

Differential Scanning Calorimetric and Free volume Study of Reactive Compatibilization by EPM-g-MA of Poly(trimethylene terephthalate)/EPDM Blends

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ABSTRACT: Differential scanning calorimetry (DSC) and positron annihilation lifetime measurements have been carried out to study the effect of the compatibilizer maleic anhydride grafted ethylene propylene copolymer (EPM-g-MA) in poly trimethylene terephthalate and ethylene propylene diene monomer (PTT/EPDM) immiscible blends. The DSC results for the blends of 50/50 and 30/70 compositions show two clear glass transition temperatures, indicating that the blends are two-phase systems. With the addition of compatibilizer, the separation between the two glass transitions decreased, suggesting an increased interaction between the blend components with compatibilizer. At 5 wt % of compatibilizer, the separation between the T_g s reduced in both 50/50 and 30/70 blends. The positron re-

sults for the blends without compatibilizer showed an increase in relative fractional free volume, as the EPDM content in the blend is increased. This suggests the coalescence of free volume of EPDM with the free volumes of PTT due to phase separation. However, the effect of compatibilizer in the blends was clearly seen with the observed minimum in free volume parameters at 5% of the compatibilizer, further suggesting that this percent of compatibilizer seems to be the optimum value for these blends. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 740–747, 2006

Key words: differential scanning calorimetry; PTT/EPDM blend; glass transition temperature; o-Ps lifetime; free volume; compatibilizer

INTRODUCTION

In recent years, because of the technological importance and the academic interest, research in the field of synthesizing polymer blends with different chemical and physical properties has grown immensely. The microstructure and morphology of the blends (mixtures) are major keys in controlling the final properties, and therefore widening the technological applications of the blends.¹ To enhance the material properties of the blends, it is important to understand the nature and the underlying factors of blending at the molecular level. Good amount of research has been carried out over the years, with a view to obtain new polymeric materials with properties needed for specific applications, which is the result of better combi-

nation of different properties.¹ The thermoplastic elastomers (TPEs) from rubber–plastic blends are such materials that combine the excellent processing characteristics of the thermoplastic materials at high temperature and a wide range of physical properties of elastomers at service temperature. But, at the molecular level, these TPEs exhibit phase-separated morphology, and therefore, most of the TPEs are immiscible and incompatible.² Melt mixing of two polymers is usually employed in the making of the polymer blends, which sometimes results in the blends that are weak and brittle. It has been observed that the low deformation modulus follows an approximately linear mixing rule but not the ultimate properties. This is probably due to the incorporation of a dispersed phase in the blend matrix, leading to the presence of stress concentrations and weak interfaces, and as such poor mechanical coupling between the phases.³ From this point of view, small and uniformly dispersed particles are advantageous for the properties of the polymer blends.⁴

It has been established that the mechanical properties of a blend or a polymer alloy will be determined not only by the properties of its components, but also by the phase morphology and interphase adhesion.³

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The applications of the immiscible blends are often limited because the adhesion strength at the interface is not strong enough. In such situation, it is worthwhile to introduce a suitable compatibilizer, which enhances the interaction between the two blend components at the interface. However, employment of a proper compatibilizer for improving interfacial adhesion of polymer blends is critical and crucial.⁴ The compatibilization leads to the modification of the interfaces in two-phase blends and the resulting phase structure and hence the properties³ may suit a particular application. One of the important effects of compatibilizers is to reduce the interfacial tension in the melt, causing an emulsifying effect, leading to a good dispersion of one phase in the other. The second major effect is to increase the adhesion at the phase boundaries, giving improved stress transfer.³ And, the third effect is to stabilize the dispersed phase against growth during annealing, thereby modifying the phase boundary interfaces.³ Compatibilization of a polymer blend is most effectively accomplished by appropriate block or graft copolymers that locate at the interface between the phase domains in the blend. These copolymers strengthen the interface between the phase domains in the blend and reduce the interfacial tension between the two phases. Reactive compatibilization has been shown to effectively enhance the interfacial properties of polymer blend.³⁻⁵ The present study involves the compatibilization of PTT/EPDM blends by the introduction of a compatibilizer precursor, namely, maleic anhydride grafted ethylene propylene copolymer (EPM-g-MA), which is physically miscible with the second phase (EPDM), but has chemical functionality (maleic anhydride group) that can react with the hydroxyl end group of PTT to form a graft copolymer at the interfaces.⁶

