reaction products of epichlorhydrin with bisphenol A. The repeat unit is :



Phenoxy resin was supplied by Union Carbide (grade PKHH). It had a quoted reduced viscosity of 0.43 dl/g measured as a 0.2 g/100 ml solution in tetrahydrofuran at 25°C, a specific gravity of 1.18, a refractive index of 1.598, a Tg of 98°C, and a linear thermal expansion coefficient of  $6.12 \times 10^{-5}$  at 25°C. It has a quoted number average molecular weight of approximately 20-25,000 g. mole<sup>-1</sup>.

### Poly(Methyl Acrylate) (PMA) and Poly(Ethyl Acrylate) (PEA)

These were obtained from Polymer Science Inc. The polymers came as 40% w/w solids solutions in toluene. In a few blends the polymer was used directly in this form. In other blends, the toluene was removed by evaporation at 70°C under reduced pressure. Further removal of toluene was carried out in a vacuum oven at 50°C and 1 mm Hg until a constant weight was obtained.

### Poly(Butyl Acrylate)

This was supplied as a solid material by a co-worker, Mr C K Sham, who obtained it from BDH, AR grade as a 40% w/w solution in toluene. He had evaporated it to dryness in a large petri dish and then dried in a vacuum oven at 1 mm Hg at 50°C for two weeks.

Poly(Methyl Methacrylate) (PMMA)

PMMA used was obtained in bead form from Polymer Science Inc. It had a quoted density of  $1.18 \text{ g cm}^{-3}$  and a refractive index of 1.49.

Poly(Propylene Oxide)

Propylan D2002, had a quoted molecular weight of 2000. It was obtained from ICI.

Poly(Tetramethylene Oxide)

Polymeg 1000 was supplied by the Chemicals Division, the Quaker Oats Co Ltd. It has a quoted hydroxyl number of 110.5 indicating a molecular weight of 1000.

Polyphenylene Oxide (PPO)

Poly (2, 6 - dimethyl phenylene oxide) had a quoted viscosity of 0.5 dl/g, a Tg of  $207^{\circ}\text{C}$ , a specific gravity of 1.06 and coefficient of thermal expansion of  $5.2 \times 10^{-5} \text{ cm}^{-1} \text{ }^{\circ}\text{C}^{-1}$ . This was obtained from GEC.

Polycaprolactone(PCL)

This was obtained from Polymer Science Inc. It is partially crystalline polymer with melting point of  $\sim 60^{\circ}\text{C}$  and a Tg of  $-60^{\circ}\text{C}$ .

Poly(Vinyl Acetate) (PVA)

PVA used was obtained from BDH Chemicals Ltd. It had a molecular weight of 45,000, a softening point  $106^{\circ}\text{C}$ , a viscosity at 8.6 weight/volume percent solution in benzene at  $20^{\circ}\text{C}$  of 6 - 8cp, a density of  $1.19 \text{ g cm}^{-3}$ , a refractive index of 1.47, and a Tg of  $28^{\circ}\text{C}$ .

Bis-Phenol A Polycarbonate

This was obtained from Polymer Science Inc. It had a Tg of  $149^{\circ}\text{C}$ , and a specific gravity of 1.2.

Poly(Vinyl Methyl Ether) (PVME)

This was obtained from Polymer Science Inc.

Poly(Ethylene Adipate)

It had a molecular weight of 2000. It was obtained from ICI. It had a quoted Tg of  $-50^{\circ}\text{C}$  and a density of  $1.183 \text{ g.cm}^{-3}$ .

3.2 LOW MOLECULAR WEIGHT ANALOGUES3.21 Tetraglyme

Tetraglyme (Tetraethylene glycol dimethylether) was obtained from BDH. This was chosen as a low molecular weight analogue for poly(ethylene oxide). It had a molecular formula,  $\text{C}_{10} \text{H}_{22} \text{O}_5$ , a quoted molecular mass of  $222.29 \text{ g.mol}^{-1}$ , a boiling point of  $275.8^{\circ}\text{C}$ , and a density of  $1.0132 \text{ g.cm}^{-3}$  at  $20^{\circ}\text{C}$ .

3.22 4-Phenoxy Diphenylsulphone (PDS)<sup>130</sup>

PDS ( $\text{C}_{18} \text{H}_{14} \text{SO}_3$ ) was used as a low molecular weight analogue of polyethersulphone. This was prepared in two stages. First 4-Chlorodiphenylsulphone was prepared from benzene-sulphonyl chloride and chlorobenzene. This was then reacted with phenol in dimethyl sulphoxide to produce PDS.

A three-necked, round bottomed flask, equipped with a stirrer, nitrogen inlet, thermometer, and condenser was charged with 176.6 g. (1 mole) of benzene sulphonyl chloride, 140 g. (1.24 moles) of chlorobenzene and 4.2 g. of ferric chloride (anhydrous). The flask was heated in an oil bath while stirring the contents. Hydrochloric acid (HCl) gas evolution started at about  $70^{\circ}\text{C}$ . The temperature was slowly raised to  $120^{\circ}\text{C}$  as more HCl gas was evolved and then maintained at  $120^{\circ}\text{C}$  for 16 hours. The temperature was then raised to  $140^{\circ}\text{C}$  and

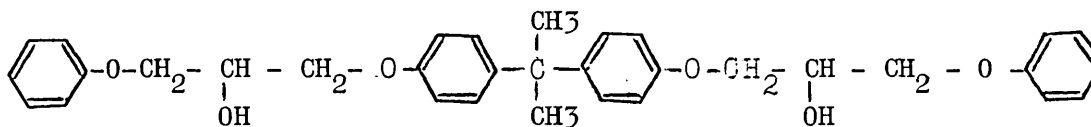
maintained there for a further one hour until no more HCl was evolved. The product was macerated with dilute HCl, filtered, and washed successively with methanolic potassium hydroxide, and water. The product was then distilled at approximately 1 mm Hg vacuum to give a colourless distillate. The product was then twice recrystallised from ethanol, filtered and washed with ethanol. It was allowed to dry at 45°C for 16 hours in a vacuum oven. The melting point of the recrystallised 4-chlorodiphenylsulphone was found to be 88°C (c.f. 87 - 90°C)<sup>130</sup>.

In the second stage sodium hydroxide 4 g. (0.1 mole) was first dissolved in 3.5 cm<sup>3</sup> of water. This was added to a three-necked flask followed by 9.4 g. (0.1 mole) of phenol, 84 g. dimethylsulphoxide and 25 g. (0.1 mole) of 4-chlorodiphenylsulphone. The flask was then heated in an oil bath to 120°C with stirring under a continuous flow of nitrogen. The temperature was then maintained at 120°C for 21 hours. The contents of the flask were cooled and poured into iced water (about 1000 cm<sup>3</sup>) with stirring. The product which precipitated from solution was filtered off and washed with hot water. The product was then recrystallised twice from methanol, filtered, washed with cold methanol and dried. It was found to melt at 88°C compared to a quoted value of 89°C.<sup>130</sup> Elemental analysis gave C-70 percent (69.68), H - 4.4 percent (4.51), S - 10.3 percent (10.32) and O by difference 15.3 percent which corresponded to the (C<sub>18</sub> H<sub>14</sub> O<sub>3</sub>) formula of the product, PDS.

### 3.23 Phenoxy Analogue

A low molecular weight analogue of phenoxy resin was required for the heat of mixing measurements. This was prepared by reacting

phenol with the diglycidyl ether of bisphenol A in the presence of a base catalyst to give a product having the following structure :



This was considered to be close to the repeat unit of phenoxy resin.

The phenoxy analogue was prepared following the method given in reference 131, where in presence of KOH catalyst the epoxy groups exclusively react with hydroxyl groups of phenol.

A three-necked round bottomed flask, equipped with a stirrer, nitrogen inlet, and thermometer was charged with 95 g. of the diglycidyl ether of bisphenol A (Epikote 828, Shell Chemicals Ltd), 47 g. phenol and 0.33 g. potassium hydroxide. This was heated on a steam bath with slow stirring under nitrogen. The temperature was maintained at 100°C for 20 hours with stirring under a continuous flow of nitrogen. After this time the presence of epoxy groups was checked for by infra-red spectroscopy. The absence of epoxy peaks at  $915\text{ cm}^{-1}$  ( $10.96\text{ }\mu$ ) and  $845\text{ cm}^{-1}$  ( $11.6\text{ }\mu$ ) confirmed that the epoxy groups had reacted with the hydroxy groups of the phenol.

### 3.3 PREPARATION OF BLENDS

There are three main methods of preparing homogeneous polymer blends, by mixing in the melt, by mixing in solution in a common solvent followed by evaporation or precipitation, and by in-situ polymerisation. Melt mixing would have problems of phase separation and thermal stability on heating. In-situ polymerisation has only been used in the past by the addition of polymerisation of double bond compound in the presence of another polymer. Mixing in a common solvent followed by evaporation

or precipitation is the commonest method used in the preparation of blends. In this case two phase structures can be formed when blends of miscible polymers are prepared. A two phase region can exist in the polymer/polymer/solvent quasi three component phase diagram which produces this effect. It is therefore not surprising to see conflicting evidence of miscibility when different solvents are used.

### 3.31 Preparation of PES/PEO Blends

Melt mixing would not seem appropriate for PES/PEO blends due to the high Tg of PES, the poor thermal stability of PEO and the known phase separation on heating. In the patent which had suggested that homogeneous blends could be prepared under some conditions<sup>108</sup>, a mixed solvent system was used. Because of the complications involved in characterising and understanding a mixed solvent system most of the blends were prepared using two separate solvents which were capable of dissolving both polymers, cyclohexanone and dimethylformamide.

Mixtures in cyclohexanone were prepared by dissolving PES in cyclohexanone at 80°C to form a 20 w/w percent solution. Various weights of PEO were added to the solution and the mixture stirred for 10 minutes at 80°C. Solutions prepared in this way, with a wide range of compositions, were put into graduated cylinders, sealed, and placed in a water bath at 95°C. Phase separation was observed in some of the solutions. The separate phases were analysed using NMR (220 MHz).

Blend compositions were prepared by pouring the solutions into glass petri dishes and removing the solvent by evaporation in a vacuum oven until constant weight was obtained. Some blends were prepared by evaporation at 95°C and others at 70°C. The absence of solvent was checked by infra-red spectroscopy by observing the absence of the

carbonyl absorption band at about  $1700\text{ cm}^{-1}$ .

Mixtures in dimethylformamide (DMF) were prepared by dissolving PES at room temperature to form a 20 w/w percent solution. PEO (molecular weight 4000) was also dissolved in DMF to form a 20 w/w percent solution by warming to  $30^{\circ}\text{C}$  and stirring. Mixtures at various compositions were prepared by mixing the two solutions. All mixtures were clear. Blends were prepared by evaporation of solvent from the mixed solutions in petri dishes at  $50^{\circ}\text{C}$  in a vacuum oven. The samples were dried to constant weight and infra-red analysis used to check the absence of solvent. Blends could also be prepared by precipitating the solutions by stirring while pouring into petroleum ether ( $60\text{--}80^{\circ}\text{C}$  bp). Samples could then be pressed to produce samples suitable for characterisation.

Blends up to 10/90 PES/PEO composition could also be prepared by dissolving PES in molten PEO (molecular weight 4000) at  $70^{\circ}\text{C}$  by prolonged stirring for 10 - 12 hours. These blends were used for melting point depression studies.

### 3.32 Preparation of PES/Phenoxy Blends

Mixtures in DMF were prepared by dissolving PES and phenoxy both separately at room temperature to form 10% w/w solutions. Blends of various compositions were prepared by mixing the two solutions in the desired proportions. All mixed solutions were clear. Approximately 25 mls of the mixtures were poured into petri dishes and dried in a vacuum oven at  $40^{\circ}\text{C}$ . Samples were dried to constant weight. The absence of solvent was checked by infra-red analysis. Films containing more than 60 w/w percent phenoxy resins were slightly hazy, possibly because of a solvent effect. Due to this haziness, blends of PES and phenoxy resins were prepared, in the same way as above, in dimethyl

sulphoxide (DMSO) and N-methyl-2-pyrrolidone (NMP) as solvents.

The absence of solvent was checked by constant weight as infra-red spectra would have been difficult to resolve. These blends were found to be clear at all compositions. Blends from DMSO were eventually used in all the tests.

### 3.33 Preparation of PES blends with Polymers other than PEO and Phenoxy Resins

In general polymers other than PEO and phenoxy resins used in this work were dissolved in dimethylformamide (DMF) to give 10 w/w percent solution. Blend compositions of 80/20, 50/50 and 20/80 PES/polymer were prepared by mixing a 10 w/w percent PES solution with a 10 w/w percent solution of the other polymer. The mixtures were then dried at 40°C in a vacuum oven as before. Blends were judged as miscible if they were optically clear. The results of polymers examined in this way are given in Table 3.1.

Polycarbonate, poly(ethyleneterephthalate) and poly(phenylene oxide) (PPO) did not dissolve in DMF. Polycarbonate and poly(phenylene oxide) solutions in chloroform were mixed with a 10 w/w percent solution of PES in chloroform. On mixing, these solutions gave cloudy precipitates and hence the polymers were considered immiscible. The melt mixing of these polymers was not tried because the processing equipment (roll mill) was not suitable for high temperature mixing.

Table 3.1 PES BLENDS WITH POLYMERS OTHER THAN PEO AND PHENOXY

| Other polymer used                | Solvent         | Optical Clarity                                                       | Inference  |
|-----------------------------------|-----------------|-----------------------------------------------------------------------|------------|
| Poly(methyl acrylate)             | DMF             | Dried film - opaque                                                   | immiscible |
| Poly(ethyl acrylate)              | DMF             | Mixture solutions<br>clear<br>Dried film - opaque                     | immiscible |
| Poly(methyl methacrylate)         | DMF             | Mixture solutions<br>clear<br>Dried film - opaque                     | immiscible |
| Poly(ethylene adipate)            | DMF             | Mixture solutions<br>clear<br>Dried film - opaque                     | immiscible |
| Poly(propylene oxide)             | DMF             | Mixture solutions<br>clear<br>Dried film - cloudy                     | immiscible |
| Poly(tetramethylene glycol)       | DMF             | Mixture solutions<br>clear<br>Dried film - cloudy                     | immiscible |
| Polycaprolactone                  | DMF             | Mixture solution<br>clear<br>Dried film - cloudy                      | immiscible |
| Poly(vinyl acetate)               | DMF             | Mixture solutions<br>cloudy<br>Dried film - cloudy                    | immiscible |
| Poly(vinyl methyl ether)          | DMF             | Solutions slightly<br>cloudy<br>Dried film separates<br>in two layers | immiscible |
| Poly phenylene oxide              | Chloro-<br>form | Solutions and dried<br>film - cloudy                                  | immiscible |
| Polycarbonate of bis-<br>phenol A | Chloro-<br>form | Solutions and dried<br>film - cloudy                                  | immiscible |

### 3.4 METHODS OF ESTABLISHING MISCIBILITY AND CLOUD POINTS

There are many different methods of establishing the miscibility of two polymers, for example, by the presence of a single glass transition, using mechanical, thermal or dielectric methods, by the observation of optical clarity, by various scattering methods or by the direct observation of the phase structure using visible or electron microscopy. The same techniques can also be used to observe the phase separation which may take place on heating. All the methods can give misleading information in some cases and therefore more than one method are used to confirm the miscibility and phase separation phenomenon.

#### 3.41 Optical Clarity

First the films were assessed for optical clarity. This is the first indication of miscibility but not a sufficient proof of homogeneity.

#### 3.42 Dynamic Mechanical Analysis<sup>132</sup>

In the glassy state, large scale molecular motion is "frozen-in". At the  $T_g$ , the onset of molecular motion characteristic of the rubber state begins to take place. The mechanical responses of such long chain molecules are viscoelastic. They are time dependent and described by stress-relaxation and creep. Stress-relaxation is defined as the decrease in the force (stress) required to sustain the deformation under constant strain. Creep responds to progressive increase in strain over a long period under a constant stress.

If a sinusoidal strain  $\epsilon$  is applied to a viscoelastic material at a frequency  $\omega$  and with a small amplitude, the stress,  $\sigma$ , also varies sinusoidally but is out of phase with the strain by a phase angle  $\delta$ , as shown in Figure 3.1.

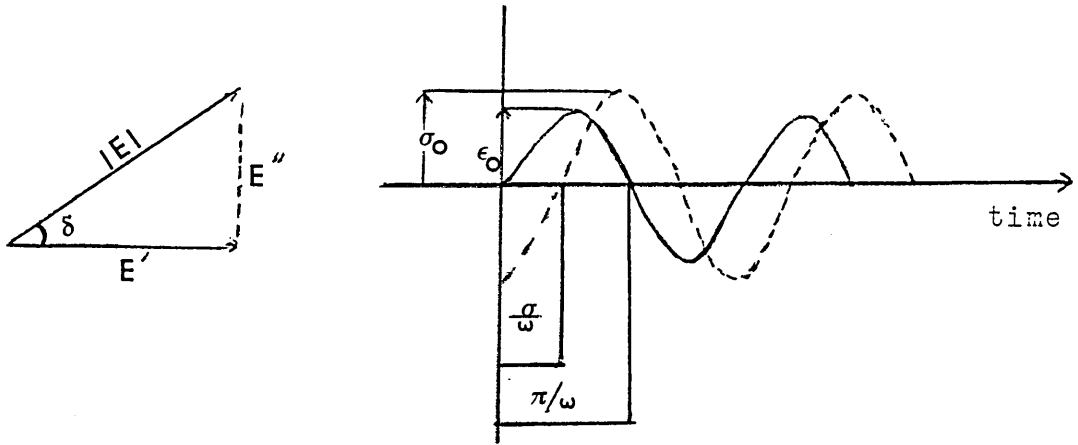


Figure 3.1 Schematic relation between various parameters in dynamic mechanical relaxation measurements  $\epsilon_0$  is the input strain and  $\sigma_0$  the output stress.

A phase lag results from the time necessary for molecular rearrangements which are associated with the relaxation. The stress,  $\sigma$ , and strain,  $\epsilon$ , can be expressed as follows :

$$\sigma = \sigma_0 \sin (\omega t + \delta) , \quad \epsilon = \epsilon_0 \sin \omega t \quad 3.1$$

where  $\omega$  is the angular frequency and  $\delta$  is the phase angle,  $\epsilon_0$  and  $\sigma_0$  represent maximum stress and strain respectively. Expanding  $\sigma$  gives :

$$\sigma = \sigma_0 \sin \omega t \cos \delta + \sigma_0 \cos \omega t \sin \delta \quad 3.2$$

Hence stress can be resolved into two components,  $\sigma_0 \cos \delta$  which is in-phase with the strain and is related to the stored elastic energy, and  $\sigma_0 \sin \delta$ , which is out of phase. Since modulus is defined as stress/strain, when these are divided by the strain, the modulus can be separated into in phase (real) and out of phase (imaginary) components, ie :

$$E' = \frac{\sigma_0}{\epsilon_0} \cos \delta \quad \text{and} \quad E'' = \frac{\sigma_0}{\epsilon_0} \sin \delta \quad 3.3$$

where  $E'$  is the storage modulus and  $E''$  is the loss modulus. The loss of energy per cycle or damping in the system, can be measured from the "loss tangent"  $\tan \delta$  defined as :

$$\tan \delta = \frac{E''}{E'} \quad 3.4$$

A maximum in  $\tan \delta$  marks the onset of main chain segmental mobility corresponding to the glass transition.

Dynamic mechanical measurements were used to confirm the phase structure of the blends. These were carried out using a Rheovibron viscoelastometer (Model DDV-II, Toyo measuring Instrument Co Ltd). A strip of the sample (20 x 5 x 0.3 mm) was subjected to an imposed oscillatory frequency of 11 Hz. A temperature range of 20 to 200°C was scanned at a 2°C/minute heating rate. A plot of loss tangent  $\delta$  against temperature was constructed.

### 3.43 Differential Scanning Calorimetry (DSC)

The blends were examined by differential scanning calorimetry (Perkin-Elmer, DSC-1) in order to establish their glass transition ( $T_g$ ) and melting ( $T_m$ ) temperatures. Sample weights were about 10 mg. A nitrogen flow was maintained through the sample chamber.

An empty sample pan was used as a reference. The samples were scanned from 50 to 350°C. The T<sub>g</sub> was taken to be the point of intersection of the extrapolated low temperature base line with the line of maximum slope encountered during the shift. T<sub>m</sub> values were recorded at the beginning of the melting curve. Crystallisation points of the blends containing crystalline components were determined from the beginning of the crystallisation exotherm of the DSC curve.

Other measurements were made using a Du Pont, 990 thermal analyser with a DSC cell at a sensitivity of 0.2 m.cal.sec<sup>-1</sup> and a heating rate of 10°C min<sup>-1</sup>. The heat flow difference between ~ 10 mg. of a sample in an aluminium pan and similar empty pan was recorded as before.

#### 3.44 Optical Microscopy

An optical microscope (Carl Zeiss, Jena Ltd) fitted with a hot stage was used to determine cloud points and study the change in phase structure on heating and cooling. A heating or cooling rate of 2°C/minute was used.

A microscope (Olympus BHB) was used to study the morphology of a thin sample before and after the phase separation. The phase separated sample was prepared by heating above the phase separation temperature prior to quenching in liquid nitrogen.

#### 3.45 Electron Microscopy

This technique and its application to polymers have been described by Rabek<sup>133</sup> and Collins et al<sup>134</sup>. Great care is needed in the preparation of the specimen for electron microscopy. An ultra-microtome (LKB Sweden), was used. A glass knife was freshly prepared for each sectioning, using a LKB knife-maker. Most of the sections for this work were cut at ambient temperature as the T<sub>g</sub> of the samples

were above room temperature. Ultra thin sections were made by setting the specimen advance control to 700 - 1000<sup>0</sup>A which causes the specimen mounting arm to extend by small increments due to resistance heating. Sections were floated on water and collected on a copper grid. The grids were left to dry before putting in the specimen chamber of the microscope. A JEM, 100B, Transmission Electron Microscope with 3.5 A<sup>0</sup> resolution was used to investigate the structure of the blends which were phase separated above the cloud point and chilled in liquid nitrogen. A few sections of the blends which were not phase separated were also examined for comparison.

### 3.46 Light Scattering Turbidimetry

A transparent homogeneous mixture can be brought to a cloudy turbid state by a variation of the temperature, pressure, or composition of the mixture. The cloud point corresponds to this transition point - the point of initial phase separation. The cloud point is usually measured by light scattering turbidimetry<sup>82</sup>. Stein<sup>135</sup> and Olabisi<sup>47</sup> have described the basis of light scattering.

Turbidity measurements have been used in studying the cloud point curves of solutions by Cowie and Saeki<sup>33</sup>, of oligomers by Chong<sup>82</sup> and of solid mixture by Reich and Cohen<sup>136</sup>. A light scattering instrument specially designed by Chong<sup>82</sup>, has been used for the determination of cloud points. The films were supported between two pieces of glass in a sample holder located in a thermostatically controlled aluminium block. Light from a 12 volt tungsten lamp was focussed on to the sample and the intensity of light scattered at 45<sup>0</sup> was measured using a photodiode. The temperature of the block could be altered at a controlled rate. A data logger is used to take readings at periodic intervals of the temperature and intensities. A plot of scattered

light intensity against temperature was obtained. The temperature of first deflection from a straight line was taken as the cloud point temperature. The experiment was repeated for the whole range of compositions to obtain the cloud point curve.

### 3.5 METHODS OF STUDYING THE THERMODYNAMICS

#### 3.51 Heats of Mixing

The heats of mixing of various mixtures of low molecular weight analogues were measured using a modified NBS batch type calorimeter. The microcalorimeter is fully described by Chong<sup>82</sup>. The instrument has an accuracy of  $\pm 0.02 \text{ J.g}^{-1}$  as determined by an acid-base reaction, however, the viscosity of the analogues used in this work made mixing difficult and it is estimated that an error of  $\pm 0.1 \text{ J.g}^{-1}$  may be more appropriate. The machine was calibrated electrically using a 100 ohm resistor immersed in a 50/50 w/w % mixture of the system under investigation. The stability of the temperature of the instrument was within  $0.001^\circ\text{C}$ . The total weight of the two components which were mixed was about 1.5 grams. The samples were kept at the temperature of the experiment for at least 3 hours before starting mixing. The heats of mixing of each mixture were measured at least three times and an average taken. Because of the high melting point ( $89^\circ\text{C}$ ) of one of the analogues (PDS) and the limitations of the microcalorimeter, the heat of mixing measurements were possible only at one temperature,  $90^\circ\text{C}$ .

Heats of mixing of 4-phenoxydiphenyl sulphone (PDS) an analogue of PES with tetraglyme, an analogue of PEO and with a phenoxy resin analogue, were measured in this work. The phenoxy resin analogue was very viscous and therefore errors in the heat of mixing measurements may be even larger than  $\pm 0.1 \text{ J g}^{-1}$  in this case.

### 3.52 Melting Point Depression

The crystallisation and melting of PEO in the PES:PEO blends were studied by DSC (Perkin Elmer Model 1) and by light scattering turbidimetry. Both of the techniques, in both heating and cooling, have problems in determining the equilibrium thermodynamic melting point. In a DSC determination, samples were heated at least 10°C above the melting endotherm and kept at this temperature for 15 minutes before cooling. The samples were cooled at the minimum rate available on the instrument, (1 K min<sup>-1</sup>). The beginning of the crystallisation exotherm was taken as the crystallisation point.

In light scattering turbidimetry, a film of the PES/PEO blend was put between glass plates as described earlier in section 3.46. The samples were heated or cooled at a rate of 0.1 K per minute. The change in intensity of light was plotted against temperature. The temperature of first deflection from straight line during heating or cooling was taken as the melting or crystallisation point. Because of the slower rate of temperature change turbidimetry is preferred. The PES/PEO system produces large scale heterogeneity and a very sharp increase in turbidity on cooling into the crystalline region. The actual melting points and crystallisation points vary markedly with the method of measurement and the rate of temperature change, but the melting point depressions do not vary very much and are within experimental error (which is quite large) in most cases.

### 3.53 Density Measurements

The densities of the low molecular analogues of PES and phenoxy resins and of low molecular weight PEO 4000, were measured using a pycnometer. All the density measurements were done at high

temperatures, The density of PEO 4000 was determined at 60 and 80°C, that of PDS at 100°C, that of tetraglyme at 90°C and that of the phenoxy analogue at 70°C and 99°C. High temperatures were necessary because the melting point of PDS was 89°C, that of PEO about 56°C and because the phenoxy analogue was very viscous at ambient temperatures.

### 3.6 SORPTION OF WATER VAPOUR

108

As mentioned earlier it has been suggested that at certain compositions (80/20 and 90/10 PES/PEO) blends of PES with PEO absorb less water than pure PES. These measurements were done by soaking thin films of blends in water. Accurate measurements of water vapour sorption in PES/PEO blends were, therefore, required.

When the uptake of penetrant is greater than 0.2% of the dry weight of the polymer, a quartz spiral balance of the McBain and Bakr<sup>137</sup> type can be used. The working principle is simple. The uptake of the vapour is measured by the extension of the spring which is measured by a cathetometer. The apparatus is illustrated in Figure 3.2. A thin sheet of sample (P) was suspended, by a small piece of copper wire, from the quartz spiral (S) (Thermal Syndicate Ltd). The spiral was suspended inside a vertical, cylindrical glass envelope (C) immersed in a water bath (W) which was thermostated to  $\pm 0.05^\circ\text{C}$ . The bath had two plate glass sides so that the spring extension could be measured using a cathetometer. The spring was calibrated at atmospheric pressure using known weights.

The vapour pressure in the system was measured with a strain-gauge pressure transducer (T) (0 - 15 psi absolute, obtained from Bell and Howell Ltd), operated from a stable 10 volts DC supply. The voltage signal from the transducer was measured by a sensitive potentiometer and was directly proportional to

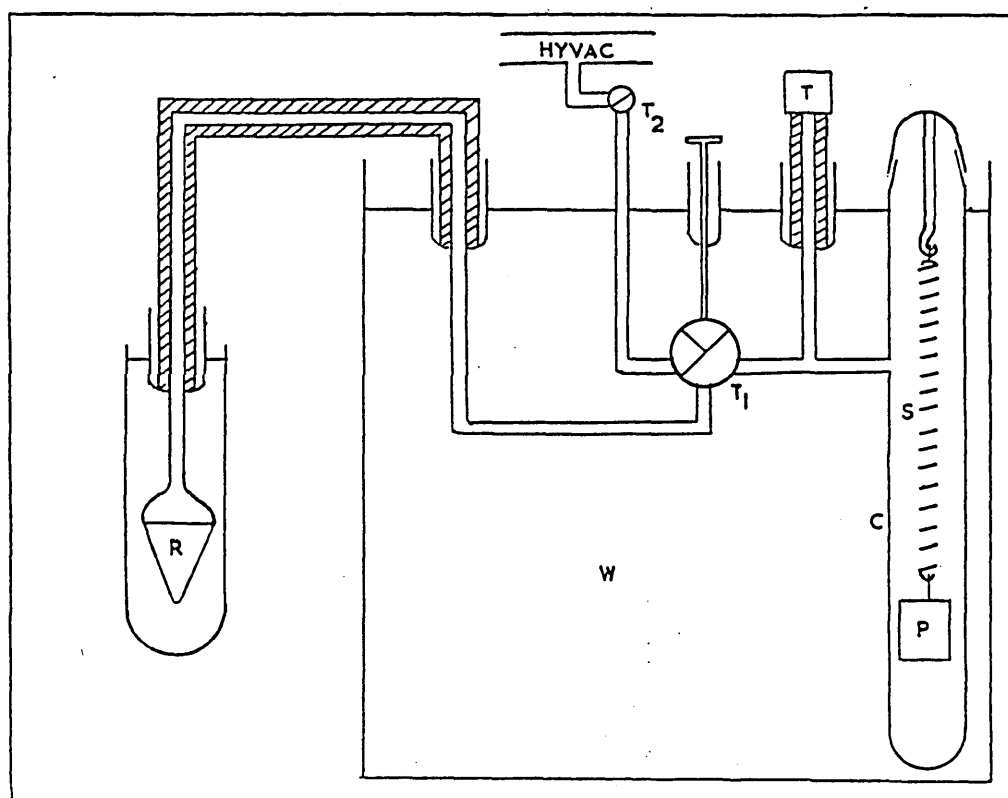


Figure 3.2 The sorption apparatus for relatively large uptakes of vapour.

the applied pressure. The transducer was calibrated against a mercury manometer. The pressures were measured to within about  $\pm 0.02$  cm.Hg.

A three-way tap ( $T_1$ ) connected the balance system either to the hyvac line via ( $T_2$ ) or to a liquid reservoir (R). The glass tubing connecting (R) with (W) and (T) with (W) was jacketed with heating tape to prevent condensation of vapour.

The essential features of the pumping system are shown in Figure 3.3. A one stage mercury diffusion pump (B) backed by an Edwards two-stage rotary oil pump (A) produced an ultimate vacuum of about  $10^{-6}$  mm. Hg. An Edwards Pirani gauge was attached to the "hyvac" line as a check on leak and outgassing rates.

Distilled water was introduced into a pear shaped flask and connected to vacuum for a short while to evacuate air from the system. The water was then frozen slowly with liquid nitrogen and the frozen ice pumped for about an hour until most of the trapped air had been removed. The ice was finally allowed to thaw, being occasionally connected to vacuum to remove any air released. The procedure was repeated four or five times and this was considered sufficient to remove all the air present.

The system was outgassed until the length of the quartz spring was constant; a vacuum of  $\sim 10^{-5}$  mm.Hg was obtained and there was no drop in vacuum after closing the system. After thermal equilibrium was established at the required temperature, the initial length of the spring and the transducer output were determined. A small amount of water vapour was then introduced to the polymer blend sample and spring section by momentarily opening the three-way valve.

