

Morphological reasoning for the enhanced charge carrier mobility of a hole transport molecule in polystyrene*

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Abstract: Pai and coworkers have reported that the charge carrier mobility of the hole transport molecule *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) is higher with polystyrene (PS) as the host polymer, in comparison to bisphenol A polycarbonate (PC) as the binder. It was proposed that the enhanced interaction of TPD with PC and the effect of the carbonyl dipole are responsible for such a phenomenon. We present a morphological study that lends support to the above proposal. The morphology and thermal behavior of TPD/polystyrene (TPD/PS) composites have been investigated as a binary solid solution and compared with that of the TPD/polycarbonate (TPD/PC) pair. The depression of the glass-transition temperature (T_g) with the concentration of TPD is more pronounced with PC than with PS. On the other hand, the recovery of the T_g upon annealing is significantly higher in the case of PS. Fourier transform infrared (FTIR) study shows that the molecular-level interaction between TPD and PS is not as significant as in the case PC. Molecular modeling based on the MM+ molecular mechanics calculations also shows an electrostatic component to the total interaction energy in the case of PC. In addition, small crystals are present in the as-prepared films of TPD/PS that, upon chaining, could enhance the charge carrier mobility. Thus, it is suggested that the enhanced interaction between TPD and PC as well as the small crystals of TPD in PS are responsible for the higher mobility in the latter. PS serves as an inert host, while there are specific interactions between TPD and PC.

INTRODUCTION

Molecular doping of charge transport molecules in polymer matrices is a common route to organo-electronic device fabrication for a range of applications such as photoreceptors, organic light-emitting diodes (OLEDs), and electrochromic devices [1,2]. The charge transport in organic systems is a thermally assisted hopping event, and this involves charge exchange between neighboring molecules. The drift mobility, which is determined by the time-of-flight technique, is a measure of the charge exchange rate. It is a function of the chemical structure of the charge transport molecule, its concentration in the matrix, the electric field, and temperature. As for the role of the chemical structure of the transport molecule, it has been shown that the charge mobility decreases exponentially with an increase in the dipole moment [3–5]. The dispersion of the active molecule and the intermolecular distance influence the charge transport [2,6]. It is preferable to have the maximum possible concentration of the transport molecule in the polymer since the drift mobility increases with its concentration in the matrix.

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The hole transport molecule, *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-[1,1'-biphenyl]-4,4'-diamine (TPD) is known to be electron donor and is employed in organic photoreceptors in the charge transport layer (CTL) [1]. It was realized about a decade ago that the polymer matrix also plays a role in the charge transport characteristics. The effect of several types of polymer binders on the charge mobility has been studied [2,7–11] to demonstrate that the binder does have an influence on the properties of the CTL. Higher charge mobility has been found in the case of TPD/polystyrene (TPD/PS) film in comparison to the TPD/polycarbonate (TPD/PC). These results were interpreted [11] as due to (i) the solubility of the molecule in the binder. Yuh and Pai [11] reported that the solubility of TPD in PS is better than that in polycarbonate (ii) local dipoles on the binder. The dipole moments of PS and PC are 0.1 and 1.0 D, respectively [4]. It was rationalized that at low concentrations of the TPD, the small molecule is surrounded by the carbonyl dipole, and mobility is reduced. With an increase in concentration, the TPD ($\mu = 1.5$ D) is surrounded by its own dipole in addition to that of the PC, and the effect of the binder becomes less pronounced. In the absence of such a polar group, the mobility in PS is higher. The difference is significant at low molecular doping levels.

In a recent paper [12], we described the phase-separation behavior in model charge transport films, with TPD in two different types of polycarbonates (PCs), and related it to the molecular flexibility of the polymers, and their interaction with the TPD molecule. The specific interaction between the PC and TPD was evident from the infrared frequency shifts in the aromatic region of the spectrum. The glass transition (T_g) of the PC was reduced significantly with the addition of TPD, and partly recovered upon crystallization of TPD with annealing. However, the extent of recovery of the T_g was not commensurate with the crystallinity of TPD as measured by thermal analysis and X-ray diffraction. It was proposed that the microcrystals of TPD actually plasticize the PC.

As mentioned above, the significant difference in carrier mobility between PC and PS as host matrices was interpreted as due to the differences in the solubility of the TPD and its molecular interaction with the polymer. In this paper, we describe our studies on the phase separation induced by annealing of films containing TPD and PS. The relative stability of this pair as compared with the PC as the host matrix will be discussed. Annealing temperatures in the range of 80–90 °C were used for varying lengths of time. Below this temperature range, no significant crystallization occurs. The reason for choosing this temperature range is to compare these results with those of the TPD/BPAPC system, which was annealed at 10–20 °C below the T_g of the host polymer. We will discuss the differences and similarities between TPD/PS, TPD/BPAPC, and TPD/PCZ systems, the latter being with the polymer that is conformationally more rigid than PS and BPAPC. The difference between the annealing temperature and the T_g affects the extent of crystallization of the TPD.

EXPERIMENTAL

The sample of TPD was courtesy of Xerox Research Centre of Canada. PS, with an average molecular weight (M_w) of 250 000, was purchased from Across Organics.

