Ionomeric Blends of Poly(ethyl acrylate-*co*-4-vinylpyridine) with Zinc-Neutralized Sulfonated Poly(ethylene terephthalate). 1. Effect of Specific Interactions upon the Amorphous Phase

C.-W. Alice Ng, Martin J. Lindway,[†] and William J. MacKnight*

Department of Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

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ABSTRACT: Compatibilization of an immiscible polymer pair, poly(ethyl acrylate) and poly(ethylene terephthalate), was accomplished by incorporating vinylpyridine groups and zinc-neutralized sulfonate groups, respectively, along the polymer chains. The compatibility of this multiphase ionomeric blend resulted from the formation of a zinc-pyridine-sulfonate group coordination complex between polymer chains. The nature and degree of this complexation were successfully probed with FTIR spectroscopy. Two blend compositions with one containing a stoichiometric amount of the interacting groups were prepared. The degree of compatibility was established with DSC and DMTA. It was found that the level of mixing depended upon the extent of specific interactions between the polymer chains. In addition, interesting phase behavior of the blends was discovered by DMTA. Results showed that upon crystallization the PET-SO_3Zn-rich phase in both ionomeric blends exhibited an increase in the temperature of the loss peak associated with segmental motions accompanying T_g, while the EAVP-rich phase showed a decrease in the temperature of its corresponding loss peak.

Introduction

Multiphase polymer systems are of considerable scientific and technological interest, as can be seen in some of the more recent monographs and reviews.[1-11] The term "multiphase polymer system" is a very broad classification of materials, including segmented polymers, block copolymers, composites, immiscible polymers, partially compatible polymers, liquid crystalline polymers, semicrystalline polymers, and ionomers. These materials have received considerable attention because of their unique morphologies and the wide range of mechanical properties which have been observed.

The well-known challenges confronting the development of multiphase polymer systems or polymer blends have been in relation to the thermodynamics of the system, which typically favors polymer pair immiscibility. The unfavorable thermodynamic conditions of high molecular weight pairs for miscibility are typically associated with a low entropy of mixing and a positive enthalpy of mixing. The enthalpy term relates to the temperature and composition dependence of the differences in the energetic interactions between the polymer pair and their self-interactions, which also dictates the interfacial properties of an intimately mixed blend. The interfacial mixing or the degree of interfacial adhesion is ultimately responsible for the resulting mechanical properties of the system, especially in the case of multiphase polymer blends. In a practical sense, only the enthalpy term can be adjusted for an enhanced degree of compatibilization or interfacial adhesion between polymer pairs. One general approach, which has been recently reviewed,[9,11] has been the incorporation of ionic moieties to act as specific sites for intermolecular interactions between immiscible polymer pairs.

Eisenberg and co-workers[12] have demonstrated that pairwise interactions of a minimum of 5 mol % of ionic moieties along a polymer backbone is necessary for compatibilization of immiscible polymer blends containing polystyrene and poly(ethyl acrylate), as demonstrated from dynamic mechanical thermal analysis (DMTA). The ionic moieties evaluated in this study consisted of the free acid form of sulfonated polystyrene and poly(ethyl acrylate-*co*-vinylpyridine). The improved compatibility of the ionomeric blend was achieved by proton transfer by the sulfonic acid to the base vinylpyridine, which led to the formation of a coulombic bond.

Peiffer and co-workers[13] examined transition metal complexes formed between the zinc and copper salts of sulfonated EPDM with poly(styrene-*co*-4-vinylpyridine) as a means of compatibilizing and controlling the melt viscosity. They observed significantly higher melt viscosities for stoichiometric blends along with Fourier transform infrared (FTIR) spectroscopy results which indicated a complexation involving a 1:1 stoichiometry of sulfur and nitrogen.

MacKnight and co-workers[14-16] have examined both acid-base interactions and zinc transition metal complexes of sulfonated polystyrene and poly(ethyl acrylate-*co*-4-vinylpyridine) blends. They have thoroughly characterized the degree of compatibilization in relation to ionic contents up to 10 mol % and have observed various degrees of compatibilization. Their results indicate a predominantly immiscible two-phase system existing below ionic contents of less than 5 mol % and a single mixed phase system as the dominant phase above 5 mol %, as evidenced by DMTA.

