

## **MISCIBILITY BEHAVIOUR OF POLY(ETHER SULPHONE)/NYLON-6 BLENDS**

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### **Abstract**

Binary blends of poly(ether sulphone) (PES) and Nylon-6 were prepared in a whole range of composition by melt extrusion. Miscibility behaviour of the blends were studied using thermal analytical techniques like differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). Due to the rapid crystallization of Nylon-6 as it is cooled from the melt state, its glass transition behaviour could not be detected even in the quenched samples by DSC. Furthermore, the crystallization and melting behaviour of the blends have been studied by DSC. DMA results show that the dynamic storage modulus of the blends were in-between those of the constituent polymers. Also the glass transition of Nylon-6 phase as determined by the peak in loss tangent remains constant which shows that the two polymers are immiscible. Thermal expansion coefficient of the blends as determined by TMA is greater than that of Nylon-6 signifying the increased dimensional stability of the blends at higher temperatures. Morphological studies done by scanning electron microscopy (SEM) show the biphasic nature of the blends, with clear cut boundaries between the phases because of poor interfacial adhesion. Dispersed particle size is small when Nylon-6 is the dispersed phase because of its lower melt viscosity as compared to PES. Thermal stability of the blends was measured using thermogravimetric analysis (TG). Two-step decomposition behaviour was observed because of macro-phase separated morphology.

**Keywords:** glass transition temperature, miscibility, Nylon-6, poly(ether sulphone), polymer blends

### **Introduction**

The growing demand for polymeric materials with good mechanical properties, high service temperature and improved chemical resistance has led to active research in the development of new high performance polymeric materials. Blending is a particularly interesting way to new engineering polymers. It allows a number of properties to be obtained that are difficult to achieve in a single polymer. Furthermore, blending gives rise to a range of properties in the final product by changing the blend compositions [1–3].

Poly(ether sulphone) is an amorphous engineering polymer that has been recognized as an important plastic offering a high heat distortion temperature, excellent

impact strength and high resistance to hydrolysis. However, it is notch sensitive and easily cracks under stress, as it is common with other amorphous polymers [4]. Hence, there are good reasons to blend PES with crystalline polymers [5]. Nylon-6 is a well known engineering polymer offering high toughness and high resistance to chemicals and oils. However, Nylon-6 has the shortcoming that its glass transition temperature ( $T_g$ ) and heat distortion temperature are very low [6]. Moisture uptake is another important problem to be solved in Nylon-6. The absorption of humidity involves the decrease of the  $T_g$ , thus affecting dimensional stability and lowering performance of manufactures. In these respects, the shortcomings of each polymer can be overcome when PES and Nylon-6 are blended. If miscible, PES might increase Nylon-6  $T_g$  and decrease water uptake, whereas Nylon-6 would enhance the solvent resistance and stress-crack resistance of PES.

In a previous study [7], PES and Nylon-6 were found to be immiscible when blended by solution mixing and the blends were further compatibilized by a block copolymer of Nylon-6 and PES. In the present investigation the miscibility behaviour of the blends of the two polymers obtained by melt-mixing has been discussed. The melting and crystallization behaviour of different compositions of Nylon-6/PES blends were studied by DSC measurements. Dynamic mechanical properties have been determined by DMA and morphological studies of the blends were carried out by SEM analysis.

## Experimental

### *Materials*

Nylon-6 used in the polymer blends under present investigation has been supplied by Gujarat State Fertilizer corporation (GSFC), India, and has a melt flow index of  $28 \text{ g } 10 \text{ min}^{-1}$  (at  $230^\circ\text{C}$ ) and melting point ( $T_m$ ) of  $221^\circ\text{C}$ . PES was procured from Amoco corporation, USA, under the trade name Radel A-300 and has a  $T_g$  equal to  $220^\circ\text{C}$ . Both materials were used without any further purification.