Coating solutions were prepared by dissolving appropriate mixtures of TPD and the polymer in THF of laboratory grade. Methylene chloride was also used as the solvent in some instances. Concentrations of 10–50 % (wt) of TPD in PS were used. Films were coated on a glass substrate using an electrically driven film coater, and these were then dried at a very low rate of the solvent evaporation at ambient conditions for at least 48 h, and then at 35 °C for 24 h in the vacuum oven. The final thickness of the films was about 10–15 μm . Samples were annealed using a vacuum oven with an accuracy of ± 1 °C at different temperatures for various lengths of time.

Thermal analysis, infrared spectroscopy, X-ray diffraction, and optical microscopy were used as described before [12] to study the effect of annealing on the structure and morphology of these films.

RESULTS AND DISCUSSION

Depression of the glass-transition temperature

Differential scanning calorimetry (DSC) analysis of TPD showed an endothermic peak at about 171 °C with a heat of fusion 17.78 cal g⁻¹. The glass-transition temperature of PS film was 93 °C. As expected, the T_g of the PS was depressed by the addition of TPD. The variation of T_g of PS with the concentration of TPD is shown in Fig. 1 for the as-prepared film. The depression of the T_g , i.e.,

$$\Delta T_g = T_g(\text{PS}) - T_g(\text{composite}) \quad (1)$$

is also shown in the inset. With 50 % TPD, the T_g of PS is reduced to as low as 45 °C. We express the compositions of the composites in terms of weight percent, which is a common practice for investigations related to these types of devices. For conversions of these to the molar volume, note that the molecular weight of TPD is 516.66 g mol⁻¹, which is five times higher than that of the repeat unit of PS (104.1 g mol⁻¹). The TPD crystallizes [13] with the P2₁2₁2₁ symmetry, and the density is 1.202 g cm⁻³. The reported density of PS is 1.05 g cm⁻³.

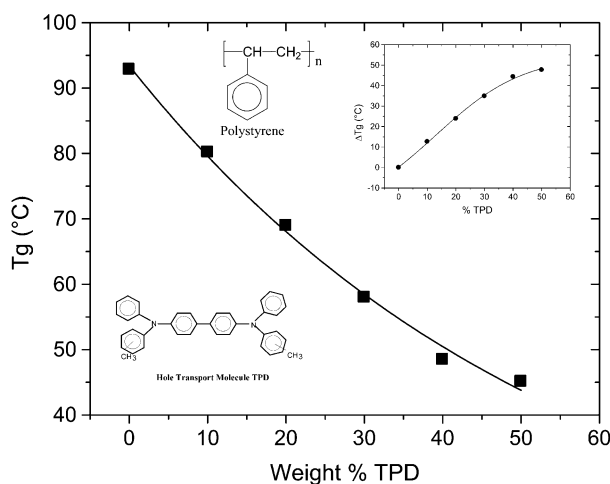


Fig. 1 The variation of T_g of the PS with different concentrations of TPD. The inset shows the depression ΔT of the T_g .

The T_g of PS is depressed by 45 °C with 40 % TPD and by 48 °C with 50 %. The DSC measurements show a small endothermic peak at 163 °C for the film with TPD/PS: 50/50, which is attributed to the melting of the TPD. This indicates that the T_m of the TPD is depressed by about 8°, in the presence of PS. It was reported [12] that the depression of T_m is 5 °C for 50 % of TPD in BPAPC. Similar depression of the T_m of the small molecule has been noted in the cases of diphenyl terephthalate and diphenyl isophthalate dispersed in a liquid-crystalline polymer [14] and poly(styrene-*co*-*n*-butyl acrylate) [15].

In the presence of TPD, the depression of the T_g of the polymer is expected to depend on the type and the molecular conformation of the polymer matrix. For example, with 40 (wt%) of TPD, the T_g of the BPAPC was depressed by 63 and by 78 °C with 50 % [12]. With 40 and 50 % concentrations of TPD in PCZ, the depression of T_g was 94 and 97 °C, respectively. The depression of T_g is much more pronounced in the case of PCZ than with PS and BPAPC. We noted before [12] that the depression of the glass-transition temperature is more pronounced when the T_g of the host polymer is high. With regard to BPAPC and PCZ, it was shown before that the extent of mutual molecular interaction between TPD and PCZ is more significant, based on IR spectra and molecular modeling. The extent of depres-

sion of T_g was correspondingly higher. With PS as the host, the extent of depression of T_g is significantly smaller.