The ionomeric blend systems, which have been cited or previously discussed, contained predominantly noncrystalline components. For the initial investigations into the structure-property relationships of ionomeric blends, these systems offered the desired simplicities of having single-phase components. In recent years, semicrystalline/amorphous blends have aroused considerable interest in the ionomer field.[17-19] The semicrystalline components undoubtedly add further complications in assessing the compatibility of two polymeric materials. However, their phase behavior can be utilized effectively to probe the compatibilization of polymer blends as will be demonstrated in this series of studies.

[†] Current address: General Electric Plastics, CPP Technology, 1 Lexan Lane, Mt. Vernon, IN 47620-9364.

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The semicrystalline component selected for the present investigation was sulfonated poly(ethylene terephthalate). The level of sulfonation was 7 mol % and the degree of crystallinity was optimized to ~30%, as determined by differential scanning calorimetry (DSC). Ion exchange procedures were developed which exchanged the initial sodium ion of sulfonated PET for hydrogen and subsequently hydrogen ion for zinc. The zinc-neutralized form of sulfonated PET (PET-SO_3Zn) was used to prepare blends with poly(ethyl acrylate-*co*-4-vinylpyridine) (p(EA-*co*-VP)). In this study, the level of zinc transition metal complexation was probed by FTIR spectroscopy. The degree of compatibilization was examined by both DSC and DMTA in comparison to blends containing poly(ethyl acrylate) (p(EA)) without the vinylpyridine component and PET-SO_3Zn. In a later communication, the study will focus on the semicrystalline phase in which the crystallization kinetics, melting behavior, and morphologies of the blend will be examined in relation to the influence of specific intermolecular interactions among polymer chains.

Experimental Section

Materials Used. Poly(ethylene terephthalate) (PET) modified with 7 mol % of sodium 5-sulfoisophthalate was obtained from AKZO Corporate Research, Arnhem Holland (IV = 0.44 dL/g; inherent viscosity of a solution in trifluoroacetic acid at a concentration of 0.5 g/dL at 30 °C). The sulfonate groups were incorporated into PET by a standard two-step melt polycondensation reaction in which 7 mol % of sodium dimethyl 5-sulfoisophthalate was substituted for the equivalent mole percent of dimethyl terephthalate. Poly(ethyl acrylate) ($\bar{M}_n$ = 230 000 and $\bar{M}_w/\bar{M}_n$ = 3.87) and poly(ethyl acrylate-*co*-4-vinylpyridine) containing 5.2 and 10.6 mol % of 4-vinylpyridine ($\bar{M}_n$ = 201 000, $\bar{M}_w/\bar{M}_n$ = 2.02 and $\bar{M}_n$ = 161 000, $\bar{M}_w/\bar{M}_n$ = 1.96, respectively) were prepared and characterized as reported previously.[14] The average molecular weights were determined by GPC and were based on polystyrene standards. All other chemicals were purchased from Aldrich Chemical Co. Trifluoroacetic acid (TFAA) (99% purity) and 1,1,1,3,3,3-hexafluoro-2-propanol (99% purity) (HFIP) were used without further purification.

Ion-Exchange Procedures. The sodium salt of the sulfonated PET (PET-SO_3Na) was subjected to a procedure to exchange the initial sodium ions for hydrogen ions and subsequently for zinc ions. PET-SO_3Na (15 g) was dissolved in 150 mL of TFAA, and the solution was filtered through glass wool and precipitated into acetone. The fine white precipitate was washed with acetone to remove residual TFAA. The precipitate was stirred in 20% hydrochloric acid solution for 1 h and filtered. This batch process was repeated four times to ensure complete exchange of the sodium ions for hydrogen ions. Then the precipitate was washed thoroughly with distilled deionized water (DDI) until the filtrate tested neutral with pH paper. Next, the polymer was stirred in concentrated zinc acetate solution (30 g in 100 mL of DDI water) for 1 h and filtered. This batch process was also repeated four times to ensure complete exchange of ions. Finally, the polymer was washed with a large amount of DDI water until no detectable unreacted zinc acetate was left by testing the filtrate with 0.1 M NaOH solution for precipitation of zinc hydroxide. The polymer was dried in air and then under vacuum at 60 °C for 3 days. A sample was subjected to elemental analysis to ensure complete conversion of the sulfonated PET to the zinc form. Anal. Calcd for $C_{10}H_{7.93}O_{4.21}S_{0.07}Zn_{0.035}$: C, 60.06; H, 4.00; S, 1.12; Zn, 1.14. Found: C, 58.53; H, 4.27; S, 1.18; Zn, 1.16. The elemental analysis was performed by the Microanalysis Laboratory at the University of Massachusetts.