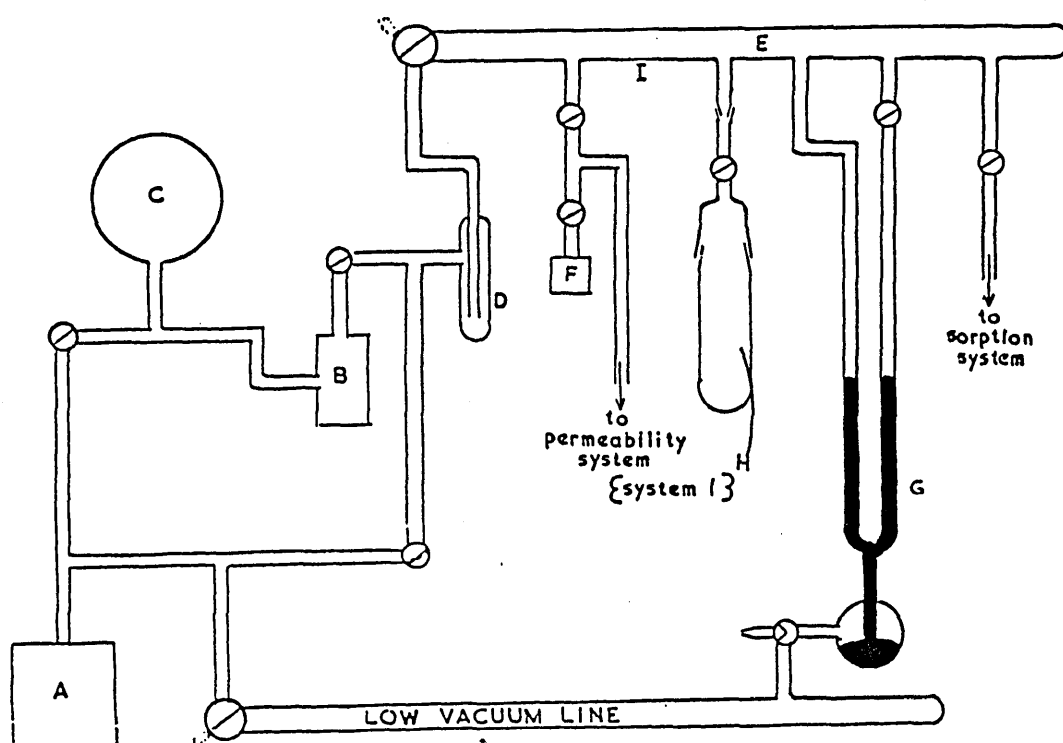


Figure 3.3 The pumping system for the sorption apparatus.

The increase of the length of spring was measured at one minute intervals for up to 30 minutes and then every hour. The sample was then left to equilibrate. A constant length of spring and a constant reading of the pressure transducer indicated that equilibrium had been attained. Further charges of vapour were admitted and the procedure repeated.

The percent sorption was calculated from the extension of the spring at each vapour pressure from :

$$\% \text{ sorption} = \frac{\Delta h \times 100}{K \times W} \quad 3.5$$

where  $\Delta h$  is the extension of the spring in cm,  $K$  is the sensitivity of the spring in  $\text{cm g}^{-1}$  and  $W$  is the initial weight of the sample in g.

The amount of water vapour absorbed is also calculated from the extension of the spring using

$$Q = \frac{\Delta h \times 2.24 \times 10^4}{K \times M} \quad 3.6$$

where  $Q$  is the amount of water vapour sorbed in cc (STP) and  $M$  is the molecular weight of water. The correction for buoyancy being negligible is not taken into account.

The concentration  $C$  ( $\text{cc (STP) cm}^{-3}$ ) of sorbed water was obtained from  $C = Q/V$  3.7

where  $V$  is volume of polymer samples in  $\text{cm}^3$ .

The solubility coefficient,  $\sigma$  ( $\text{cc (STP) cm}^{-3} (\text{cm Hg})^{-1}$ )

was given by  $\sigma = \frac{C}{p}$  3.8

where  $p$  is the surrounding vapour pressures in cm Hg.

The spiral extensions  $E_t$  (cm) at time  $t$  (secs) were calculated and  $\frac{E_t}{E_{\infty}}$  plotted against  $(\frac{t}{l})^{1/2}$  for sorption, where  $l$  (cm) was the sample thickness measured with a micrometer and  $E_{\infty}$  (cm) the equilibrium extension.

The mean diffusion coefficients  $\bar{D}$  ( $\text{cm}^2 \text{sec}^{-1}$ ) were obtained from the 'half time' expression<sup>158</sup>:

$$\bar{D} = \frac{.049 l^2}{t_{1/2}} \quad 3.9$$

The permeability coefficient  $P$ , the amount of penetrant (water vapour) passing through the membrane of unit area and unit thickness under unit pressure difference, is calculated from the diffusion and solubility coefficients.

$$P = \bar{D} \sigma \quad 3.10$$

The error in sensitivity of the spring was within  $\pm 1$  percent. The largest errors were in the pressure measurements. This was due to the sensitivity of the pressure transducer used in this work (0 - 15 psi) and the temperature of measurements. Most of the measurements were done at  $30^\circ\text{C}$  and at this temperature the maximum saturation vapour pressure of water is approximately 3cm. Therefore with the transducer used the errors even at saturation vapour pressure could be 7 - 8 percent. At lower pressure, the errors are much higher. The errors involved in weighing of the samples and through fluctuation of temperature were considered as negligible.

## CHAPTER 4

### RESULTS AND INTERPRETATION

#### 4.1 BLEND PREPARATION

In the literature<sup>108</sup> it was reported that a mixture of N-methyl-2-pyrrolidone (NMP)/dichloromethane was used for dissolving PES/PEO blends. In this work we preferred to use single component solvents because of the complications involved in characterising and understanding a mixed solvent system. In the early stages of this work PES and PEO were separately dissolved in dichloromethane. Both the polymers gave clear solutions. When these solutions were mixed together a white precipitate formed. This implied that the affinity of the solvent for the two polymers is not the same or that polymer-polymer affinity is greater than polymer-solvent affinity. This effect will be discussed further in Chapter 5. Results similar to those obtained using dichloromethane were obtained when other chlorinated solvents which dissolved both the polymers such as 1,1,2 trichloroethane and chloroform were used. It was found that PEO was not soluble in N-methyl-2-pyrrolidone therefore this could not be used. The two single component solvents DMF and cyclohexanone which dissolved both PES and PEO and did not cause phase separation, were used for this work.

#### 4.11 Polymer-Polymer Solvent Mixtures

When cyclohexanone was used as a common solvent, all the three component mixtures prepared at 80°C, were clear. Many of

the solutions, however, separated on heating to between 82 and 135°C. Clear solutions in cyclohexanone were heated at 95°C for 100 hours in sealed graduated tubes, the layers separated and the compositions of the separated phases analysed at 100°C by NMR (220 MHz) by measuring the peak areas for the mixtures. PES peaks appeared at 7.9 – 8.2 and 8.7 – 8.9δ, PEO at 4.3 – 4.4 δ and cyclohexanone at 2.3 – 2.7 and 3 – 3.25δ. Compositions were calculated as follows :-

$$x = \frac{\text{Peak area due to total PES peaks} \times \text{molecular weight of the PES repeat unit}}{\text{number of protons}}$$

$$x = \frac{\text{Peak area of total PES peaks} \times 232}{8}$$

$$y = \frac{\text{Peak area PEO peaks} \times 44}{4}$$

$$z = \frac{\text{Peak area of total cyclohexanone peaks} \times 98}{10}$$

$$\therefore \text{ weight percent of PES in the mixture} = \frac{x}{x + y + z} \times 100$$

The percentage composition of PEO and cyclohexanone were obtained in the same way as for PES. Typical NMR spectrograph obtained for a sample of 32/11/57 PES/PEO/cyclohexanone is shown in Figure 4.1. The phase compositions thus found are given in Table 4.1. and the resultant three component phase diagram is shown in Figure 4.2. Compositions outside the two phase region remained clear.

Other temperatures and solvents were not studied in such detail, but a few observations were made. Solutions in DMF were all homogeneous at 50°C as used in preparing blends. Compositions of 90/10 to 10/90 w/w percent PES/PEO in DMF showed phase

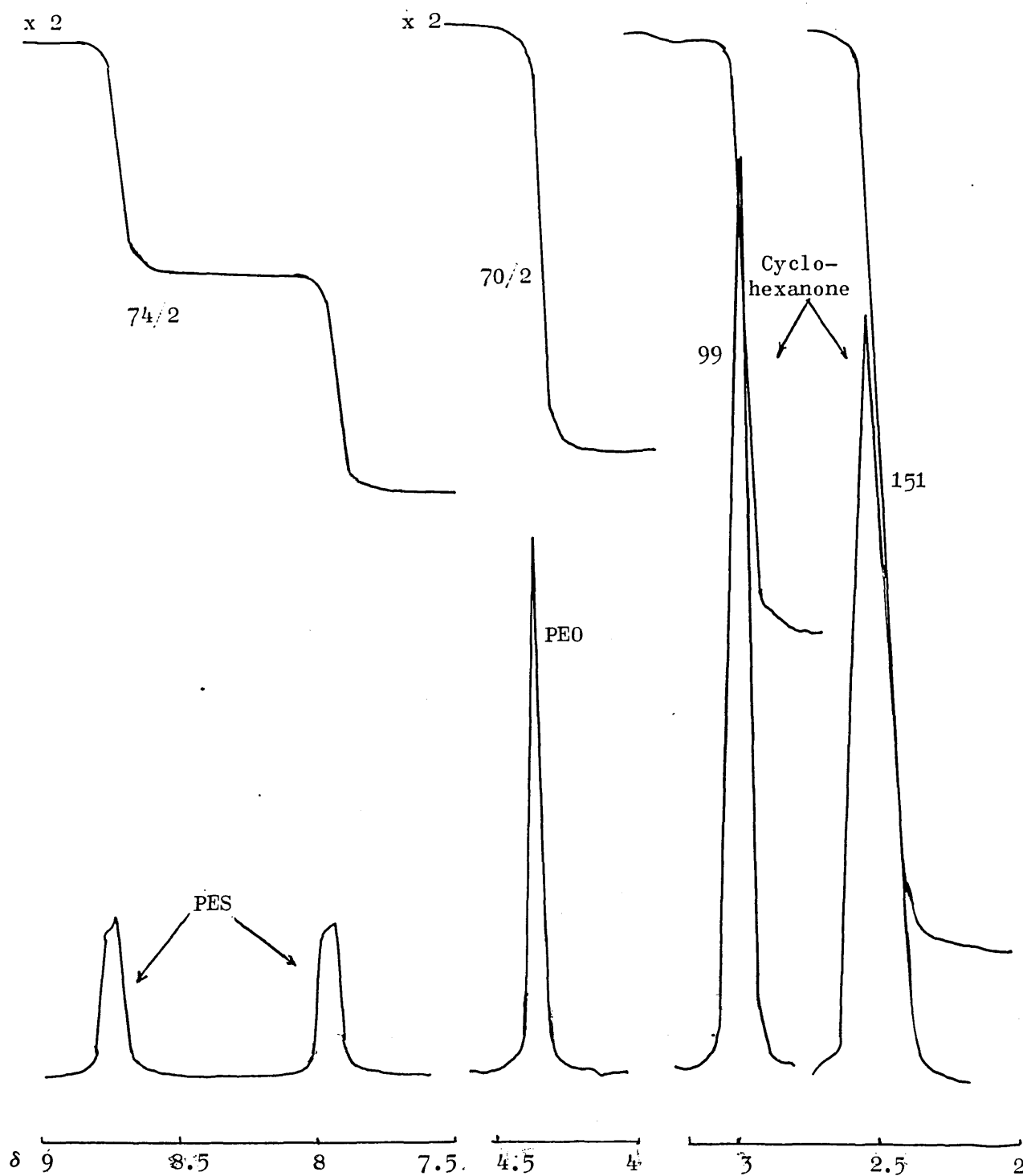


Figure 4.1 Typical NMR spectra for a 32/11/57 (weight, ratio) PES/PEO/Cyclohexanone blend at 100°C., 220 MHz.

| Original<br>Initial<br>PES/PEO | PES/PEO Soln. in<br>Cyclohexanone |       |                    | Composition of Phase I |               |                    |             | Composition of Phase II |      |                    |             |
|--------------------------------|-----------------------------------|-------|--------------------|------------------------|---------------|--------------------|-------------|-------------------------|------|--------------------|-------------|
|                                | PES                               | PEO   | Cyclo-<br>hexanone | PES                    | PEO           | Cyclo-<br>hexanone | PES/<br>PEO | PES                     | PEO  | Cyclo-<br>hexanone | PES/<br>PEO |
| 93.75: 6.25                    | 24.2                              | 1.6   | 74.2               | -                      | -             | -                  | -           | -                       | -    | -                  | -           |
| 83 :17                         | 23.5                              | 4.75  | 71.75              | -                      | -             | -                  | -           | -                       | -    | -                  | -           |
| 75 :25                         | 22.80                             | 7.60  | 69.6               | -                      | NO SEPARATION |                    | -           | -                       | -    | -                  | -           |
| 71 :29                         | 22.40                             | 9.0   | 68.6               | -                      | -             | -                  | -           | -                       | -    | -                  | -           |
| 65 :35                         | 21.76                             | 11.76 | 66.48              | 13                     | 16            | 71                 | 45/55       | 31.8                    | 9.4  | 58.5               | 77/33       |
| 62 :38                         | 21.46                             | 13.00 | 65.54              | 12                     | 18.2          | 69.8               | 39/61       | 27.5                    | 9.8  | 62.7               | 74/26       |
| 55 :45                         | 20.7                              | 17.3  | 62.00              | 14.1                   | 20.7          | 65.2               | 41/59       | 32                      | 9    | 59                 | 78/22       |
| 50 :50                         | 21.25                             | 21.25 | 57.5               | 8.2                    | 27.3          | 64.5               | 23/77       | 35.6                    | 12.2 | 52.2               | 75/25       |
| 45.4:54.6                      | 19                                | 22.8  | 58.2               | 8.0                    | 27.0          | 65                 | 23/77       | 39.5                    | 10.5 | 50.0               | 79/21       |
| 40 :60                         | 19.43                             | 28.57 | 52.0               | 6.9                    | 34.7          | 58.4               | 16/84       | 45.6                    | 14.0 | 40.4               | 76/24       |
| 25 :75                         | 15.0                              | 44.5  | 40.5               | 6.5                    | 49            | 44.5               | 12/88       | 53.0                    | 15.0 | 32.0               | 78/22       |
| 15 :85                         | 8.8                               | 51.7  | 39.5               | 4.7                    | 54.3          | 41.0               | 8/92        | 31.0                    | 39.5 | 29.5               | 45/55       |
| 5 :95                          | 4.0                               | 76.0  | 20.0               | 3.4                    | 80            | 16.6               | 4/96        | 33.3                    | 58.4 | 8.3                | 36/65       |

Table 4.1 Composition of Separated Phases at 95°C.

separation in the temperature range of 70 to 150°C. This confirmed previous observations<sup>108</sup>. Solutions in mixed NMP/dichloromethane (75:25 to 40:60) at 90/10 to 10/90 PES/PEO compositions also showed phase separation between 80 to 150°C. This explains the two phase structure of many blends prepared from these solvents and shows phase separation on heating to be a common feature of these solutions. Areas of immiscibility within three component systems are not uncommon. They have been observed for polymers dissolved in mixed solvents<sup>139</sup> and for mixed polymers with one co-solvent<sup>140</sup>. Such studies were not carried out on the PES/Phenoxy /solvent solutions.

#### 4.12 Polymer/Polymer Miscibility

A 83/17 PES/PEO mixture when dissolved in cyclohexanone (28.25 w/w percent solids) was inside the one phase region of the phase diagram in Figure 4.2. It gave a clear film on drying. A mixture of 50/50 PES/PEO dissolved in cyclohexanone (42.5 w/w percent solids) was within the two phase region. It gave a cloudy film on drying. The solutions which phase separated from the 50/50 PES/PEO solution above had 75/25 and 23/77 PES/PEO compositions. The 75/25 solution, when separated, produced a clear film on evaporation of the solvent. The 23/77 PES/PEO solution, however, gave a cloudy film (even at the melting temperature of PEO). One can see that this would have to pass through other parts of the two phase region to reach the PES/PEO axis. Similar behaviour was observed at other compositions of the phase diagram in Figure 4.2

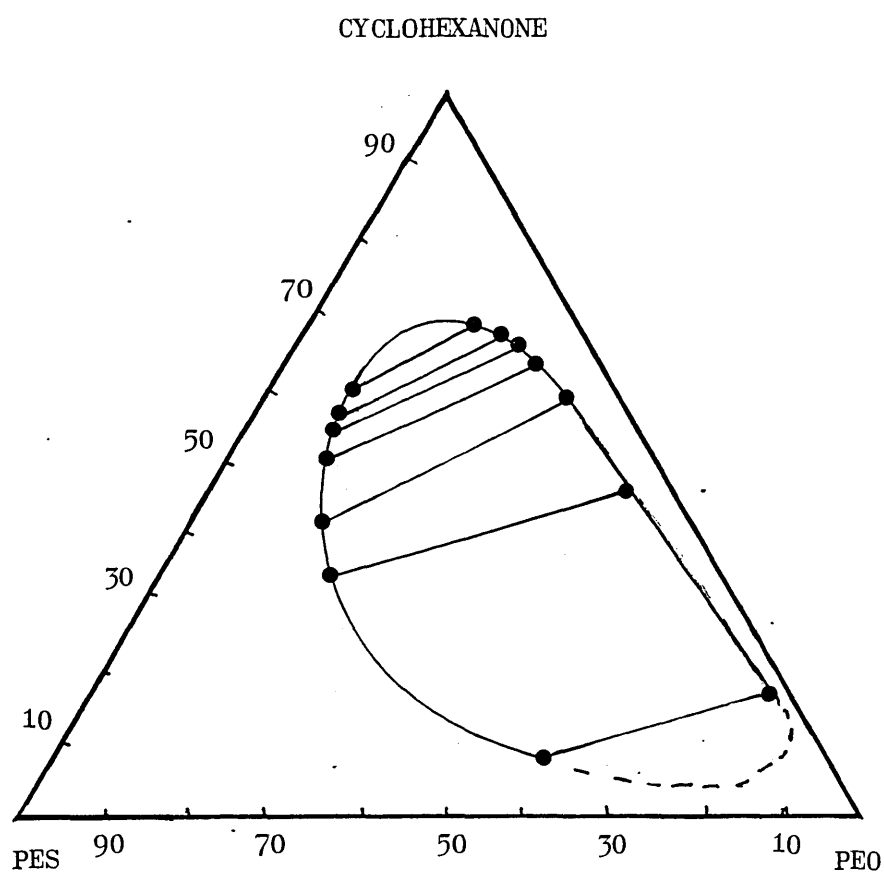


Figure 4.2 The three component phase diagram for mixtures of cyclohexanone, polyethersulphone (PES) and poly(ethylene oxide) (PEO) at 95°C showing the two-phase region and tie lines.

By using the solutions "under" the two phase region it was possible to prepare clear films over a wide range of compositions. The binary mixtures of PES/cyclohexanone and PEO/cyclohexanone did not phase separate on heating as would be expected from the phase diagram in Figure 4.2.

It was found that up to 10 weight percent PES could be dissolved in PEO at 4000 molecular weight in the absence of any solvents by continuous prolonged stirring at 70°C to produce clear solutions. This mixture was found to phase separate on heating as described later. It is theoretically possible to obtain homogeneous mixtures of higher percentage of PES in PEO at 70°C but the high viscosity of PES makes it progressively more difficult and there is an obvious limit as one reaches the T<sub>g</sub> of the mixture.

Clear films were also prepared from dimethylformamide (DMF) solutions. Mixtures of PES/PEO from 90:10 to 10:90 composition at 20 weight percent solids, were dried in petri dishes at 50°C in a vacuum oven for two to four weeks. The absence of DMF was checked by infra-red analysis (no peak at 1667 $\text{cm}^{-1}$ ). Compositions containing more than 40 percent PEO in the blend became opaque at room temperature, possibly due to crystallisation of PEO from the blend. However, they were very clear when maintained above the PEO melting point.

PES/phenoxy blends prepared by solvent casting from 10 weight percent solids in dimethyl sulphoxide (DMSO) and drying in a vacuum oven at 40°C gave clear films over the entire composition range. The absence of solvent from films was checked by drying to a constant weight as infra-red frequencies of DMSO were very close to PES and therefore difficult to detect. Similarly,

blend films prepared from N-methyl pyrrolidone were also clear at all compositions. PES/phenoxy blends when cast from DMF at 10 weight percent solids, however, on drying were found to give hazy films at compositions containing greater than 60 weight percent phenoxy resin in the blend. These differences may be due to the differences in the solubility of the component polymers in different solvents.

Blends of other polymers with PES from DMSO or DMF solvents were investigated and were found to give opaque films on drying. The results of visual observations of blend solutions and dried films have been given in Table 3.1 in section 3.33.

#### 4.2 LIGHT SCATTERING TURBIDIMETRY

Light scattering turbidimetry is used to determine the cloud point, the temperature of initial phase separation, of the blend compositions. By measuring the cloud point for a range of compositions a cloud point curve is obtained which normally lies between the binodal and spinodal curves although it could be affected by kinetics. The theoretically simulated phase diagrams are compared to this cloud point curve.

##### 4.21 The PES/PEO Blends

All compositions from 99:1 to 1:99 PES/PEO were found to phase separate on heating. Some of the plots of the scattered intensities obtained by turbidimetry for PES/PEO (molecular weight 4000) are shown in Figure 4.3. The plots show a sharp increase in the intensity of scattered light at the cloud point. The resultant cloud point curves for the blends of PES with PEO of molecular weights of 4000, 20,000 and 200,000 are shown in Figure 4.4. An increase in molecular weight of PEO from 4000 to 200,000 decreases

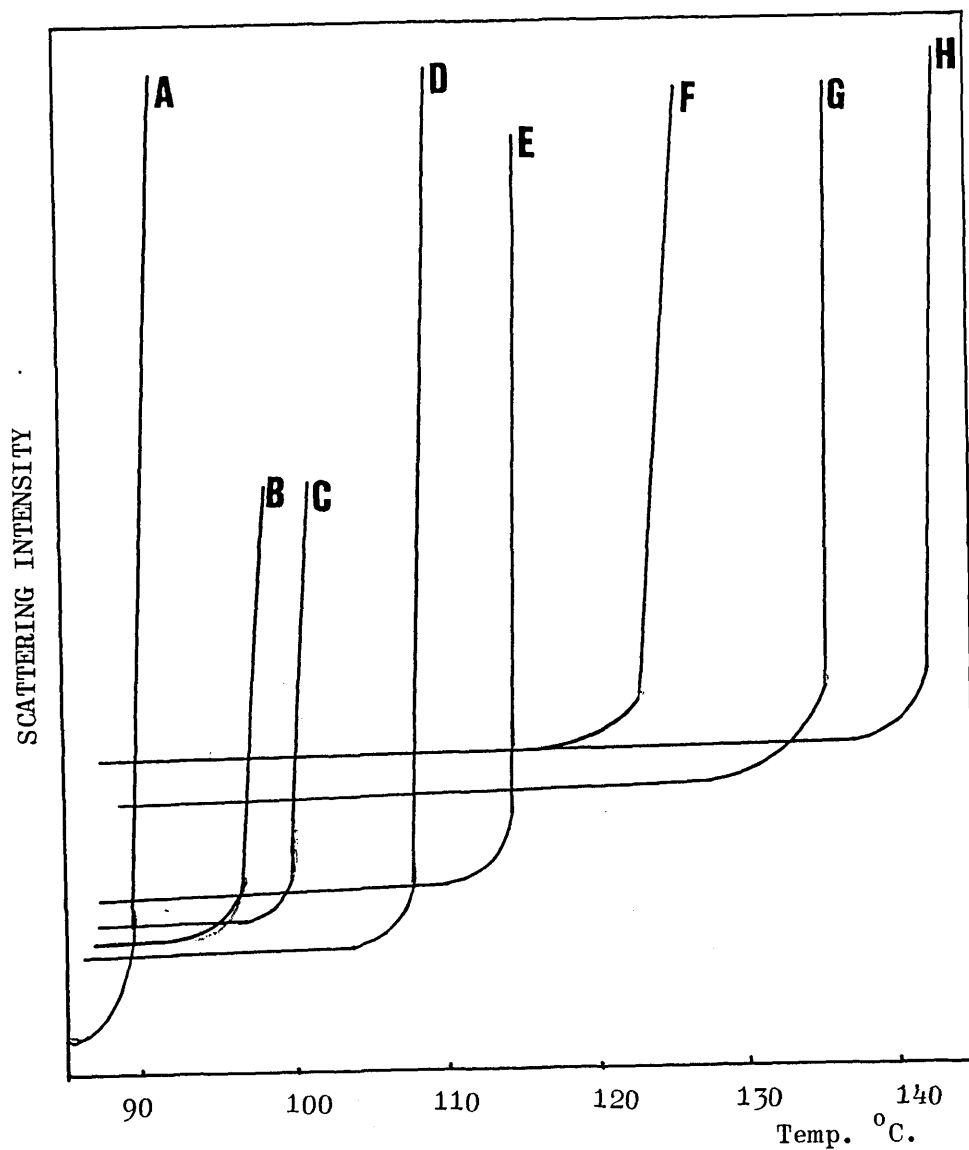


Figure 4.3 Plots of scattering intensities (arbitrary units) against temperature for blends of PES : PEO at (A) 20:80, (B) 30:70, (C) 40:60, (D) 50:50, (E) 60:40, (F) 70:30, (G) 80:20, (H) 90:10 weight ratio (PEO 4000 used).

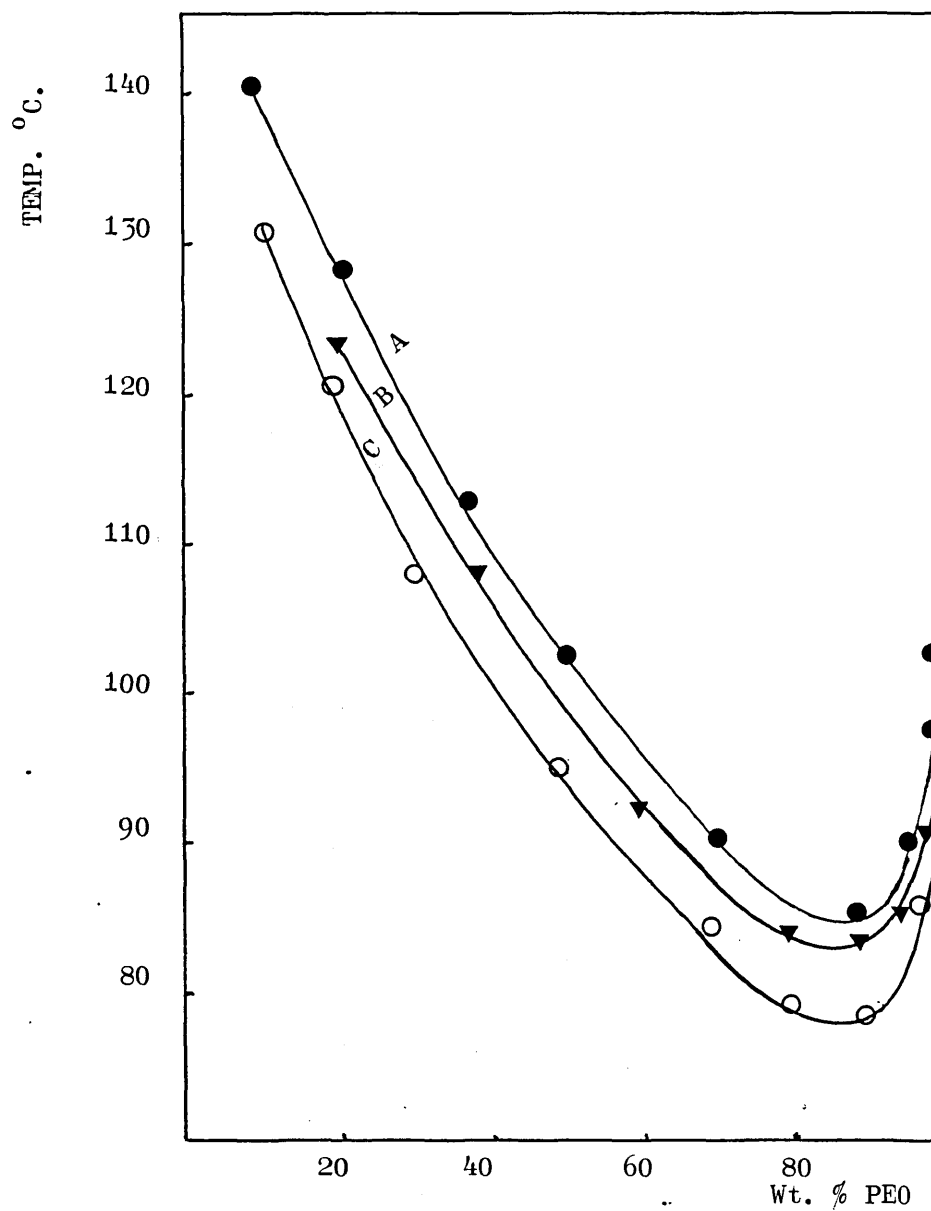


Figure 4.4 Plots of cloud points against composition for PES blends with (A) PEO 4000, (B) PEO (molecular weight 20,000), (C) PEO WSRN 80 (molecular weight 200,000).

the cloud point temperature as expected<sup>22</sup> but not to the extent seen in other systems. The minimum in the cloud point curve appears close to a 10:90 PES:PEO ratio. This composition varies little with molecular weight of PEO. The skew nature of the curves appears, therefore, to be independent of molecular weight.

#### 4.22 The PES/Phenoxy Blends

All compositions from 90/10 to 10/90 PES/phenoxy were found to phase separate on heating. Only 50/50 PES/phenoxy blend compositions could be studied using the light scattering turbidimeter. This plot of scattered intensities against temperature is shown in Figure 4.5. Cloud points of other PES/phenoxy compositions could not be measured by this method, because of the upper temperature limit of 200°C on the light scattering instrument used. The phase separation temperature of other PES/phenoxy compositions were visually observed on a hot plate at a heating rate of 2°C/minute. The temperatures were measured by putting a probe of a digital thermometer near the sample. These results could have an error of  $\pm 5^\circ\text{C}$  due to difficulty in knowing the real specimen temperature. The resultant phase diagram is shown in Figure 4.6. This cloud point curve is symmetrical and not skewed as with the PES/PEO blends. This may be due to there being less differences in the state parameters of the two components.

#### 4.3 GLASS TRANSITION TEMPERATURE MEASUREMENTS

The measurement of glass transition temperatures ( $T_g$ ) is the most widely used test for establishing the miscibility of two polymers. As stated earlier (section 1.32) a blend of two polymers giving a single  $T_g$ , usually intermediate between two polymers, is

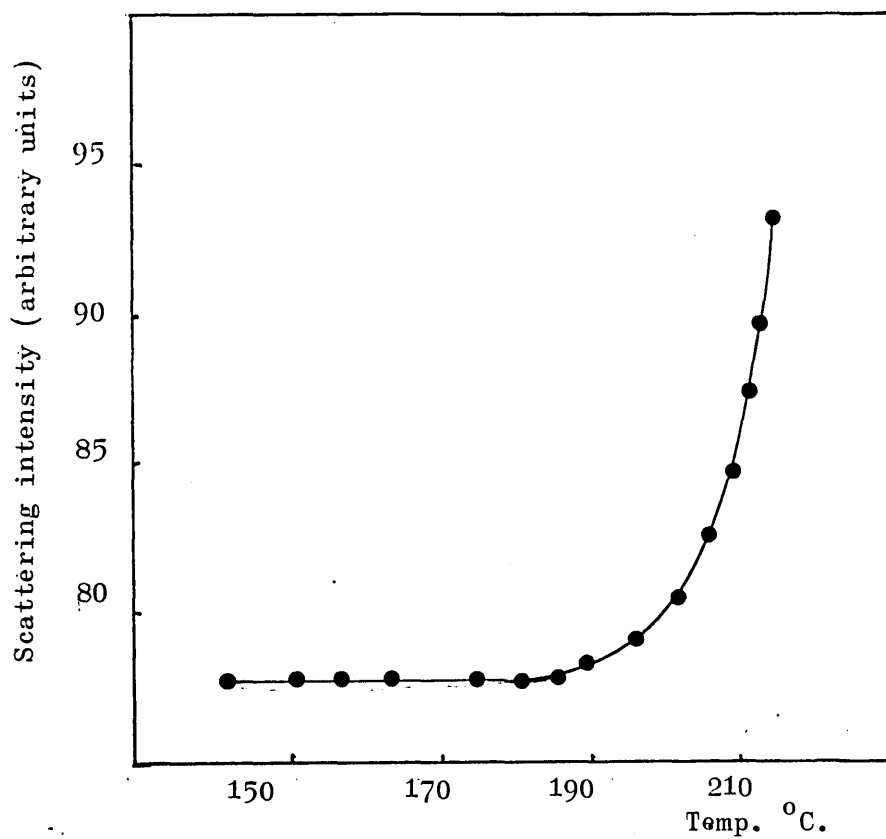


Figure 4.5 Plot of scattering intensities (arbitrary units) against temperature for a blend of PES:phenoxy at 50:50.