Figure 2 shows the Fourier transform infrared (FTIR) spectrum of TPD/PS (50/50) composite film along with those of pure TPD and PS film. In probing for specific interaction between TPD and the polymer, we monitor the shifts in the absorption frequencies of the polymer in the regions of the

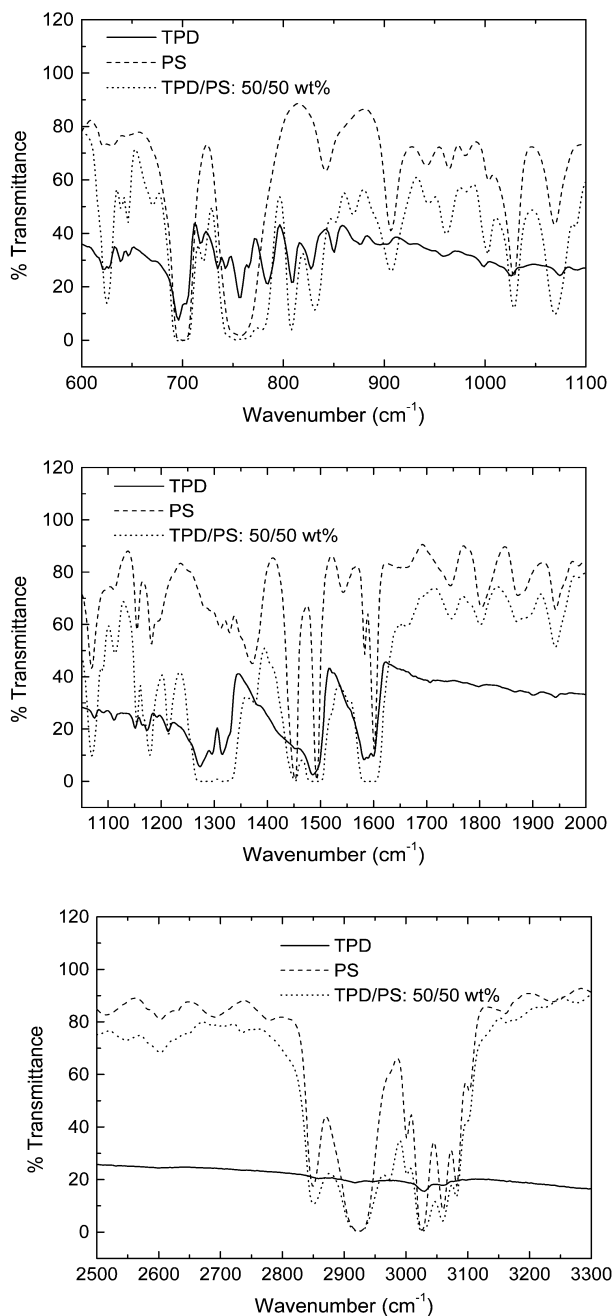


Fig. 2 FTIR spectra of TPD, PS, and TPD/PS: 50/50 film.

spectrum that correspond to the aromatic group, viz. 540, 697, 758, 1029, 1220, 1494, 1601, and 3000–3100 cm^{-1} . The band at 1601 cm^{-1} in the PS spectrum corresponds to the aromatic ring quadrant stretch. With an increase in the concentration of TPD in PS, a broader band is observed and shifts to lower frequency by 10 cm^{-1} in the spectrum of TPD/PS: 50/50 (wt%). There is no significant shift in the positions of peaks in the region 3000–3100 cm^{-1} that correspond to aromatic CH stretches.

While there is a modest shift in IR frequencies of PS in the presence of TPD, the shifts in the case of PCs were much more pronounced with the addition of TPD [12]. The extent of depression of T_g was also more significant in the case of PCs. In addition, even with a concentration of 30 % TPD in PS, tiny crystals are seen, as in the optical micrographs shown in Fig. 3. Their number increases with the concentration of TPD. The SEM image of the cross-section of the TPD/PS: 30/70 film is shown in Fig. 3c.