Blend Preparation. Modified blends with one containing stoichiometric amounts of vinylpyridine groups and zinc-neutralized sulfonate groups and the other an excess amount of sulfonated groups were prepared. Unmodified blends with the same corresponding blend ratios but containing no vinylpyridine groups were also made for comparison purposes. The compositions and the nomenclature of the blends are listed in Table 1.

Table 1. Compositions and Nomenclature of Polymer Blends

polymer	mol % of VP	wt % of p(EA-*co*-VP)	wt % of PET-SO_3Zn
PET-SO_3Zn	0	0	100
EAVP/PET-SO_3Zn-25/75[a]	10.6	25	75
EA/PET-SO_3Zn-25/75	0	25	75
EAVP/PET-SO_3Zn-58/42[b]	5.2	58	42
EA/PET-SO_3Zn-58/42	0	58	42

[a] Nonstoichiometric blend. [b] Stoichiometric blend.

Individual homopolymers were predried at 60 °C under vacuum for 2 days prior to use. The homopolymers were separately dissolved in HFIP to yield a 5% (w/v) polymer solution. The p(EA) or p(EAVP) solution was added to the PET-SO_3Zn solution under vigorous stirring. The blend solution was stirred for 1 day at room temperature to ensure thorough mixing. The polymer solution was then cast onto an aluminum pan under a slow stream of nitrogen. After removal of most of the solvent under ambient conditions, the film was allowed to dry under vacuum at 60 °C for 3 days.

FTIR Study. Infrared spectra were obtained on an IBM IR44 FTIR spectrometer. A total of 128 scans at a resolution of 1 cm^{-1} were signal averaged. The samples were cast on KBr plates from a solution of HFIP and dried under vacuum at 60 °C for 3 days.

Inherent Viscosity Measurement. The inherent viscosity (IV) of PET-SO_3Zn (7 mol % sulfonation) was determined using a Cannon-Ubbelohde viscometer at 30 °C in TFAA. The polymer concentration was 0.5 g/dL.

DSC Measurement. A DuPont DSC 10 equipped with a Thermal Analyst 2000 was used to obtain the DSC thermograms at a heating rate of 10 °C/min and was calibrated with indium. The scans were run with samples ranging from 10 to 15 mg from −75 to +250 °C under a nitrogen purge to prevent oxidative degradation. The glass transition temperature, T_g, was taken as the midpoint of the change in heat capacity at the transition. All samples were heated to above melting and held at 250 °C for 10 min to render the samples completely amorphous. Amorphous samples were obtained by quenching from above melting temperature to −20 °C. Semicrystalline samples were prepared by annealing the quenched samples in the DSC at 150 and 175 °C for 1 h for all the blends and zinc-neutralized sulfonated PET, respectively. The percent crystallinity of the annealed samples was estimated by assuming an enthalpy of melting of 113 J/g for 100% crystalline PET.[20]

DMTA Measurement. The dynamic mechanical properties of polymer samples were measured using a Polymer Laboratories PL-DMTA instrument at a frequency of 1 Hz. The modified blends and zinc-neutralized sulfonated PET samples were prepared by compression molding at ~240 °C under vacuum and low pressure. Amorphous samples were made by removing the molten samples from the press and quenching them between two cold metal plates. Semicrystalline samples were prepared by annealing the quenched samples under a nitrogen atmosphere at 150 and 175 °C for 1 h for the blends and zinc-neutralized sulfonated PET, respectively. The poly(ethyl acrylate) and poly(ethyl acrylate-*co*-4-vinylpyridine) were compression molded between two aluminum foils at 50 °C. The sample sizes were all approximately 2.5 × 1.2 × 0.5 mm^3. The single-cantilever mode was used with a 2-mm free length. Samples were scanned from −50 to +150 °C at 3 °C/min. The glass transition temperatures were taken as the peaks in the tan δ plots.

Results and Discussion

FTIR Study. The level of specific intermolecular interactions between vinylpyridine and zinc sulfonate pairs was probed with the use of FTIR spectroscopy. Figure 1 shows the resulting FTIR spectra: (a) p(EA-*co*-VP) (10.6% VP), (b) EAVP/PET-SO_3Zn-25/75, and (c) EAVP/PET-SO_3Zn-58/42 in the 1550–1650 cm^{-1} region.