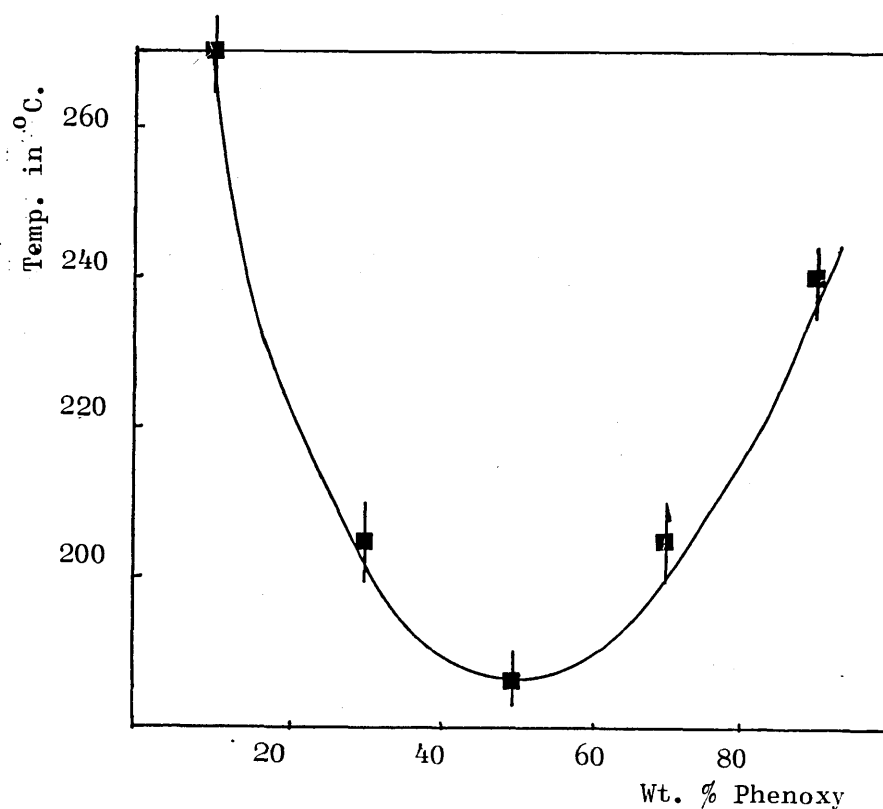


Figure 4.6 Plot of Cloud point against compositions for PES blends with phenoxy resin.

considered miscible and that giving two Tg's immiscible. The measurement can also give an indication of polymer-polymer interactions. Dynamic mechanical analysis and differential scanning calorimetry were used to determine the Tg's of the blends in this work. These techniques have been discussed in sections 3.42 and 3.43.

#### 4.31 Dynamic Mechanical Analysis (DMA)

Table 4.2 gives the glass transition temperatures for PES/PEO and PES/phenoxy blends as determined by the DMA method and for comparison theoretical values calculated using the Fox equation (1.10). Figures 4.7 and 4.8 show the typical plots of  $\tan \delta$  against composition for the two systems. The blends for both systems show a single composition dependent Tg. Compositions containing more than 60 weight percent PEO were too fragile to be tested by DMA. In the case of PES/phenoxy blends containing more than 70 weight percent PES, these could not be examined because of the temperature (200°C) limitation of the DMA instrument.

Figures 4.9 and 4.10 show plots of Tg against composition of PES/PEO and PES/phenoxy blends respectively compared to the Fox equation (1.10). In Figure 4.9 the Fox equation result is very dependent on the value of Tg used for PEO which has to be extrapolated for amorphous samples. We used a value of  $-73^{\circ}\text{C}^{102}$  but values as high as  $-20^{\circ}\text{C}$  have been suggested<sup>106</sup>. The experimental values of Tg follow a smooth curve to 60/40 PES/PEO compositions. With higher PEO content the samples curve away from the expected line possibly because of PEO crystallisation. For the PES/phenoxy blends the experimental Tg's of the blend fall almost on a straight line. The experimental Tg's for both the systems show a positive

Table 4.2 T<sub>g</sub> against blend composition for PES/PEO and PES/Phenoxy blends

| Ratio of Blend Components | PES : PEO        |                          | PES : Phenoxy |                          |
|---------------------------|------------------|--------------------------|---------------|--------------------------|
|                           | Experimental     | Theoretical Fox Equation | Experimental  | Theoretical Fox Equation |
| 100 : 0                   | 226*             | 226*                     | 226*          | 226*                     |
| 90 : 10                   | 168              | 162                      | -             | 207                      |
| 83 : 17                   | 132              | 125                      |               |                          |
| 80 : 20                   | 128              | 111                      |               |                          |
| 75 : 25                   | 110              |                          |               |                          |
| 70 : 30                   | 100              | 72                       | 182           | 174                      |
| 65 : 35                   | 84               |                          |               |                          |
| 60 : 40                   | 68               | 39.5                     |               |                          |
| 50 : 50                   | 54               | 13.0                     | 157           | 145                      |
| 40 : 60                   | 45               | - 10                     |               |                          |
| 30 : 70                   | -                | -29                      | 130           | 119                      |
| 20 : 80                   | -                | -46                      | 115           | 109                      |
| 10 : 90                   | -                | -60                      | 98            | 96                       |
| 0 : 100                   | -73 <sup>+</sup> | -73 <sup>+</sup>         | 87            | 87                       |

\* Quoted value, as given by ICI for Victrex 200P

<sup>+</sup> Value given in reference 102

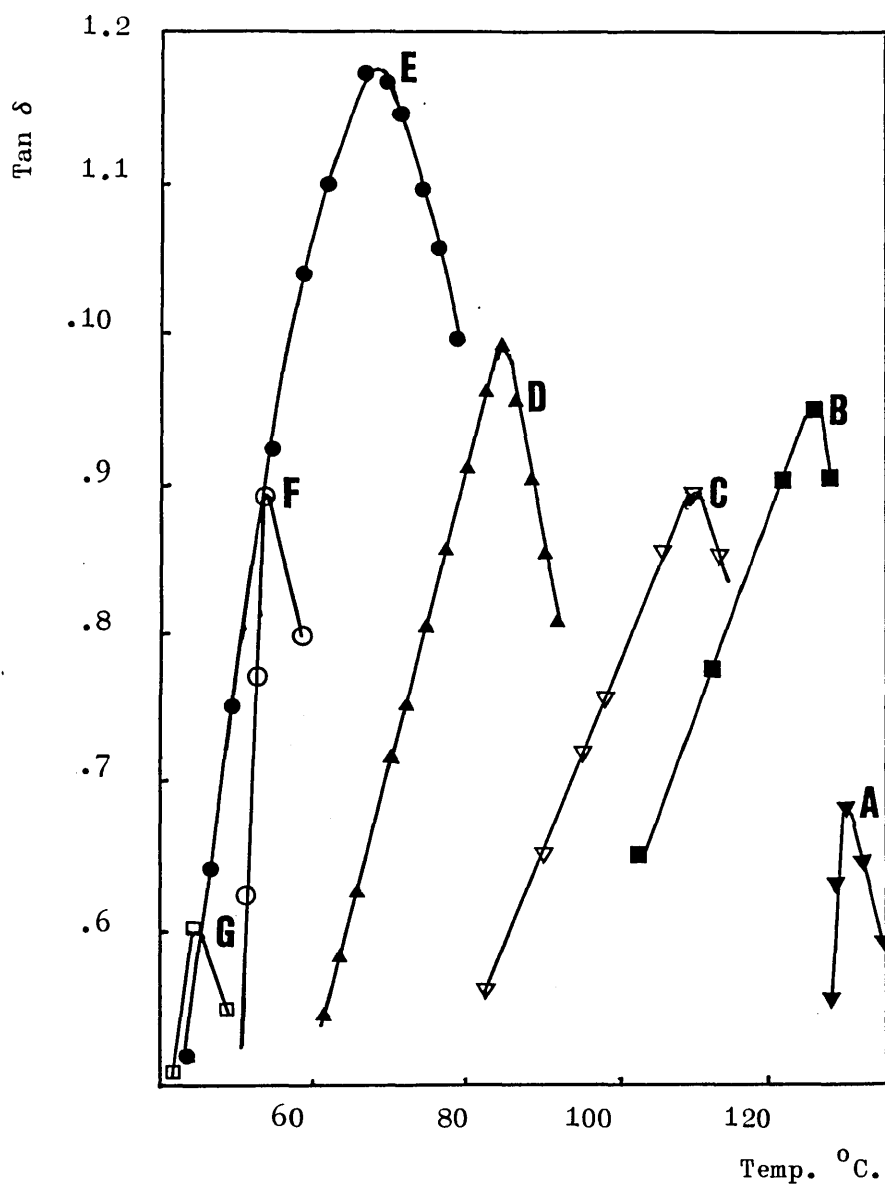


Figure 4.7 Plots of  $\tan \delta$  against temperature for blends of PES with PEO at (A) 83:17, (B) 80:20 (C) 75:25, (D) 65:35, (E) 60:40. (F) 50:50 (G) 40:60 weight ratio.

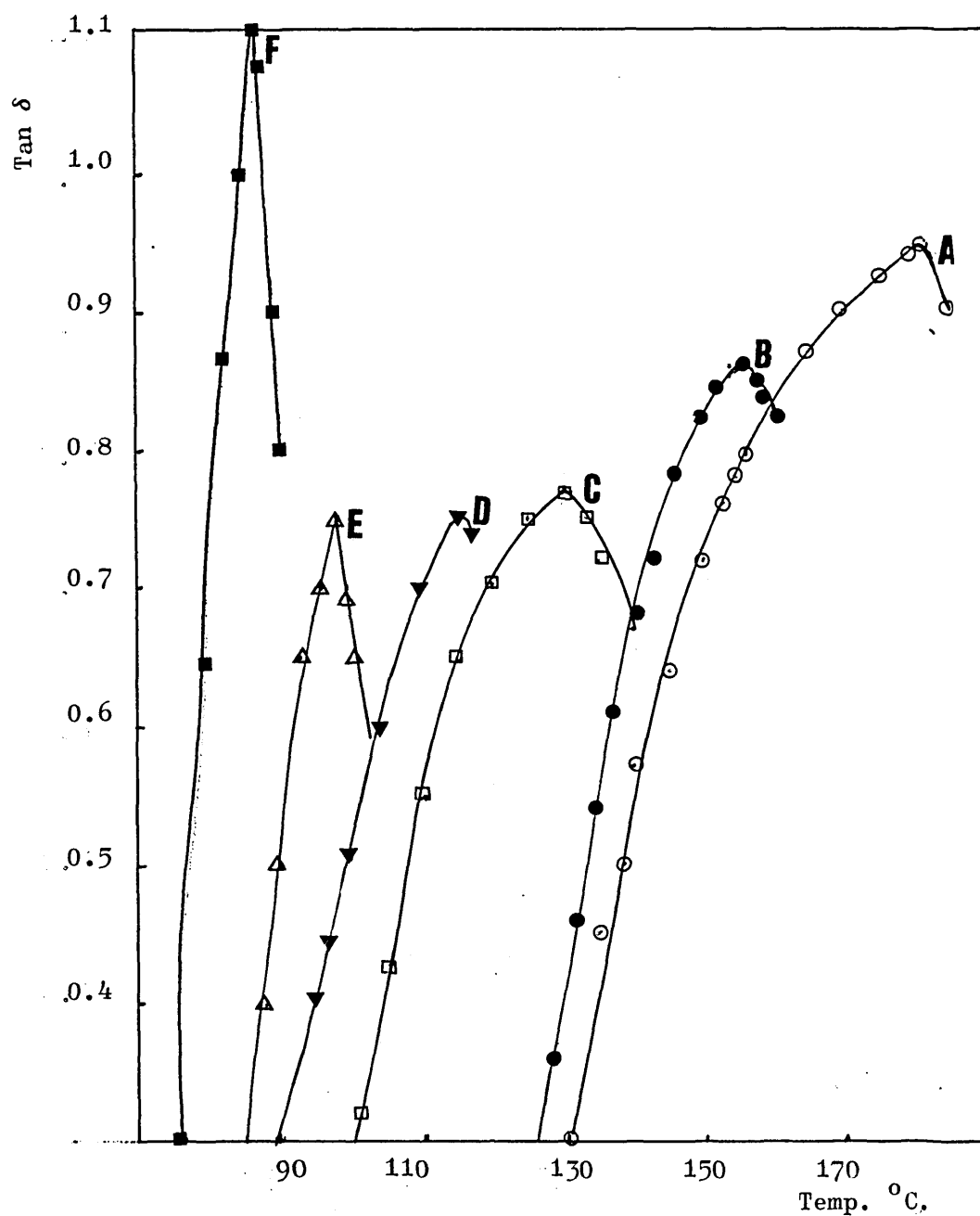


Figure 4.8 Plots of  $\tan \delta$  against temperature for blends of PES with phenoxy resin at (A) 70:30, (B) 50:50, (C) 30:70, (D) 20:80, (E) 10:90, (F) 0:100 weight ratio.

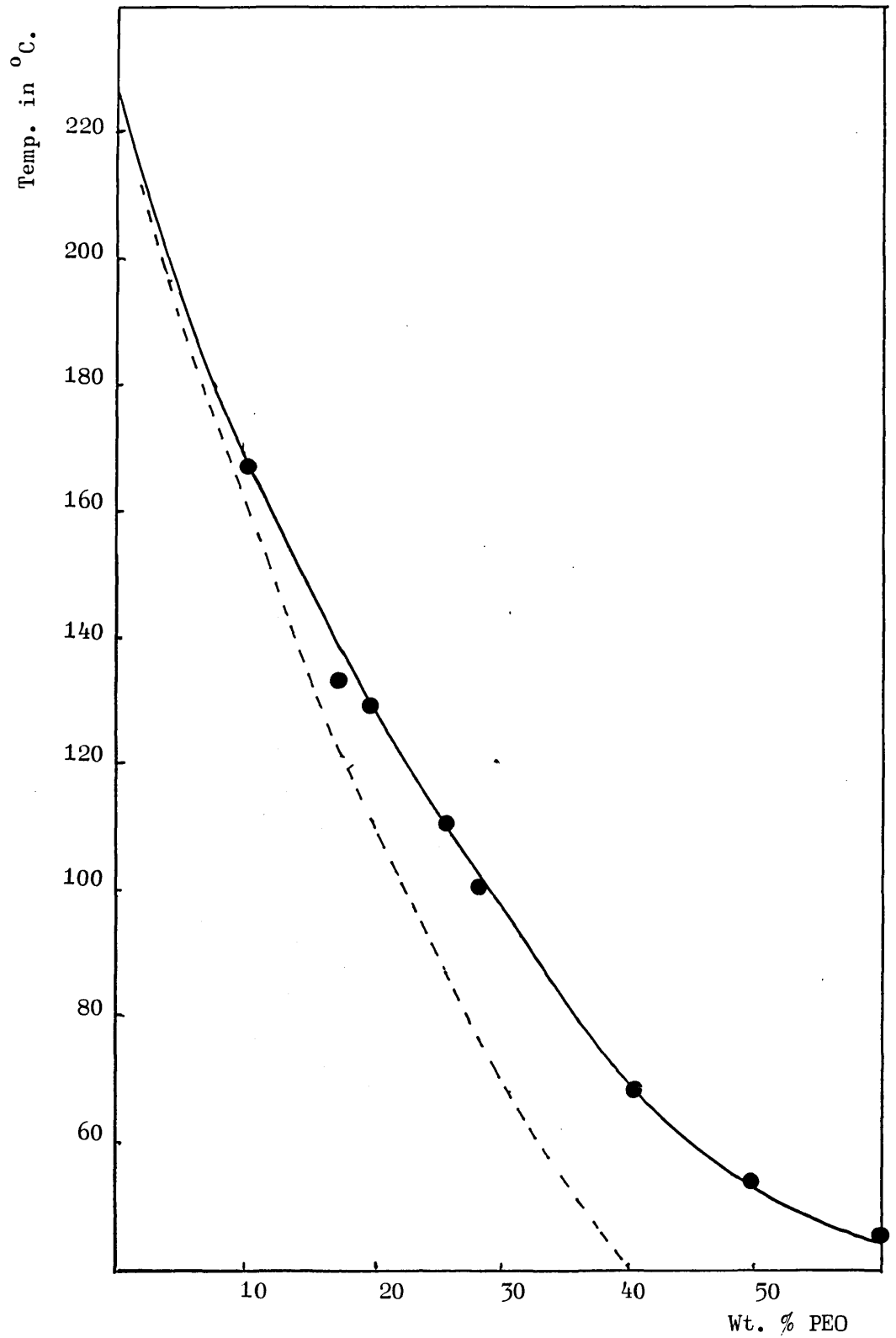


Figure 4.9 Plot of  $T_g$  against composition for PES blends with PEO; solid line - experimental, dotted line - Theoretical (Fox Equation). This plot is for PEO 4000, but other molecular weights were not significantly different.

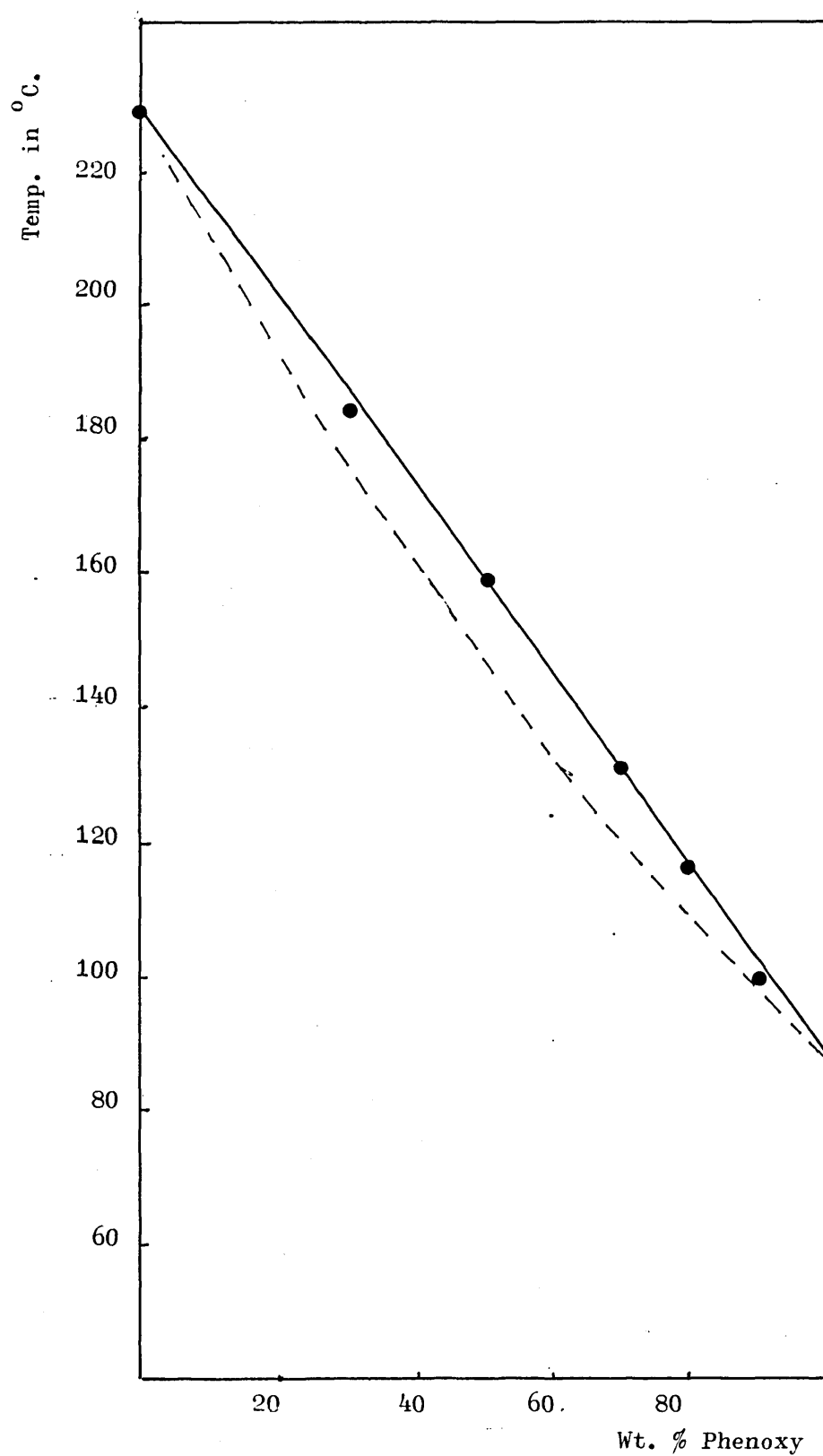


Figure 4.10 A plot of  $T_g$  against composition for PES with phenoxy resin. Solid line experimental  $T_g$  from DMA and dotted line - theoretical calculated from Fox equation.

deviation from the theoretical Fox equation implying a strong interaction between the polymers<sup>141</sup>. Blends prepared from PEO molecular weight 20,000 (Carbowax 20M) and 200,000 (Polyox WSRN 80) did not show significantly different Tg's from those of the PEO molecular weight of 4000 used in the above work.

$$\text{The Gordon-Taylor equation } T_{g_b} = \frac{W_1 T_{g_1} + K W_2 T_{g_2}}{W_1 + K W_2} \quad 4.1$$

is often semiquantitatively related to the strength of the interaction between the two polymers.  $T_{g_b}$  is the glass transition temperature of the blend and  $T_{g_1}$  and  $T_{g_2}$  those of respective polymers.  $W_1$  and  $W_2$  are the weight fraction of the two polymers and  $K$  is the Gordon-Taylor parameter.

The above equation can be reorganised to give

$$(T_{g_1} - T_{g_b}) = K \frac{W_2}{W_1} (T_{g_b} - T_{g_2}) \quad 4.2$$

A plot of  $(T_{g_1} - T_{g_b})$  against  $\frac{W_2}{W_1} (T_{g_b} - T_{g_2})$  gives a straight line and the slope of this gives the value of Gordon-Taylor parameter. These plots of PES/PEO and PES/phenoxy blends are given in Figure 4.11. The values of  $K$  obtained from the plots are 1.52 and 1.0. These values of  $K$  for the two systems suggest that the interaction between PES and PEO is stronger than that between PES and phenoxy resin.

Figure 4.12 shows a DMA plot for a 20/80 PES/phenoxy blend before and after phase separation. The phase separation was carried out by heating the sample to 250°C (~20°C above the cloud point). The sample was 'sandwiched' between two glass slides to avoid distortion. The temperature of the sample was maintained for ten minutes at 250°C and then it was rapidly quenched in liquid nitrogen. The miscible blend shows a single Tg at 115°C, whereas the

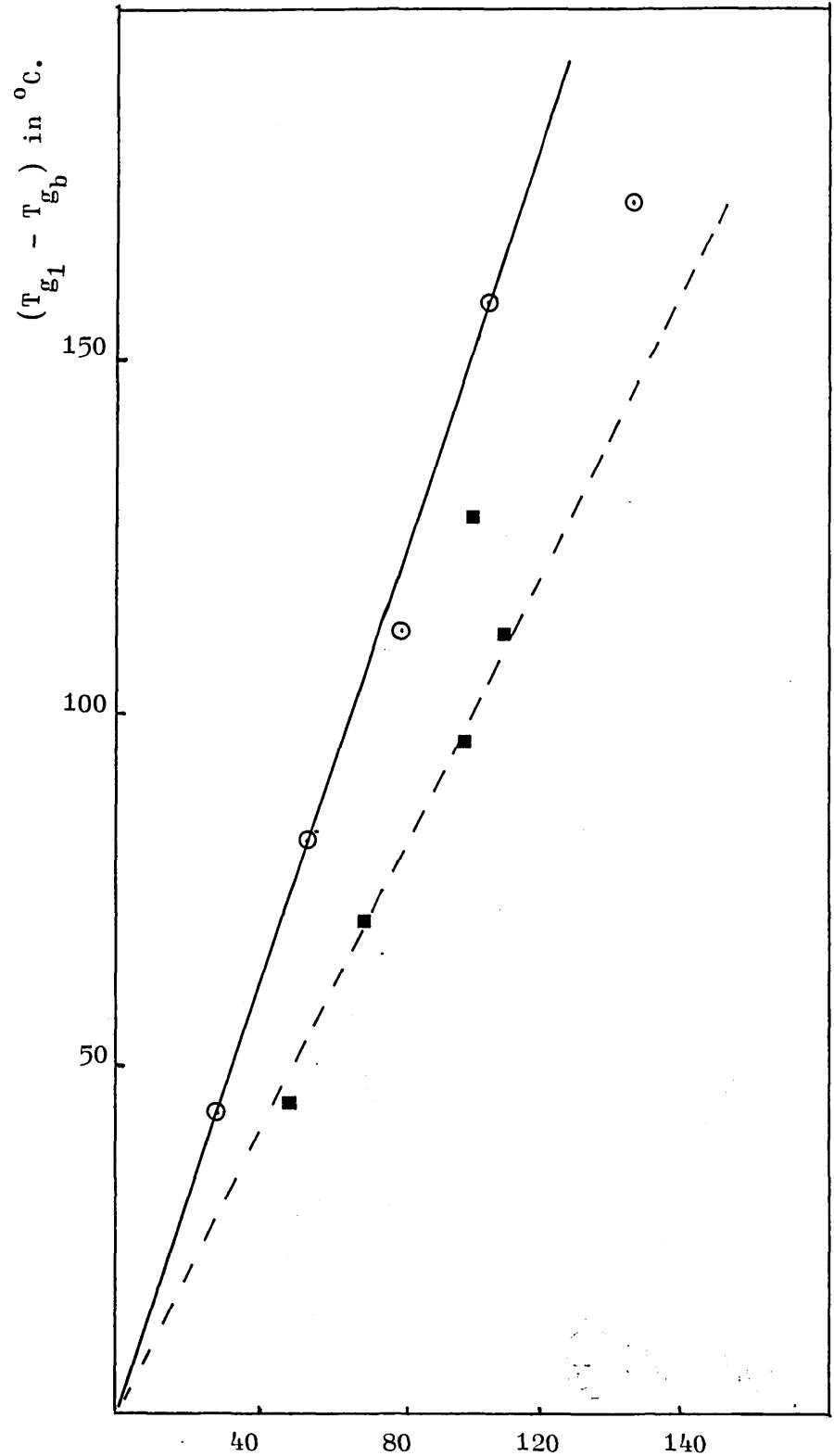


Figure 4.11 A plot of  $(T_{g1} - T_{gb})$  against  $\frac{W_2}{W_1} (T_{gb} - T_{g2})$   
solid line - PES/PEO blends, dotted line PES/  
phenoxy blends

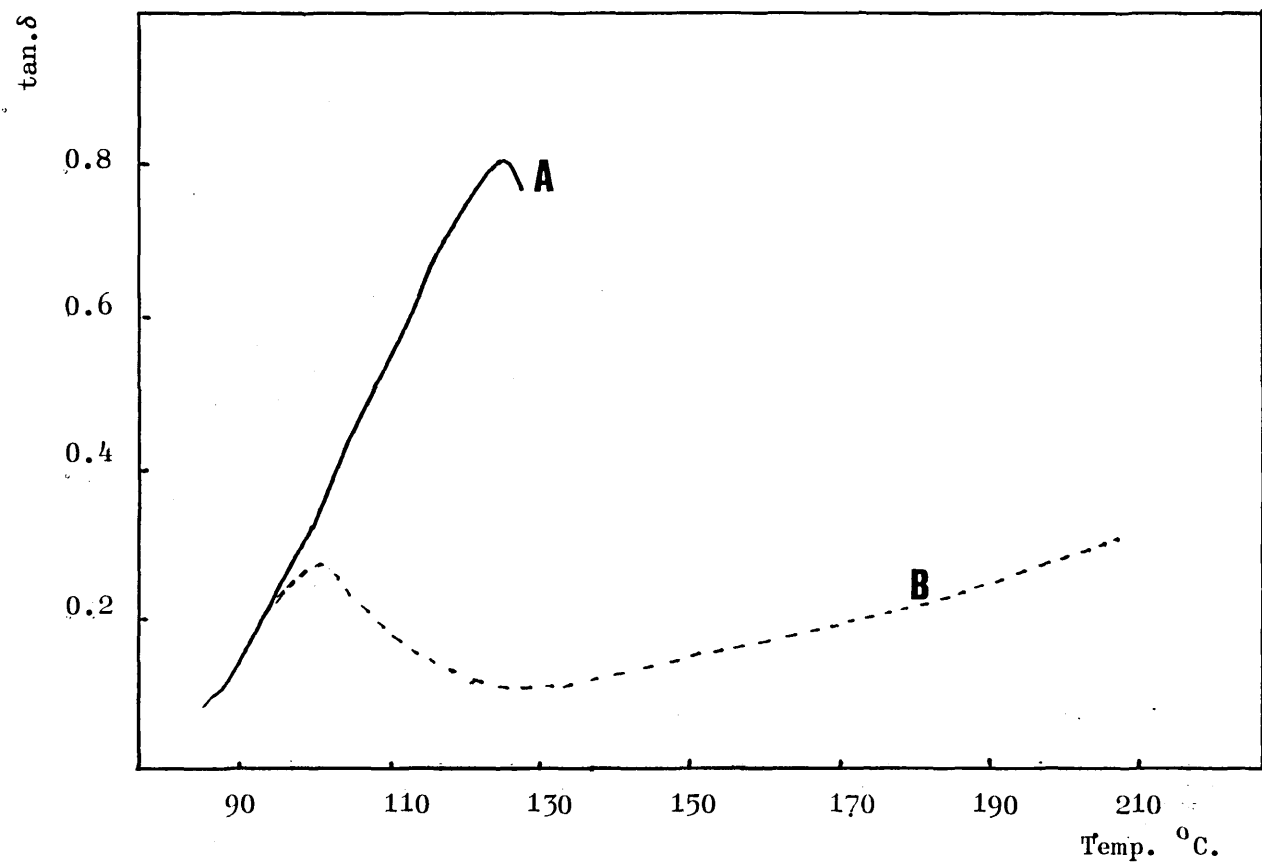


Figure 4.12 A plot of  $\tan \delta$  against temperature for PES with phenoxy resin at 20:80 weight ratio; (A) homogeneous blend, (B) phase separated blend.

phase separated sample shows a  $T_g$  at  $90^{\circ}\text{C}$  (nearer to the phenoxy  $T_g$ ) and possibly another nearer the PES  $T_g$  of  $226^{\circ}\text{C}$ . The latter could not be accurately determined because of the instrumental limitations. This confirms the observed phase separation from the turbidity measurements.

#### 4.32 Differential Scanning Calorimetry (DSC)

Typical DSC results for various PES/PEO and PES/phenoxy blend compositions at a heating rate of  $10^{\circ}\text{C min}^{-1}$  are shown in Figures 4.13 and 4.14 and the  $T_g$ 's obtained from them are given in Tables 4.3 and 4.4 respectively. For the PES/PEO blends DSC  $T_g$  results are given up to 60/40 PES/PEO compositions. The results obtained for compositions containing more than 40 weight percent PEO in the blend were unreliable because of the melting of PEO crystallites. No melting peak was given by blends containing less than 40 weight percent PEO. This problem, however, does not arise in PES/phenoxy blends because both polymers are amorphous.

A 70/30 PES/phenoxy blend which gave a single  $T_g$  of  $188^{\circ}\text{C}$  was phase separated by heating to  $230^{\circ}\text{C}$ , a temperature  $25^{\circ}\text{C}$  above the phase separation temperature, and quenched in liquid nitrogen to freeze the structure. This phase separated sample was found to give two  $T_g$ 's, one at  $135^{\circ}\text{C}$  and the other at  $218^{\circ}\text{C}$ . These  $T_g$ 's were not those of the individual components but were shifted towards intermediate temperatures probably because complete separation of the components did not take place. This result confirms that the PES/phenoxy blends phase separate on heating. In general DSC results were  $8 - 10^{\circ}\text{C}$  higher than DMA  $T_g$ 's, as expected, possibly because of the fast heating rate and because DSC

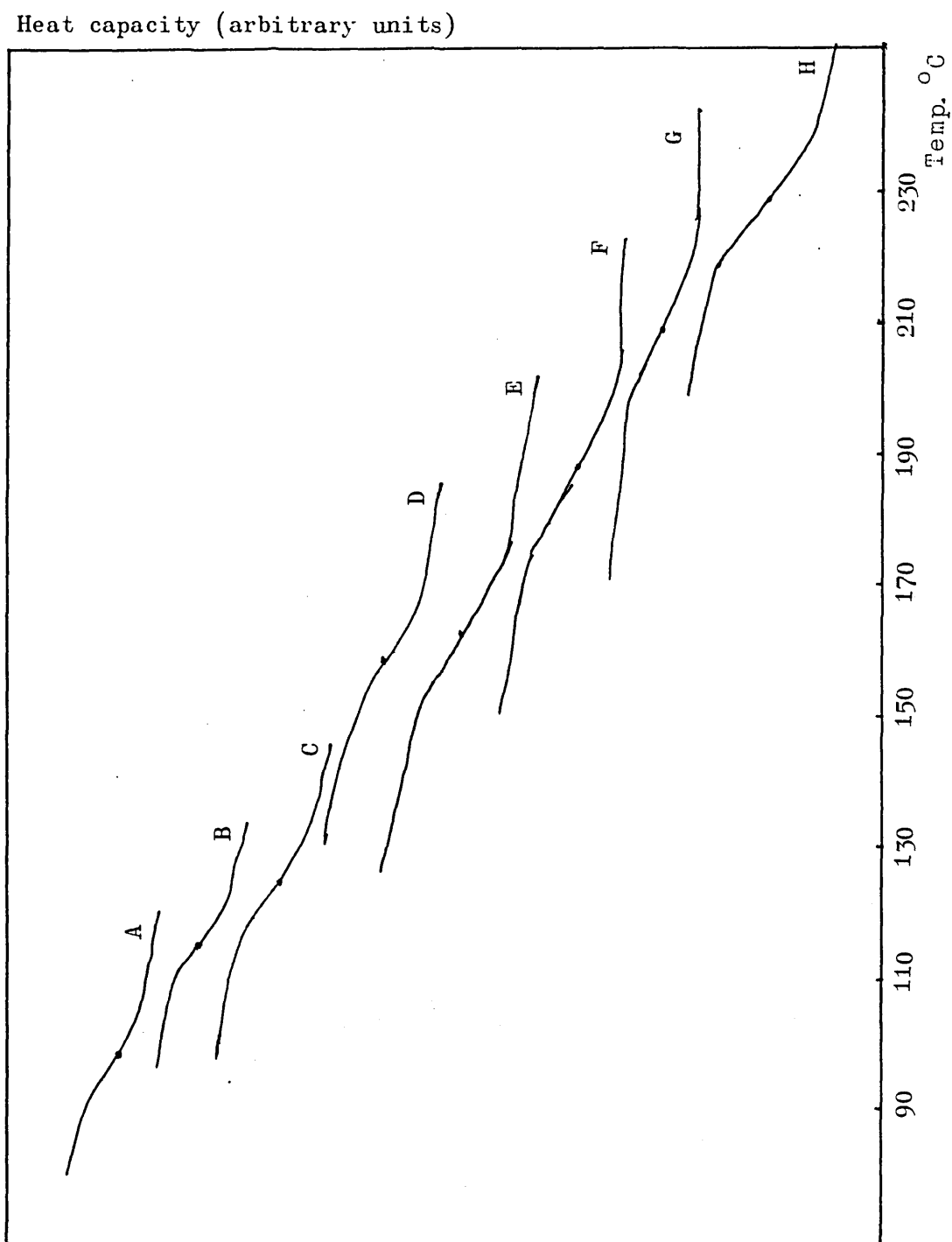


Figure 4.13 Plots of DSC thermograms of heat capacities against temperature for PES blends with PEO at (A) 60:40, (B) 70:30, (C) 75:25, (D) 80:20, (E) 85:17, (F) 89:11, (G) 94:6 and (H) 100:0 weight ratio.