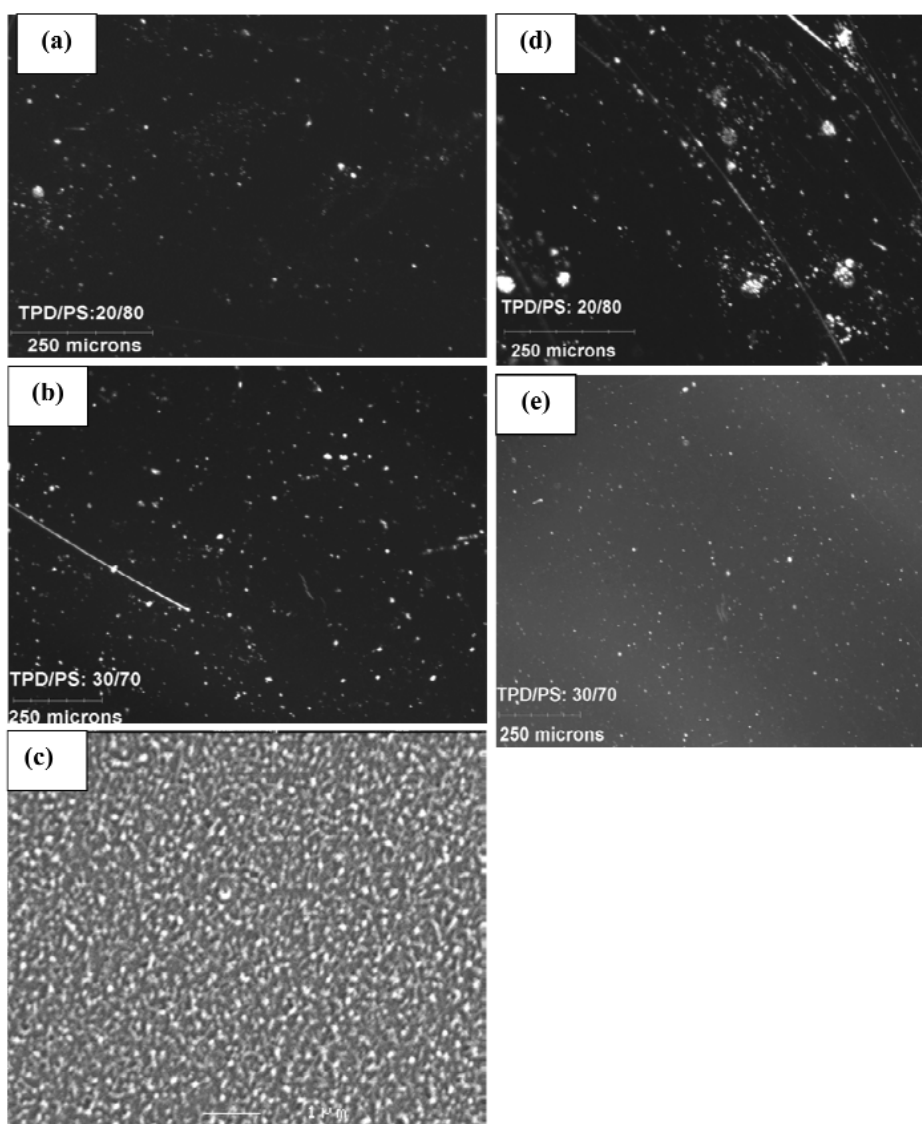


Fig. 3 Transmission optical micrographs of as-prepared films of TPD/PS. (a) 20:80 and (b) 30:70 (wt%) with THF as the solvent; (d) 20:80 and (e) 30:70 (wt%) with methylene chloride as the solvent. (c) is the SEM image of the cross section of the 30:70 (wt%) film with THF as the solvent. The scale bar in (c) is 1 μm .

It is seen that the crystals of submicron size (the scale bar is 1 μm) are present through the thickness of the film. Since these crystals are small, the film itself remains visibly clear, although brittle. In contrast, these were sporadic in the case of the PC films with the same concentration of TPD. Thus, the solubility or interaction of TPD with the PC is more favorable than with PS.

To compare the molecular interactions between the TPD/PS and TPD/PC pairs, a simple molecular modeling was performed. Using HyperChem software, models of TPD, and a trimer of PS were energy-minimized. Pairs of TPD/PS were then created by placing the TPD molecule in the proximity of the PS model. The pair was then energy-minimized. Relatively, the energies of the TPD, and the trimers of PS were 16.3 and 1.2 kcal mol⁻¹, respectively. The energy of the TPD/PS pairs reduced to -4.6 kcal mol⁻¹. The extent of lowering of the energy is thus 6 kcal mol⁻¹ for the TPD/PS relative to that of the polymer. Similar modeling studies of TPD/BPAPC and TPD/PCZ systems showed a much larger decrease in the energy of the polymer than TPD/PS [12]. The decrease in energy was larger for the TPD/PCZ pair than for TPD/BPAPC. This accords with the larger depression of the T_g of PCZ compared to BPAPC. Thus, the extent of depression of the T_g , IR spectra and modeling studies show that the molecular interaction between TPD and the PC is more favorable than with PS. It was also noted in the modeling studies using the MM+ force field, that the electrostatic contribution to the total energy of the BPAPC trimer and the TPD/BPAPC pair was -3.3 kcal mol⁻¹, whereas in the case of PS, it was almost zero.

Recovery of the T_g

Annealing these composites at different temperatures below the T_g of PS results in crystallization of TPD to varying degrees. Upon the crystallization of the TPD, the T_g of the PS is partially recovered, the extent of recovery depending on the temperature and time of annealing and the concentration of the TPD. The results of the recovery of T_g with annealing time is shown in Fig. 4, for temperatures of 80, 85, and 90 °C, for 40 and 50 % concentration of TPD in PS. With both 40 and 50 % concentrations of TPD, the T_g recovery is sharp during the first thirty minutes, and levels off. Beyond 1 h, no significant increase is observed. For the TPD/PS (40/60) film, annealing at 80 °C for 2 h increases the T_g from 49 to 67 °C, and at 90 to 72 °C. The recovery of T_g is slightly higher for the TPD/PS: 50/50 composite. Thus, the difference in the T_g recovery is significant when the annealing temperature is increased by 10°.

The recovery of T_g in this case upon annealing contrasts significantly with that of TPD/BPAPC. In the latter, almost 2 h of annealing was required for the T_g recovery to level off, whereas the maximum recovery was reached within 30 min with the TPD/PS composite. The recovery was only about 10° in the case of TPD/BPAPC (50/50 wt%), after annealing at 140 °C (10° below the T_g of the host) for 4 h. However, a recovery of 30° is noted for TPD/PS for annealing at 85 °C (10° below the T_g of the host). Thus, the phase separation and the resulting T_g recovery are substantial. It is seen from Fig. 4c that upon annealing, the TPD/PS (50/50 wt%) film at 90 °C for 2 h, the T_g increases from 45 to 75 °C. Referring to Fig. 1, it is the equivalent of the T_g of the film with about 15 wt% of TPD. Thus, a profuse crystallization has occurred. In the case of the TPD/BPAPC, although the crystallinity measured by DSC and X-ray diffraction was significant, the T_g recovery was small. It was proposed that the sub-micron crystals of TPD serve to plasticize the polymer, i.e., the increase of T_g due to phase separation was moderated by the crystals of TPD acting as a plasticizer.