Many investigations on the rheological, morphological, mechanical, and thermal properties of the compatibilized blends have been made in the past.⁷⁻⁹ However, not much work has been carried out to understand the effects of compatibilizer at molecular level in such blends. In the present article, we have made an attempt in this direction, using a novel technique like positron lifetime spectroscopy, which measures directly the nanometer-sized free volume cavities and their content in immiscible systems of PTT/EPDM blends with and without the compatibilizer (EPM-g-MA). For this purpose, the concentration of the graft copolymer (compatibilizer) was varied to see whether there is enhancement in the interfacial interactions. Differential scanning calorimetry has also been used to supplement the positron results by characterizing the glass transition temperatures of the blends.

Here, we briefly outline the positron annihilation lifetime spectroscopy (PALS). In recent years, PALS has emerged as a unique and versatile tool for char-

acterizing the free volume properties of polymers and blends.^{10,11} PALS is one of the sophisticated tools currently available for determining directly the nanometer-sized free volume cavities and their relative number density (concentration) in polymers¹⁰⁻¹⁴ and recently, in polymer blends.¹⁰ To enunciate the versatility of this method, we mention only a few of the interesting studies carried out using this technique: water sorption in contact lens polymers,¹⁵ polymers containing silver nanoparticles,¹⁶ structural relaxation of polyethylene terephthalate and polycarbonate,¹⁷⁻¹⁹ ageing studies on polymers,²⁰ etc. When positrons from a radioactive source (²²Na) are injected into a molecular medium like polymers or blends, they reach thermal energy in a very short time (~ 1 ps), through the interaction with the surrounding atoms and molecules, losing the energy by inelastic collisions. During such a slowing down process, and at nearly thermalized stage, a positron, the antiparticle of the electron, will annihilate with the electron of the medium. The positron may annihilate as a free positron or get trapped in defects present in crystalline, crystalline-amorphous interface regions and then annihilates, or form a bound state with an electron of the medium (e^+e^-) called the Positronium (Ps) atom. Ps can exist in one of the two allowed spin states: para-Positronium (p-Ps), if the spins of e^+e^- pair are aligned antiparallel and annihilates into two gamma rays with a lifetime of 125 ps, or ortho-Positronium (o-Ps) if the spins are parallel and annihilates into three gamma rays with a lifetime of 140 ns in free space. However, in molecular media like polymers, o-Ps annihilates through a fast channel called pick-off annihilation, where the positron of o-Ps picks up an electron from the surrounding medium and annihilates, thereby its lifetimes gets shortened to few nanoseconds. It has been clearly established that, o-Ps preferentially scans the free volume holes of the polymer system.^{10-17,21} Therefore, the o-Ps lifetime parameters, namely lifetime (τ_3) and its intensity ($I_3\%$), have been widely used in the study of microstructural behavior of polymeric materials. Also, it is a common practice to correlate the relative concentration of the free volume holes to the viscoelastic properties of the system under investigation. Even though the PALS technique has been successfully used in the study of polymers for more than two decades,²² only recently it has been used to study microstructural behavior of polymer blends and their miscibility property.^{23,24}

EXPERIMENTAL

Blend preparation

The blend components namely PTT (Dupont) and EPDM (DSM, Netherlands) along with the compatibilizer (DSM, Netherlands) were obtained from the re-

TABLE I
Glass Transition Temperature Evaluated from DSC Data for P50E50

| Compatibilizer (wt%) in P50E50 | T_{g1} (°C) | T_{g2} (°C) | T_{m2} (°C) |
|-----------------------------------|---------------|---------------|---------------|
| 0 | -55 | 54 | 230 |
| 2.5 | -53 | 40 | 229 |
| 5 | -50 | 30 | 230 |
| 10 | -55 | 40 | 230 |

spective agencies. Blends with different compositions (P70E30, P50E50, and P30E70) were prepared by melt blending technique. The densities and number-average molecular weights of the homopolymers PTT and EPDM are 1.33g/cc and 0.86g/cc, and 38,000 and 60,000, respectively. In the blends P70E30, P50E50, and P30E70, P represents the PTT, E stands for EPDM, and the numbers indicate the weight percentage of the respective homopolymer. PTT was melted first at a temperature of 230°C, and then EPDM was added after 2 min. The blends were prepared in an internal mixer with a rotor speed of 60 rpm; the total mixing time was fixed as 4 min. The samples were compression molded at 230°C with a pressure of 20 kg cm⁻² for 2 min, into sheets. Similarly the compatibilized blends were also prepared by adding 1, 2.5, 5.0, 10 wt % of EPM-g-MA into P70E30, P50E50, P30E70 blends, with the same mixing time and rotor speed.