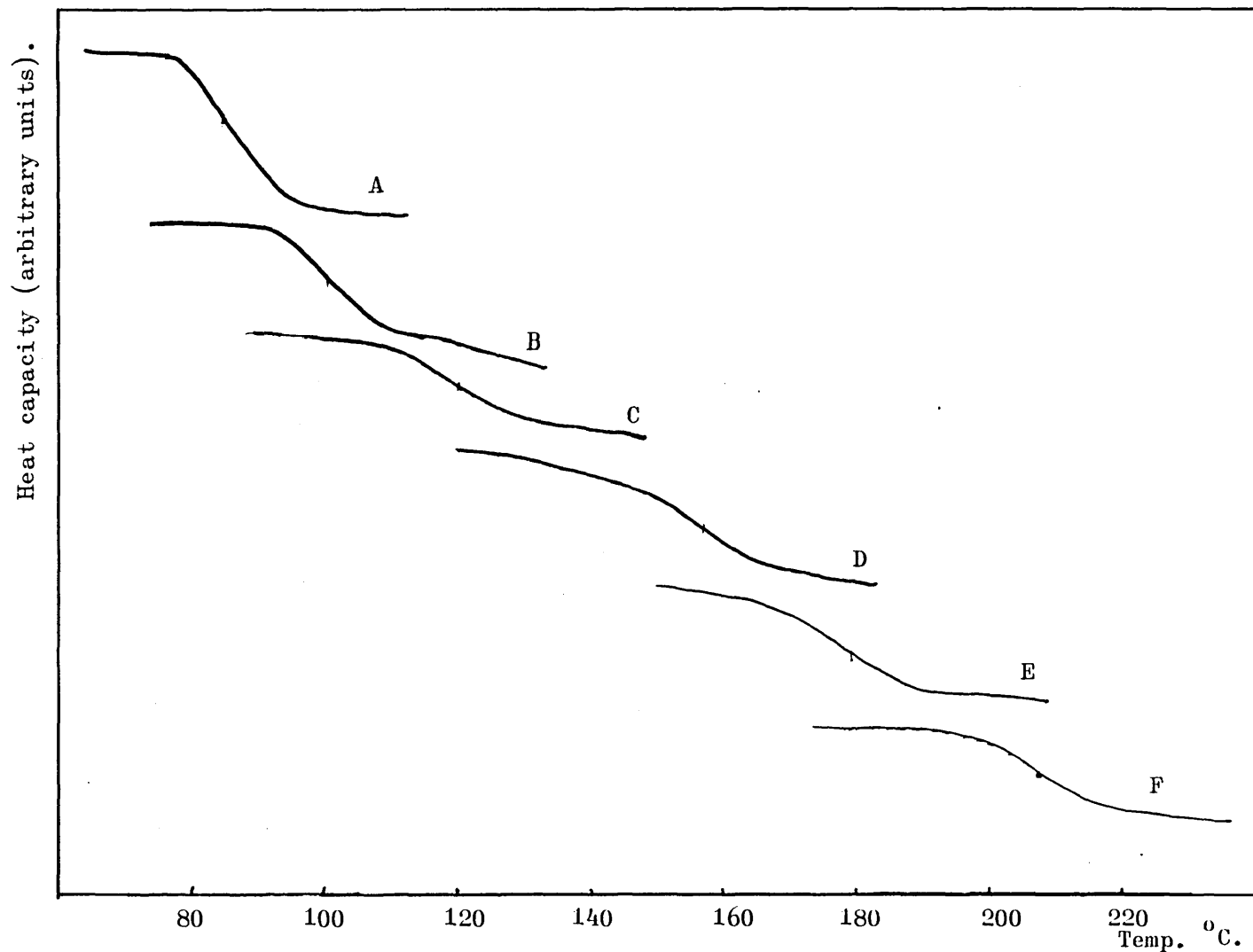


Figure 4.14 Plots of DSC thermograms of heat capacities (arbitrary units) against temperature for PES : Phenoxy blends at (A) 0:100, (B) 10:90, (C) 30:70, (D) 50:50, (E) 70:30 and (F) 90:10 weight ratio.

measurements involve longer range motions compared to the micro-brownian motions responsible for the dynamic mechanical loss peak.

Table 4.3 Tg's obtained by DSC for PES/PEO blends

| Composition<br>w/w % PES/PEO | Tg( <sup>o</sup> C) obtained by DSC |
|------------------------------|-------------------------------------|
| 100/0                        | 226                                 |
| 94/6                         | 208                                 |
| 83/17                        | 163                                 |
| 80/20                        | 157                                 |
| 75/25                        | 125                                 |
| 70/30                        | 115                                 |
| 60/40                        | 98                                  |

Table 4.4 Tg's obtained by DSC for PES/Phenoxy blends

| Composition<br>w/w % PES/<br>Phenoxy | Tg( <sup>o</sup> C) obtained by DSC |
|--------------------------------------|-------------------------------------|
| 100/0                                | 226                                 |
| 90/10                                | 215                                 |
| 70/30                                | 188                                 |
| 50/50                                | 163                                 |
| 30/70                                | 129                                 |
| 10/90                                | 110                                 |
| 0/100                                | 94                                  |
| 70/30 PES/Phenoxy<br>Phase separated | 135      218                        |

In DSC plots at or above 60 weight percent PES, no PEO melting endotherm was observed. However, above 40 weight percent PEO in the blend a monotonic increase in melting endotherm was noticed (similar to that shown in other systems)<sup>102, 18</sup>. The area under the melting endotherm gives an estimate of the heat of fusion of crystalline PEO in the blends. If the areas under the melting endotherms are plotted against the blend composition, a straight line is obtained which intersects the composition axis at 40 weight percent PEO (Figure 4.15). This shows that up to a 60/40 PES/PEO composition, the blends are possibly amorphous and no detectable PEO crystallites are present. If the crystallinity of PEO is known, from Figure 4.15 one can calculate the amount of crystalline PEO in the blend at ambient temperature.

#### 4.4 OPTICAL AND ELECTRON MICROSCOPY

The phase separation of the PES/PEO blends were studied using an optical microscope fitted with a hot stage. The phase separation on heating and disappearance of separated phases on annealing below the phase separation temperature were observed. The cloud point was taken as the onset of phase separation on heating. The cloud points thus determined for PES/PEO (molecular weight 4000) blends are given in Table 4.5. These were similar to those obtained by light scattering turbidimetry. Figure 4.16 shows pictures of an 80/20 PES/PEO blend examined in this way. Picture A is of a clear blend at room temperature and it is observed to stay clear up to the phase separation temperature of 128°C (in this case). At the phase separation temperature, a phase separated structure as shown in picture B appears. In another 10 seconds the phase separated domains grow bigger in size as shown in picture C.

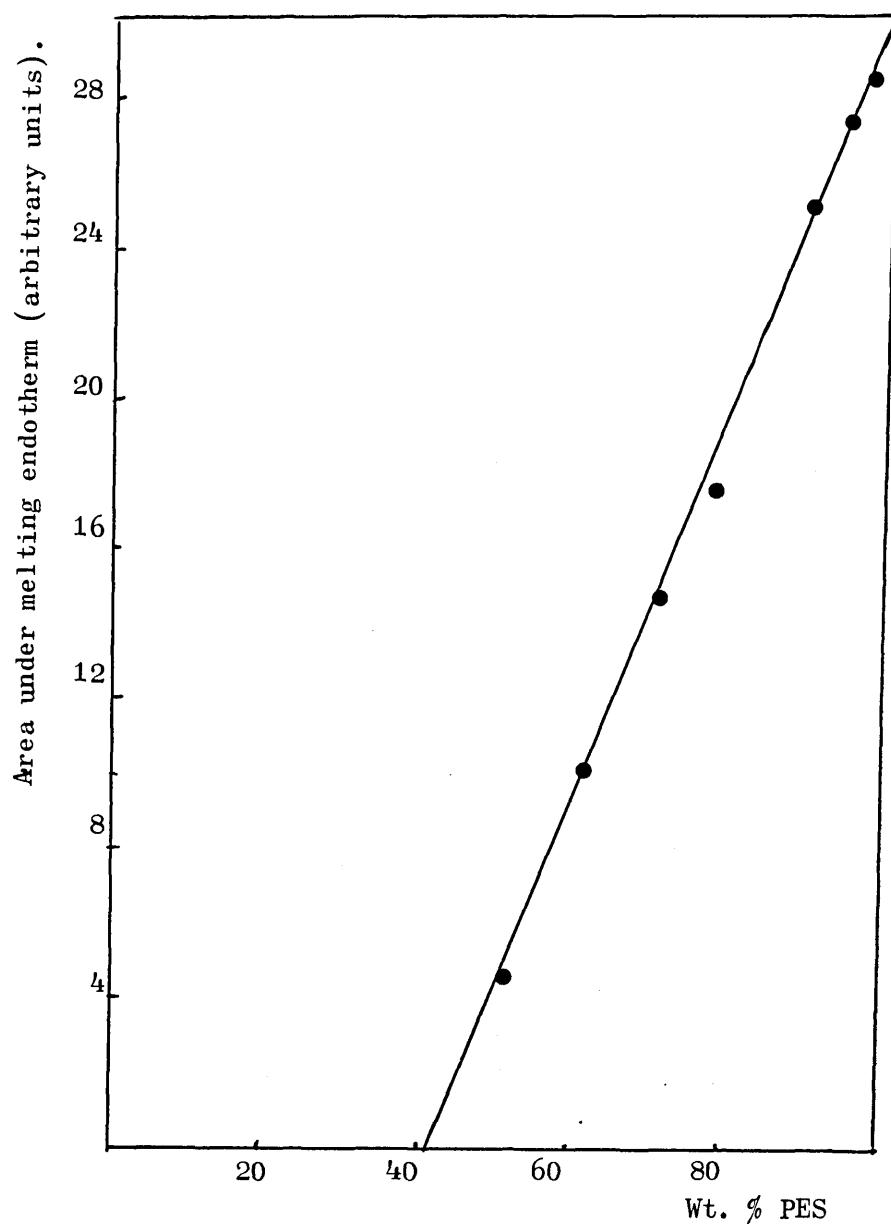


Figure 4.15 A plot of area under the melt endotherm for PES/PEO blends containing greater than 40 wt % PES in the blend.

Very quickly within a temperature change of  $1^{\circ}\text{C}$ , the sample becomes completely opaque. On cooling, the process reverses but it takes longer to clear. Complete clarity was noticed at  $122^{\circ}\text{C}$  in about 4 - 5 minutes.

Table 4.5 Cloud Points by Hot Stage Microscope.

| Blend Composition<br>PES:PEO | Cloud Point $^{\circ}\text{C}$ |         | Cloud Point $^{\circ}\text{C}$<br>by turbidimetry |
|------------------------------|--------------------------------|---------|---------------------------------------------------|
|                              | Heating                        | Cooling |                                                   |
| 80 : 20                      | 128                            | 122     | 128                                               |
| 60 : 40                      | 115                            | 110     | 110                                               |
| 50 : 50                      | 103                            | 98      | 103                                               |
| 40 : 60                      | 97                             | 88      | 96                                                |
| 20 : 80                      | 85                             | 70      | 85                                                |

Other blend compositions also showed similar behaviour and thus confirmed that the phase separation on heating is a common feature of these blends.

In the case of PES/phenoxy blends the phase separation on heating or rehomogenisation on cooling is not as quick as with PES/PEO blends. These were examined by an optical microscope before and after phase separation. Clear film sample before phase separation did not show any structure. Figure 4.17 shows a picture of a 50/50 PES/phenoxy blend after phase separation. This sample was phase separated by heating the blend to  $200^{\circ}\text{C}$  (the cloud point for a 50/50 blend is  $185^{\circ}\text{C}$ ), keeping at this temperature for 10 minutes and then quenching in liquid nitrogen to avoid remixing on cooling. Phase separated domains are clearly seen.

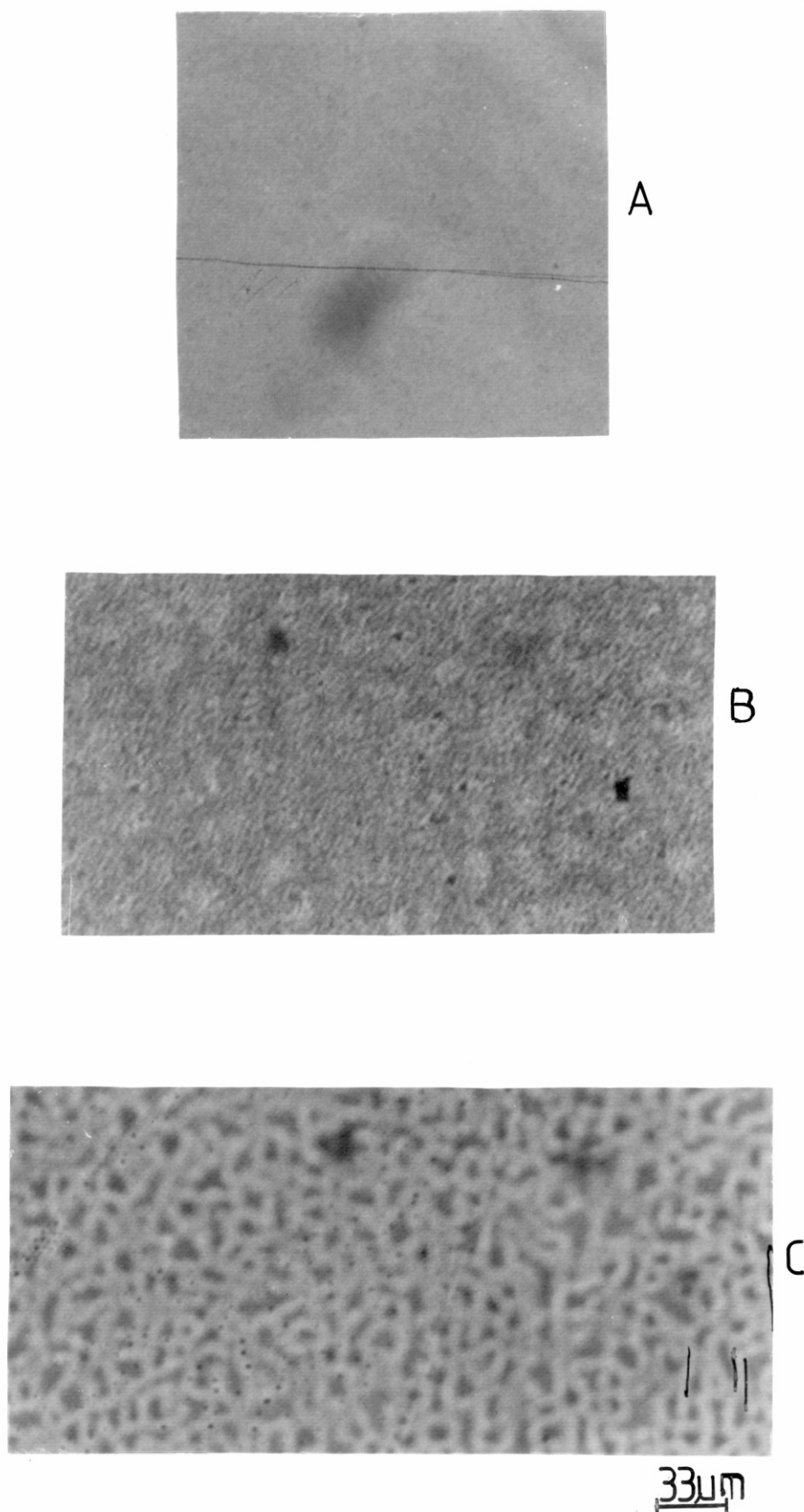


Figure 16 Optical microscope pictures of an 80:20 (weight ratio) PES:PEO blend, (A) at room temperature as prepared, and (B) and (C) at 128°C showing the structure which develops, (B) as soon as the first signs of phase separation are detected, and (C) 10 seconds later.

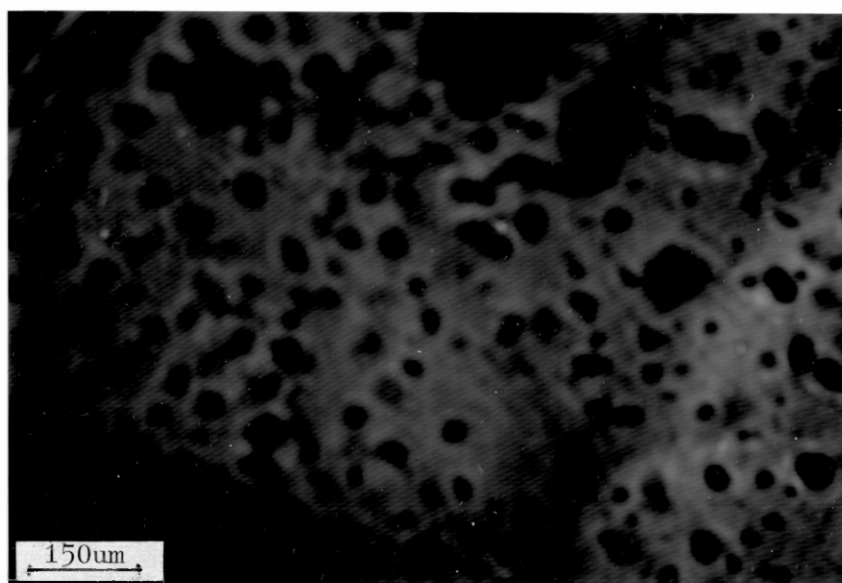


Figure 4.17 Optical microscope picture of an 50:50 PES:Phenoxy blend after phase separation at 200°C and chilling.

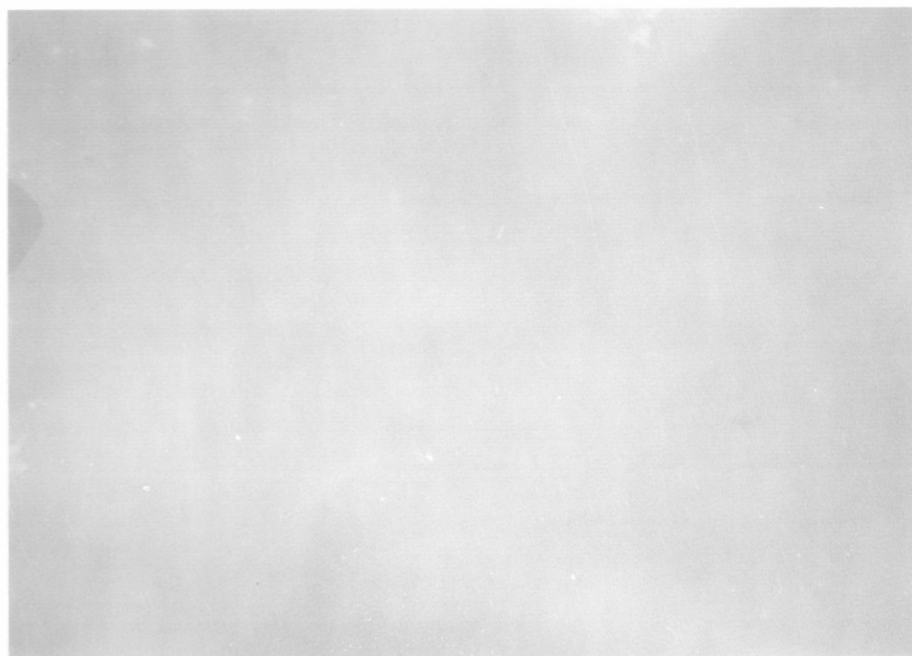
The morphological features of blends of PES/PEO were also studied using transmission electron microscopy. An example of a 83.5/16.5 PES/PEO (molecular weight 4000) blend before and after phase separation as examined in the transmission electron microscope is shown in Figure 4.18. The sample was phase separated by heating to 150°C (20° above the cloud point), and then quenched in liquid nitrogen. In picture B (Figure 4.18) phase separated domains are clearly visible. PEO domain sizes appear to be approximately 0.25 $\mu$ m. A picture of 70/30 PES/PEO blend before and after phase separation, observed through a scanning transmission electron microscope is also shown in Figure 4.19. The two phase structure is clearly seen. The samples show a natural contrast in electron microscopy because of the higher electron density of PES due to the presence of heavy sulphur atoms and aromatic rings in the PES (dark phase).

Electron microscopy was not attempted in the case of PES/phenoxy blends. These structurally similar polymers might have resulted in poor phase contrast.

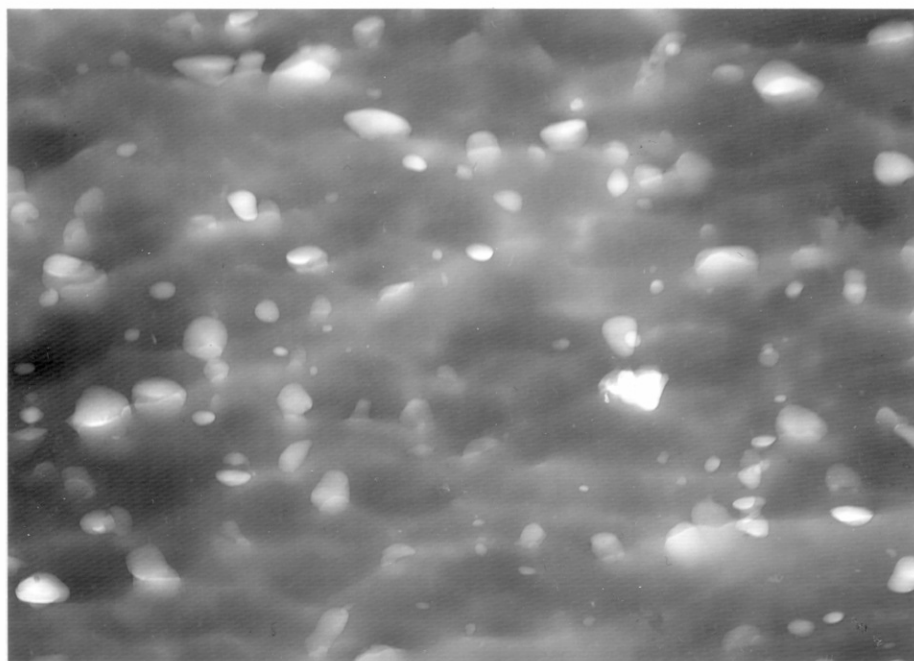
#### 4.5 THE PROPERTIES OF PURE COMPONENTS

The following properties of the pure components were either measured experimentally or obtained from the literature. They were used for the simulation of theoretical phase boundaries of the miscible polymer-polymer systems.

- (a) The specific volume,  $v_{sp} = \frac{1}{d}$
- (b) The thermal expansion coefficient,  $\alpha = \frac{1}{v} \left( \frac{\partial v}{\partial T} \right)_P$
- (c) The thermal pressure coefficient,  $\gamma = \left( \frac{\partial P}{\partial T} \right)_V$
- (d) The surface area per unit core volume ratio of the two components,  $\frac{S_2}{S_1}$



A



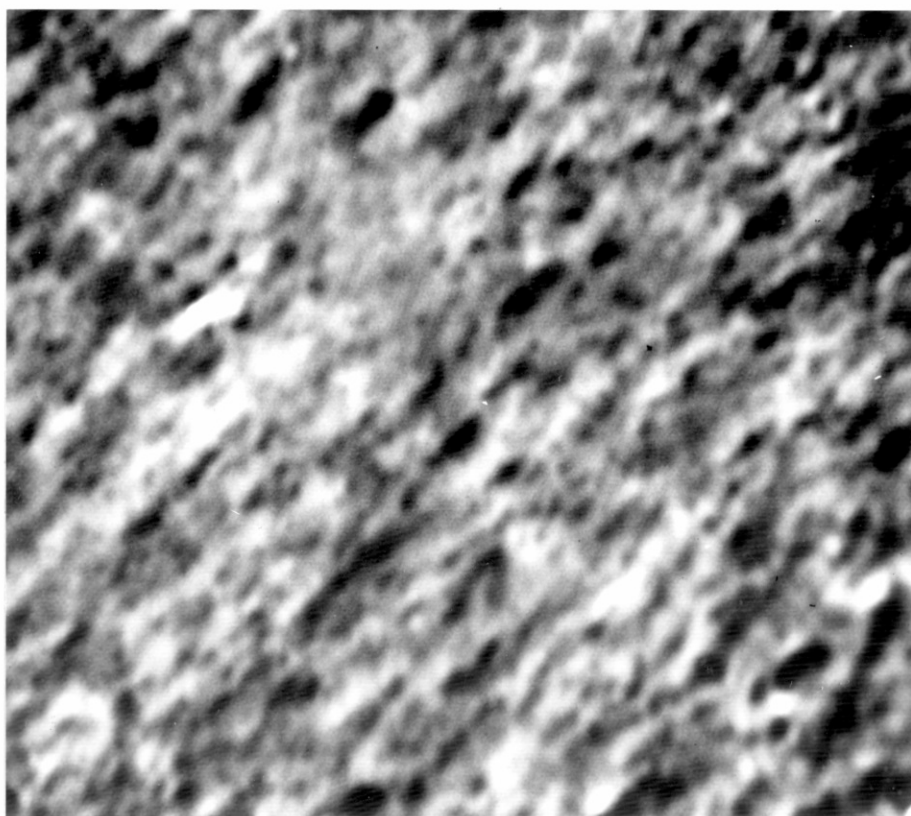
B

0.5μm  
└────────┘

Figure 18 Electron micrograph of an 83.5:16.5 (weight ratio) PES/PEO blend, (A) at room temperature as prepared, and (B) after heating to 150°C and quickly quenching. The system shows a natural contrast. The PEO appears light.



A



B

Figure 19 Scanning transmission electron micrograph of 70:30 (weight ratio) PES/PEO blend, (A) at room temperature as prepared and (B) after phase separation at 150°C and quickly quenching.

1  $\mu$ m

(a) The Specific Volume of the Components

The specific volumes of the pure components are normally obtained from the densities ( $v_{sp} = \frac{1}{d}$ ) at a particular temperature. The temperature dependence of the specific volume is given by :

$$v_{sp} = v_{sp}^0 e^{\alpha \Delta T} \quad 2.103$$

The densities of 4-phenoxy diphenylsulphone, tetraglyme, the phenoxy analogue and PEO (molecular weight 4000) were measured at different temperatures using a 25 ml. pycnometer. Densities of PES<sup>143</sup>, high molecular weight PEO<sup>142</sup> and phenoxy resins<sup>144</sup> were taken from the manufacturers product data information. The values thus obtained are given in Table 4.6.

Table 4.6 Densities and Specific Volumes of Pure Components

| Material                      | Temperature<br>°C | Density gcm <sup>-3</sup> | Specific Volume<br>cm <sup>3</sup> -g <sup>-1</sup> |
|-------------------------------|-------------------|---------------------------|-----------------------------------------------------|
| PES                           |                   | 1.37 (quoted)             | 0.7299                                              |
| PEO (molecular weight 4000)   | 80                | 1.089 ± .0005             | 0.9183 ± .0004                                      |
|                               | 60                | 1.096 ± 0.0005            | 0.9124 ± .0004                                      |
| PEO (molecular weight 20,000) | 20/80             | 1.065 (quoted)            | 0.9389                                              |
| Phenoxy resin                 | 30                | 1.18 (quoted)             | 0.8475                                              |
| 4-Phenoxy diphenylsulphone    | 100               | 1.2441 ± .0005            | 0.8048 ± .0004                                      |
| 4-Phenoxy diphenylsulphone    | 90                | 1.2469 ± .0005            | 0.8020 ± .0004                                      |
| Tetraglyme (PEO analogue)     | 90                | 0.9860 ± .0005            | 1.0420 ± .0004                                      |
| Phenoxy resin (analogue)      | 99                | 1.1426 ± .0005            | 0.8752 ± .0004                                      |
| Phenoxy resin (analogue)      | 80                | 1.1476 ± .0005            | 0.8714 ± .0004                                      |

(b) The Coefficient of Thermal Expansion

The expansion of a material on heating is a phenomenon which depends on internal - mostly intermolecular - forces. The coefficient of thermal expansion is obtained either from densities or from dilatometric measurements of the samples. The latter provides more accurate values for  $\alpha$  at various temperatures. The density measurements tend to give slightly higher values due to trapped air in the oligomeric materials. The temperature and pressure dependence of  $\alpha$ , can be calculated from theoretical considerations when it is written in terms of reduced variables and provided its value is known at one particular temperature and pressure :

$$\alpha = \frac{1}{v} \frac{\partial v}{\partial T} = \frac{\gamma}{T v} \left( \frac{\partial v}{\partial T} \right)_P \quad 4.3$$

$$\partial \alpha (T, P) = \left( \frac{\partial \alpha}{\partial T} \right)_P dT + \left( \frac{\partial \alpha}{\partial P} \right)_T dP \quad 4.4$$

where

$$\left( \frac{\partial \alpha}{\partial T} \right)_{P=0} = (7 + 4 \alpha T) \alpha^2 / 3 \quad 4.5$$

and

$$\left( \frac{\partial \alpha}{\partial P} \right)_T = -(T\alpha/\gamma) \{ 1 + 13 \alpha T/3 + 4 (\alpha T)^2 / 3 \} \quad 4.6$$

Neglecting the pressure dependence of  $\alpha$  at atmospheric pressure gives :

$$\alpha = \alpha_0 + \alpha_0^2 (7 + 4 \alpha_0 T) \Delta T / 3 \quad 2.104$$

This equation was used to calculate  $\alpha$  at the required temperatures.

The thermal expansion coefficient of PES and phenoxy resin were estimated from their linear thermal expansion coefficients<sup>143, 144</sup>.

That for PEO was taken from the literature and density measurements.<sup>142</sup>

The  $\alpha$  values for polymer analogues were obtained from the density measured at two temperatures. The values of the thermal expansion coefficients thus obtained are given in Table 4.7.