In Figure 1a, the broad absorbance peak at 1600 cm^{-1} corresponds to a pyridine ring stretching. In Figure 1b, the 1618 cm^{-1} band corresponds to a pyridine ring

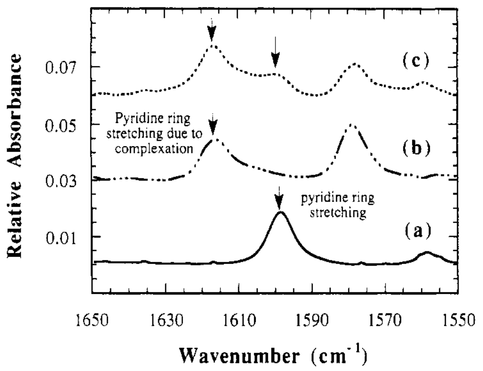

Figure 1. FTIR spectra for (a) p(EA-*co*-VP) (10.6% VP), (b) EAVP/PET-SO$_3$Zn-25/75, and (c) EAVP/PET-SO$_3$Zn-58/42.

stretching as a result of the formation of the zinc–pyridine complexes. This assignment is supported by similar findings of two separate FTIR spectroscopy studies of ionomeric blends containing p(EA-*co*-VP). In the first study, Peiffer and co-workers examined a blend of p(EA-*co*-VP) with zinc-neutralized sulfonated EPDM.[13] They assigned the absorbance band at 1618 cm^{-1} to the pyridine ring stretching as a result of the formation of zinc–pyridine complexes. In the second study, MacKnight and co-workers examined a blend of zinc sulfonated polystyrene with p(EA-*co*-VP) and their respective model compounds.[16] They assigned the absorbance band at 1620 cm^{-1} to be the pyridine ring stretching with zinc–pyridine complexation. In Figure 1c, the absorbance band at 1618 cm^{-1} corresponds again to pyridine ring stretching with zinc–pyridine complexation as primarily observed for EAVP/PET-SO$_3$Zn-25/75, and the absorbance band at 1598 cm^{-1} corresponds to free pyridine ring stretching.

On the basis of the spectroscopy results, the formation of zinc–pyridine complexes is considered to be nearly complete in the blend of EAVP/PET-SO$_3$Zn-25/75. However, the double peak observed for the blend of EAVP/PET-SO$_3$Zn-58/42 indicates the presence of both coordinated and free pyridine rings. The high degree of complexation in the 25/75 blend is possibily due to the presence of an excess amount of sulfonate groups. Another possible explanation could be the presence of a higher concentration of ionic moieties (10 mol % of VP) per unit p(EA-*co*-VP) chain in the 25/75 blend, which in turn provides more interacting sites for complexation to occur.

Degree of Compatibility. As stated before, the objective of this investigation was to examine an ionomeric blend system containing a multiphase (semicrystalline) component. The degree of crystallinity of the semicrystalline component is an important determinant of blend compatibility; its influence on the degree of compatibilization has been evaluated by DSC and DMTA. The annealing temperatures, determined as the temperature at which a maximum ΔH_m was observed, for PET-SO$_3$Zn and EAVP/PET-SO$_3$Zn-25/75 occurred at 175 and 150 °C, respectively. The optimum annealing time at these selected temperatures in relation to ΔH_m (maximum) was chosen as 60 min, at which point the rate of increase of ΔH_m has significantly decreased. The selected annealing conditions for EAVP/PET-SO$_3$Zn-25/75 were also applied to other blends listed in Table 1. The optimum annealing conditions for pure PET to maximize crystallinity require considerably longer time periods (>16 h) at temperatures very close to the T_m.[21] For this study, similar conditions would not be practical due to the thermal instability of the ionomeric systems. However, it is believed that the selected annealing conditions are sufficient to elucidate the effect of crystallinity upon the blend compatibilization.

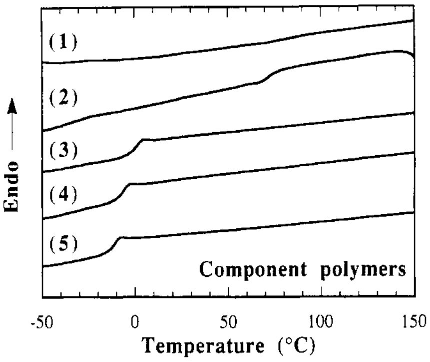

Figure 2. DSC thermograms of component polymers: (1) PET-SO$_3$Zn (annealed); (2) PET-SO$_3$Zn (quenched); (3) p(EA-*co*-VP) (10.6% VP); (4) p(EA-*co*-VP) (5.2% VP); (5) p(EA).