Differential scanning calorimetric measurements

Differential scanning calorimetric measurements (DSC) have been carried out to characterize the glass transition temperature (T_g) and melting points (T_m) of the homopolymers and their blends. For this purpose, we have used Universal V3.0G TA instrument type DSC 2010 connected to liquid nitrogen cooling accessory with a nitrogen purge facility. The samples weighing in the range 10–20 mg were allowed to cool from room temperature to -65°C. Before starting the measurements, the samples were equilibrated at -65°C for 10 min. The DSC scans were then recorded at a heating rate of 10°C/min from -65 to 250°C. The thermal data so obtained are reported in the Tables I and II for 50/50 and 30/70 blends, respectively.

Positron annihilation lifetime measurements

Positron annihilation lifetime (PALS) measurements have been carried out at room temperature with a conventional fast-fast coincidence system having a time resolution of 220 ps, measured with Cobalt-60 prompt spectrum. The PALS consists of conical shaped BaF₂ scintillators coupled to photo multiplier tubes of type XP2020/Q with quartz window as de-

TABLE II
Glass Transition Temperature Evaluated from DSC Data for P30E70

| Compatibilizer (wt%) in P30E70 | T_{g1} (°C) | T_{g2} (°C) | T_{m2} (°C) |
|-----------------------------------|---------------|---------------|---------------|
| 0 | -55 | 50 | 230 |
| 1 | -45 | 35 | 230 |
| 2.5 | -47 | 10 | 229 |
| 5 | -45 | -10 | 230 |
| 10 | -45 | 20 | 230 |

tectors. The ²²Na positron source (Amersham) with an activity of ~6 × 10⁵ Bq (17 μCi) was prepared on a 0.0127-mm thick pure Kapton foil, and was sandwiched between two identical pieces of the sample. This sample-source sandwich was placed between the two detectors of PALS to get the lifetime spectrum. Two to three positron lifetime spectra with more than a million counts under each spectrum were recorded.

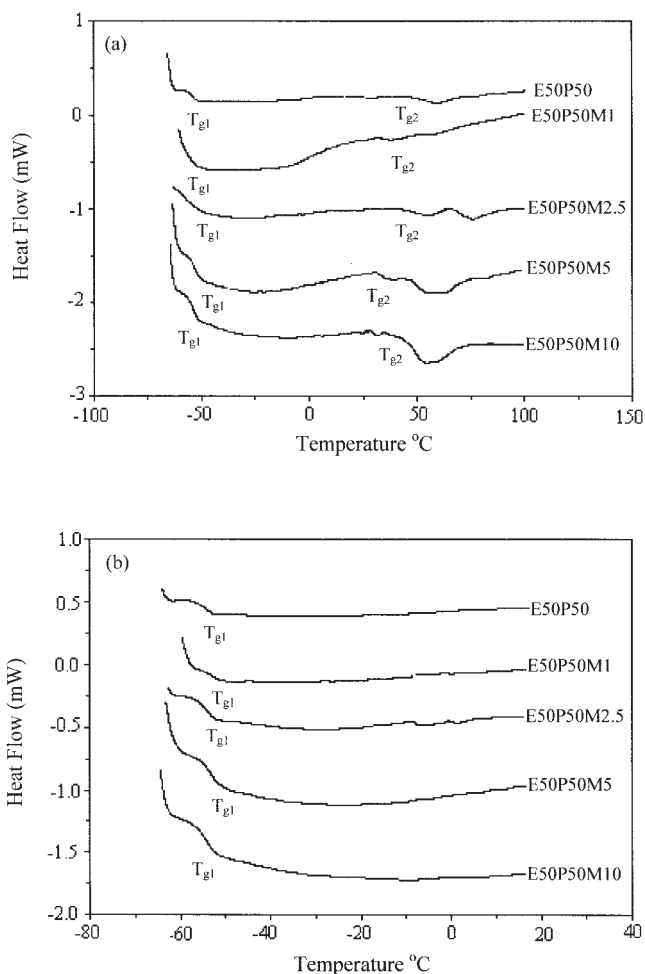


Figure 1 (a) DSC scans of P50/E50 blend and blends with 1, 2.5, 5, and 10 wt % of compatibilizer. (b) For clarity the regions of $T_{g,s}$ are expanded in DSC scans of P50/E50, and blends with 1, 2.5, 5, and 10 wt % of compatibilizer.