Table 4.7  $\alpha$  Values of Pure Components at 25°C

| Material                  | $\alpha \times 10^4 \text{ (K}^{-1}\text{)}$ |
|---------------------------|----------------------------------------------|
| PES                       | 1.65                                         |
| PEO                       | 5.5                                          |
| Phenoxy resin             | 2.0                                          |
| PDS (PES analogue)        | 2.65                                         |
| Tetraglyme (PEO analogue) | 7.0                                          |
| Phenoxy analogue (80°C)   | 2.6                                          |

(c) The Thermal Pressure Coefficients,  $\gamma$ 

Reliable values for the thermal pressure coefficients of polymers are not generally available because of the practical difficulties of measuring this quantity. The thermal pressure coefficients of the pure polymers can be estimated either from the ratio of thermal expansion coefficient,  $\alpha$ , to isothermal compressibility,  $\beta_T$ , as  $\gamma = \frac{\alpha}{\beta_T}$ , or from the solubility parameter. The solubility parameter is related to the cohesive energy density (CED) and hence to the strength of the internal pressure of the molecules. The internal pressure,  $P_i$ , at a given temperature is related to  $\gamma_i$  by<sup>145</sup>

$$P_i \approx T \gamma_i \quad 4.7$$

$$\text{where } P_i = m (\text{CED}) = m \delta_i^2 \quad 4.8$$

$$\text{or } m \delta_i^2 = T \gamma_i \quad 4.9$$

where  $m$  for most polymers is close to one. Thus, knowing the solubility parameter of the components,  $\gamma$  can be calculated at any temperature. The solubility parameter can be obtained from group contributions using tabulated data<sup>142</sup>. These calculations normally give  $\delta$  and  $\gamma$  at 25°C, where the temperature dependence of  $\gamma$  at atmospheric pressure is given by :

$$\frac{\partial \gamma}{\partial T} = -\gamma (1 + 2 \alpha T)/T \quad 4.10$$

$$\gamma = \gamma_0 - \gamma_0 (1 + 2 \alpha_0 T) \Delta T/T \quad 2.105$$

The thermal pressure coefficients of the pure materials at 25°C calculated according to equation 4.9 are given in Table 4.8.

Table 4.8 The Thermal Pressure Coefficients of Pure Components at 25°C

| Material                  | $\gamma$ (J Cm <sup>3</sup> g <sup>-1</sup> ) |
|---------------------------|-----------------------------------------------|
| PES                       | 1.4                                           |
| PEO                       | 1.2                                           |
| Phenoxy Resin             | 1.23                                          |
| PDS (PES analogue)        | 1.5                                           |
| Tetraglyme (PEO analogue) | 1.08                                          |
| Phenoxy analogue          | 1.25                                          |

(d) The Surface per Unit of Core Volume Ratio of the Two Polymers : S<sub>2</sub>/S<sub>1</sub>

This ratio can be calculated from the method of group contributions given by Bondi<sup>147</sup>. Bondi listed the volume of molecules impenetrable to thermal collision, the so called van der Waals volumes, and the corresponding area per molecule. In the case of PES the corresponding data for the C = O group was used as an approximation for the SO<sub>2</sub> group, since this was not available. The surface area per unit core volume can also be calculated by casting shadows of molecules for various orientations, where the area for monomer unit is estimated from the area of the projections<sup>7</sup>. A spherical shape for small molecules and a cylindrical shape for polymers was assumed. Another alternative is the use of the Abe and Flory<sup>119</sup> equation :

$$\frac{S_1}{S_2} = \left( \frac{V_1^*}{V_2^*} \right)^{-1/3} = \left( \frac{r_1}{r_2} \right)^{-1/3} \quad 4.11$$

where  $V^*$  is the product of  $v_{sp}^*$  and the molecular weight of the corresponding component. None of these methods, however, give a precise value for  $\frac{S_1}{S_2}$  and the agreement between the different methods is poor.

The ratio of  $\frac{S_2}{S_1}$  is close to unity when two polymers or two solvents are mixed, unless there is a strong specific interaction within the molecules of one of the components. The ratios of  $\frac{S_2}{S_1}$ , calculated from Bondi's approximation, for the systems investigated, are presented in Table 4.9. In this calculation the intermolecular interactions of the two components were ignored.

Table 4.9  $\frac{S_2}{S_1}$  Ratio's for the Components

| Materials             | $\frac{S_2}{S_1}$ |
|-----------------------|-------------------|
| PEO/PES               | 1.2               |
| Tetraglyme/PDS        | 1.2               |
| Phenoxy resin/PES     | 1.084             |
| Phenoxy analogues/PDS | 1.087             |

#### 4.6 MELTING OR CRYSTALLISATION POINT DEPRESSION

In polymer blends where one of the components is crystalline or partially crystalline, values of the melting point depression can be used to calculate values of the interaction parameter. The crystallisation and melting behaviour of PEO in the PES:PEO blends was studied by DSC and by light scattering turbidimetry. Both of the techniques, in both heating and cooling, have problems in determining the equilibrium thermodynamic melting point. In heating, equilibrium is difficult to achieve because of slow diffusion rates

and initial large scale inhomogenities and in cooling, the problem is supercooling. The DSC used has a minimum rate of heating or cooling of  $1 \text{ K min}^{-1}$ , whereas the turbidimeter has a minimum rate of  $0.1 \text{ K min}^{-1}$  and therefore turbidimetry measurements are preferred. The beginnings of the melting or cooling thermograms were taken as melting or crystallisation points. Similarly the beginning of the increase in the intensity of light during heating or cooling in turbidimetry was taken as the melting or crystallisation point. Others have taken, the peak<sup>102</sup> or the end<sup>30, 88</sup> of the melting thermographs as the melting or crystallisation points. Since two techniques respond to different physical properties of the system their sensitivity will be different for different systems. This system produces large scale heterogeneity and a very sharp increase in turbidity on cooling into the crystalline region and therefore turbidimetry was used at a very low cooling rate. The actual melting and crystallisation points vary markedly with the method of measurement and rate of temperature change. The melting point depressions do not vary very much and are within experimental error (which is quite large) in most cases. The interaction parameters calculated from these results therefore also agree within experimental error. For PES/PEO systems this method gives good turbidity measurements for the higher molecular weight PEO used. The details of experimental procedure are given in Section 3.52.

The measured crystallisation points are given in Table 4.10 along with the extrapolated results for pure PEO (since turbidity plots were not good for this). All temperatures could be determined reproducibly to within  $0.10$  to  $0.2^{\circ}\text{C}$  and the same error is estimated in

the extrapolated value. Only blends containing 75 volume percent PEO or greater had measurable melting or crystallisation points.

Table 4.10 Crystallisation Temperature of PES/PEO Blends

| Volume fraction of PES | Crystallisation temperature of PEO in °C |                               |
|------------------------|------------------------------------------|-------------------------------|
|                        | Polyox WSRN 80 (MW 200,000)              | Carbowax M20 (MW 15000-20000) |
| 0                      | 54.5                                     | 52.4                          |
| 0.008                  | 54.3                                     | 52.3                          |
| 0.016                  | -                                        | 52.2                          |
| 0.04                   | 53.8                                     | 51.85                         |
| 0.08                   | 53.0                                     | 51.2                          |
| 0.17                   | 51.1                                     | 49.6                          |
| 0.25                   | 49                                       | -                             |

A generalised form of the melting point depression equation, 1.15, as given by Kwei and Frisch<sup>88</sup>,

$$\Delta H_u (T_m^0 - T_m) / \phi_1 R T_m^0 - T_m / m_1 - \phi_1 T_m / 2m_2 = C/R - b\phi_1 \quad 1.15$$

is used to calculate the interaction parameter  $\chi'_{21}$ . The interaction parameter  $\chi$  is related to  $b$  through the expression

$$\chi'_{21} = a + b/T \approx b/T \quad 4.12$$

where  $a$  is a constant which is considered negligible and  $T$  is the melting temperature.

Values of  $\Delta H_u = 8.79 \text{ K J mol}^{-1}$ <sup>107</sup>,  $V_2 = 38.9 \text{ cm}^3 \text{ mol}^{-1}$ <sup>107</sup> and

$V_1 = 169 \text{ cm}^3 \text{ mol}^{-1}$  (calculated), were used. The values of the LHS of equation 1.15 and the crystallisation point depression for blends of PES with PEO of molecular weight 200,000 and 20,000 respectively are given in Table 4.11.

Table 4.11 LHS of Equation 1.15, &  $\Delta T$  for PES/PEO Blends

| Vol Fraction of<br>PES: $\phi_1$ | Polyox WSRN 80                |              |                 | Carbowax M20                  |              |                 |
|----------------------------------|-------------------------------|--------------|-----------------|-------------------------------|--------------|-----------------|
|                                  | Crystallisation Temperature K | $\Delta T$ K | LHS of Eq. 1.15 | Crystallisation Temperature K | $\Delta T$ K | LHS of Eq. 1.15 |
| 0.0                              | 327.8                         |              |                 | 325.7                         |              |                 |
| 0.008                            | 327.6                         | $0.2 \pm .2$ | $79 \pm 79$     | 325.6                         | $.1 \pm .2$  | $39.5 \pm 79$   |
| 0.016                            | -                             | -            |                 | 325.5                         | $.2 \pm .2$  | $39.5 \pm 39.5$ |
| 0.04                             | 327.1                         | $0.7 \pm .2$ | $55.5 \pm 16$   | 325.2                         | $.5 \pm .2$  | $43.5 \pm 17$   |
| 0.08                             | 326.3                         | $1.5 \pm .2$ | $59.45 \pm 8$   | 324.5                         | $1.2 \pm .2$ | $47.5 \pm 8$    |
| 0.17                             | 324.6                         | $3.2 \pm .2$ | $63.3 \pm 4$    | 322.9                         | $2.8 \pm .2$ | $52.5 \pm 4$    |
| 0.25                             | 322.3                         | $5.5 \pm .2$ | $69.6 \pm 2.5$  |                               |              |                 |

Plots of the LHS of the above equation against  $\phi_1$ , the volume fraction of PES in the blend are shown in Figure 4.20. From the slope  $b$ , and hence  $\chi'_{21}$  were calculated. The intercept gives  $C/R$ , the morphological contribution. The values of  $\chi'_{21}$  and  $C/R$  obtained at  $60^\circ\text{C}$  for PEO (WSRN 80) (molecular weight  $2 \times 10^5$ ) and Carbowax 20M (molecular weight  $2 \times 10^4$ ) are given in Table 4.12.

There are very large errors inherent in this procedure which are difficult to reduce, since points at higher

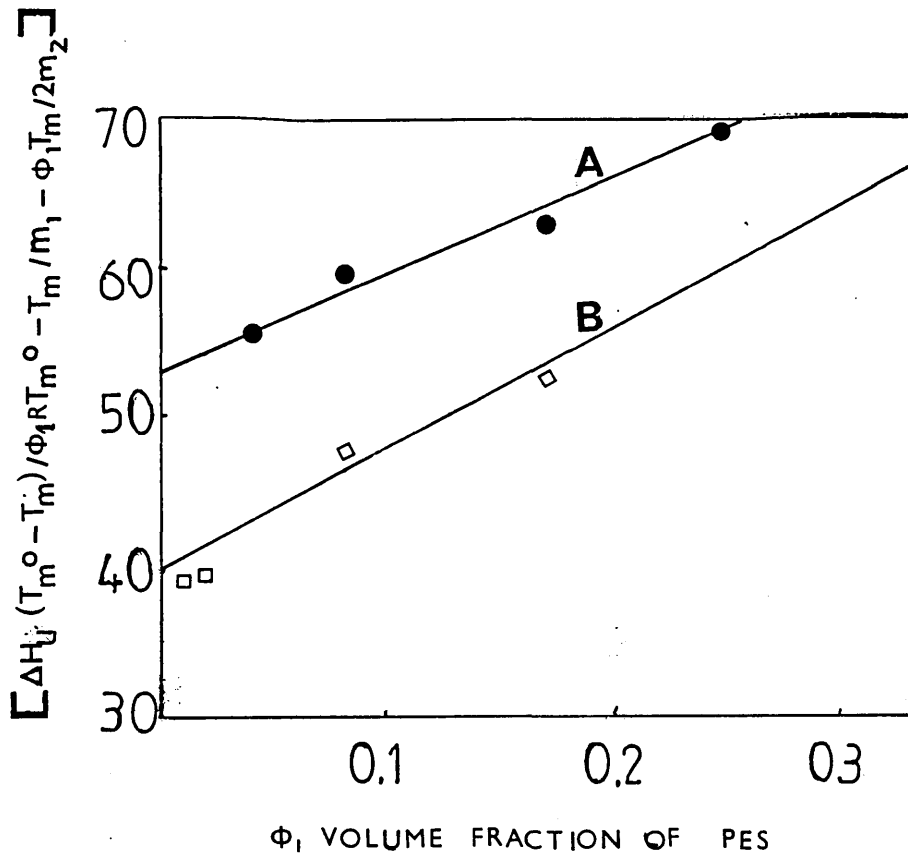


Figure 4.20 A plot of the left hand side of Eq. 1.15 against volume fraction of PES ( $\phi_1$ ) in blends with PEO; (A) PEO WSRN 80 (Mol. Wt. 200,000) and (B) PEO M20 (Mol. Wt. 20,000).

PEO content are more reliable (due to less likelihood of supercooling) but less accurate (due to low  $\Delta T$  values). Along with the above reservations about the effect of morphological contributions we can, therefore, attach very little significance to the absolute values of  $\chi$ , except to say that they appear to be negative which is in agreement with the observed miscibility of the two polymers at the temperature of measurements.

Table 4.12 The Values of  $\chi_{21}^i$  and  $\frac{C}{R}$  obtained from crystallisation point depression.

| PEO used (mol.mass<br>g.mol <sup>-1</sup> ) | $\chi_{21}^i$ | $C/R$ (K <sup>-1</sup> ) |
|---------------------------------------------|---------------|--------------------------|
| WSRN 80 (2 x 10 <sup>5</sup> )              | -0.20         | -53                      |
| Carbowax M20 (2 x 10 <sup>4</sup> )         | -0.23         | -39                      |

The term  $C/R$  represents the effect of morphological factors such as imperfections in crystals and reduction in lamellar thickness. From the data it seems that the morphological effects are large in both cases.  $C/R$  appears to increase with an increasing molecular weight of PEO. This is contrary to the findings reported by Kwei and Frisch<sup>88</sup>. However, the differences should be interpreted with caution because of the errors involved in the procedure. We could better say that the morphological effects are probably similar in both cases.

The melting point depression equation 1.15, which has been modified in terms of the equation of state theory<sup>129</sup>, is given in Chapter 2 section 2.42. Equation 2.107 and 2.109 (reproduced here) have been used with the melting point data in Table 4.11 to obtain values of  $\bar{X}_{12}$  ( $\bar{X}_{12} = X_{12} - T_v^{\infty} Q_{12}$ ).

$$\begin{aligned}
& \frac{\Delta H_u (T_m^0 - T_m)}{\phi_1 R T_m^0} - \frac{T}{m_2} \left( \frac{\ln \phi_2}{\phi_1} - \left(1 - \frac{r_2}{r_1}\right) \right) \\
& - \frac{P_2^* V_2^*}{R \phi_1 m_2} \left\{ 3T_2 \ln \frac{(\tilde{v}_2^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right\} \\
& = \frac{V_2^* \bar{X}_{12} \theta_1^2 S}{\phi_1 R \tilde{v} m_2} + \frac{C}{R}
\end{aligned} \tag{2.107}$$

$$\begin{aligned}
& \frac{\Delta H_u (T_m^0 - T_m)}{\theta_1 R T_m^0} - \frac{T}{m_2} \left( \frac{\ln \phi_2}{\theta_1} - \left(1 - \frac{r_2}{r_1}\right) \frac{\phi_1}{\theta_1} \right) \\
& - \frac{P_2^* V_2^*}{R \theta_1 m_2} \left\{ 3T_2 \ln \frac{(\tilde{v}_2^{1/3} - 1)}{(\tilde{v}^{1/3} - 1)} + \frac{1}{\tilde{v}_2} - \frac{1}{\tilde{v}} \right\} \\
& = \frac{V_2^* \bar{S} \bar{X}_{12} \theta_1}{R \tilde{v} m_2} + \frac{C'}{R}
\end{aligned} \tag{2.109}$$

The total interaction parameters were estimated for the mixtures with different molecular weights of PEO. Within the range of data used it was assumed that  $\bar{X}_{12}$  is temperature independent. If the LHS of equation 2.107 was plotted against  $\phi_1$  and the LHS of equation 2.109 against  $\theta_1$  (site fraction of species 1). The slope of the first would give

$$\frac{V_2^* \bar{S} \bar{X}_{12}}{m_2 R \tilde{v}} \left[ \frac{\theta_1}{\phi_1} \right]^2 \approx \frac{V_2^* \bar{X}_{12}}{m_2 R \tilde{v}_2 S} \tag{2.108}$$

as  $\phi_1$  tends to zero.

The slope of the second (from equation 2.109) would give :

$$\frac{V_2^* \bar{S} \bar{X}_{12}}{R \tilde{v} m_2} \approx \frac{V_2^* \bar{S} \bar{X}_{12}}{R \tilde{v}_2 m_2} \tag{2.110}$$

whichever above equation is used, in order to calculate  $\tilde{v}$ , a value of  $X_{12}$  is needed to be used in equation 2.68.

If the entropy correction parameter  $Q_{12}$  is zero then  $\bar{X}_{12} = X_{12}$  and the equations can be solved iteratively but if  $Q_{12}$  is not zero then an exact solution is not possible. It was found that the resulting value of  $\bar{X}_{12}$  was not very dependent on the value of  $X_{12}$  chosen to calculate  $\bar{V}$  and a good estimate of  $\bar{X}_{12}$  could be obtained within a reasonable range of values of  $X_{12}$ .  $\bar{X}_{12}$  was thus calculated by a computational method. The resulting values of  $\bar{X}_{12}$  for  $X_{12}$  values of -20, -40 and -60 J cm<sup>3</sup> are given in Table 4.13. The experimental error in these values of both  $\bar{X}_{12}$  and  $C/R$  is  $\pm 25$  percent as estimated from the graphs. There are also uncertainties in the interpretation of the origin of  $C/R$  based on the assumption that morphological contribution will contribute to the free energy proportional to  $\theta_1$  and  $\phi_1$  respectively, neither of which may be valid assumptions. This makes the absolute value of  $\bar{X}_{12}$  very doubtful.

#### 4.7 HEATS OF MIXING

Measurement of the heats of mixing of low molecular weight analogues is the most simple method of studying the interaction between the two polymers. This may not always give reliable results due to differences between the high polymers and the analogues used. Heats of mixing of various compositions of low molecular weight analogues were determined at 90°C using a modified NBS batch type calorimeter<sup>82</sup> (see section 3.51).

The heats of mixing results for 4-phenoxy diphenylsulphone (PDS) (an analogue of PES) with tetraglyme (an analogue of PEO) and for PDS with an analogue of the phenoxy resin are given in Table 4.14 and these are plotted in Figure 4.21. The plot shows that for PES/PEO analogues

TABLE 4.13

Values of  $\bar{X}_{12}$  and  $C/R$  ( $C'/R$ ) obtained from melting point depression results from two different PEO samples using different estimated values of  $X_{12}$ .

| PEO<br>g mol <sup>-1</sup> | From the LHS of equation 2.109 against $\theta_1$           |     |                                                             |     |                                                             |     |
|----------------------------|-------------------------------------------------------------|-----|-------------------------------------------------------------|-----|-------------------------------------------------------------|-----|
|                            | $X_{12} = -20 \text{ J cm}^{-3}$                            |     | $X_{12} = -40 \text{ J cm}^{-3}$                            |     | $X_{12} = -60 \text{ J cm}^{-3}$                            |     |
|                            | $\bar{X}_{12} \text{ J cm}^{-3} \text{ C/R or C'/R K}^{-1}$ |     | $\bar{X}_{12} \text{ J cm}^{-3} \text{ C/R or C'/R K}^{-1}$ |     | $\bar{X}_{12} \text{ J cm}^{-3} \text{ C/R or C'/R K}^{-1}$ |     |
| $2 \times 10^4$            | -43                                                         | -43 | -45                                                         | -43 | -47                                                         | -43 |
| $2 \times 10^5$            | -35                                                         | -59 | -37                                                         | -59 | -39                                                         | -59 |
|                            | From the LHS of equation 2.107 against $\phi_1$             |     |                                                             |     |                                                             |     |
| $2 \times 10^4$            | -48                                                         | -35 | -50                                                         | -35 | 53                                                          | -35 |
| $2 \times 10^5$            | -42                                                         | -48 | -44                                                         | -48 | -46                                                         | -48 |

the heats of mixing are negative for all the compositions. This suggests a favourable interaction between two polymers and miscibility. Clearly the enthalpies of mixing are composition dependent and the maximum favourable heat of mixing obtained is at about 70 percent PEO in the blend. The heat of mixing curve is skewed towards the high PEO compositions. The heats of mixing of the PDS/phenoxy analogue are, however, very close to zero albeit slightly negative. In this case the phenoxy analogue was very viscous and this may have caused problems during mixing. Because of the viscosity of the materials errors involved in the measurements are large ( $\pm 0.1 \text{ J g}^{-1}$ ). The heat of mixing results for PES/phenoxy analogues suggest that this system has a very small negative free energy of mixing. The results were used to calculate  $X_{12}$ , the interactional energy parameter.

Table 4.14 Heats of Mixing of PDS/Tetraglyme and PDS/Phenoxy Analogue

| PDS/Tetraglyme |                               | PDS/Phenoxy analogue |                               |
|----------------|-------------------------------|----------------------|-------------------------------|
| Composition    | $\Delta H_M \text{ J g}^{-1}$ | Composition          | $\Delta H_M \text{ J g}^{-1}$ |
| 70/30          | $- 6.7 \pm 0.1$               | 90/10                | $- 0.05 \pm 0.1$              |
| -              | -                             | 85/15                | $+ .017 \pm 0.1$              |
| -              | -                             | 72/28                | $- 0.13 \pm 0.1$              |
| 50/50          | $- 9.6 \pm 0.1$               | 66/34                | $- 0.08 \pm 0.1$              |
| -              | -                             | 50/50                | $- 0.18 \pm 0.1$              |
| 20/80          | $- 8.0 \pm 0.1$               | 34/66                | $- 0.15 \pm 0.1$              |
| 15/80          | $- 4.4 \pm 0.1$               | 16/84                | $+ .02 \pm 0.1$               |
| 10/90          | $- 3.6 \pm 0.1$               |                      |                               |

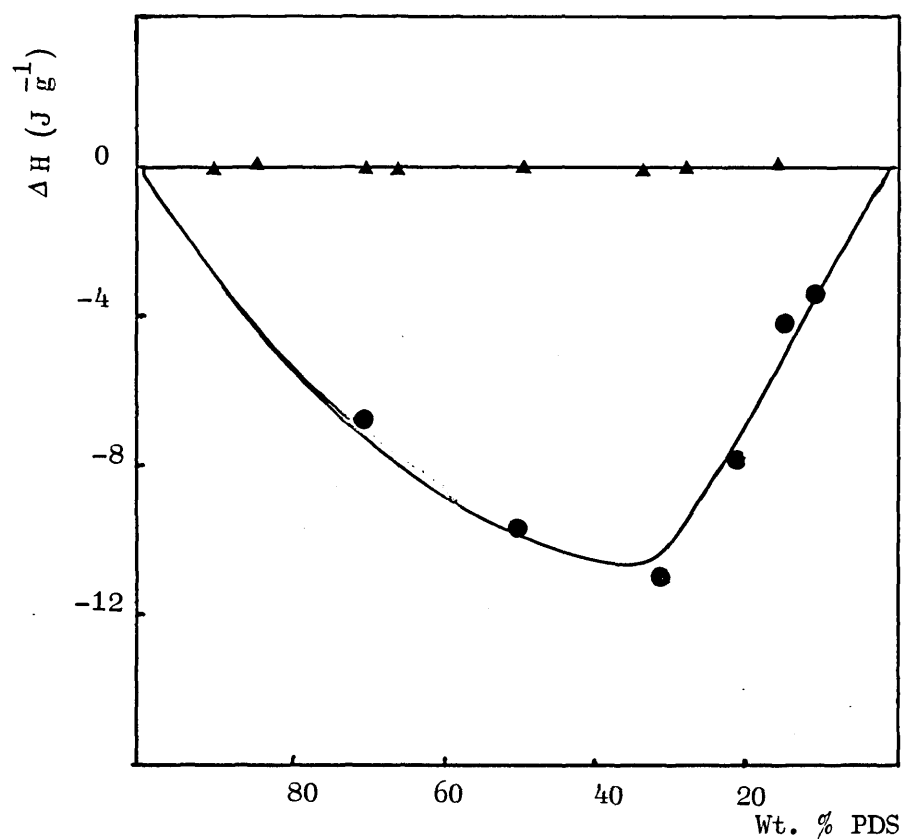


Figure 4.21 A plot of the heat of mixing ( $\Delta H_m$ ) against composition for mixtures of 4-phenoxy diphenylsulphone (PDS), an analogue of PES, with tetraglyme, an analogue of PEO, (●) and PDS with an analogue of phenoxy (▲).

#### 4.71 The Interactional Energy Parameter $X_{12}$

To obtain  $X_{12}$  of the mixture, the theoretical heat of mixing equation 2.73 given by Flory's equation of state theory was fitted to the experimental heat of mixing.

$$\Delta H_m = \bar{r}NV^* \{ \phi_1 P_1^* / \bar{v}_1 + \phi_2 P_2^* / \bar{v}_2 - P^* / \bar{v} \} \quad 2.73$$

$$P^* = \phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \phi_2 X_{12} \quad 2.68$$

To utilise the heat of mixing equation, the pure component state parameters, densities, thermal expansion coefficients, thermal pressure coefficients, which are given in Section 4.5 are required. Knowing the pure component state parameters and a guessed value of  $X_{12}$ , one can calculate  $P^*$  of the mixture using equation 2.68. These values can be substituted in the heat of mixing equation 2.73 in order to calculate values of  $\Delta H_m$ . The value of  $X_{12}$  was varied until a best fit to the experimental  $\Delta H_m$  values was obtained. The results of this fitting process for PES/PEO are shown in Figure 4.22 for a value of  $X_{12} = -40 \text{ J cm}^{-3}$ . As shown, the experimental heat of mixing is skewed towards the region richer in tetraglyme. The theoretical heat of mixing curve, on the other hand, is more symmetrical which is probably due to the fact that the theory does not take account of specific interaction effects in the mixture. The value of  $X_{12}$  obtained in this way for oligomeric mixtures was assumed to be equivalent to that of the corresponding polymeric mixtures and was used for further calculations.

For the PES analogue (PDS) and Phenoxy analogue Figure 4.23 shows that a value of  $X_{12} = -1.5 \text{ J cm}^{-3}$  gives a theoretical curve similar to experimental heat of mixing curve. Both theoretical and

experimental curves are symmetrical in this case. For comparison theoretical curves with  $X_{12} = -1$  and  $-2 \text{ J cm}^{-3}$  are also shown. These curves also lie within the experimental error of the measurements. This value of  $X_{12}$  was used to simulate spinodals.

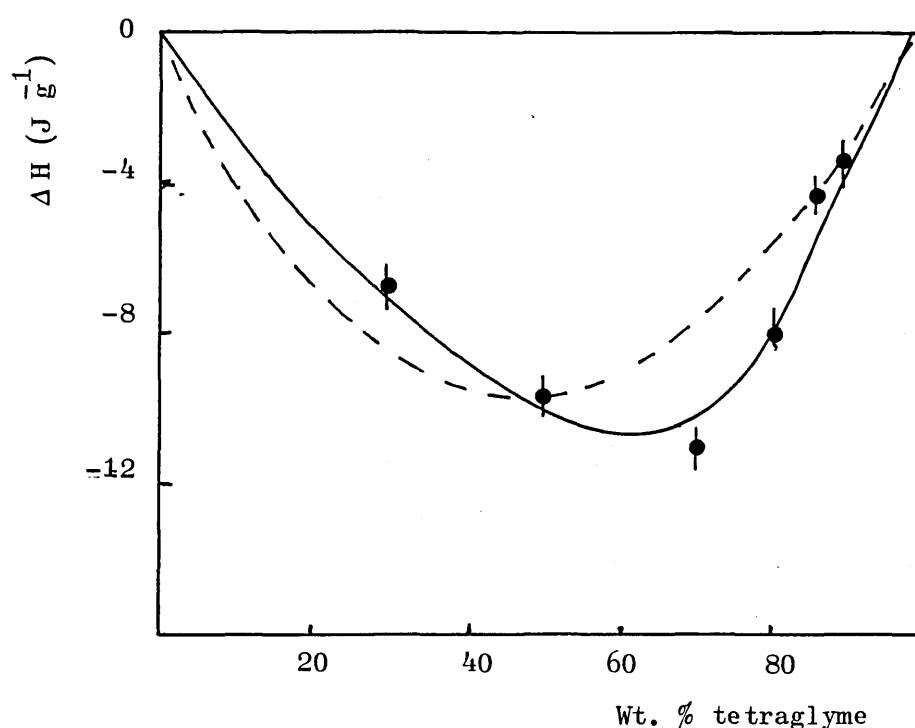


Figure 4.22 A plot of the heat of mixing ( $\Delta H_m$ ) against composition for mixtures of tetraglyme, an analogue for PEO, with 4-phenoxy diphenyl sulphone, an analogue for PES. The solid line follows the experimental results, the dashed line is theoretical result based on equation 2.73 and 2.68 with a value of  $X_{12} = -40 \text{ J cm}^3$ .

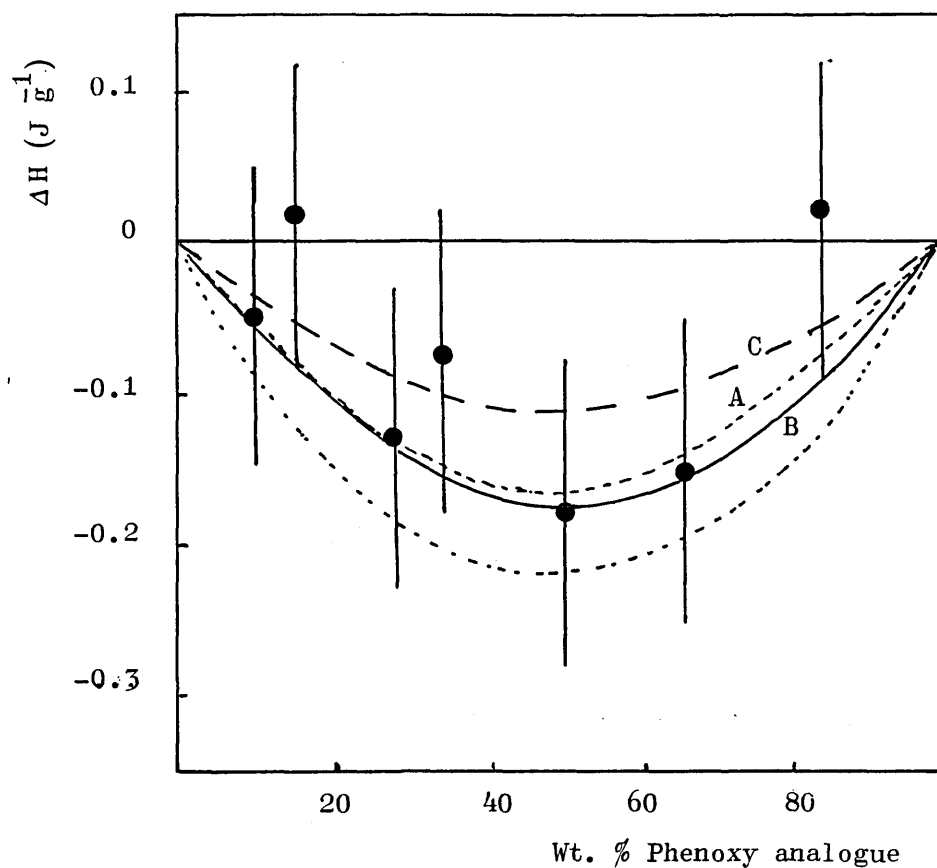


Figure 423 A plot of the heat of mixing ( $\Delta H_m$ ) against composition for mixtures of an analogues of phenoxy resin with 4-phenoxy-diphenylsulphone, an analogue for PES. The experimental points are shown with error bars and dotted lines (A) with a value of  $X_{12} = -1.5$ , (B)  $X_{12} = -2$  and (C)  $X_{12} = -1.0 \text{ J cm}^3$ .

#### 4.8 SIMULATION OF THE SPINODAL PHASE DIAGRAM

To simulate the spinodal curves for mixtures the procedure was to calculate a value of the interactional energy parameter,  $X_{12}$ , from heat of mixing data (as given in Section 4.71). The combinatorial entropy parameter  $Q_{12}$  was then used as an adjustable parameter to fit the minimum of the spinodal to the minimum of the cloud point curve. Finally the full spinodal curve was calculated using these values and compared to the measured cloud point curve.