### *Preparation of blends*

All the polymers were vacuum dried for 24 h before using them for blending. Nylon-6 was vacuum dried at  $60^\circ\text{C}$ , whereas PES was vacuum dried at  $100^\circ\text{C}$ . Nylon-6 and PES were blended at  $260^\circ\text{C}$  in the ratio Nylon-6/PES=100/0, 75/25, 50/50, 25/75, 0/100 and given the sample code as PESN-0, PESN-25, PESN-50, PESN-75 and PESN-100 respectively. All the compositions were first physically mixed and then were melt blended in a CSI Maxwell Mixing Extruder (model CS194-AV) [8]. These extruded rods were further cut into small pellets for further molding and characterization. Blends were molded into sheets of 4 mm thickness using a 2.5 ton hydraulic press. All samples were stored in desiccator under  $\text{P}_2\text{O}_5$  before examination.

## Characterization

### *Differential scanning calorimetry*

A DSC 2910 Differential Scanning Calorimeter (TA Instruments) was used to determine the  $T_g$ ,  $T_m$  and  $\Delta H_f$  of the blend and pure samples. A heating rate of  $20^\circ\text{C min}^{-1}$  was used. All the samples were first run through a first heating cycle from ambient to  $250^\circ\text{C}$  and it was kept at this temperature for two minutes to destroy any previous thermal history and crystallization. Then the samples were immediately quenched into liquid nitrogen and a second heating run was carried out on these quenched samples again from ambient to  $250^\circ\text{C}$  at  $20^\circ\text{C min}^{-1}$ . The whole analysis was carried out in nitrogen atmosphere with a flow rate of  $60\text{ ml min}^{-1}$ .

### *Dynamic mechanical measurements*

Dynamic mechanical measurements were carried out on a DMA 2980 Dynamic Mechanical Analyzer (TA Instruments). A frequency of 10 Hz and a heating rate of  $3^\circ\text{C min}^{-1}$  was used. Dimensions of a typical sample were  $60\times 15\times 4\text{ mm}$  and the analysis was carried out from room temperature to  $170^\circ\text{C}$ .

### *Thermomechanical analysis*

Thermomechanical measurements were carried out on TMA2950 Thermomechanical Analyzer (TA Instruments) by penetration mode on specimens having a diameter of  $1.5\pm 0.1\text{ mm}$ . The penetration test was performed perpendicular to the axis of the cylindrical specimens, using a wedge shaped probe. A heating rate of  $4^\circ\text{C min}^{-1}$  was used and tests were carried out in nitrogen atmosphere.

### *Thermogravimetric analysis*

Thermal stability of blends were measured by a Hi-Res TGA 2950 Thermogravimetric Analyzer (TA Instruments). A sample mass of 10–12 mg was used. Heating rate of  $20^\circ\text{C min}^{-1}$  and nitrogen atmosphere was used during the analysis.

### *Scanning electron microscopy*

The extruded blends were fractured in liquid nitrogen and then the fractured surface was observed in a scanning electron microscope (JEOL JSM – 35CF). The samples were coated with a thin layer of gold prior to SEM observations.

## Results and discussion

Figures 1a and 1b show the overlay DSC curves of Nylon-6/PES blends obtained after the first and second heating run respectively. These heating scans were used to determine the melting behaviour of the components in the blend, such as the onset melt-