Figures 4b and 4d show the change in T_g as a ln-ln plot with annealing time. The slopes of the curves for 80, 85, and 90 °C are similar. Ideally, these could be superimposed with a shift factor. The rate of change of T_g with time is similar for the annealing temperatures studied in this case.

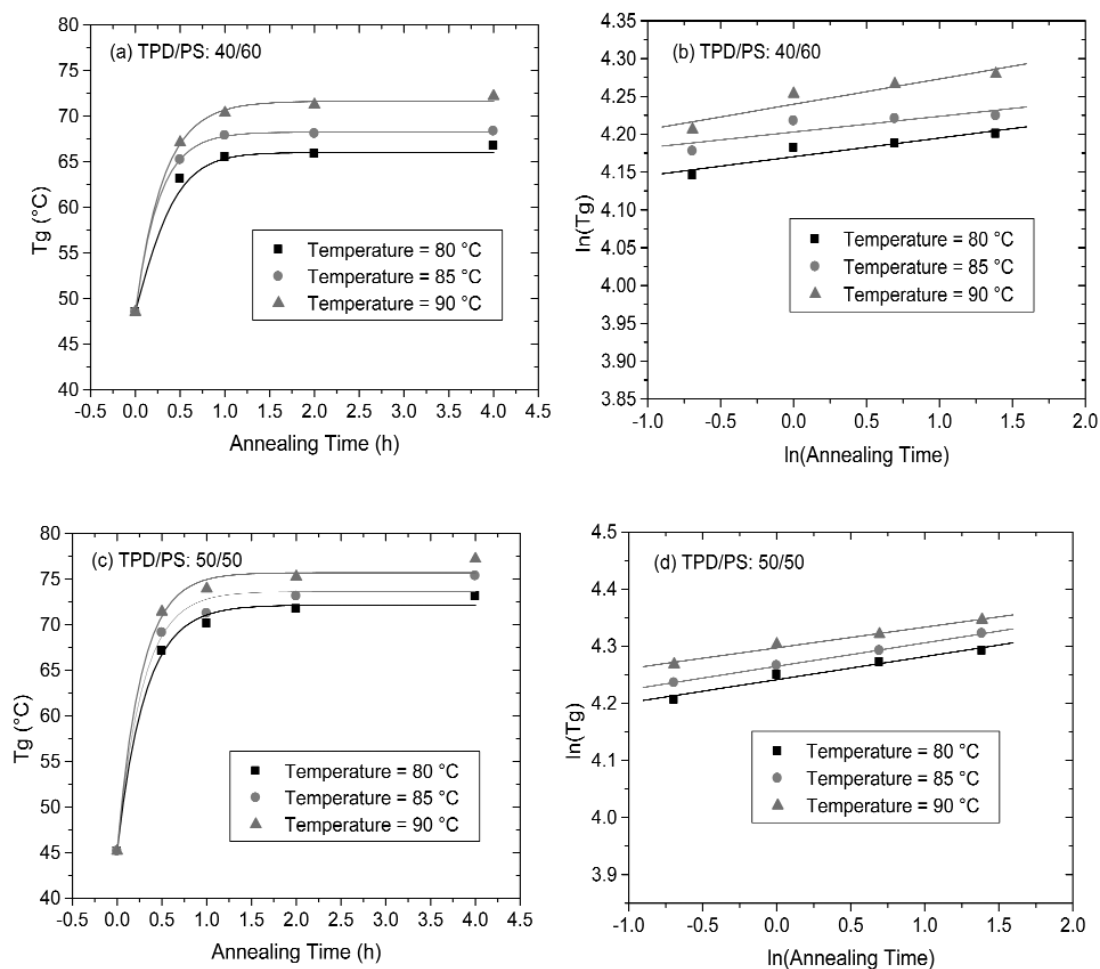


Fig. 4 Glass-transition temperature (T_g) vs. annealing time of TPD/PS film: (a) 40/60 (c) 50/50 (wt%). (b) and (d) show the \ln - \ln plot of (a) and (c), respectively.