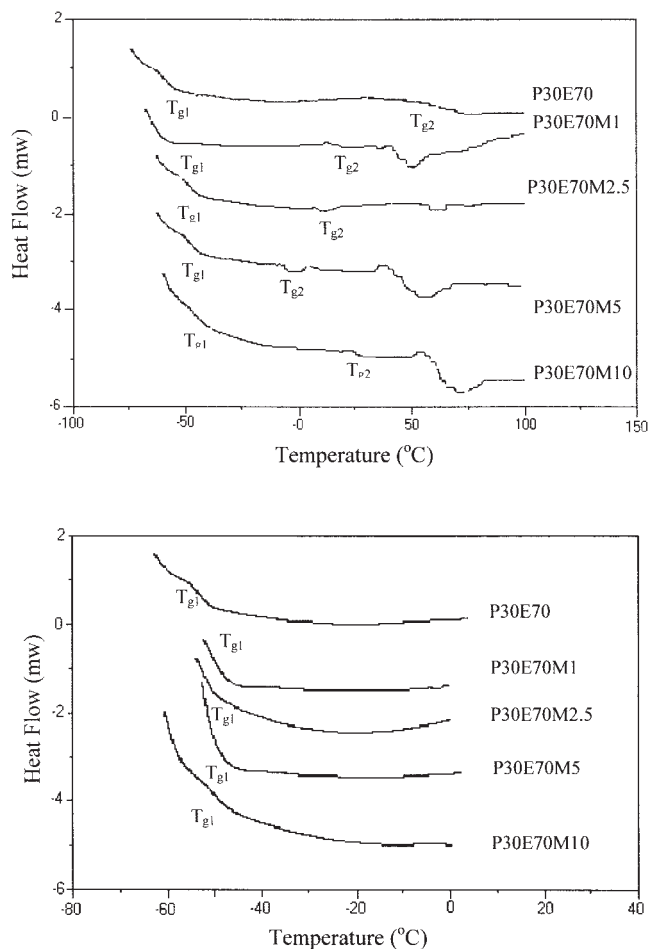


Figure 2 (a) DSC scans of P30/E70, and blends with 1, 2.5, 5, and 10 wt % of compatibilizer. (b) For clarity the regions of T_g s are expanded in DSC scans of P30/E70 blends with 1, 2.5, 5, and 10 wt % of compatibilizer.

The measured lifetime spectra were resolved into three lifetime components with the help of the computer program PATFIT-88,²⁵ with proper source and background corrections. Source correction term and resolution functions were estimated from the lifetime of well-annealed aluminum, using the program RESOLUTION.²⁵ In the present study, three Gaussian functions were used for the resolution function in the analysis of blends lifetime spectra with and without

the compatibilizer, since a single Gaussian resolution function failed to give good convergence.

RESULTS AND DISCUSSION

Differential scanning calorimetric results

The glass transition temperature T_g and the melting temperature T_m of the blend play a major role in differentiating the blend as phase-separated or single-phase system.^{1,2} In the present DSC measurements, T_g is taken as the onset of the transition. The component PTT is a crystalline polymer, which exhibits a $T_g = 50^\circ\text{C}$, and a well-defined crystalline melting point of 230°C , with $\Delta H_m = 109 \text{ J/g}$, where ΔH_m is the change in enthalpy of the system. The second component EPDM is an elastomer with -55 and 42°C as the T_g and T_m , respectively. Figures 1 and 2 show the variation in glass transition temperatures of P50E50, P30E70 blends and the same composition blends with different compatibilizer composition (1, 2.5, 5, and 10), respectively. The P50E50 and P30E70 blends show two glass transition temperatures, indicating micro phase-separated structures consisting of microdomains of rubbery EPDM and glassy PTT segments.²⁶ The glass transition (T_{g2}) is related to the rich PTT phase, while T_{g1} to EPDM phase.²⁷ Several studies have reported that if two T_g s were found in the blend, the separation between the T_g s gets shifted. This shift reduces sometimes, as the weight percentage of one of the components was increased. Such blends were termed as partially miscible blends.^{24,28} The DSC scans for the present blends (Figs. 1 and 2), show two glass transition temperatures, indicating clearly the two-phase systems of PTT/EPDM. With the compatibilizer added to the blends, we observe a clear shifting of two glass transition temperatures such that the separation between the two T_g s gets reduced. These results are tabulated in the Tables I and II. As can be seen from the Figures 1 and 2, the shifting is predominant at 5% of compatibilizer in both the blends (50/50 and 30/70). This suggests that an increased interaction between the components of the blends occurs at 5% compatibilizer, and this seems to be the optimum concentration of the compatibilizer to achieve in-