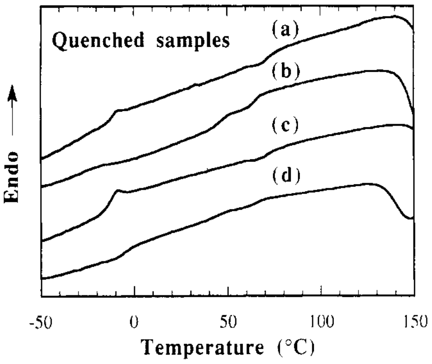

Figure 3. DSC thermograms of polymer blends in the quenched state: (a) EA/PET-SO$_3$Zn-25/75; (b) EAVP/PET-SO$_3$Zn-25/75; (c) EA/PET-SO$_3$Zn-58/42; (d) EAVP/PET-SO$_3$Zn-58/42.

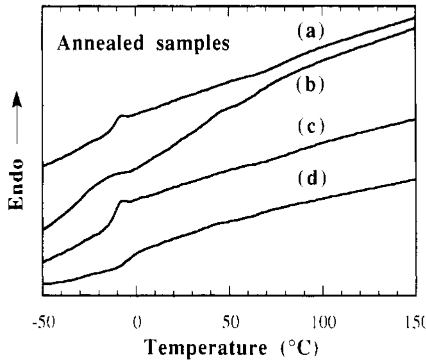

Figure 4. DSC thermograms of polymer blends in the annealed state: (a) EA/PET-SO$_3$Zn-25/75; (b) EAVP/PET-SO$_3$Zn-25/75; (c) EA/PET-SO$_3$Zn-58/42; (d) EAVP/PET-SO$_3$Zn-58/42.

DSC Study. DSC thermograms of the component polymers and the quenched and annealed blends are shown in Figures 2–4, respectively. The DSC results for the component polymers and the blends are summarized in Table 2.

In determining the degree of compatibility for multiphase blends by DSC, a general limitation occurs when the T_g's of the components are too similar. A minimum difference in T_g's of ~30 °C can usually be resolved by DSC with a significant degree of confidence. As shown in Table 2, the difference in T_g for the individual components is greater than 70 °C. Unmodified blends of EA/PET-SO$_3$Zn-25/75 and –58/42, both quenched and annealed samples, are considered immiscible since there is no measurable shift in their T_g's and the value for the ΔT_g's remains constant in comparison to the transitions of their respective homopolymers.

For the modified blend of EAVP/PET-SO$_3$Zn-25/75, the quenched sample displays T_g's at 43 and 63 °C. The T_g at 63 °C, a downward shift of 10 °C from that of the

Table 2. DSC Results: T_g's for the Component Polymers and the Quenched and Annealed Blends

	quenched samples		annealed samples		
polymer	T_g (°C)	ΔT_g (°C)	T_g (°C)	ΔT_g (°C)	% crystallinity[a]
PET-SO3Zn	73	10	79	25	30
p(EA)	−13	5			
p(EA-*co*-VP) (5.2% VP)	−7	8			
p(EA-*co*-VP) (10.6% VP)	−1	8			
EAVP/PET-SO3Zn-25/75	43	12	38	27	27
	63	6	69	28	
EA/PET-SO3Zn-25/75	−14	6	−13	6	24
	72	10	77	24	
EAVP/PET-SO3Zn-58/42	−5	14	−5	12	26
	66	22	66	17	
EA/PET-SO3Zn-58/42	−15	7	−13	6	24
	73	10	80	32	

[a] % crystallinity was normalized per unit gram of PET-SO3Zn.