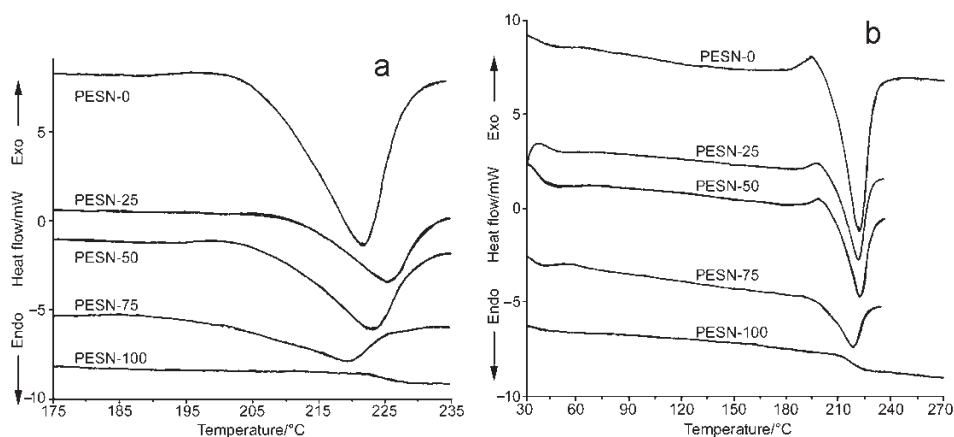


Fig. 1 DSC heating curves of PES/Nylon-6 blends: a – 1<sup>st</sup> heating scan; b – 2<sup>nd</sup> heating scan

ing temperature ( $T_i$ ), the melting peak temperature ( $T_{max}$ ), the completion of melting ( $T_f$ ) and also the heat of fusion ( $\Delta H_f$ ). The degree of crystallinity ( $X_c$ ) of the nylon-6 phase in the blend was calculated by means of the following relation:

$$X_c = 100(\Delta H_{blend}) / (\Delta H_{nylon-6}^{\circ}) \times \text{mass fraction of nylon in the blend}$$

where  $\Delta H_{blend}$  is the heat of fusion per gram of the blend and  $\Delta H_{nylon-6}^{\circ}$  is the heat of fusion per gram of 100% crystalline nylon. Value of  $\Delta H_{nylon-6}^{\circ}$  has been taken as 207.0 J g<sup>-1</sup>. The data obtained from the DSC heating scans are shown in Tables 1 and 2. Because of rapid crystallization of Nylon-6 from the melt state both in pure state and in blends, its  $T_g$  could not be obtained even in the quenched samples. Furthermore, the crystallization and melting behaviour of the blends were studied mainly from data obtained from DSC curves of the second heating scan because of the same thermal history of all samples in this scan. No crystallization exotherm was observed in the first heating run because of the inherent crystalline nature of the samples. The second heating run carried out on quenched samples does show a crystallization exotherm. But as soon as the crystallization process starts, small and unstable crystals present in the sample start to melt because of which crystallization exotherm gets overshadowed by the melting endotherm. For the pure Nylon-6 this crystallization process starts at 180°C, but in case of blends, because of the restriction imposed by the PES phase, onset temperature of crystallization is around 187°C. Both Tables 1 and 2 show negligible dependence of  $T_m$  on PES content. The small variation in the melting point parameters can be attributed to morphological effects (lamella thickness, defects, spherulitic morphology) as reported by several authors [9–11]. Onset melting temperature ( $T_i$ ) in case of blend having PES less than 50% was slightly greater than that of pure Nylon-6 which may be because of formation of more stable crystals at these compositions. Further increasing the PES ratio leads to a decrease in the  $T_i$  of Nylon-6 phase in blend than that of pure Nylon-6, because of the complete

phase separation that occurs at these compositions. So, Nylon-6 crystallizes at these compositions independently of PES phase and hence the observed behaviour. Also, the melting peak temperature decreases by about 2°C, beyond a blend composition of 50% PES. The dependence of  $\Delta H_f$  (heat of fusion normalized to Nylon-6 content) on composition is more complex, in both as extruded and quenched samples, and a minimum followed by a maximum is shown off.  $\Delta H_f$  of PESN-75 sample is even greater than that of pure Nylon-6. We do not have a definite explanation but the phenomena occurring during the extrusion might give some suggestions. The phase dispersion in the melt and consequently the blend morphology could affect the apparent heat of fusion [12]. Another interesting observation is that the  $\Delta H_f$  value obtained for the quenched samples is greater than that for the as extruded samples. Though the result is contrary to expectation, probably the recrystallization melting phenomenon in quenched samples has something to do with it. Percentage crystallinity of both as extruded and quenched samples obtained from the heat of fusion value are also shown in Tables 1 and 2. The obtained values have been compared with those calculated from the additivity rule.