TABLE III
Free Volume Size Evaluated from Positron Data

| EPDM (wt %) | τ_3 (ns) (± 0.015) ^a | I_3 (%) (± 0.29) ^a | V_f (\AA^3) (± 1.16) ^a | $F_{VR} = V_f I_3$ (%) |
|-------------|---|--|---|---------------------------|
| 0 | 1.57 | 15.26 | 59.58 | 9.1 |
| 30 | 2.04 | 17.48 | 101.31 | 17.7 |
| 50 | 2.16 | 19.54 | 113.65 | 22.3 |
| 70 | 2.28 | 20.48 | 124.77 | 25.5 |
| 100 | 2.37 | 28.57 | 133.90 | 38.3 |

^a The average errors on the measured parameters.

creased interaction. The shifting of two glass transition temperatures in the case of P30E70 at 5% of the compatibilizer is more predominant than P50E50 blend. This is probably due to the larger composition of EPDM (70%). Thus, the thermal analysis of blends indicates that the blends exhibit the phase-separated structure even in the presence of the compatibilizer; but, we observe increased interaction between the two blend components at 5% of compatibilizer.

Positron annihilation lifetime results

All the measured positron lifetime spectra were resolved into three lifetime components $\tau_1, \tau_2,$ and τ_3 with intensities $I_1, I_2,$ and $I_3,$ respectively. The lifetime spectra were resolved into three lifetime components since it gave better χ^2 -value and standard deviations than the two- and four-component analyses. Hence, three-component analysis results are presented here. The attribution of these lifetime components is as follows.^{12–21} The shortest lifetime component τ_1 (0.130–0.170 ns) with intensity I_1 (45–50%) is attributed to p-Ps and free positron annihilations. The intermediate lifetime component τ_2 with intensity I_2 (25–35%) is usually considered to be due to the annihilation of positrons trapped at the defects present in the crystalline regions or at the crystalline–amorphous interface boundaries (0.410–0.470 ns). The longest-lived component τ_3 (1.57–2.37 ns) with intensity I_3 (15–29%) is due to pick-off annihilation of the o-Ps in the free volume sites present mainly in the amorphous regions of the polymer matrix.^{11,29} A simple relation developed by Nakanishi et al.³⁰ relates o-Ps lifetime τ_3 to the free volume hole size, which is based on the quantum mechanical models of Tao³¹ and Eldrup et al.³² In this model, positronium atom is assumed to be localized in a spherical potential well having an infinite potential barrier of radius R_0 with an electron layer in the region $R < r < R_0$. Accordingly, the relation between τ_3 and the radius R of the free volume hole or cavity is given by

$$(\tau_3)^{-1} = 2 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right] \text{ns}^{-1} \quad (1)$$

where $R_0 = R + \delta R$ and δR is an adjustable parameter. By fitting eq. (1) with τ_3 values for known hole sizes in porous materials like zeolites, a value of $\delta R = 0.1657$ nm was obtained. It has been verified that this value of δR also holds good for the present lifetime values in homopolymers and blends of PTT and EPDM. Hence, with this value of δR , the free volume radius R has been calculated from eq. (1), and the average size of the free volume holes V_f is evaluated as $V_f = (4/3)\pi R^3$ for the blends with and with out compatibilizer. The

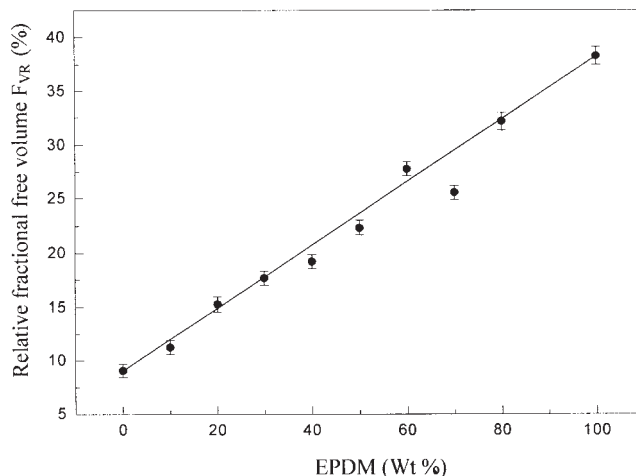


Figure 3 Variation of relative fractional free volume F_{VR} ($V_f I_3$) as a function of EPDM weight percentage.