amorphous, pure PET-SO3Zn polymer, is considered to be associated with the PET-SO3Zn-rich phase resulting from the partial mixing of the polymer pair. The T_g occurring at 43 °C is found to be intermediate between the T_g's of the respective homopolymers. Hence, it is postulated that the T_g at 43 °C originates from a mixed phase containing approximately equal amounts of the two constituents. As for the EAVP-rich phase, if any, its T_g cannot be discerned from the DSC measurements possibly because (1) its ΔC_p is too small to be detected or (2) the domain size is beyond the detection limit of the instrument. Upon annealing, both T_g's observed in the quenched sample broaden significantly as shown by the ΔT_g values. The T_g associated with the PET-SO3Zn-rich phase experiences a slight upward shift from 63 to 69 °C. This shift is probably due to the development of crystallinity in the sample which influences the amorphous PET-SO3-Zn-rich phase. However, the T_g due to the mixed phase decreases from 43 to 38 °C upon annealing. One of the possible explanations could be that the amount of the amorphous phase of the PET-SO3Zn component decreases upon annealing, which leads to an increase in the relative amount of the EAVP phase in the mixed phase, and therefore the T_g of the mixed phase decreases accordingly.

Unlike the blend of EAVP/PET-SO3Zn-25/75, which displays significant compatibilization upon mixing, the modified blend of EAVP/PET-SO3Zn-58/42 displays compatibilization but to a lesser extent as indicated by the relative shift of both T_g's and a moderate increase in ΔT_g's, as compared to the respective homopolymers in both the amorphous and semicrystalline states. It is also noted that both the T_g and ΔT_g values remain more or less the same after annealing, unlike the behavior observed in the case of the EAVP/PET-SO3Zn-25/75 blend.

It is a well-known fact that the glass transition is accompanied by micro-Brownian segmental motion in the amorphous phase of the polymer. Upon annealing of a multiphase polymer blend, crystallization takes place at the expense of the amorphous phase. As a result, with the reduction in the amount of amorphous material in the blend, the heat capacity change (ΔC_p) at the glass transition decreases to such an extent that the transition becomes much less prominent. In this respect, the determination of the T_g becomes ambiguous in the semicrystalline polymer blends. In view of this inherent uncertainty, the DMTA technique was employed to further investigate the phase behavior of the polymer blends.

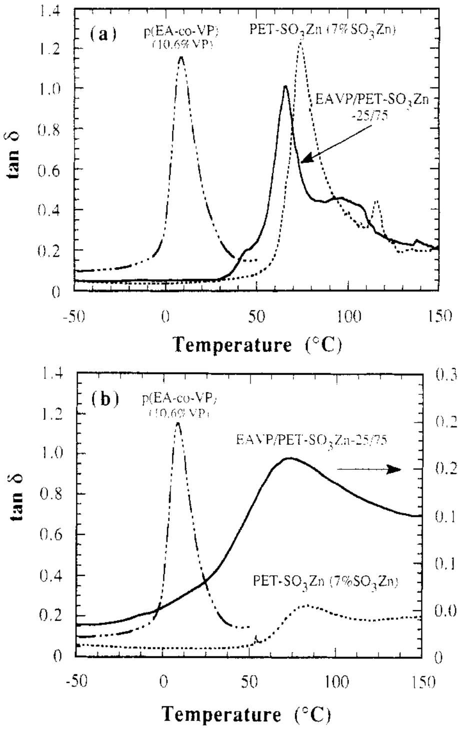

Figure 5. Temperature dependences of tan δ at 1 Hz for EAVP/PET-SO3Zn-25/75 and its homopolymers: (a) quenched and (b) annealed samples.

Table 3. DMTA Results (1 Hz): tan δ for the Component Polymers and Their Polymer Blends

	tan δ (°C)	
polymer	quenched	annealed
p(EA-*co*-VP) (5.2% VP)	−1	
p(EA-*co*-VP) (10.6% VP)	8.5	
PET-SO3Zn	74	84
EAVP/PET-SO3Zn-25/75	45, 65.5	8.5, 72
EAVP/PET-SO3Zn-58/42	8, 65	4, 69

DMTA Study. It is known that DMTA is more sensitive in detecting T_g than DSC.[19] Therefore, this technique is used to further probe the phase behavior of the blends. The unmodified blends will not be considered here because they showed no miscibility by DSC. Both quenched and annealed samples were examined to investigate the effect of crystallinity on the level of compatibilization. The tan δ results are summarized in Table 3.

Both modified blends exhibit two different relaxation processes characteristic of their respective component phases. For both quenched samples, the two tan δ peaks are narrow and distinct as shown in Figures 5a and 6a. The merging of the two peaks indicates that the polymer pairs are partially miscible on a 50–100-Å level as a result of the specific intermolecular interactions between the salt groups and the vinylpyridine. For the annealed samples, the tan δ peaks broaden as presented in Figures 5b and 6b. This indicates that a range of microenvironments is present which relax at slightly different temperatures. However, the changes of the temperatures of the tan δ peaks from those of the pure constituents are still evident.