**Table 1** DSC results for Nylon-6/PES blends (first heating scan)

Composition	$T_i/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$T_f/^\circ\text{C}$	$\Delta H_f/\text{J g}^{-1}$	$X_{\text{ce}}$	$X_{\text{cc}}$
PESN-0	207.4	221.5	238.0	64.5	31.1	31.1
PESN-25	208.4	221.3	234.5	29.3	14.2	23.3
PESN-50	205.5	220.6	234.0	56.0	27.0	15.5
PESN-75	199.3	217.3	231.6	66.8	32.3	7.8
PESN-100	—	—	—	—	—	—

$T_i$ =onset melting temperature,  $T_{\text{max}}$ =peak melting temperature,  $T_f$ =final melting temperature,  $\Delta H_f$ =heat of fusion normalized with respect to Nylon-6 content,  $X_{\text{ce}}$ =experimental percentage of crystallinity,  $X_{\text{cc}}$ =calculated value of percentage of crystallinity

**Table 2** DSC results for Nylon-6/PES blends (second heating scan)

Composition	$T_c/^\circ\text{C}$	$T_i/^\circ\text{C}$	$T_{\text{max}}/^\circ\text{C}$	$T_f/^\circ\text{C}$	$\Delta H_f/\text{J g}^{-1}$	$X_{\text{ce}}$	$X_{\text{cc}}$
PESN-0	180.6	202.3	219.9	236.0	71.1	34.4	34.4
PESN-25	187.3	204.5	219.9	233.2	42.6	20.6	25.8
PESN-50	187.7	204.8	220.8	233.0	58.6	28.3	17.2
PESN-75	—	199.1	217.4	233.0	73.2	35.3	8.6
PESN-100	—	—	—	—	—	—	—

$T_c$ =onset crystallization temperature

Figures 2 and 3 show the temperature dispersions of the dynamic storage modulus ( $E'$ ) and  $\text{Tan}\delta$  (loss tangent) for Nylon-6, PES and their various blend compositions. The peak in the  $\text{Tan}\delta$  curve at temperature around 60°C corresponds to the  $T_g$  of Nylon-6 phase. It can be seen in the figure that the  $T_g$  of Nylon-6 phase does not vary much with composition, which shows that the two polymers are immiscible in the

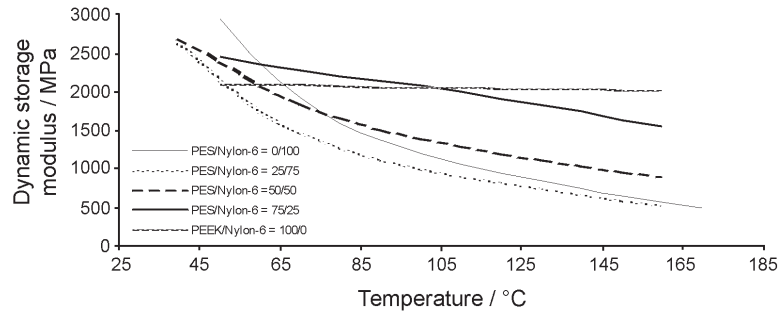


Fig. 2 Temperature dependence of dynamic storage modulus ( $E'$ ) for PES/Nylon-6 blend