fractional free volume or the free volume content (F_v) can then be estimated as

$$F_v = CV_f I_3 \quad (2)$$

where C is a structural constant and V_f and I_3 are the parameters described above. The parameter C has to be estimated from an independent experiment. Since we have not measured the C value, in the present case, we use the relative fractional free volume $F_{VR} = V_f I_3$ to understand the changes in fractional free volume.

As said before, it is appropriate that we consider only o-Ps lifetime τ_3 and its intensity I_3 in understanding the changes in free volume properties of the blends with and without compatibilizer. Since the Ps atom probes the local molecular environment, and the free volume is the result of it, the PAL results shall provide appropriate basis for understanding the interactions at molecular level.^{10,11} The positron data for the different composition of the blends are displayed in Table III.

Of the few existing free volume theoretical models applied to polymer blends, we consider the Kelley and Bueche linear additivity rule,³³ which is derived on the basis of additivity of free volumes of the blend constituents at all temperatures. According to this, the relative fractional free volume of a polymer blend will be the sum of the free volumes of the two components of the blend and is given by

$$F_v = w_1 F_{v1} + w_2 F_{v2} \quad (3)$$

where F_v is the relative fractional free volume of the blend, F_{v1} and F_{v2} , and w_1 and w_2 are the relative fractional free volumes and the weight fractions of the constituents 1 and 2, respectively.

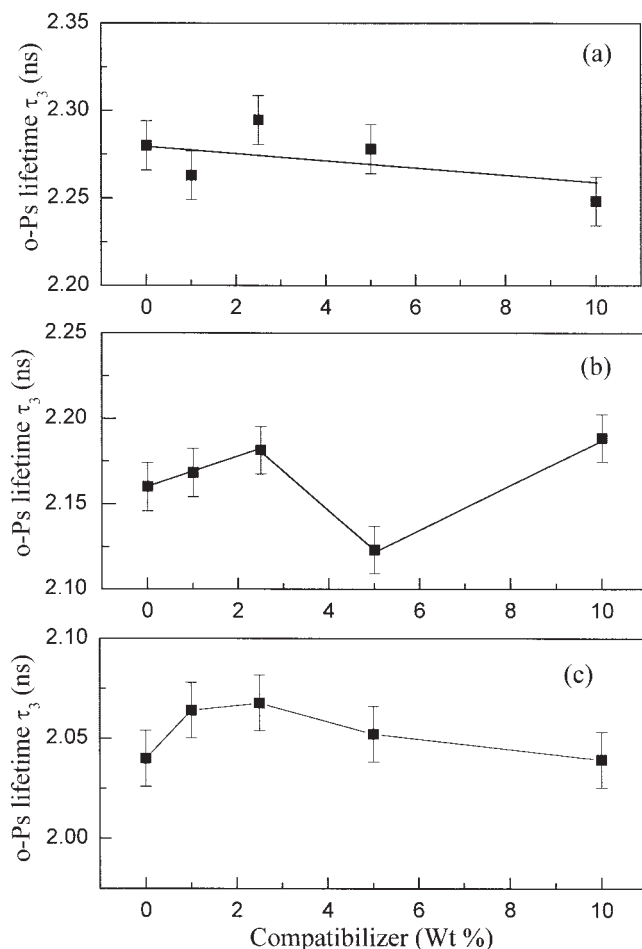


Figure 4 (a) Variation of *o*-Ps lifetime τ_3 and free volume hole size (V_f) in P70/E30 blend as a function of compatibilizer wt %. (b) Variation of *o*-Ps lifetime τ_3 and free volume hole size (V_f) in P50/E50 blend as a function of compatibilizer weight percentage. (c) Variation of *o*-Ps lifetime τ_3 and free volume hole size (V_f) in P30/E70 blend as a function of compatibilizer weight percentage.