It can be expected that the T_g recovery would depend on the difference ΔT between the T_g of the polymer and the annealing temperature. Figure 5a shows the variation of the extent of T_g recovery with ΔT , after annealing (at 80, 85 and 90 °C) for 2 and 4 h. It is seen that there is a linear variation of T_g recovery with the ΔT . The variation of T_g recovery with ΔT in Fig. 5a can be expressed in the following form

$$T_{g(\text{rec})} = 31.00 - 0.35 \Delta T_{\text{ann}}; R = 0.99 \text{ for } 2.0 \text{ h} \quad (2)$$

$$T_{g(\text{rec})} = 33.05 - 0.36 \Delta T_{\text{ann}}; R = 0.99 \text{ for } 4.0 \text{ h} \quad (3)$$

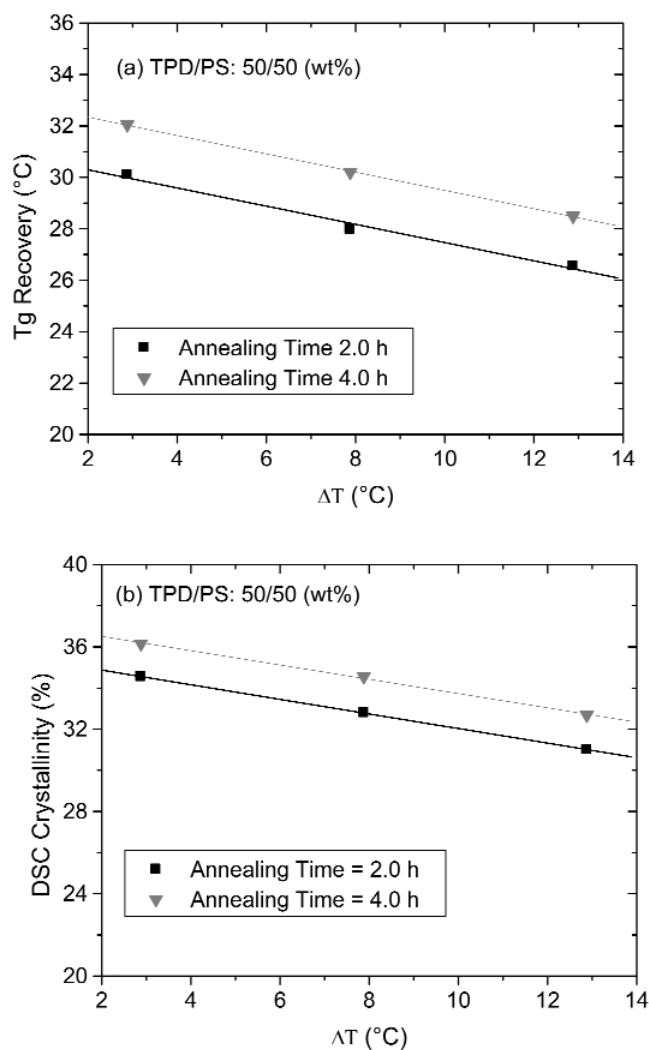


Fig. 5 T_g recovery (a) and the DSC crystallinity (b) plotted as a function of the difference ΔT between the T_g of the polymer and the annealing temperature.

Crystallinity of phase-separated TPD

The crystallinity of the phase-separated TPD was determined from the heat of fusion and X-ray diffraction. Typical changes in the X-ray diffraction profile upon annealing are illustrated in Fig. 6, for the TPD/PS: 50/50 (Fig. 6a) and for TPD/BPAPC: 50/50 (Fig. 6b) films. The results of the calculated crystallinity are given in Fig. 7 for TPD/PS: 50/50 film, with annealing time. Before annealing, no crystalline peak is seen in either Figs. 6a or 6b. This could be taken to mean that TPD is molecularly dispersed, and no aggregation has taken place. However, it is seen from Fig. 3 that tiny crystals are present in the as-prepared films of TPD/PS. Indeed, a broad peak is seen in Fig. 6a at about $2\theta = 20^\circ$. Thus, although there are crystals present, they are not of sufficient size and perfection that could be detected by X-ray diffraction. After 0.5 h, the peaks due to TPD begin to appear. The crystalline peaks are far less pronounced with the TPD/PS system compared to TPD/BPAPC. This could be attributed in part to the size of the crystals. Figure 8 shows the optical micrographs of TPD/PS and the TPD/BPAPC films, after annealing at a temperature 5–10° lower than the T_g of the host polymer for 4 h. While