Using the value of  $X_{12} = -40 \text{ J cm}^{-3}$  obtained in the previous section from the heats of mixing of the PES analogue with the PEO analogue at  $90^\circ\text{C}$ , together with the data given in Tables 4.6, 4.7, 4.8, and 4.9, the spinodal curves of the PES/PEO mixtures were simulated by means of equation 2.101 using the procedure given above.

$$\begin{aligned} \frac{\partial}{\partial \phi_2} \left( \frac{\Delta \mu_1}{RT} \right) = & 1/\phi_1 + (1 - r_1/r_2) + (P_1^* V_1^*/(RT_1^*)) \left( -D/(\tilde{v} - \tilde{v}^{2/3}) \right) \\ & + P_1^* V_1^* D/(RT \tilde{v}^2) + P V_1^* D/(RT) \\ & + V_1^* X_{12}^2 \theta_2^2 \theta_1 / (RT \tilde{v} \phi_1 \phi_2) - V_1^* X_{12}^D \theta_2^2 / (RT \tilde{v}^2) \\ & - V_1^* Q_{12}^2 \theta_2^2 \theta_1 / (R \phi_1 \phi_2) \end{aligned} \quad 2.101$$

In these simulations a value of  $Q_{12}$  was chosen to match the minimum point of the spinodal curve to that of the cloud point curve. A constant value of  $Q_{12} = -0.048 \text{ J cm}^{-3} \text{ K}^{-1}$  thus obtained for a value of  $X_{12} = -40 \text{ J cm}^{-3}$  was used to simulate the whole spinodal curve. Results of these simulations together with an experimental cloud point curve for a PEO molecular weight of  $200,000 \text{ g mol}^{-1}$  are shown in Figure 4.24. The dependence of the spinodal curve on the molecular weight of PEO is also shown. Figure 4.24 shows that as the

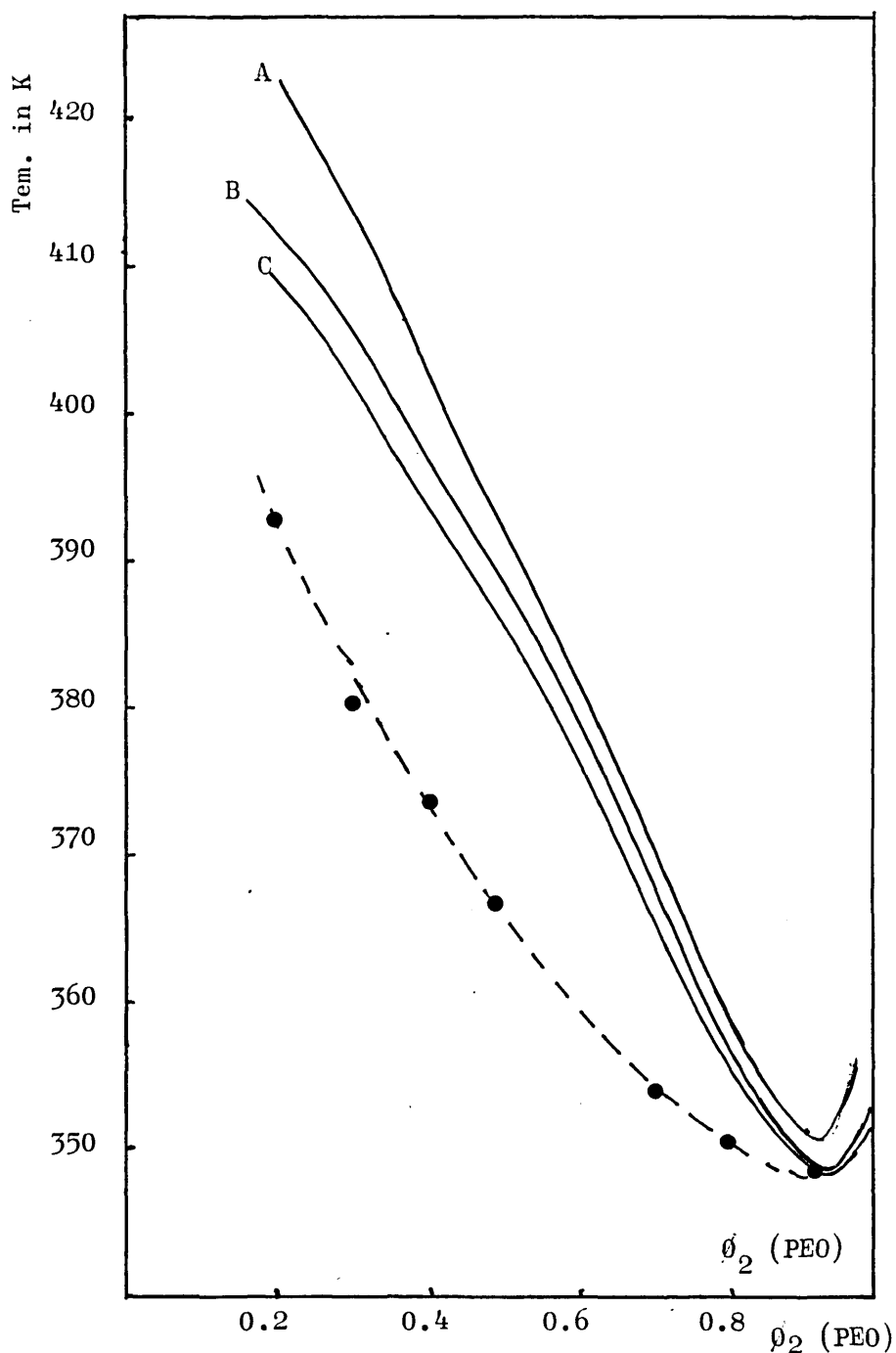


Figure 4.24 Plots of the cloud point curve (dashed line) and simulated spinodal curves for PES-PEO mixtures. The cloud point curve shown is for PEO of molecular weight 200,000 g.mol<sup>-1</sup>. The simulated spinodals are for PEO molecular weight 4000 g.mol<sup>-1</sup> (A), 20,000 (B) and 200,000 (C). The spinodal curves were calculated using a value of  $X_{12} = -40 \text{ J cm}^3$  and a value of  $Q_{12} = -0.048 \text{ J cm}^3 \text{ K}^{-1}$  adjusted to fit the cloud point curve at its minimum.

molecular weight of PEO decreases, the range of miscibility of the mixture increases by only a few degrees which is consistent with the experimental observations. The shape of the simulated spinodals and the position of the minimum are largely as a result of the value of  $S_2/S_1$  and its effect on the last three terms of equation 2.101.

In the case where  $Q_{12} = 0$  is used, a value of  $X_{12} = -18 \text{ J cm}^{-3}$  ( $\equiv \bar{X}_{12}$ ) is required to simulate the spinodal curves. The simulated spinodal curves for various molecular weights of PEO using this value of  $\bar{X}_{12}$  are shown in Figure 4.25. The value of  $\bar{X}_{12}$  from the melting point depression method as given in Table 4.13 are larger than this value. This could either be explained by the large random and systematic errors inherent in this method or by the fact that this value was obtained between 30 and 40°C below the phase boundary. In many systems  $\bar{X}_{12}$  has been found to decrease with temperature.

The simulated spinodals by both these methods lie well inside the observed cloud point curve. This may be due to the fact that the cloud point curve approximates much more closely to the binodal. The mobility of the polymers in this system is very high and the phase separation process is readily reversible on annealing below the cloud point which agrees with this interpretation.

Following a procedure similar to that used for PES/PEO mixtures and using the value of  $X_{12} = -1.5 \text{ J cm}^{-3}$  obtained from the heats of mixing of PES analogue with phenoxy analogue at 90°C, together with the data given in Section 4.5, the spinodal curves of PES/phenoxy mixtures were simulated by means of equation 2.101. Curves were also simulated for values of  $X_{12} = -2$  and  $-3 \text{ J cm}^{-3}$  for comparison. The results of these simulations together with an experimental cloud points are shown in Figure 4.26. When  $X_{12} = -1.5 \text{ J cm}^{-3}$  was used a

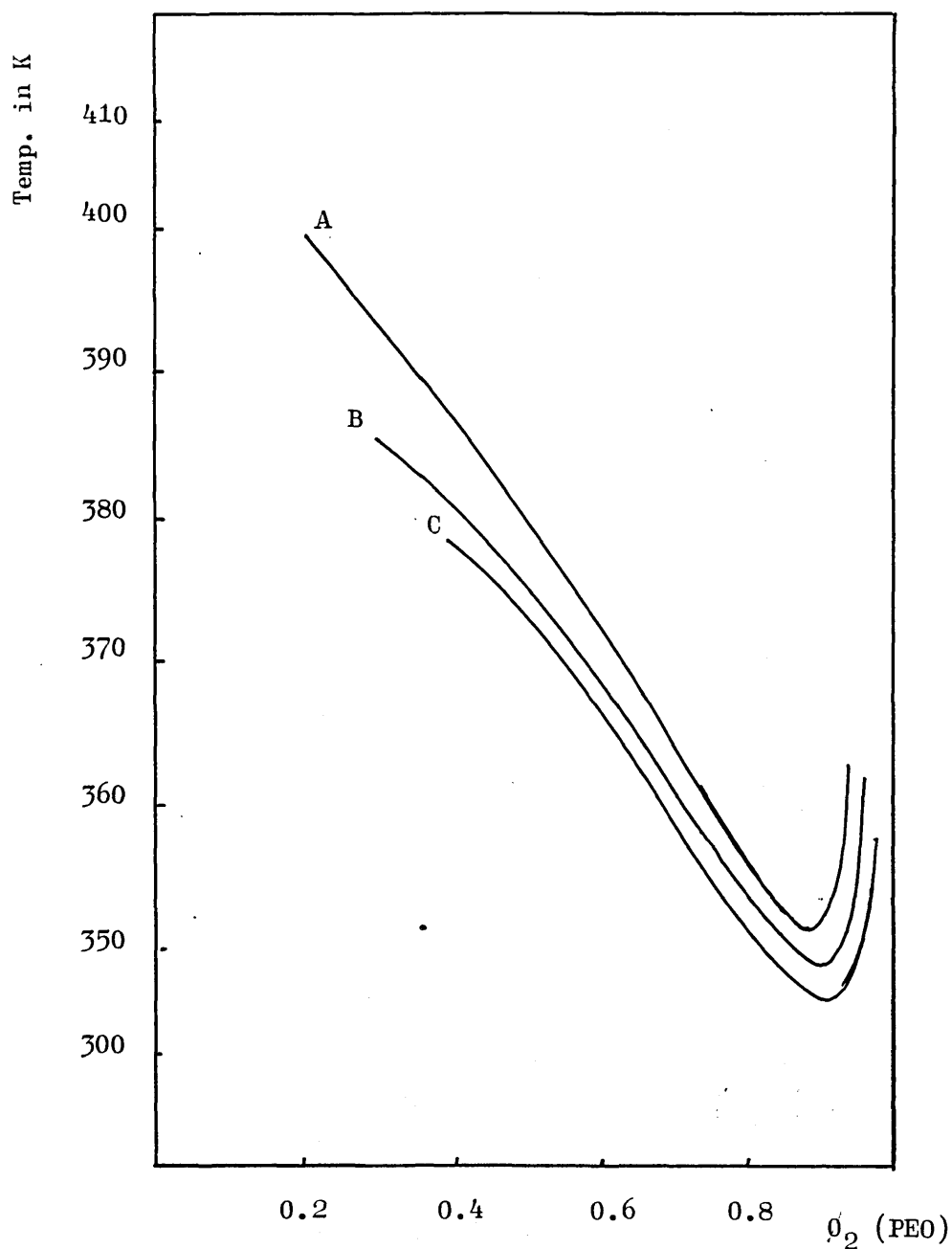


Figure 4.25 Plots of the simulated spinodals for PES with PEO of molecular weight  $4000 \text{ g mol}^{-1}$  (A),  $20,000 \text{ g mol}^{-1}$  (B) and  $200,000 \text{ g mol}^{-1}$  (C). These were calculated assuming  $Q_{12} = 0$  and an adjusted  $X_{12}$  value ( $\bar{X}_{12}$ ) of  $-18 \text{ J cm}^3$ .

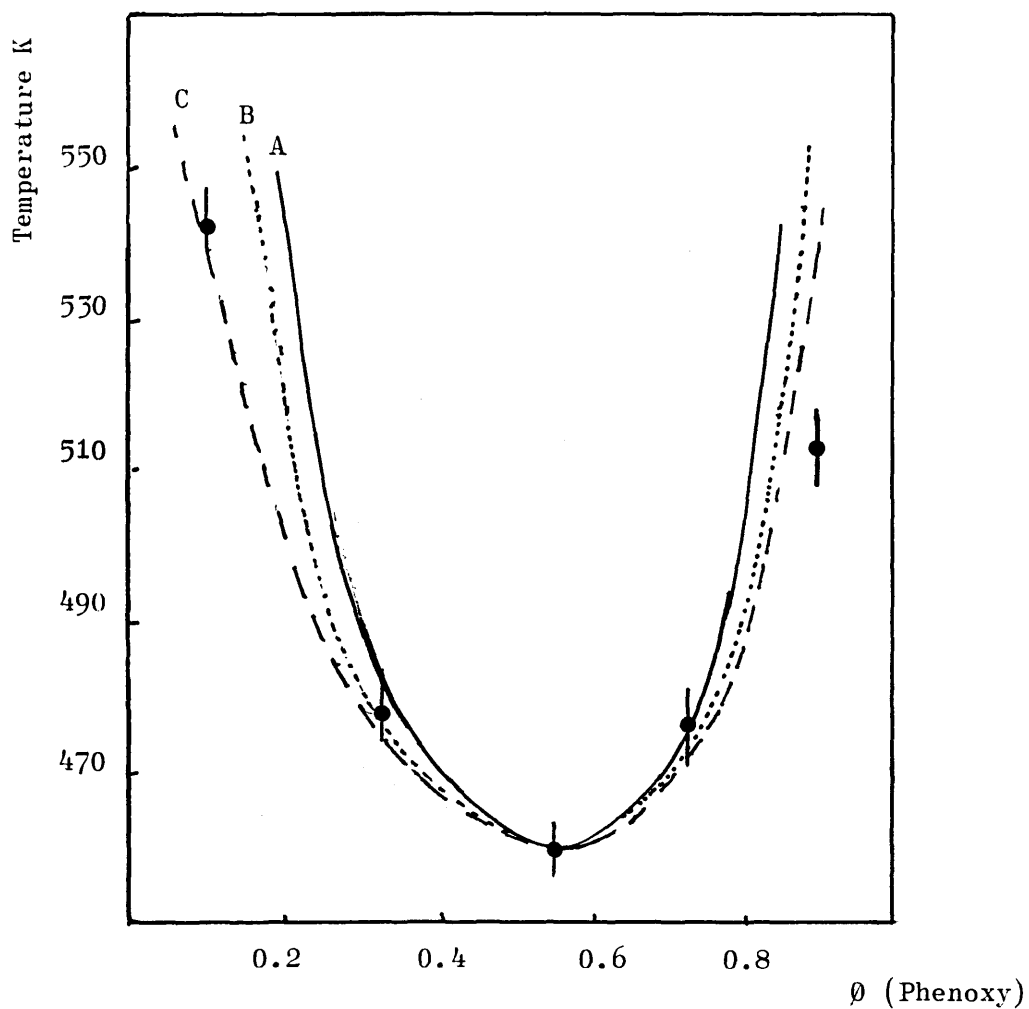


Figure 4.26 Plots of the simulated spinodals for PES with phenoxy resin. These were calculated with  $X_{12} = -1.5$  (A),  $-2.0$  (B) and  $-3.0 \text{ J cm}^3$  (C), and a value of  $Q_{12} = 0.0027$ ,  $-0.00373$  and  $0.00575 \text{ J cm}^3 \text{ K}^{-1}$  respectively adjusted to fit the cloud point curve at its minimum. Experimental cloud points are shown with error bars.

value of  $Q_{12} = -0.0027 \text{ J cm}^3 \text{ K}^{-1}$  was necessary to simulate the spinodal. For a value of  $X_{12} = -2 \text{ J cm}^3$ ,  $Q_{12} = 0.0038 \text{ J cm}^3 \text{ K}^{-1}$  and for a value of  $X_{12} = -3 \text{ J cm}^3$ , a value of  $Q_{12} = -0.00575 \text{ J cm}^3 \text{ K}^{-1}$  gave spinodals to fit the cloud point curve. Thus it seems for a smaller value of  $X_{12}$ , a smaller value of  $Q_{12}$  was required. The best fit to the experimental cloud point was obtained with a value of  $X_{12} = -2.0 \text{ J cm}^3$  and  $Q_{12} = -0.0038 \text{ J cm}^3 \text{ K}^{-1}$ . A decrease in  $X_{12}$  makes the spinodal flatter and an increase makes it sharper. In these calculations the molecular weight of PES and phenoxy were taken as 20,000. The effect of increasing the molecular weight of phenoxy by a factor of two was checked. It was found that a value of 40,000 will make the spinodal curve much flatter and skewed towards the higher molecular weight component, which is in agreement with other findings<sup>22</sup>. An increase in the molecular weight of phenoxy resin to 30,000 and a corresponding change in the value of segmental ratio,  $r_2/r_1$ , did not make significant changes in the simulated spinodal curve. A change in the value of the coefficient of thermal expansion of either component changes the shape of the spinodal and moves it up or down. In this case the minimum of the cloud point is at  $185^\circ\text{C}$  and therefore there is large doubt in the  $\alpha$  value for the phenoxy component because of the lower  $T_g$  of phenoxy. Generally  $\alpha$  values quoted are for the glassy condition. This value can change rapidly above the glass transition temperature. A change in the value of  $\frac{S_2}{S_1}$  from 1.08 to 1.04 did not seem to have much effect on the calculated spinodal in this case.

Considering the large errors involved in the heat of mixing measurement, the simulated spinodals appear to have an excellent fit with the experimental curve.

#### 4.9 SORPTION OF WATER VAPOUR

The water vapour sorptions of PES/PEO and PES/phenoxy blends were measured using the standard McBaine and Bakr type quartz spiral balance. The details are given in Section 3.6.

The sorption isotherms at 30°C for PES, PEO (amorphous) (calculated), PEO (partially crystalline) (experimental) and, 95/5, 90/10, 80/20, 70/30 and 60/40 PES/PEO blends are given in Figure 4.27. The errors involved in the measurement of the water regain were negligible. The greatest errors were in the measurement of pressure (especially at lower activities) and are reflected in the errors of the  $X$  parameter calculated as described in Section 1.43 and given in Table 4.16.

PEO is a crystalline polymer and the isotherm in Figure 4.27 (dotted line) refers to the amorphous phase calculated on the assumption that the degree of crystallinity is unaffected by the sorption of water. This assumption is clearly not valid at the higher activities where eventually complete dissolution of the crystallites occurs. For this reason the isotherm for the amorphous content is only given for lower activities where dissolution of crystallites is less likely. For the amorphous PEO isotherm, the PEO was considered to have 50 weight percent crystallinity<sup>107</sup>. The level of sorption for the PES and for the PES/PEO blends are similar up to activities of approximately 0.6. At activities greater than 0.6, sorption at a given activity increased monotonically with the amount of PEO in the blend. A similar sorption isotherm was obtained for a PEO/polyurethane mixture<sup>146</sup>. Water regains less than for PES were not observed for any of the blends at unit or lower activities as had been reported<sup>108</sup> for 80/20 and 90/10 PES/PEO blends at unit activities.

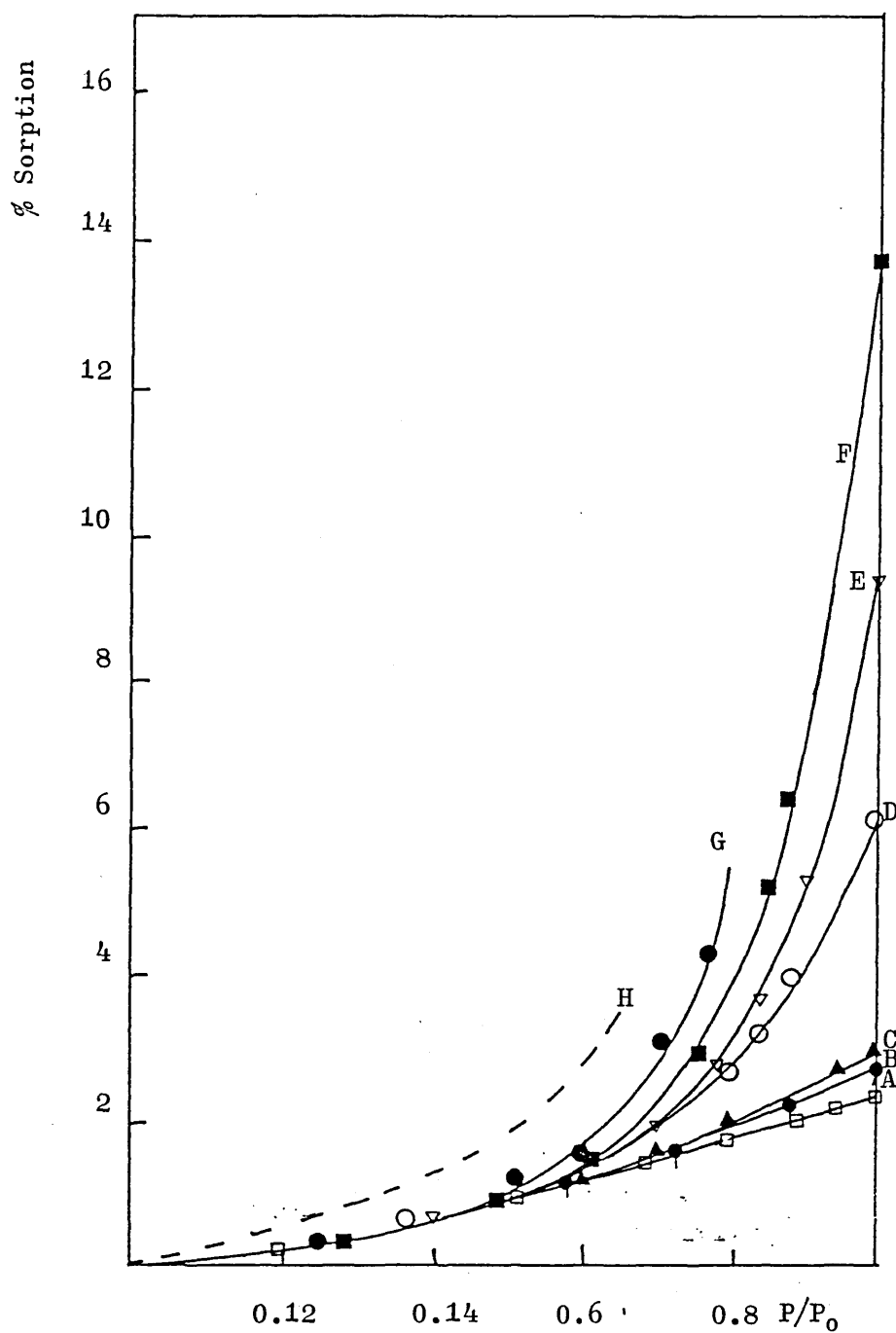


Figure 4.27 Plots of wt. % sorption against relative vapour pressure of water for (A) PES, (G) PEO (semi-crystalline), (H) PEO amorphous and PES:PEO blends at (B) 95:5, (C) 90:10, (D) 80:20 (E) 70:30 and (F) 60:40 weight ratio.

Sorption isotherms were not obtained for blends containing more than 40 percent PEO, because crystallites if present in the blend would have complicated the interpretation of the results. As mentioned earlier (Section 4.2) the crystallisation and melting point behaviour of blends showed no indication of PEO crystallisation up to this value. At higher fractions of PEO there is evidence (from the melting endotherm) of some degree of crystallisation of the PEO component.

The effect of temperature on the sorption of water vapour was studied for the 80/20 PES/PEO blend. Isotherms obtained at 30, 40 and 50°C were virtually coincident over the entire range of activities as shown in Figure 4.28, indicating that the heat of sorption is close to the heat of condensation of water.

The shapes of the isotherms at lower activities were not measured with sufficient accuracy to detect any initial Langmuir type curvature associated with specific localised interactions.

For the homogeneous blends the experimental isotherms lie below that predicted by the additivity rule, calculated using a PEO isotherm for the amorphous phase. Typical examples are shown in Figure 4.29. The uncertainty in the isotherm for the PEO amorphous phase will be reflected in the isotherm predicted by the additivity rule at higher activities because the percentage of crystalline phase is uncertain. For this reason the latter is given for the lower activities only.

The effect of phase separation on the isotherm is shown in Figure 4.30 for an 80/20 PES/PEO miscible blend at 30°C. Phase separation produced by heating at 150°C and chilling, resulted in an increased regain at higher activities consistent with the formation of PEO rich domains with a water regain more characteristic of

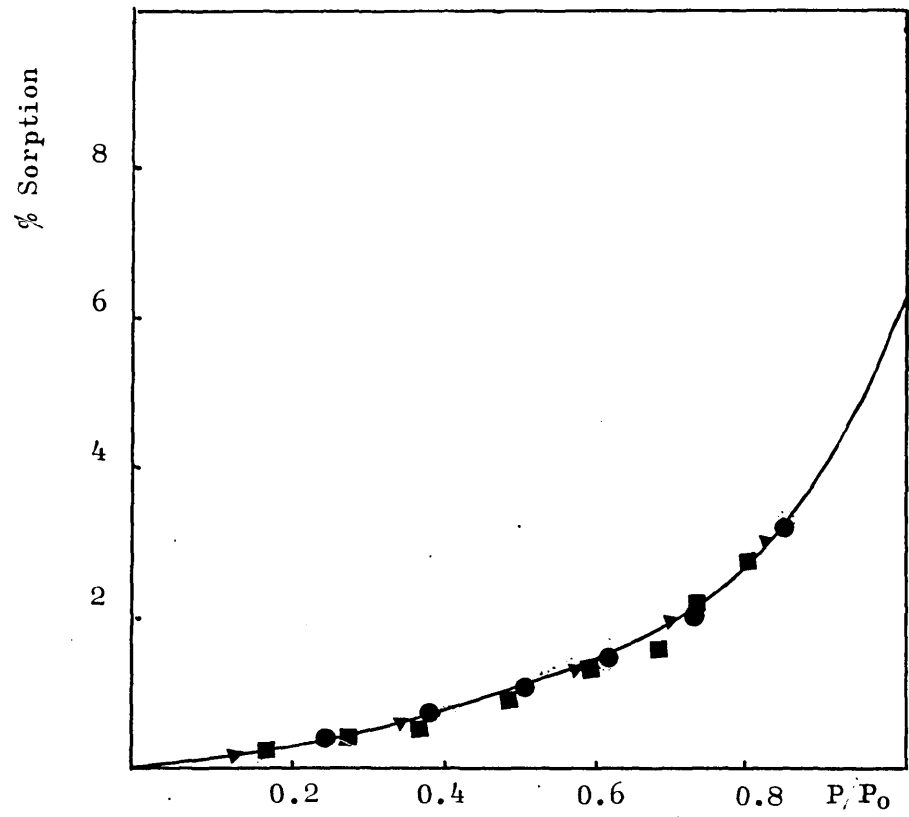


Figure 4.28 Plots of % sorption against the activity of water for 80/20 (weight ratio) PES/PEO miscible blends at 30°(▲), 40°(●) and 50°C(■).

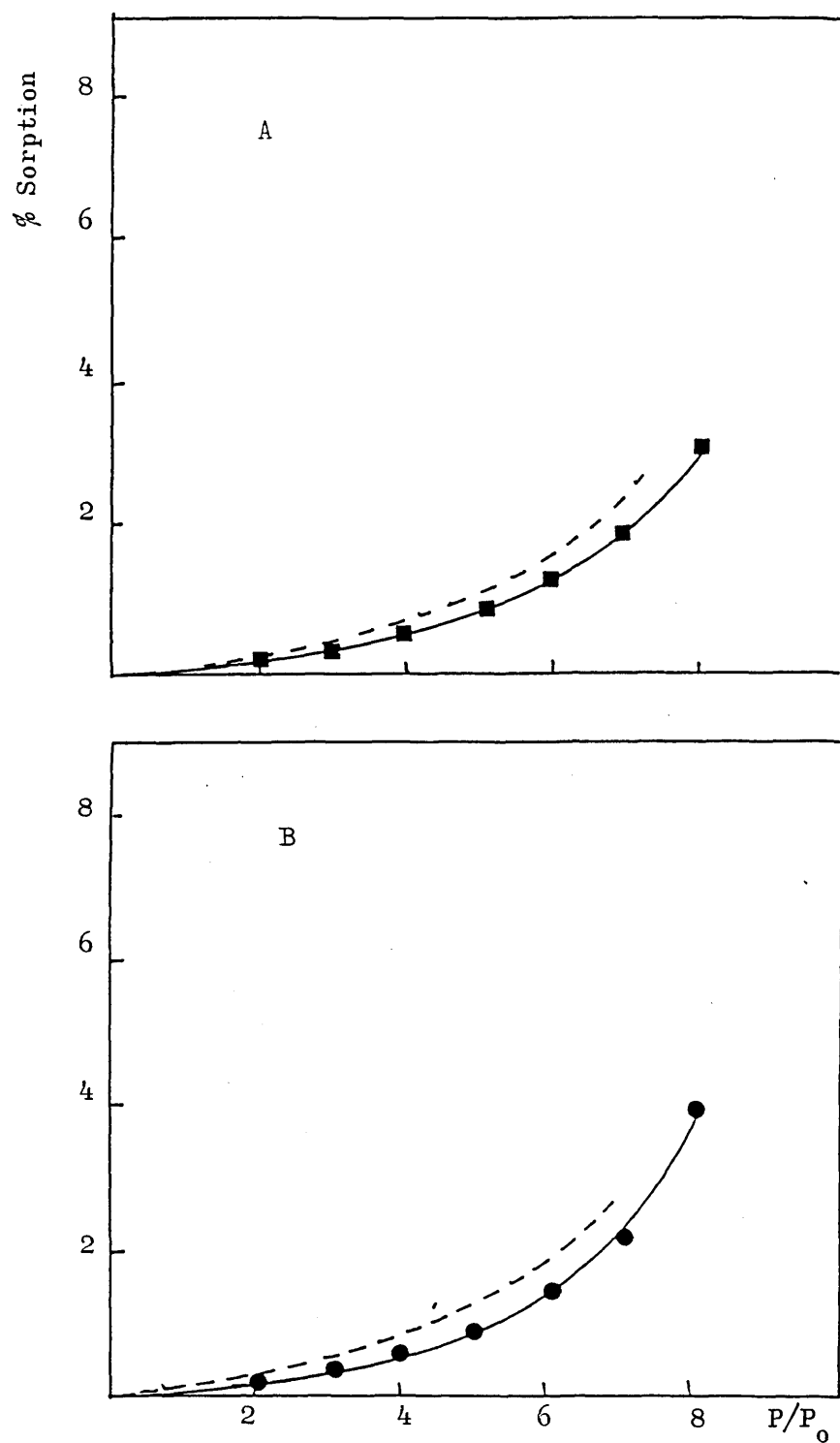


Figure 4.29 Sorption isotherms for PES:PEO at 70:30 (A) and 60:40 (B) wt.ratio. Experimental isotherms (solid line) compared to those calculated by additivity rule.

bulk PEO. There was no significant extraction of PEO from the phase separated blend after prolonged soaking in water consistent with discrete PEO rich domains dispersed in a PES continuum.

Estimates of the average diffusion coefficients were obtained from the half time expression using the plots of  $E_t/E_{\infty}$  against  $(\frac{t}{l^2})^{\frac{1}{2}}$  for sorption. The solubility and the permeability coefficients were calculated from the sorption data using equations given in Section 3.6. The diffusion solubility and permeability coefficients obtained were in the range  $1 \times 10^{-6}$  (PEO) to  $5 \times 10^{-8}$  (PES)  $\text{cm}^2 \text{sec}^{-1}$ , 8.46 (PEO) to 5.37 (PES) cc,  $\text{cm}^{-3} (\text{cm Hg}^{-1})$  and  $8.1 \times 10^{-6}$  (PEO) to  $2.9 \times 10^{-7}$  (PES) c.c (STP)  $\text{cm sec}^{-1} \text{cm}^2 (\text{cm Hg}^{-1})$  respectively (see Table 4.15)

TABLE 4.15 Diffusion, Permeability and Solubility Coefficients of PES/PEO Blends

| Blend Composition    | Activity | Average Diffusion Coefficient $\text{cm}^2 \text{sec}^{-1}$ | Average Permeability Coefficient $\text{cc(STP)} \frac{\text{cm}}{\text{sec}^{-1} \text{cm}^2 (\text{cm Hg}^{-1})}$ | Average Solubility Coefficient $\text{cc.cm}^{-3} (\text{cm Hg}^{-1})$ |
|----------------------|----------|-------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------|------------------------------------------------------------------------|
| 100% PES             | 0.18     | $5.5 \times 10^{-8}$                                        | $2.9 \times 10^{-7}$                                                                                                | 5.37                                                                   |
| 90/10 PES/PEO        | .084     | $6.8 \times 10^{-8}$                                        | $3.4 \times 10^{-7}$                                                                                                | 5.04                                                                   |
| 80/20 PES/PEO        | .06      | $6.8 \times 10^{-8}$                                        | $5.2 \times 10^{-7}$                                                                                                | 7.68                                                                   |
| 70/30 PES/PEO        | .097     | $1.96 \times 10^{-8}$                                       | $1.5 \times 10^{-7}$                                                                                                | 8.0                                                                    |
| 60/40 PES/PEO        | .084     | $1.12 \times 10^{-7}$                                       | $9 \times 10^{-7}$                                                                                                  | 8.13                                                                   |
| 100% PEO (Amorphous) | 0.12     | $0.96 \times 10^{-6}$                                       | $8.1 \times 10^{-6}$                                                                                                | 8.46                                                                   |

From the sorption data of pure PES and PEO and equation 1.13, the interaction parameter  $\chi_{12}$  and  $\chi_{13}$  for  $H_2O$ /PES and  $H_2O$ /PEO were found to be 2.66 and 2.22 respectively. Knowing  $\chi_{12}$  and  $\chi_{13}$  and the sorption for different blend compositions  $\chi'_{23}$  values were calculated using equation 1.12. These values of  $\chi'_{23}$  for different blend compositions at various activities are given in Table 4.16. Large errors are involved in the pressure measurements especially at low activities. The errors in the  $\chi'_{23}$  values due to errors in pressure were calculated and are also given in Table 4.16. A mean value of  $\chi'_{23}$  was found by weighting

Table 4.16 Interaction Parameter Values at Different Activities for 90/10, 80/20, 70/30 and 60/40 PES/PEO Blends

| Blend Composition<br>PES/PEO  | Water Vapour<br>Activity | $\chi'_{23} \pm \text{Error}$ |
|-------------------------------|--------------------------|-------------------------------|
| 90/10                         | 0.27                     | $-0.33 \pm 2.5$               |
|                               | 0.49                     | $-0.99 \pm 1.5$               |
|                               | 0.60                     | $-0.47 \pm 1.2$               |
| 80/20                         | 0.36                     | $-0.47 \pm 1.26$              |
|                               | 0.60                     | $-0.61 \pm 0.76$              |
| 70/30                         | 0.38                     | $-0.8 \pm 0.66$               |
|                               | 0.51                     | $-0.43 \pm 0.65$              |
|                               | 0.60                     | $-0.79 \pm 0.62$              |
| 60/40                         | 0.37                     | $-0.86 \pm 0.74$              |
|                               | 0.50                     | $-0.55 \pm 0.58$              |
| Calculated mean<br>(See text) |                          | $-0.64 \pm 0.26$              |

each result according to :  $w_i = (\text{Error})^{-2}$  and so that

$$\chi'_{23} = \frac{\sum \chi'_{23} w_i}{\sum w_i} \quad 4.13$$

and a weighting for this average given by

$$w = \sum w_i$$

This gave a result  $\chi'_{23} = -0.64 \pm 0.26$ . Because of the large errors involved in the experimental procedure we cannot put any emphasis on the actual numbers except to say that the PES/PEO interaction parameter is negative which is in agreement with the observed miscibility and negative values obtained from the melting point depression data (Section 4.6).