Literature reveals that the studies on polymer blends by PALS are scanty, and only few blends have been studied so far. Of these, few blends have showed negative deviation from the linear additivity rule (eq. (3)), and hence were concluded as miscible; only two of them showed positive deviation, and hence were concluded as immiscible; and one of the blends showed agreement with the linear additivity rule but still was concluded as immiscible.^{26,34}

Figure 3 shows the variation of relative fractional free volume as a function of EPDM weight percentage. From this, we observe that the relative fractional free volume increases as the EPDM weight percentage increases, and it exhibits good agreement with the linear additivity rule (eq. (3)). This can be construed as incompatible or immiscible nature of the blends.

In Figures 4–6, we show the variations of positron lifetime parameters, namely τ_3 , I_3 , and F_{VR} , as a function of compatibilizer weight percentage for P70E30,

P50E50, and P30E70 blends, respectively. These blends are selected to see the effect of compatibilizer at the interfaces of the blends. It is expected that improved interaction at the interfaces result in decreased positron parameters.³³ As is evident from Figures 4–6 that the P70E30 and P30E70 blends do not show any marked decrease in value of the positron parameters, namely τ_3 , I_3 , and F_{VR} , as the concentration of compatibilizer in the blend is increased. On the other hand, the blend with 50/50 composition shows that τ_3 , I_3 , and F_{VR} decreases as the compatibilizer concentration increases. For the 50/50 blend at 5% of compatibilizer, F_{VR} shows minimum value, beyond which there is an increase of F_{VR} . Similar behavior was noticed in the SEM micrographs, as observed by the Aravind et al.⁶ We conclude that 5% of MA is the optimum concentration of compatibilizer, which could be treated as critical micelle concentration. Further we suggest that, beyond this concentration, the

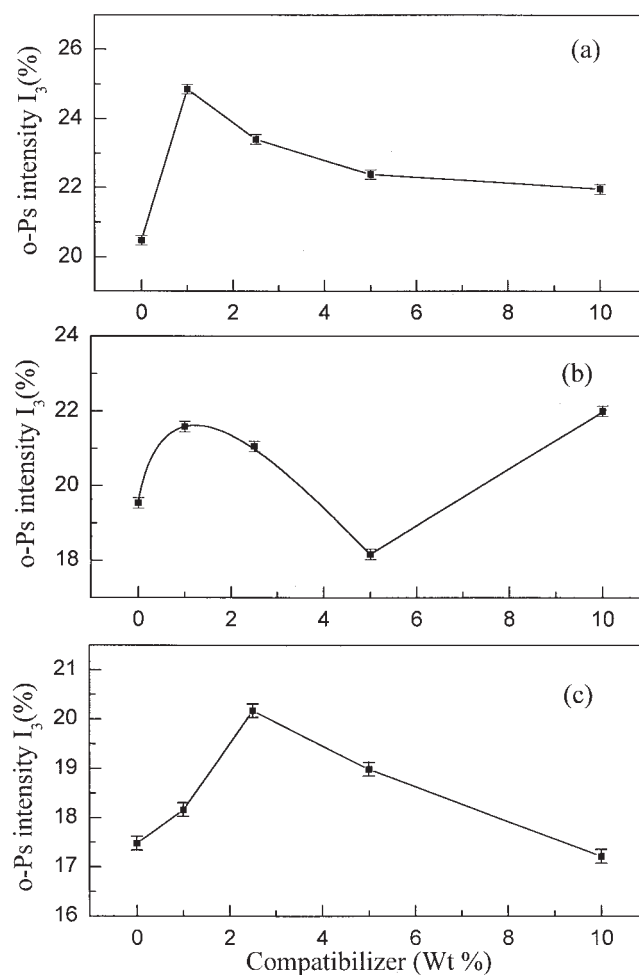


Figure 5 (a) Variation of *o*-Ps intensity I_3 in P70/E30, blend as a function of compatibilizer weight percentage. (b) Variation of *o*-Ps intensity I_3 in P50/E50 blend as a function of compatibilizer weight percentage. (c) Variation of *o*-Ps intensity I_3 in P30/E70 blend as a function of compatibilizer weight percentage.

formation of micelle may take place at the blend interface, which might be the reason for increased values in positron data. Although the positron parameters show some decrease as compatibilizer concentration increases in the case of 70/30 and 30/70 blends, the change is small that we do not see any critical value from these graphs. Hence, 50/50 data are considered.