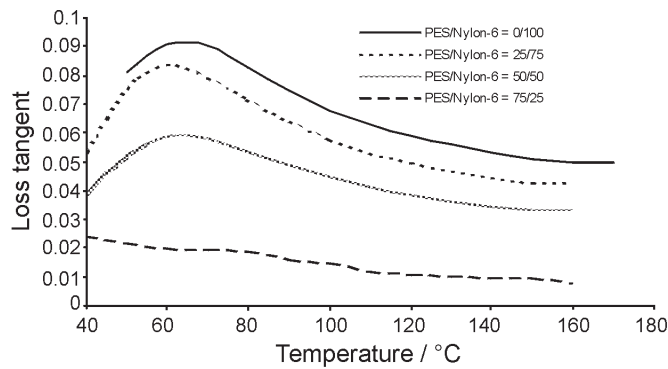


Fig. 3 Temperature dependence of loss tangent ( $\text{Tan}\delta$ ) for PES/Nylon-6 blend

blend. Figure 2 shows that the dynamic storage modulus of PES/Nylon-6 blends is in-between those of the constituent polymers. Whereas at low temperature, modulus of blends is inferior to Nylon-6, at higher temperatures the former shows better behaviour than the latter. Figure 4 shows dependence of  $E'$  at 50, 70 and 150°C on PES concentration in the blend. The reason why these three temperatures were chosen is as follows: 50°C is below the  $T_g$  of amorphous phase in Nylon-6, 70°C is just above the  $T_g$  of Nylon-6 and 150°C is a temperature far from the  $T_g$  of Nylon-6. Important

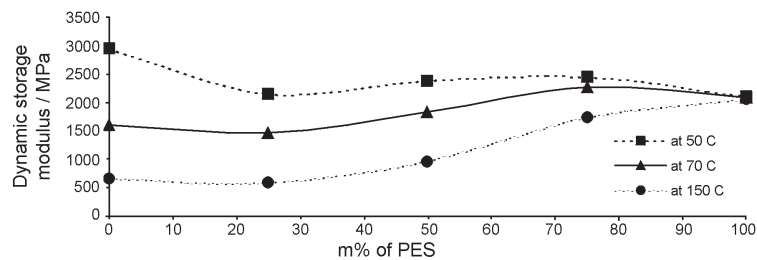


Fig. 4 Dependence of dynamic storage modulus ( $E'$ ) at various temperatures on PES content in the blend

observation from this figure is that  $E'$  values of various blend compositions are greater than those of pure Nylon-6 at temperatures above its  $T_g$ .

Results of TMA studies are shown in Fig. 5, where coefficient of thermal expansion (CTE) is plotted as a function of temperature. CTE increases as the  $T_g$  of the polymer is reached and shows a maximum in the temperature region 50–60°C after which it decreases slightly, may be because of the recrystallization phenomenon and then increases again. Figure 5 shows that the CTE decreases as the PES concentration increases in the blend. Since the thermal expansion coefficient is an expansion of free volume, low thermal expansion coefficient results are reasonable because of small free volume. This decrease in the free volume also results in the increased dimensional stability of blend compositions at higher temperature compared to Nylon-6.

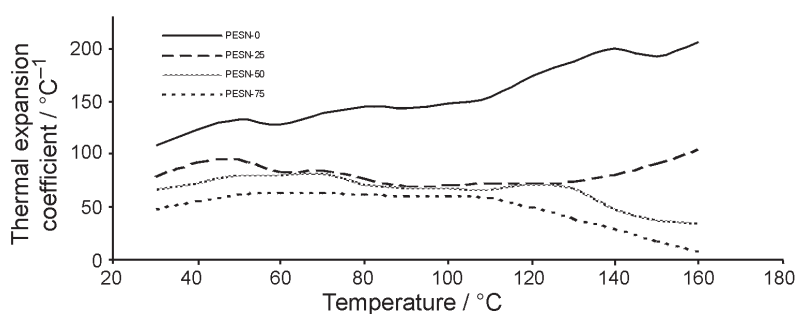


Fig. 5 Variation of thermal expansion coefficient with temperature for PES/Nylon-6 blend