For comparison with other data a value of  $\chi'_{23}$  of  $-0.64$  is equivalent to a value of  $\bar{X}_{12}$  of  $-34 \pm 14 \text{ J cm}^{-3}$  which is, within experimental errors, similar to that obtained from melting point depression data.

The sorption of water vapour in PES/phenoxy mixtures was not studied in such detail as for PES/PEO mixtures. The sorption isotherms at  $30^\circ\text{C}$  for PES, phenoxy, 70/30 and 50/50 PES/phenoxy blends are given in Figure 4.31. The sorption isotherms were again similar up to activities of 0.6. For activities greater than 0.6, the water regains increased with increasing phenoxy content of the blend. None of the blends tested showed water regains less than PES. The polymer-polymer interaction parameters for 70/30 and 50/50 PES/phenoxy blends calculated from sorption at different activities of water vapour are given in Table 4.17. The average value found was  $-0.15 \pm .21$ , which again is a negative value implying miscibility of this system. This value of  $\chi'_{23}$  is equivalent to a value of  $X_{12}$  of  $-9 \pm 12 \text{ J cm}^{-3}$ , which considering

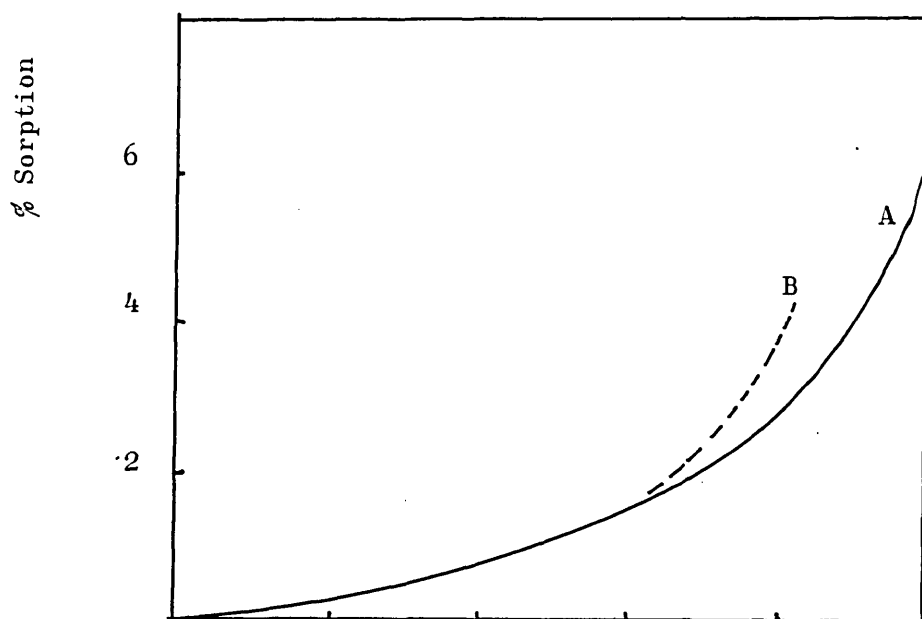


Figure 4.30 Plots of % Sorption against activity of water for 80/20 PES/PEO blend before (A) and after phase separation.(B).

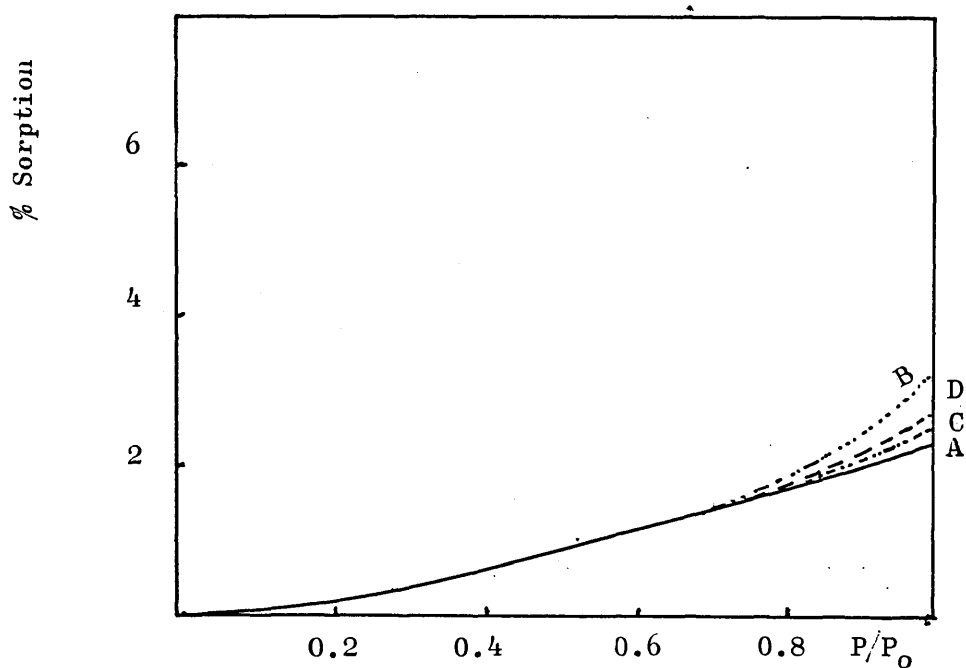


Figure 4.31 Plots of % sorption against activity of water for (A) PES, (B) phenoxy, and PES, phenoxy blends at (C) 70:30 and (D) 50:50 weight ratio.

the errors involved agrees with the previous estimates.

The results show that the water absorption in PES/PEO and PES/phenoxy blends over the whole of the activity and composition range was always greater than for pure PES. The results thus do not agree with previously reported findings of less water absorption by some PES/PEO blends and these blends are not useful to reduce water absorption of PES itself.

Table 4.17  $X'_{23}$  Interaction Parameter Values at Different Activities  
For 70/30 and 50/50 PES/Phenoxy Blends

| Blend Composition<br>PES/Phenoxy | Water Vapour<br>Activity | $X'_{23} \pm \text{Error}$ |
|----------------------------------|--------------------------|----------------------------|
| 70/30                            | 0.15                     | $-0.34 \pm 1.86$           |
|                                  | 0.34                     | $-0.10 \pm 1.1$            |
|                                  | 0.54                     | $-0.072 \pm 0.68$          |
|                                  | 0.67                     | $-0.21 \pm 0.55$           |
|                                  | 0.81                     | $-0.02 \pm 0.46$           |
| 50/50                            | 0.14                     | $-0.21 \pm 20$             |
|                                  | 0.25                     | $-0.2 \pm 0.75$            |
|                                  | 0.41                     | $-0.44 \pm 0.80$           |
|                                  | 0.49                     | $-0.26 \pm 0.6$            |
|                                  | 0.64                     | $-0.058 \pm 0.5$           |
| Calculated mean                  |                          | $-0.15 \pm 0.21$           |

## CHAPTER 5

### DISCUSSION

The results of the miscibility studies of polyethersulphone with two different polymers, poly(ethylene oxide) and phenoxy resin have been presented in the previous Chapter. The results appear to correlate with the current theories of polymer-polymer miscibility and are further discussed below. Other polymers were found not to be miscible with PES and the reasons for this are also considered.

#### 5.1 BLEND PREPARATIONS

The solvents used for preparation of blends were selected on the basis that they dissolved both the polymers and did not cause phase separation on mixing. Cyclohexanone dissolved PES only at temperatures above 70 - 80°C and therefore phase separation studies were limited to temperatures above 80°C.

Similar phase separation studies could have been possible using dimethylformamide; the other solvent used in this work but this was not attempted. A major problem for the solvents used, DMF and cyclohexanone, was the difficulty in attaining complete removal of them from cast films. It was found essential to leave the films of PES/PEO or PES/phenoxy blends at 50°C under vacuum for at least two to three weeks for complete removal of solvents. Residual solvent in the film can affect the glass transition results by having a plasticising effect.

The use of chlorinated solvents was very attractive because of the fast removal of solvent from the blend. Both PES and PEO were found to dissolve in dichloromethane and chloroform but formed a precipitate when mixed. This may have been due to the diff-

erences in polymer/solvent and polymer-polymer interactions.

The origin and shape of the three components (PES/PEO/cyclohexanone) phase diagram shown in Figure 4.2 could be attributed to (a) the strength of polymer-polymer interactions in preference to the polymer-solvent interactions and (b) the difference in the strengths of the two separate polymer-solvent interaction parameters i.e. on the " $\Delta\chi$ " effects ( $\Delta\chi = \chi_{12} - \chi_{13}$ ). Theoretical simulations by Zeman and Patterson<sup>148</sup> showed that at high concentrations the polymer incompatibility is associated with the polymer-polymer interaction ( $\chi_{23}$ ) but at low concentration it is mainly due to differences between  $\chi_{12}$  and  $\chi_{13}$ . Robard et al<sup>149</sup> confirmed this " $\Delta\chi$ " effect for polystyrene/poly(vinyl methyl ether). They found a closed two phase region as predicted by the " $\Delta\chi$ " effect for this system. According to the authors, a homogeneous system is attained only with a suitably small " $\Delta\chi$ " in addition to the necessary requirement of a very small interaction parameter  $\chi_{23}$ . It is thought that " $\Delta\chi$ " effects are responsible for the phase diagram obtained in the present system. The skewness of the phase diagram is perhaps due to the large differences in the two polymer-solvent interactions similar to Ahroni's speculation<sup>45</sup>. The direction of the tie lines in Figure 4.2 also signify a " $\Delta\chi$ " effect.

PES/PEO compositions in dimethylformamide and mixed N-methyl-2-pyrrolidene and dichloromethane also showed phase separation on heating and would have given rise to two phase regions in the multi component phase diagram. Similar effects have been reported for polymers dissolved in mixed solvent<sup>139</sup> and mixed polymers dissolved in co-solvent<sup>149</sup>. The above observations explain the two phase regions of many polymer mixtures prepared from these solvents and shows phase separation on heating to be a common feature of these

solutions.

## 5.2 POLYMER-POLYMER MISCIBILITY

General thermodynamic reasons for the polymer-polymer miscibility have been given in Section 1.1. A majority of polymer pairs which show specific interactions resulting in favourable heats of mixing have been found to be miscible<sup>151, 42, 150, 75</sup>. Structural similarity has been described as the other reason for miscibility<sup>39, 14</sup>. In these cases the polymers with small unfavourable heats of mixing could be miscible if they are outweighed by favourable entropies of mixing.

In this work PES/PEO mixtures and PES/phenoxy mixtures have been found to be miscible. Overwhelming evidence of miscibility has been presented by the observation of optical clarity, single Tg of the blend compositions and phase separation on heating. Low molecular weight analogues of PES and PEO have been found to give large negative heats of mixing. This showed that the miscibility of PES and PEO mixtures results from the strong specific interactions. In the case of PES/phenoxy mixtures, the heats of mixing of the low molecular weight analogues were very small, albeit favourable.

The polyethersulphone repeat unit contains two aromatic rings, one ether oxygen in between two aromatics and one strong electron withdrawing sulphone group. Due to this it can act as an electron acceptor. In the case of PEO every third atom along the polymer backbone is an oxygen atom having two unshared pair of electrons. Because of this it can act as an electron donor. Thus when PES and PEO are mixed together strong specific interaction between donor-acceptor molecules can be expected to take place and the polymers are found to be miscible. It is not certain, which groups of the

PES molecule interact with PEO. It is possible that the interaction is between  $\pi$  electrons of the aromatic groups with two ether oxygen electrons of the PEO.  $n-\pi$  interactions between free electrons of the ester group and the aromatic ring between benzene-ester mixtures were reported by Grollier et al<sup>152</sup>. Similar interactions between aromatic moieties of polystyrene and poly(vinyl methyl ether) have been postulated<sup>43</sup>. Cruz et al<sup>97</sup> have suggested the possibility of  $n-\pi$  complex formation between the electrons of ester carbonyl groups and the aromatic rings of polycarbonate in their work on the miscibility of various polyesters with polycarbonates. The miscibility of modified polystyrene with a number of polyacrylates, poly(vinyl methyl ether), polyphenylene oxide, polycarbonate copolymer, polyamides and polyesters has been suggested due to hydrogen bonding<sup>153</sup>. Polymers containing carbonyl and carboxyl groups such as acrylates and esters were examined for their compatibility with PES. As shown in Section 3.33 none of the polymers examined, poly(ethylene adipate), poly(methyl acrylate), poly(ethylacrylate) and poly(methylmethacrylate) were found to be miscible. Poly(vinyl methyl ether) which contains an ether oxygen, similar to PEO was also found to be immiscible with PES. This implied that the oxygen electrons which are freely available in PEO are somehow restricted in poly(vinyl methyl ether) possibly because of steric restrictions. Poly(propylene oxide), poly(tetramethylene oxide), poly(vinylacetate), and polycaprolactone were also found to be immiscible with PES. More work is needed to understand this specific interaction. It is however still possible that some of these polymers are thermodynamically miscible with PES but the solvents used in the blend preparation have prevented homogeneous blend formation.

In order to understand the reasons for the miscibility of various polyacrylates with PVC, Walsh and Cheng<sup>154</sup>, examined the heats of mixing of various oligomers with chlorinated paraffin (an analogue of PVC). They found that oligomers containing intermediate number of carbonyl groups gave favourable heats of mixing and those containing the lowest and highest number of carbonyl groups unfavourable heats of mixing. This was consistent with the observed miscibility. These results were explained in terms of the summation of the effects of the specific interactions and the dispersion forces. The measured heat of mixing can be represented as

$$\Delta H_m = \Delta H_{\text{dispersive}} + \Delta H_{\text{specific}}$$

The dispersive contribution can be calculated from the solubility parameters using Hilderbrand's equation 1.5

$$\Delta H_{\text{dispersive}} = V \phi_1 \phi_2 (\delta_1 - \delta_2)^2$$

and the contribution from the specific interaction would depend on the concentration of reactive group present in the polymer. The contribution from the specific interactions to the heat of mixing thus can be calculated by subtracting the dispersive contribution from the observed heat of mixing. This analysis shows that a large difference in the solubility parameters of the two polymers would contribute to the large dispersive effects (unfavourable contributions). For the two polymers to be miscible, this large dispersive effect must be outweighed by the large contribution from the specific interactions. Walsh and Cheng<sup>154</sup> found in case of immiscible poly(methyl acrylate)/PVC blends a large contribution from the specific interactions was outweighed by a

large unfavourable contribution from the dispersive forces.

The calculated values for  $\Delta H_{\text{dispersive}}$  and  $\Delta H_{\text{specific}}$  for the PES/PEO and PES/phenoxy mixtures are shown in Table 5.1.

Table 5.1  $\Delta H_{\text{dispersive}}$  and  $\Delta H_{\text{specific}}$  for PES/PEO and PES/phenoxy blends.

| Blend Composition 50:50 | Experimental Heat of Mixing $\text{Jg}^{-1}$ | $\Delta H_{\text{dispersive}}$ from Equation 1.5, $\text{J g}^{-1}$ | $\Delta H_{\text{specific}}$ $\text{J g}^{-1}$ |
|-------------------------|----------------------------------------------|---------------------------------------------------------------------|------------------------------------------------|
| PES/PEO                 | - 9.7                                        | + 1.69                                                              | - 11.39                                        |
| PES/Phenoxy             | - 0.18                                       | + 0.38                                                              | - 0.56                                         |

The results show that the contributions from the specific interactions are larger in the case of PES/PEO when compared to PES/phenoxy blends. In the case of PES/phenoxy blends, the heat of mixing of low molecular weight analogues had a very small, slightly negative value which implied a very weak specific interaction. The miscibility may be possibly helped by the structural similarity of PES and phenoxy resin and closeness of state parameters.

It has been pointed out<sup>155</sup> that blends of random copolymers and a homopolymer can have a negative exchange interaction if the "repulsion effect" is strong enough. This happens in a situation for which the value of the exchange interaction parameter between the monomers which make up the copolymer is larger than the values of both the other interaction parameters involved. In this extreme case all three interaction parameters can be positive and yet mis-

cibility occurs. Hence specific interactions are not always necessary for miscibility. Paul and Barlow<sup>156</sup> explained the miscibility of poly-(methyl methacrylate) with styrene acrylonitrile (SAN) copolymers on the basis of the simple binary interaction model. Chai<sup>157</sup> has shown that the compatibility in the system in which dispersion forces dominate, is determined by the degree of similarity of the equation of state parameters of the pure components. In PES/phenoxy blends the specific interaction is possibly either through the hydroxyl group of the phenoxy which can act as either an electron donor or acceptor or through the aromatic  $\pi$  electrons. The equation of state parameters as given in Section 4.5 for PES and phenoxy resins are also in the same order of magnitude. Thus, similar structural and equation of state parameters seem to contribute towards the miscibility of PES/phenoxy blends.

### 5.3 THE PHASE DIAGRAMS

The T<sub>g</sub>, T<sub>m</sub> and cloud point phase diagram for the PES/PEO system is shown in Figure 5.1. The cloud point curve actually meets the T<sub>g</sub> curve for the blend at very high PES content and yet cloud points are still obtainable. Because of this, the T<sub>g</sub> measurements in this region are likely to be affected by phase separation and may be meaningless. The ability to measure cloud points in this region shows the very great mobility apparent in this system which must in part be due to the low molecular weights used and lack of branching in the polymers. The high mobility of the system was also confirmed by optical microscopy where phase separation was observed on heating and remixing of phases on cooling. The rapid remixing of phases was a common feature of PES/PEO blends at all compositions.

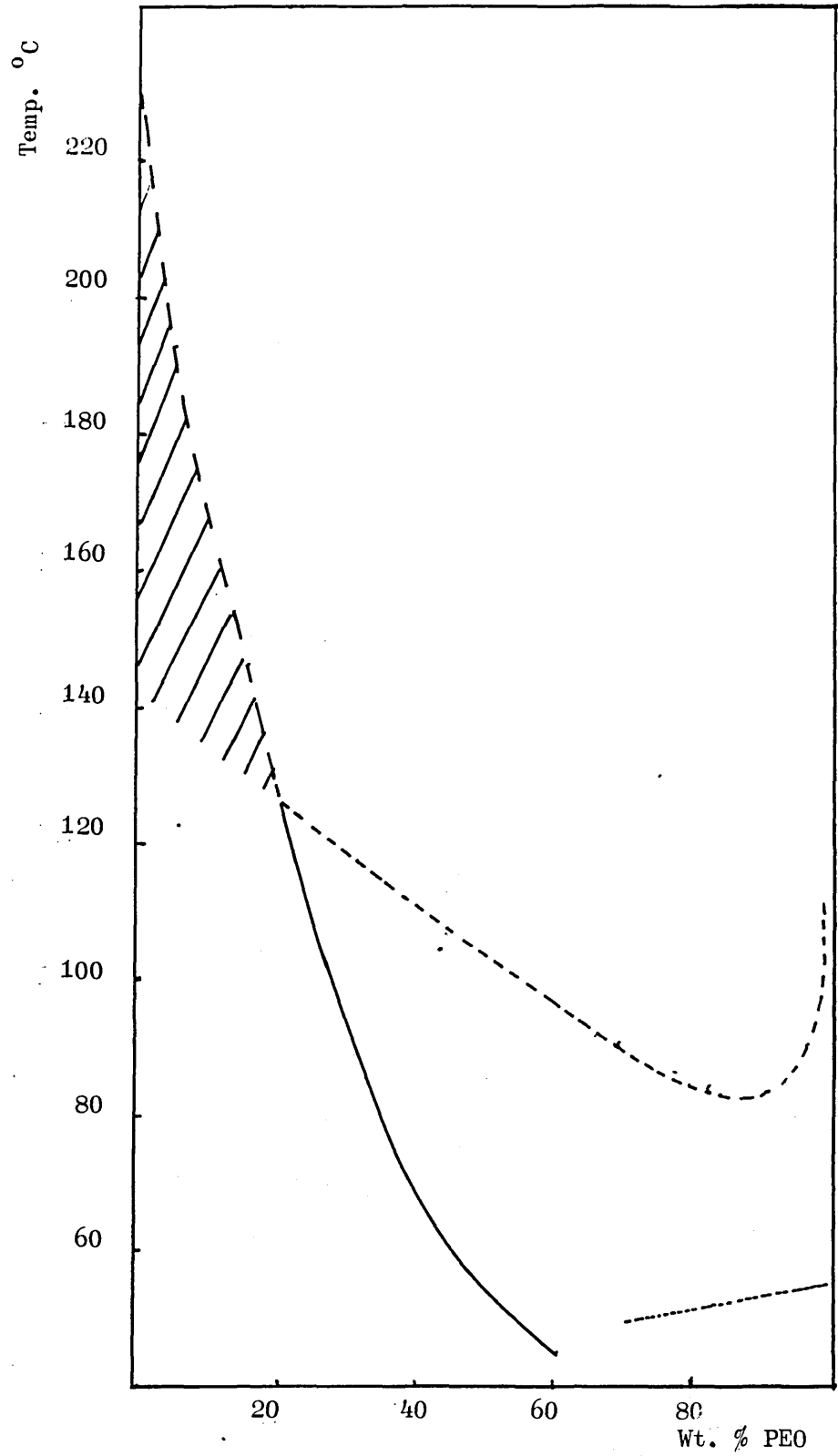


Figure 5.1 Phase diagram for PES/PEO blends (PEO molecular weight 200,000) showing melting points of PEO (dotted line), cloud point curve (dashed line), and  $T_g$  of blends (solid line) shaded area shows uncertainty in this region.

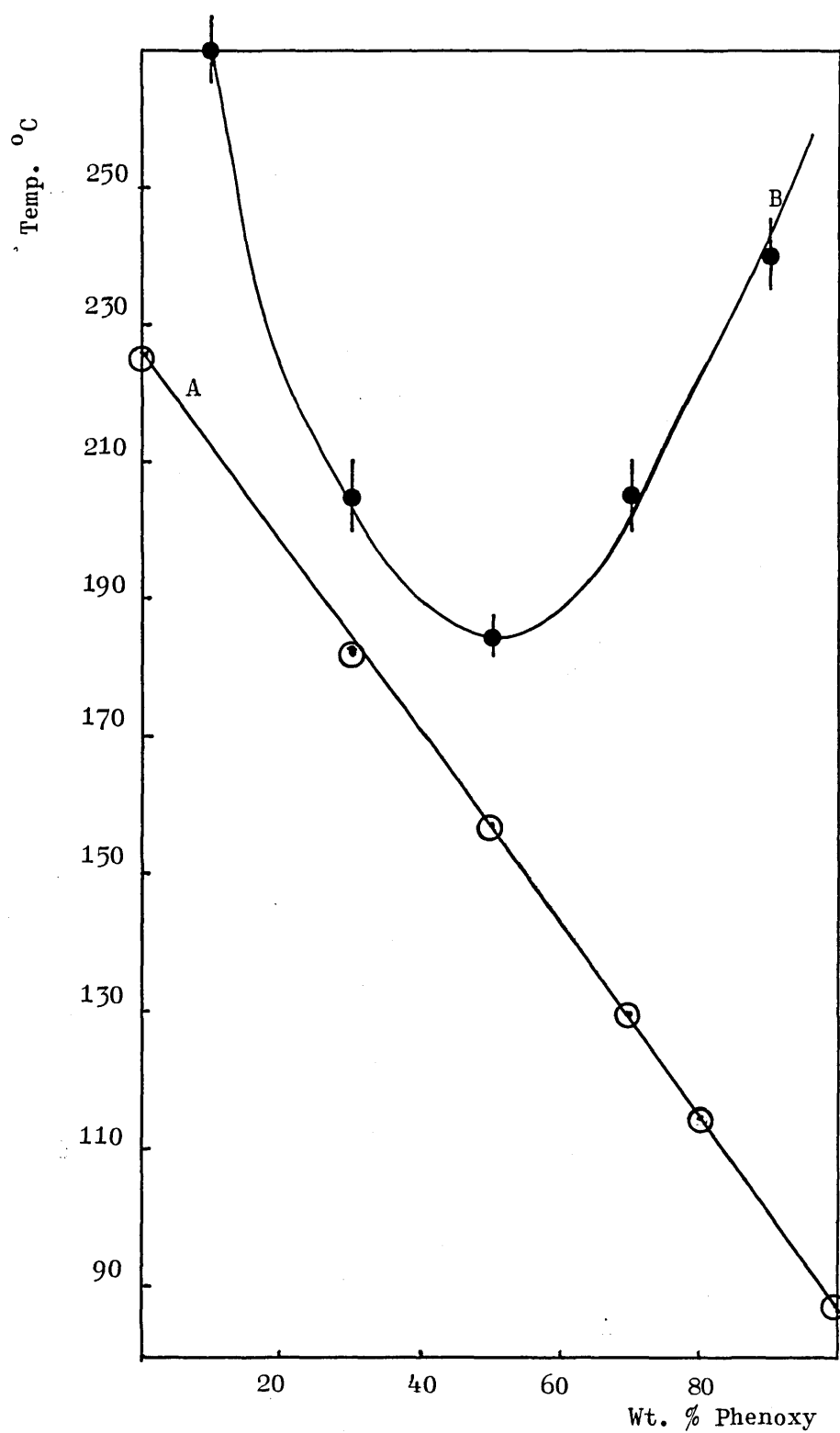


Figure 5.2 Phase diagram for PES/Phenoxy blends showing  $T_g$  (A) and cloud point (B) curves.

Figure 5.2 shows the phase diagram for PES/phenoxy blends. Here no problem of overlap of cloud point and T<sub>g</sub> arises. The cloud point curves lies well above the T<sub>g</sub> curve. The rate of phase separation on heating and remixing on cooling is also less rapid than for PES/PEO blends.

The phase morphology of a PES/PEO phase separated sample observed by electron microscopy showed that PEO domains sizes were of the order of 0.1 to 0.25  $\mu\text{m}$ . In a phase separated 80/20 PES/PEO blend the PEO domains appear to be surrounded by PES matrix and possibly because of this it was difficult to extract PEO from the phase separated blend.

#### 5.4 POLYMER-POLYMER INTERACTION PARAMETERS

Three methods, melting point depression, water vapour sorption and heats of mixing, have been used to calculate polymer-polymer interaction parameters. Where one of the component copolymers is crystalline, melting point depression is the most direct method for obtaining the Flory-Huggins interaction parameter,  $\chi$ . This method has large errors inherent in the procedure, because of the difficulty of determining the equilibrium melting point during heating or crystallisation point during cooling. In PES/PEO blends the points at higher PEO content were more reliable (due to less likelihood of supercooling but gave less accurate interaction parameters (due to low  $\Delta T$  values). Melting point depression has been assumed to be the result of thermodynamic interactions between the crystal and the miscible polymer-polymer amorphous phase with which it is in equilibrium. The melting point can vary with environment and can also vary with blend composition. Thus the value of  $\chi$  obtained by this method may not be reliable.  $\chi$  could be calculated only at one

temperature ie. at crystalline melting point of the polymer. The value obtained was however negative which agreed with the observed miscibility.

The melting point expression has been modified by Walsh et al.<sup>129</sup> to calculate  $\bar{X}_{12}$  (the total interaction energy parameter). In this calculation  $\bar{X}_{12}$  has been assumed to be independent of temperature and calculated at 50°C. The experimental errors in the values of both  $\bar{X}_{12}$  and  $C/R$  are very large ( $\pm 25$  percent as estimated from the graphs). There are uncertainties in the origin of  $C/R$  because it has been assumed that the morphological contribution will contribute to the free energy proportional to site fraction or segment fractions. None of the assumptions may be valid and therefore absolute values of  $\bar{X}_{12}$  obtained by this method are doubtful. However, the simulated spinodal curves obtained by using the  $\bar{X}_{12}$  values were in reasonable agreement with the observed cloud point curves.

The Flory-Huggins polymer-polymer interaction parameters for PES/PEO and PES/phenoxy mixtures were also obtained from water vapour sorption measurements. In both cases, negative values were obtained, which confirmed miscibility. The values of  $X_{12}$  calculated from the values of  $\chi'_{23}$  obtained from the sorption method agreed reasonably well within experimental errors. The interaction parameter measured by this method for PES/PEO blends has a higher negative value compared to PES/phenoxy blends. This implied that the interaction between PES and PEO is stronger compared to that between PES and phenoxy. This method is direct but inherently has large errors as mentioned in Sections 3.6 and 4.9 respectively and therefore emphasis should not be placed on the actual values obtained. Sorption studies with other solvents which act as solvents for blend components could

possibly have given more accurate results. This method is useful but samples take a long time to reach equilibrium and it is therefore time consuming. In Figure 4.28 the experimental isotherm for PES/PEO blends lies below the theoretical isotherms obtained by the additivity rule. This provides further proof of polymer-polymer interaction.

Heat of mixing measurements of low molecular weight analogues of the component polymers are the most accurate but indirect method of obtaining values of the interaction parameters. In the case of PES/PEO blends, large negative heats of mixing were obtained, which again suggests that the mixing is through strong specific interactions. In this method it is assumed that the polymeric mixtures behave in the same way as the low molecular analogues. This assumption is not necessarily valid and therefore an exact fit of the experimental and theoretical data is not necessarily obtained.

In the case of PES/phenoxy blends, the heats of mixing of low molecular weight analogues obtained was marginally negative which implies weak interactions. The value of  $X_{12}$  obtained in this case was also small and negative.

Another indication of polymer-polymer interaction was obtained from Tg measurements. Theoretical Tg values of blend compositions have been obtained using the Fox equation. A positive deviation of Tg values of both systems over a wide range of compositions has been detected implying that there are interactions between the polymers. The positive deviation for PES/PEO blends was greater than that for the PES/phenoxy system. This shows that the interaction between PES/PEO is stronger than the PES/phenoxy interaction.

Further confirmation of this effect is reflected in the strength of Gordon-Taylor parameter,  $K$ , which was 1.52 for PES/PEO and 1.0 for PES/phenoxy blends.

PES/PEO blends containing more than 50 weight percent PEO in the blend showed significantly higher  $T_g$ 's compared to the theoretical  $T_g$ 's. This possibly happens because of the presence of crystalline material (PEO) in the blend. Crystallisation of some of the PEO reduces the amount present in the amorphous phase of the blend. Crystallation of one component also has stiffening effect on polymer chains. A similar effect has been reported for phenoxy/PEO blends<sup>102</sup>.