The minimum in free volume parameters seen in P50E50 at 5% of compatibilizer can be interpreted as follows. The graft copolymer (EPM-g-MA) seems to reduce the interfacial tension and enhances the coalescence behavior. Therefore, the 50/50 blend with 5% compatibilizer produces a blend with increased interaction between the blend components and strengthens the adhesion. This argument is in line with the earlier studies on the physical and reactive compatibilization of immiscible polymer blends, in which the theoretical predictions of compatibilization suggest that a critical

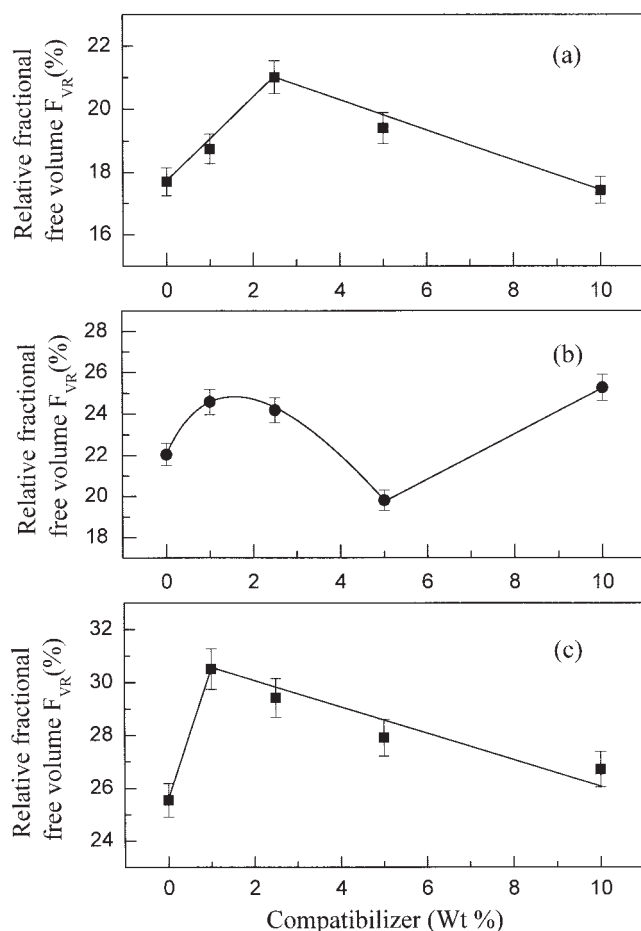
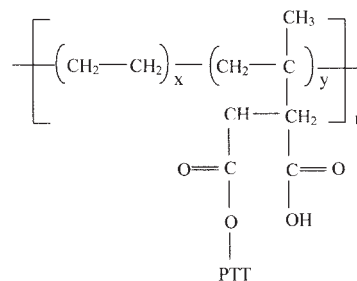


Figure 6 (a) Variation of relative fractional free volume F_{VR} as a function of compatibilizer weight percentage in P70/E30 blend. (b) Variation of relative fractional free volume F_{VR} as a function of compatibilizer weight percentage in P50/E50 blend. (c) Variation of relative fractional free volume F_{VR} as a function of compatibilizer weight percentage in P30/E70 blend.



Structure of PTT

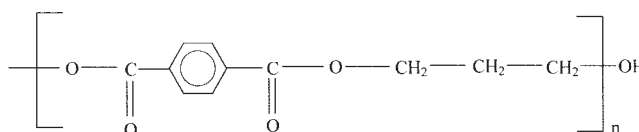


Figure 7 Possible chemical interaction of PTT and EPM-g-MA.

concentration of compatibilizer is required to saturate the interface of binary polymer blends.³ Above this critical concentration, the compatibilizer will not modify the interface further, but forms micelles in the bulk phase. The most possible reaction of the anhydrides with the hydroxyl group of polyester has been reported by Fokes et al.³ and recently by Aravind et al.,⁶ which is shown in Figure 7. Based on the present results, we also expect that intermolecular dipole-dipole interactions and interchain reactions between OH, —COOH groups in the compatibilized blends. This increased interaction reduces the free volume of the blend, and the observed results support this argument.

CONCLUSIONS

Differential scanning calorimetric results of blends without the compatibilizer show two distinct glass transition temperatures (T_g s). The shifting of T_{g2} toward T_{g1} is observed, when the EPM-g-MA is added to the system. The PALS results in P50E50 blend show minimum values of positron parameters at 5% compatibilizer, suggesting increased interaction between the blend components and hence increased compatibility.

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