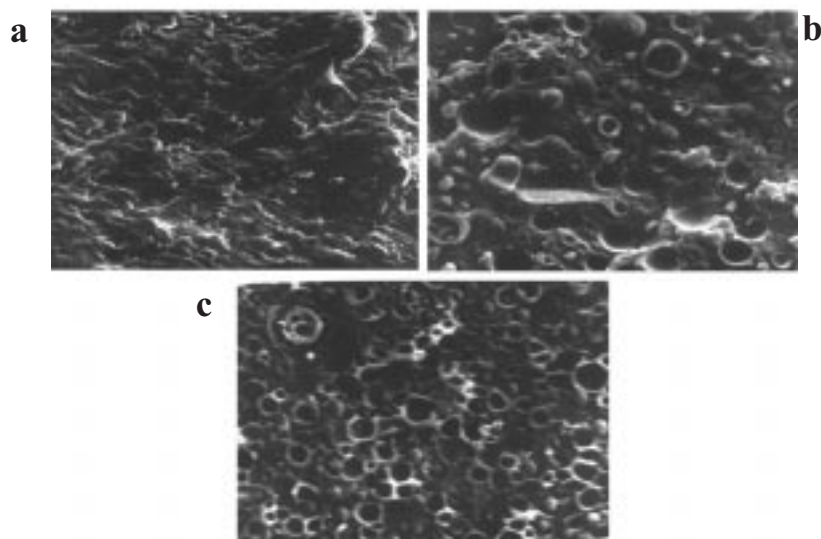


Fig. 6 a – SEM micrograph of fractured surface of PES/Nylon-6=25/75 blend  
 b – SEM micrograph of fractured surface of PES/Nylon-6=50/50 blend  
 c – SEM micrograph of fractured surface of PES/Nylon-6=75/25 blend

The morphology of fractured surfaces of Nylon-6/PES blend was observed by SEM as shown in Fig. 6a–c. Micrographs show that the morphology of PES/Nylon-6 blend does not significantly vary with composition and the dominant morphology is apparently a particle-in-matrix structure. The dispersed domain is smaller in size when Nylon-6 forms a dispersed phase than when PES does. This, among many factors, is due to the large difference in viscosity between the two components. With a higher viscosity of the dispersed phase (PES), fine break up would be more difficult [13].

Thermal stability of the blends determined from TG show two step decomposition behaviour because of macro phase separated morphology. Initial decomposition temperature ( $T_i$ ) and maximum rate of decomposition ( $T_{max}$ ) for the first decomposition step is summarized in Table 3. Decomposition behaviour of neither polymer was affected in the blend.

**Table 3** TG result of Nylon-6/PES blends

Composition	$T_o/^\circ\text{C}$	$T_{max}/^\circ\text{C}$
PESN-0	416.6	449.0
PESN-25	427.9	451.8
PESN-50	419.8	444.2
PESN-75	416.5	435.2
PESN-100	547.4	572.9

$T_o$ =onset degradation temperature taken as the intersection of double tangent on the main degradation curve

$T_{max}$ =maximum rate of degradation

## Conclusions

1. PES affects the crystallization and melting behaviour of the Nylon-6 when blended with it. This effect varies with the composition of the blend. No  $T_g$  of Nylon-6 was observed by DSC even in quenched samples because of its rapid crystallization from the melt state.
2. Glass transition temperature of Nylon-6 phase taken as the peak in loss tangent from DMA results, does not vary, indicating the immiscible nature of the blends. Dynamic storage moduli of the blends were found to be in-between those of neat polymers. It is better in the case of composition where Nylon-6 is the dispersed phase because of its better dispersion in the PES matrix.
3. TMA shows that thermal expansion coefficient of blend decreases with PES concentration leading to increased dimensional stability.
4. The morphologies of the blends were characterized by two well defined homophase of PES and Nylon-6. Disperse phase size is smaller when Nylon-6 is the dispersed phase because of its lower viscosity compared to PES.



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