#### 5.5 SIMULATION OF THE PHASE DIAGRAMS

McMaster<sup>22</sup> simulated binodal and spinodal curves for hypothetical polymer pairs with various values of the equation of state parameters. Walsh and Rostami<sup>23</sup> also simulated many hypothetical spinodal curves. The effect of changing the equation of state parameters on the spinodal curves are summarised here :

- (i) An increase in the difference of the  $\alpha$  values decreases miscibility.
- (ii) Changes in  $\gamma$  values have less effect compared to  $\alpha$  values.
- (iii) Increase in the molecular weight of polymers decreases miscibility.
- (iv) A negative  $X_{12}$  increases miscibility. Curves become flatter with an increase of  $X_{12}$ .
- (v)  $S_2/S_1$  has little effect in the absence of  $X_{12}$  (or  $Q_{12}$ ) terms. If  $S_2/S_1$  is greater than 1, the curve leans down to high volume fractions of component 2.
- (vi) A more negative value of  $Q_{12}$  makes polymers less miscible. Where a large negative  $X_{12}$  is compensated by a large negative  $Q_{12}$ , the curve can become extremely flat.

- (vii) For polydispersed polymers the spinodal curve remains unchanged if the weight average chain length is used<sup>76, 15</sup>.
- (viii) Bimodality in the spinodal curve can arise in simulations involving the variation of state parameters of pure components and binary quantities.

Olabisi<sup>26</sup> applied McMasters treatment to the poly(caprolactone)/poly(vinyl chloride) system. He obtained  $X_{12}$  by inverse gas chromatography and assumed  $Q_{12} = 0$ . The simulated curves were in poor agreement with the experimental data because he used only  $S_2/S_1$ , as an adjustable parameter.

The simulated phase diagrams obtained for PES/PEO mixtures are shown in Figures 4.24 and 4.25. Two methods were used to calculate interactional energy parameters. The heat of mixing measurements gave a value of  $X_{12}$  and the melting point depression a value of  $\bar{X}_{12}$  ( $\bar{X}_{12} = X_{12} - T \bar{v} Q_{12}$ ). The value of  $\bar{X}_{12}$  was obtained at a temperature 40°C below that of heat of mixing values. When the value of  $X_{12} = -40 \text{ J cm}^{-3}$  was used to simulate the spinodal curve of the polymer pair then a large negative value of the non-combinatorial entropy contribution parameter,  $Q_{12} = -0.048 \text{ J cm}^{-3} \text{ K}^{-1}$ , had to be used to balance the large negative  $X_{12}$  value. If a zero value of  $Q_{12}$  is chosen then a lower value of  $X_{12}$  ( $= \bar{X}_{12}$ ) =  $-18 \text{ J cm}^{-3}$  is used to simulate the spinodal curve. It is apparent that the parameter  $Q_{12}$  plays an important role in the simulation of spinodal curves. It is not possible to fit the calculated spinodal to the experimental results without using  $Q_{12}$ . For a large favourable,  $X_{12}$ , (strong specific interactions), a large unfavourable  $Q_{12}$  is necessary and vice versa.

The spinodals generated for PES/PEO are not very molecular

weight dependent as suggested by cloud point measurements. The shape of the spinodal is dominated by the values of  $S_2/S_1$  through its effect on the interactional terms in the spinodal equation.

The simulated spinodals by both these methods for PES/PEO blends lie well inside the observed cloud point curve. This may be due to the fact that the cloud point curve approximates much more closely to the binodal. The mobility of the polymers in this system is very high and phase separation process is readily reversible on annealing below the cloud point which agrees with this interpretation. There are also uncertainties in the values of various state parameters, particularly the  $S_2/S_1$  ratio.

Simulated spinodal curves for PES/phenoxy mixtures are presented in Figure 4.26. Three values of  $X_{12} = -3, -2$  and  $-1.5 \text{ J cm}^{-3}$  were used to simulate the spinodal curves. These values were balanced by the negative values of  $Q_{12}$  as before. In this case the spinodals found were very close to the experimental cloud point curve and the curves were symmetrical. Here the differences in component state parameters are not large. Small increases in the molecular weight do not seem to make much difference but when the molecular weight of one of the components was doubled the spinodal curve became skewed towards the higher molecular weight component and became more flat bottomed. An increase in the negative value of  $X_{12}$  or a change in  $\alpha$  also makes the spinodal flat bottomed. For any change in any of the parameters, a new value of the adjustable parameter  $Q_{12}$  is required to match to the minimum of the cloud point curve. The simulated spinodals thus obtained were very close to the observed cloud point curve. Small variations in the state parameter did not change the spinodal very much. Closeness of the cloud point and calculated

spinodals suggests that the phase separation is via spinodal decomposition in this case.

The simulated results are generally in agreement with the conclusions reached by McMaster<sup>22</sup>, Walsh and Rostami<sup>23</sup> and other workers<sup>26, 122</sup>. The findings agree with the effect of changes in properties on spinodal curves given at the beginning of this Section.

One problem in applying the equation of state theory to these mixtures is that in theory  $X_{12}$  is introduced as a temperature independent constant whereas in many cases the heat of mixing, and hence  $X_{12}$  is strongly temperature dependent. The problem arises because  $X_{12}$  was never intended to describe the interaction between two polymers which are dominated by a temperature dependent specific interaction.

#### 5.6 SORPTION OF WATER VAPOUR

The water vapour sorption of polymers and polymer blends were examined to explore the claim<sup>108</sup> that at certain compositions PES/PEO blends absorb less water than PES itself. It was logical to assume that if the sites which are responsible for water uptake were occupied by PEO or any other polymer, as the negative polymer-polymer interaction parameter,  $\chi_{23}$ , would suggest, the water uptake of the blend should be less than PES. However, the results presented in Section 4.9 do not support this assumption. The sorption was found monotonically to depend on the concentration of the other polymer in the blend. The penetrant, water, molecule is relatively small and in the liquid and solid state is strongly associated through hydrogen bonding. Strong localised interactions may develop between the water molecule and polar groups of a polymer, on the other hand, in relatively non-polar materials, clustering of the sorbed water is possible.

The sorptive capacity of the polymers depend on the nature of the chemical groups present and their position on the polymer chain. If the interchain hydrogen bonds are weak then swelling may occur. In general, the more polar groups present in the polymer matrix, the higher will be its affinity towards water. However, the accessibility of these groups, the degree of crystallinity of the matrix, and the strength of water-water and water-polymer bonds are important factors in deciding the total uptake of water. Because of all these factors, any simple correlation between the number of polar groups and the water uptake is not possible.

Four types of sorption isotherms as shown in Figure 5.3 have been observed. Our results for water vapour-sorption in PES, PEO, phenoxy polymers and their blends appear to follow the type IV (type III of BET Classification) isotherm described in Figure 5.3. The shapes of the isotherms at lower activities were not measured with sufficient accuracy and therefore any initial Langmuir type curvature associated with specific localised interactions was difficult to detect. At lower activities (less than 0.6) the water vapour uptake appears to be similar for the PES, PEO (semi-crystalline) and phenoxy polymers and their blends. At higher activities, in case of PEO (semicrystalline) the rapid increase in water uptake is possibly due to the breaking of PEO crystallites followed by their dissolution. In pure phenoxy water uptake is possibly related to the presence of hydroxyl groups. In PES/PEO blends explanation is complex because of the differences in polymer-polymer and individual polymer-water interactions but seems to relate to the percentage of PEO in the blend composition.

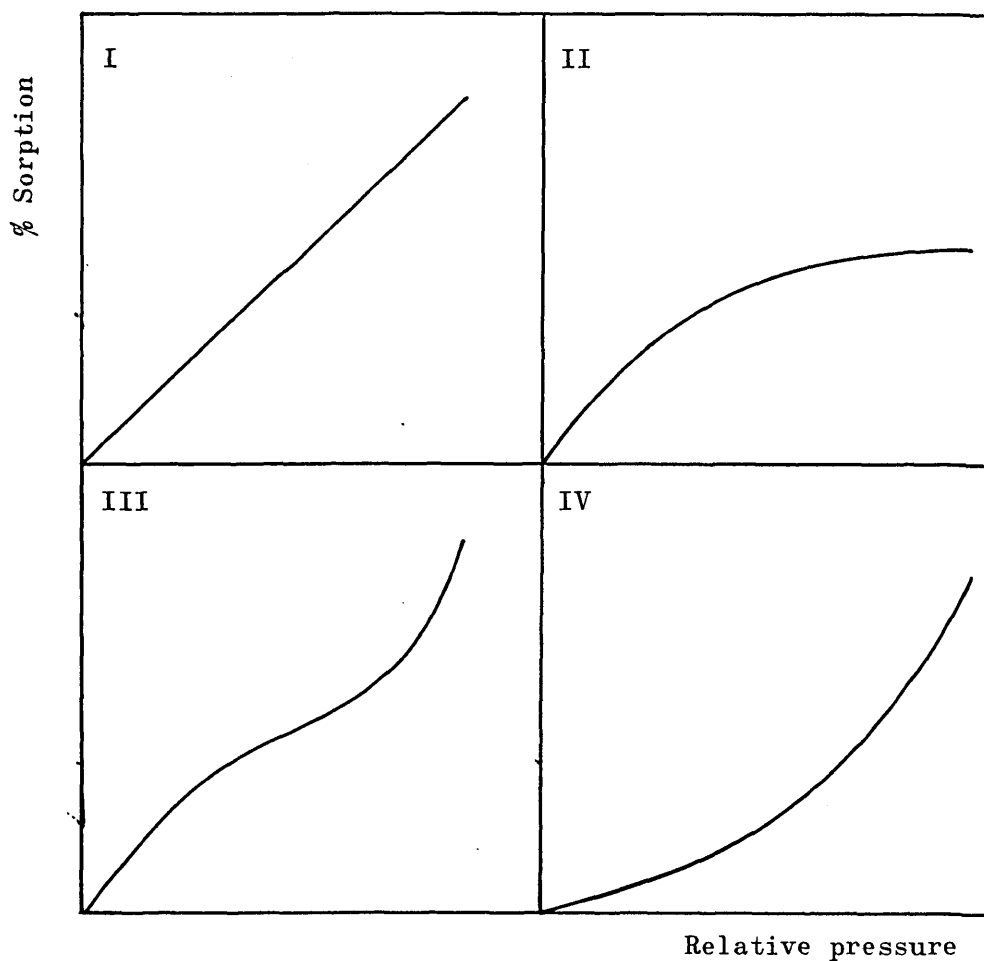


Figure 5.3 Types of sorption isotherms. Plots of sorption against relative pressure of vapour :

- I Linear isotherm following Henry's Law, no interaction between the penetrant and the polymer.
- II Langmuir-type isotherm, involves adsorption in a single layer on any adsorption site.
- III Involves multilayer surface adsorption characterised by strong penetrant-polymer interaction.
- IV Involves absorption into systems showing positive deviation from Henry's Law (Type 3 in BET classification).

The temperature independence of water asorption in a blend of 80/20 PES/PEO implied that the heat of sorption is very close to the heat of condensation of water.

Only approximate average diffusion coefficients were obtained from the sorption data using the half time expression. The conditions used were not suitable for the accurate measurement of diffusion kinetics.

However, the results obtained were reasonable.

The equilibrium sorption isotherms of water vapour in PES/PEO blends showed that none of the blend compositions sorbed water less than PES as claimed in the literature<sup>108</sup>. Flory-Huggins polymer-polymer interaction parameters for both PES/PEO and PES/phenoxy blends estimated from the sorption data, were found to be negative. The interaction parameter value was more negative for PES/PEO compared to PES/phenoxy confirming a stronger interaction for the former. These results were consistent with the observed miscibility of the systems and the polymer-polymer interaction parameters obtained by other methods in this work.

## CHAPTER 6

### CONCLUSIONS

The miscibility of polyethersulphone(PES) with a number of polymers has been investigated. Some of the polymers which contained carboxyl, (acrylates and other esters) and ether groups were found to be probably immiscible with the PES. Among the polymers examined, only poly(ethylene oxide) and phenoxy resin were proved to be miscible with the PES.

The reasons for polymer-polymer miscibility have been considered. It is postulated that the  $n-\pi$  interaction takes place between the free electrons of the ether group of PEO and the  $\pi$  electrons of the aromatic ring of PES. The predominance of this specific interaction has been confirmed by the high favourable heat of mixing values obtained from the low molecular analogues of this mixture. In the case of PES/phenoxy blends, the heats of mixing of low molecular weight analogues implied that the interactions are weak. In this case mixing is possibly helped by the structural similarity and the closeness of the state parameters of the two polymers.

Blends of PES/PEO and PES/phenoxy were prepared by solvent casting from a common solvent and were found to be miscible and show a single, composition dependent, glass transition temperature. PES/PEO mixtures in both cyclohexanone and DMF phase separated on heating and thus conditions need to be carefully chosen to obtain homogeneous blends. It has been shown that PEO and PES are miscible at all compositions within a band of temperatures between the PEO melting point and the cloud point of the blend.

The clear blends of PES/PEO and PES/phenoxy phase separated on heating, and the cloud point could be measured by turbidimetry and

confirmed by both visible and/or electron microscopy. The cloud point curve of PES/PEO was very skew with a minimum at around 10 weight percent PES content. This was not a strong function of molecular weight and the skew nature was thus presumably due to differences in the state parameters of the pure components. The cloud point curves of PES/phenoxy were, however, symmetrical giving a minimum at about 50:50 weight percent.

Three methods, melting point depression, heats of mixing of low molecular weight analogues and water vapour sorption were used to obtain polymer-polymer interaction parameters of the blends. The interaction parameters for both the systems were found to be negative which were consistent with the observed miscibility.

The simulated spinodals for both PES/PEO and PES/phenoxy blends were calculated using interaction parameters obtained from the heat of mixing measurements. In both cases, for a favourable value of  $X_{12}$ , it was necessary to assume an unfavourable non-combinatorial entropy contribution,  $Q_{12}$ , to obtain the minimum of the cloud point curve. In case of the PES/PEO blends a modified form of the equation for the melting point depression of PEO in the blend has been used to obtain values of  $\bar{X}_{12}$ . This was used to simulate the spinodals. The spinodals obtained by both the methods for PES/PEO were similar to the cloud point curve. They were not very molecular mass dependent which corresponds to the findings from the cloud point curves. It was found that the shape of the spinodals was dominated by the value of the surface area to unit volume ratio  $S_2/S_1$  through its effect on the interactional terms in the spinodal equation.

The calculated spinodals for the PES/phenoxy system were very close to the cloud point curve and therefore the phase separation

in this case may be by spinodal decomposition.

Water vapour sorption measurements in PES/PEO and PES/phenoxy blends showed a monotonic increase in vapour sorption with the increase of PEO or phenoxy component in the mixture especially at activities greater than 0.6. None of the blends showed water sorptions less than for pure PES.

PES/PEO mixtures showed very high mobility with sharp and reproducible cloud points which make them ideal for future miscibility studies. As phenoxy resins have been found to be miscible with PES, it would be interesting to examine other structurally similar polymers eg polycarbonates, poly(phenylene oxides), poly(ethyleneterephthalates) and polyetheretherketone. Success would depend on the availability of either a suitable solvent or achieving proper melt processing conditions.

# REFERENCES

- 1 Gardner, W.H. in Protective and Decorative Coatings ( J. J. Matteillo ed.) p. 1. Chapman and Hall, London, (1941).
- 2 Flory P.J. 'Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, (1962).
- 3 Hildebrand, J.H., Scott, R. L., The Solubility of Non-electrolytes, Chapter 3. p. 346, Reinhold, New York, (1950).
- 4 Dobry, A. and Boyer-Kawenoki, F., J. Polym.Sci., 2, 90 (1947).
- 5 Flory, P.J., Orwell, R.A. and Vrij, A., J.Am.Chem.Soc. 86, 3507, 3515 (1964).
- 6 Flory, P.J., J.Am.Chem.Soc. 87:9, 1833 (1965).
- 7 Eichinger, B.E. and Flory, P.J., Trans.Faraday Soc. 64, 2035 (1968).
- 8 Allen, G., Chai, Z., Chong, C.L., Higgins, J.S. and Tripathi, J., Polymer, 25, 239 (1984).
- 9 Yeh, G.S:Y. and Lambert, S.L., J.Polym.Sci., Part A2, 10, 1183 (1972).
- 10 Krause, S.. and Roman, N.; J.Polym.Sci., Part A3, 1631 (1965)
- 11 Liu, H.Z. and Liu, K.J., Macromolecules, 1, 157 (1968).
- 12 Liquori, A.M., Anzuino, G., Coiro, V.M., D'Alagni, M., D. Santis, P. and Savino, M., Nature (London), 206, 358 (1965).
- 13 Hughes, L.J. and Britt, G.E., J.Appl.Polym.Sci., 5, 337 (1961).
- 14 Carmain, B., Villoutreix, G. and Barlot, R., J.Macromol.Sci. Phys., 14 (2), 307 (1977).
- 15 Chai, Z., Ph.D. Thesis, Imperial College, London, (1982).
- 16 Doube, C.D. and Walsh, D.J., Europ.Polym.J., 17, 63 (1980).
- 17 Cruz, C.A., Barlow, J.W. and Paul, D.R., Macromolecules, 12, 276 (1979).
- 18 Ziska, J.J., Barlow, J.W. and Paul, D.R., Polymer, 22, 918 (1981).

- 19 Walsh, D.J. and McKeown, J.G., *Polymer*, 21, 1330 (1980).
- 20 Adler, K. and Paul, K.P., *Kunststoffe*, 7, 70 (1980).
- 21 Newton, A.B., Paper presented at "Macro Group" Meeting, Belgrave Square, London (1983).
- 22 McMaster, L.P., *Macromolecules*, 6, 760 (1973).
- 23 Walsh, D.J. and Rostami, S., *Polymer*, to be published.
- 24 Moskala, E.J., Painter, P.C., Coleman, M.M., Walsh, D.J. and Rostami, S., *Polymer*, 24, 1410 (1983).
- 25 Coleman, M.M. and Zarian, J., *J. Polym. Sci., Phys. Ed.* 17, 837 (1979).
- 26 Olabisi, O., *Macromolecules*, 9, 316 (1975).
- 27 Nishi, T. and Wang, T.T., *Macromolecules*, 8, 227, 909 (1975).
- 28 Paul, D.R. and Barlow, J.W., *Multiphase Polymers*, *Adv. Chem. Soc.* 176 (1979).
- 29 Bernstein, R.E., Cruz, C.A., Paul, D.R. and Barlow, J.W., *Macromolecules*, 10, 681 (1977).
- 30 Mondragon, I., Cortazar, M. and Guzman, G.M., *Makromol. Chem.* 184, 1741 (1983).
- 31 Nishi, T. and Kwei, T.K., *Polymer*, 16, 285 (1975).
- 32 Davis, D.D. and Kwei, T.K., *J. Polym. Sci., Phys. Ed.*, 18, 2337 (1980).
- 33 Cowie, J.M.G. and Saeki, S., *Polym. Bull. (Berlin)*, 6 (1-2), 75 (1981).
- 34 Shultz, A.R. and Gendron, B.M., *J. Appl. Polym. Sci.*, 16, 461 (1972).
- 35 Buchdahl, R. and Nielsen, L.E., *J. Polym. Sci.*, 15, 1 (1955).
- 36 Patterson, D. and Delmas, G., *Discussions Faraday Soc.* 49, 98 (1970).
- 37 Hammer, C.F., *Macromolecules*, 4, 69 (1971).
- 38 Nielsen, L.E., *J. Polym. Sci.*, 42, 357 (1980).
- 39 Doube, C.P. and Walsh, D.J., *Polymer*, 20, 115 (1979).
- 40 Wagner, E.R. and Robeson, L.M., *Rubber Chem. Technol.*, 43, 1129 (1970).

- 41 Walsh, D.J. and Cheng, G.L., Polymer, 23, 1965 (1982).
- 42 Walsh, D.J. and Cheng, G.L., Polymer, 25, 495 (1984).
- 43 Bank, M., Leffingwell, J. and Thies, C., Macromolecules, 4, 43 (1971).
- 44 Hsu, C.C. and Prausnitz, J.M., Macromolecules, 7, 320 (1974).
- 45 Aharoni, S.M., Macromolecules, 11, 277 (1978).
- 46 MacKnight, W.J., Karasz, F.E. and Fried, J.R., Chapter 5 "Polymer Blends". Academic Press, New York, San Francisco, London (1978).
- 47 Olabisi, O., Robeson, L.M. and Shaw, M.T., Polymer-Polymer Miscibility, Academic Press, New York, London (1979).
- 48 Gesner, B.D., Encyclopedia of Poly.Sci. and Tech., 10, 694 (1969).
- 49 Rosen, S.L., Polym.Eng.Sci. 7 (2), 115 (1967).
- 50 Bohn, L., in "Polymer Handbook", (Bandrup, J., and Immergut, E.H. eds) 2nd Ed., 111-211, Wiley (Interscience), New York (1975).
- 51 Nagumanova, E.I., Sagitov, R.Y. and Voskresenki, V.A., Kolloid Zh. 37 (3), 571 (1975).
- 52 Matsuo, M., Polym.Eng.Sci., 9, 206 (1969).
- 53 Karasz, F.E. and McKnight, W.J., Contemporary Topics in Polym.Sci. 2, 149 (1977), Plenum Press, N.Y.
- 54 Cowie, J.M.G., J. of Macromole.Sci.Phys.Ed., B18, 569 (1980).
- 55 Hichman, J.J. and Ikeda, R.M., J.Polym.Sci. Polym.Phys.Ed. 11, 1713 (1973).
- 56 Zabrzewski, G.A., Polymer, 14, 347 (1973).
- 57 Fox, T.G., Bull.Amer.Phys. Soc. 1, 123 (1956).
- 58 Kelley, F.N. and Bueche, F., J.Polym.Sci., 50, 549 (1961).
- 59 Gordon, M. and Taylor, J.S., J.Appl.Chem., 2, 493 (1952).
- 60 Dimarzio, E.A. and Gibbs, J.M., J.Polym.Sci., XL, 121 (1959).
- 61 Couchman, P.R., Macromolecules, 11, 6 (1978).

- 62 Paul, D.R. and Altamirano, J.O., Adv.Chem.Ser., 142, 371 (1975).
- 63 Manche, E.P. and Carroll, B. in "Physical Methods in Macromolecular Chemistry, Vol.2. Chapl. 4., Dekker, N.Y. (1972).
- 64 Ke.B., "Newer Methods of Polymer Characterisation", Wiley, N.Y. (1964).
- 65 Bair, H.E., Polym.Sci.Eng., 10, 247 (1970).
- 66 Flynn, J.M., Thermo.Chim. Acta., 8, 69 (1974).
- 67 Stoelting, J., Karasz, F.E. and McKnight, W.J., Polym.Eng.Sci., 10, 133 (1970).
- 68 Noland, J.S., Hsu, N.N.C., Saxon, R. and Schmitt, J.M., Adv.Chem. Ser., 99, 15 (1971).
- 69 Fried, J.R., Karasz, F.F. and McKnight, W.J., Macromolecules, 11, 150 (1979).
- 70 Eguiazabal, J.I., Irvin, J.J., Cortazar, M. and Guzman, M., Makromol. Chem., 185, 1761 (1984).
- 71 Walsh, D.J. and Rostami, S., Review, Advances in Polymer Science, to be published.
- 72 Wetton, R.E., MacKnight, W.J., Fried, J.R. and Karasz, F.E., Macromolecules, 11 158 (1978).
- 73 Akiyama, S., Kamatsu, Y. and Kaneko, R., Polymer J., 7, 172 (1975).
- 74 Rostami, S., Ph.D. Thesis, Imperial College (1983).
- 75 Walsh, D.J., Higgins, J.S., Rostami, S. and Weeraperuma, K., Macromolecules 16, 391 (1983).
- 76 Stein, R.S., Khambatta, F.B., Warner, F. and Russell, T., J.Polym. Sci, Polym.Phys.Ed. 14, 1391 (1976).
- 77 Maconnachie, A., Kambour, R., Rostami, S. and Walsh, D.J., to be published.
- 78 Koningsveld, R. and Kleintjens, L.A., Br.Polym.J., 9, 212 (1977).

- 79 Tager, A.A., Scholokhovich, T.T. and Bessanov, Yu.S., Eur.Polym.J., 11, 321 (1975).
- 80 Chai, Z., Ruona, S., Walsh, D.J. and Higgins, J.S., Polymer, 24, 263 (1983).
- 81 Rostami, S. and Walsh, D.J., Macromolecules, 17, 315 (1984).
- 82 Chong, C.L., Ph.D. Thesis. Imperial College (1981).
- 83 Braun, J.M., Guillet, J.E., Macromolecules, 9, 617 (1976).
- 84 Kwei, T.K., Nishi, T. and Roberts, R.F., Macromolecules, 7, 667 (1974).
- 85 Cates, D.M. and White, Jr., H.J., J.Polym.Sci., 20, 155, 181 (1956).
- 86 Cates, D.M. and White, Jr., H.J., J.Polym.Sci., 21, 125 (1956).
- 87 Tait, P.J. and Abushihada, M.A., Polymer, 18, 810 (1977).
- 88 Kwei, T.K. and Frisch, H.L., Macromolecules, 11, 1267 (1978).
- 89 Kimura, M., Porter, R.S. and Salee, G., J.Polym.Sci., Polym. Phys.Ed., 21, 367 (1983).
- 90 Krause, S., J. Macromol.Sci., - Rev.Macromol.Chem., 7 (21), 251 (1972).
- 91 Olabisi, O., Robeson, L.M. and Shaw, M.T., Polymer-Polymer Miscibility, Academic Press, London, N.Y. (1979).
- 92 Paul, D.R. and Barlow, J.W., J.Macromol.Sci., Rev.Macromol.Chem., C.18 (1), 109 (1980).
- 93 Shultz, A.R. and Beach, B.M. Macromolecules, 7, 902 (1974).
- 94 Robeson, L.M., Matzner, M., Fetters, L.J. and McGrath, in "Recent Advances in Polymer Blends, Graft and Blocks" (L.H. Sperling Ed.), 281 (1974), Plenum, N.Y.
- 95 Alexandrovich, A.R., Karasz, F.E. and MacKnight, W.J., Polymer, 18, 1022 (1977).
- 96 Cruz, C.A., Paul, D.R., and Barlow, J.W., J.Appl. Polym.Sci., 23 589 (1979).

- 97 Cruz, C.A., Barlow, J.W. and Paul, D.R., *Macromolecules*, 12, 726 (1979).
- 98 Paul, D.R., Barlow, J.W., Cruz, C.A., Mohn, R.N., Wassar, T.R. and Wahramund, D.C., *Am.Chem.Soc., Div. Org. Coat. Plast.Chem.*, 37 (1), 130 (1977).
- 99 Brode, G.L., Koleske, J.V., *J.Macromol. Sci., Chem.*, 6 (6)C, 1109 (1972).
- 100 Robeson, L.M., Furlek, A.B., *J.Appl. Polym.Sci.*, 23, 645 (1979).
- 101 Seefried, C.G. Jr., Koleske, J.V., Critchfield, F.E., *Polym.Eng. Sci.*, 16, 771 (1976).
- 102 Robeson, L.M., Hale, W.F. and Merrian, C.N., *Macromolecules*, 14 1644 (1981).
- 103 Smith, K.L., Winslow, A.E., Peterson, D.E., *Ind.Eng.Chem.*, 51, 1361 (1959).
- 104 Osada, Y., Sato, M., *J.Polym.Sci. Polym. Lett.Ed.*, 14, 129 (1976).
- 105 "Forming Association Compounds", F-43272, publication of Union Carbide Corp.
- 106 Bailey, F.E. and Koleske, J.V., "Poly(ethylene oxide)", Academic Press, New York (1976).
- 107 Kalfoglou, N.K., *J.Polym.Sci. Polym.Phys.Ed.* 20, 1259 (1982).
- 108 Eur. Pat. Appl. EP37, 181 (1981), ICI PLC, inv. Newton, A.B., *Chem.Abstr.* 96 7553Y (1982).
- 109 Jpn. 8235906 (1982). Kuraray Co. Ltd., Suenka, A., Hamatoto.Y. *Chem. Abstr.* 97, 25085X (1982).
- 110 Flory, P.J., *J.Chem.Phys.*, 9, 660 (1941).
- 111 Huggins, M.L., *J. Chem.Phys.* 9, 660 (1941).
- 112 Huggins, M.L., *Ann. N.Y. Acad. Sci.*, 43, 1 (1942).
- 113 Hildebrand, J.H., *J. Chem. Phys.*, 15, 225 (1947).

- 114 Longuet-Higgins, H.C., Discuss. Faraday Soc. No 15, 73 (1953).
- 115 Patterson, D. and Delmas, G., Discuss Faraday Soc. No 49, 98, (1970).
- 116 Sanchez, I.C. and Lacombe, R.H., Macromolecules, 11, 1145 (1978).
- 117 Prigogine, I., "The Molecular Theory of Solutions", Holland Pub. (1975).
- 118 Chalal, S.R., Kao, W.P. and Patterson, D., Faraday Trans. 1, 1834 (1973).
- 119 Abe, A. and Flory, P.J., J. Amer. Chem. Soc., 87 :9, 1838 (1965).
- 120 McMaster, L.P. and Olabisi, O., Amer. Chem. Soc. Div. Org. Coat. Plast. Chem. Pap. 35, 322 (1975).
- 121 Patterson, D., Macromolecules 11, 691 (1978).
- 122 ten Brinke, G., Eshuis, A., Roerdink, E. and Challa, G., Macromolecules, 14, 867 (1981).
- 123 Patterson D. and Delmas, G., Discuss. Faraday Soc. No. 49, 98 (1970).
- 124 Renuncio, J.A.R. and Prausnitz, J.M., Macromolecules, 9, 898 (1976).
- 125 Canovas, A.A., Rubio, R.G. and Renuncio, J.A.R., J.Poly.Sci. Phys. Ed. 20, 784 (1982).
- 126 Canovas, A.A., Rubio, R.G. and Renuncio, J.A.R., J.Poly.Sci. Phys. Ed. 21, 841 (1983).
- 127 Sanchez, I.C. and LaComb, R.H., J.Phys.Chem., 80, 2352, 2568 (1976).
- 128 Sanchez, I.C., J. Macromol. Sci.Phys. Ed. B17(3), 565 (1980).
- 129 Walsh, D.J. Rostami, S. and Singh, V.B., Makromol.Chem., 186, 145 (1985).
- 130 Newton, A., ICI Petrochemicals and Plastics Division, Wilton. Private Communication.
- 131 Shechler, L. and Wynstra, J., Ind.Eng. Chem., 48, 1, 86 (1956).

- 132 Murayama, T., "Dynamic Mechanical Analysis of Polymeric Materials",  
Elesvier Scientific Publishing Co. (1978).
- 133 Rabek, J.F., "Experimental Methods in Polymer Chemistry", Wiley (1980).
- 134 Collins, E.A., Bares, J. and Billmeyer Jr., F.W., Experiments in  
Polymer Science, Wiley (1973).
- 135 Stein, R.S., Chapter 9 "Polymer Blends", Paul and Newman Ed. (1978).
- 136 Reich, R., and Cohen, Y., J.Polym.Sci., Phys. Ed. 19, 1255 (1981).
- 137 McBain, J.W. and Bakr, A.N., J.Am. Chem.Soc., 48, 690 (1926).
- 138 Crank, J. and Park, G.S., in "Diffusion in Polymers", Academic Press,  
London/New York (1968).
- 139 Wolf, B.A., Willms, M.M., Makromol. Chem. 179, 2265 (1978).
- 140 Robard, A., Patterson, D. and Delmar, G., Macromolecules, 10,  
706 (1977).
- 141 Karasz, F.E. and MacKnight, W.J., Contemporary Topics in Polym.Sci.,  
"Problems in Compatibility Studies", Plenum Press, N.Y., 2, 149  
(1977).
- 142 Van Krevelen, D.W., "Properties of Polymers", Elsevier (1972).
- 143 ICI Petrochemicals and Plastics Division Product Data Sheet on  
Polyethersulphone.
- 144 Union Carbide data sheet on Phenoxy Resins.
- 145 Allen, G., Gee, G., Mangaray, D., Sins, D. and Wilson, G.J.,  
Polymer, 1, 467 (1960).
- 146 Schneider, N.S., Dusablon, L.V., Snell, E.W. and Prasser, R.A.,  
J. Macromol.Sci. Phys. B3(4), 623 (1969).
- 147 Bondi, A., J. Phys. Chem., 68, 441 (1964).
- 148 Zeman, L. and Patterson, D., Macromolecules, 5, 513 (1972).
- 149 Robard, A., Patterson, D. and Delmas, G., Macromolecules, 10,  
706 (1977).
- 150 Chai, Z. and Walsh D.J., Makromol. Chem, 184, 1544 (1983).

- 151 Walsh, D.J., Higgins, J.S. and Chai, Z., Polymer, 23, 336 (1982).
- 152 Grollier, J.P.E., Ballet, D. and Viallard, A., J.Chem. Thermodyn., 6, 895 (1975).
- 153 Pearce, E.M., Kwei, T.K. and Min, B.Y., J.Macromol.Sci., Chem.A21, 1181 (1984).
- 154 Walsh, D.J. and Cheng, G.L., Polymer, 25, 499 (1984).
- 155 Brinke, G. ten and Karasz, F.E., Macromolecules, 17, 515 (1984).
- 156 Paul, D.R. and Barlow, J.W., Polymer, 25, 487 (1984).
- 157 Chai, Z. and Sun, R., Polymer, 24, 1279 (1983).