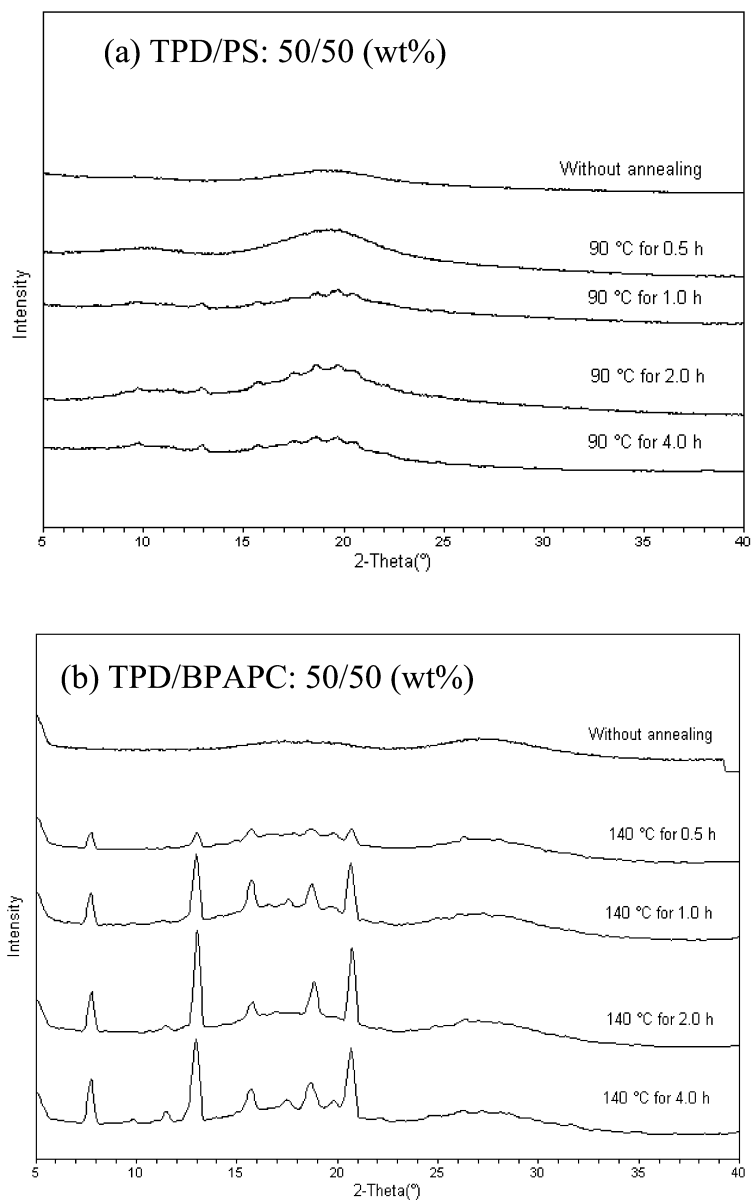


Fig. 6 X-ray diffraction traces of (a) TPD/PS: 50/50 (wt%), (b) TPD/BPAPC: 50/50 (wt%) films.

the TPD/BPAPC forms large crystals, with the size ranging from 1 to several hundred microns, those corresponding to TPD/PS are only from 1 to 20 μm .

It is seen from Figs. 7a and b that the values of the crystallinity from the DSC measurements are significantly higher than those obtained from X-ray diffraction measurements. The rate of change of crystallinity with time is also different. Such differences are due to the small size of the crystals and their detectability with X-ray diffraction, as mentioned above. With 50 % TPD, the DSC crystallinity (H_{cr}) is found to increase from 15 to nearly 35 % with annealing at 90 °C. This is consistent with the extent of the recovery of the T_g .

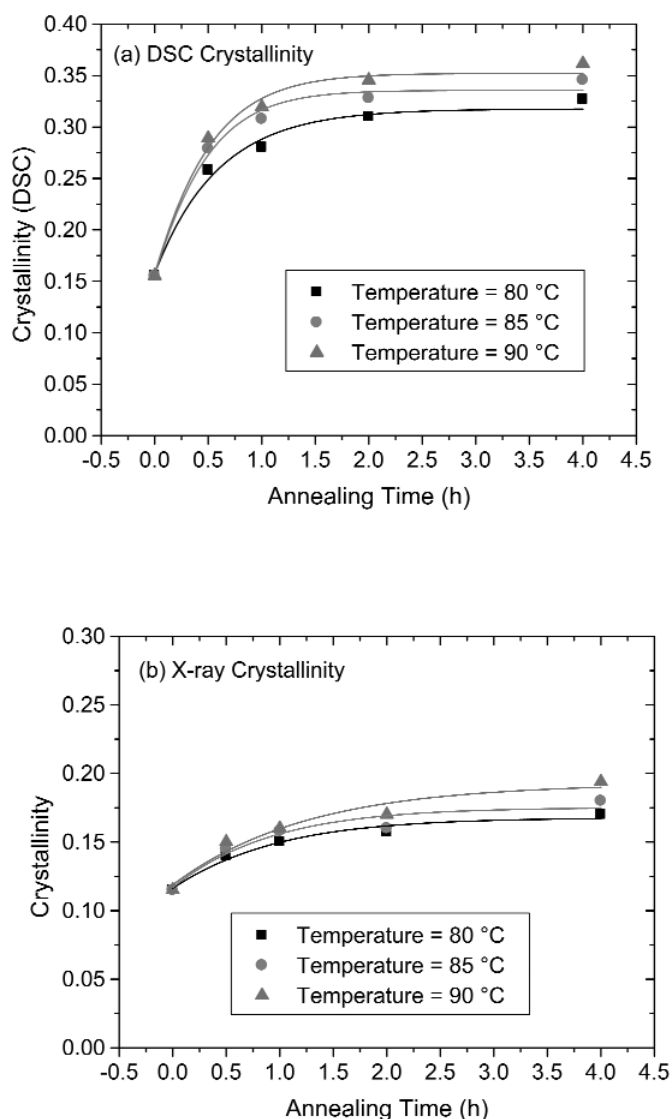


Fig. 7 DSC crystallinity (a) and X-ray crystallinity (b) of TPD/PS: 50/50 (wt%) films, as a function of annealing time at different temperatures.

Figure 5b shows the variation of the crystallinity of the phase-separated TPD as a function of ΔT the difference between the T_g of the polymer and the annealing temperature, after annealing (at 80, 85, and 90 °C) for 4 h. The DSC crystallinity is plotted here, to be consistent with Fig. 5a, showing the variation of the T_g recovery. It is seen that the crystallinity of the phase-separated TPD decreases with an increase in ΔT . The results shown in this figure can be fitted to a linear regression, with the following relationships:

$$H_{cr} = 35.58 - 0.36 \Delta T; R = 0.99; \text{ for 2 h of annealing} \quad (4)$$

$$H_{cr} = 37.21 - 0.34 \Delta T; R = 0.99; \text{ for 4 h of annealing} \quad (5)$$

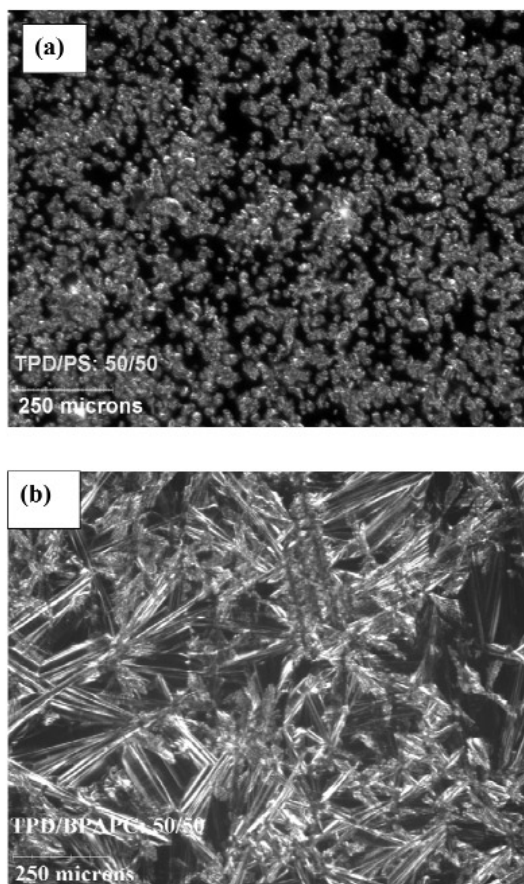


Fig. 8 Transmission optical micrographs of (a) TPD/PS: 50/50 (wt%) annealed at 90 °C and (b) TPD/BPAPC: 50/50 (wt%) annealed at 140 °C, for 4.0 h.

Figures 5a and 5b show that the slopes of the T_g recovery and the crystallinity of the phase-separated TPD with ΔT are almost the same (compare eqs. 2–5). This confirms that no other event occurs in the case of TPD/PS, such as the TPD crystals plasticizing the BPAPC.

Morphology and the carrier mobility

As mentioned in the Introduction, the higher carrier mobility of TPD with PS as the host, in comparison to PC, was attributed to the influence of the carbonyl dipole in the latter [7–11]. It was also observed that the difference is more pronounced with the lower concentrations of TPD. This is due to the fact that at lower concentrations, each TPD molecule will be surrounded by the polymer than another TPD, and experience the effect of the carbonyl dipole of the PC. At higher concentrations, each TPD molecule will be surrounded by its own kind and the effect of the dipole would become negligible.

From the current study, it is found that the molecular interaction between TPD and the PC is more significant than with PS, as shown by the depression of the T_g , recovery of the T_g upon annealing, the IR frequency shifts, and molecular modeling. As mentioned above, the electrostatic component of the total energy is about $-3.3 \text{ kcal mol}^{-1}$ in the case of PC. Further, the recovery of the T_g and the crystallinity of the phase-separated TPD is also higher with PS, indicating that the polymer in this case is a relatively inert host compared to the PC. Based on these results, the interpretation presented by Pai and collaborators [7–11] that the PC exerts an influence on the mobility of TPD is reasonable. It was also

shown above that even at TPD concentrations of 30 %, small crystals are present in the as-prepared films of PS (Fig. 3), and with 50 %, the initial crystallinity is about 15 % (Fig. 7a). The SEM of the cross-section of the film with 30 (wt%) TPD (Fig. 3c) shows the presence of submicron crystals through the thickness of the film. Chaining of these tiny crystals could also contribute to the enhanced charge carrier mobility. Note that as shown in Fig. 8, the size of the crystals, after annealing, is smaller in PS than in PC.

CONCLUSIONS

The current studies on the TPD/PS composites show that the glass-transition temperature of the PS is reduced significantly in the presence of the TPD, although the extent of the reduction is smaller as compared with PC. The IR absorption frequencies corresponding to the aromatic resonance of the PS show very little shift when mixed with TPD, indicating that the molecular interactions involving the phenyl groups is not as significant as in the case of PC. Annealing induces crystallization of the TPD due to phase separation and leads to a recovery of the T_g of the host polymer by as much as 30° for 50 % TPD in PS. The higher level of molecular interaction between PC and TPD supports the previous suggestions that such an interaction is responsible for the lower mobility than with PS as the host polymer. The presence of small crystals in the as-prepared films of TPD/PS also could be a contributing factor.

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