An examination of the PET-SO3Zn-rich phase in the pure PET-SO3Zn and both modified blends sheds additional light on the modification of the relaxation behavior induced by crystallization. The corresponding tan δ peak (the higher temperature peak in the blends) is found to shift to higher temperatures upon annealing. In addition, the width of the relaxation peak is much broader compared to the quenched sample. These observations may be explained as follows: (1) the crystals may be restricting the long-range segmental motion accompanying the glass

Table 4. Phase Compositions in the Polymer Blends Based on DSC Results

	quenched samples		annealed samples	
polymer	T_g (°C)	wt frac of EA or EAVP phase	T_g (°C)	wt frac of EA or EAVP phase
EAVP/PET-SO_3Zn-25/75	43	0.35	38	0.45
	63	0.11	69	0.10
EA/PET-SO_3Zn-25/75	−14	1.02	−13	1.00
	72	0.01	77	0.02
EAVP/PET-SO_3Zn-58/42	−5	0.97	−5	0.97
	66	0.07	66	0.12
EA/PET-SO_3Zn-58/42	−15	1.03	−13	1.00
	73	0.00	80	0.00

Table 5. Phase Compositions in the Polymer Blends Based on DMTA Results

	quenched samples		annealed samples	
polymer	T_g (°C)	wt frac of EA or EAVP phase	T_g (°C)	wt frac of EA or EAVP phase
EAVP/PET-SO_3Zn-25/75	45.0	0.39	8.5	1.00
	65.5	0.11	72.0	0.13
EAVP/PET-SO_3Zn-58/42	8.0	0.85	4.0	0.92
	65.0	0.10	69.0	0.14

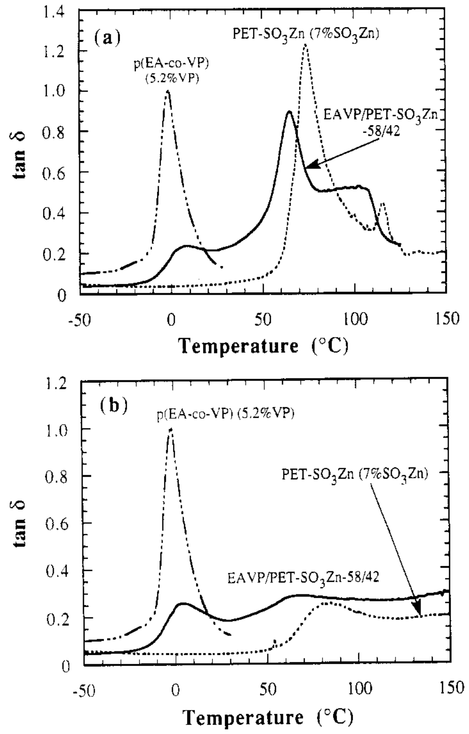

Figure 6. Temperature dependences of tan δ at 1 Hz for EAVP/PET-SO_3Zn-58/42 and its homopolymers: (a) quenched and (b) annealed samples.

transition in the amorphous phase, and thus the tan δ peak temperature is raised; (2) the semicrystalline sample is acting like a composite system in which different phases relax at slightly different temperatures, and hence the entire relaxation process is broadened.

Interestingly, the EAVP-rich phase in both modified blends behavies in an exactly opposite manner. For EAVP/PET-SO_3Zn-58/42, the tan δ peak of the EAVP phase decreases from 8 to 4 °C upon annealing unlike the behavior observed in the PET-SO_3Zn-rich phase discussed above. The explanation could be that the EAVP phase, instead of being stiffened by the crystal formation as in the PET-SO_3Zn-rich phase, is becoming richer in EAVP composition upon crystallization of the amorphous PET-SO_3Zn previously present in that phase. Therefore, the tan δ peak temperature is shifted downward. For EAVP/PET-SO_3Zn-25/75, the shoulder at 45 °C in the quenched sample is again postulated to be associated with a mixed phase of both polymers which has already been observed from the thermal behavior shown by DSC. However, the lower tan δ peak associated with the EAVP-rich phase could not be detected here because either the amount of material is too small or it is totally incorporated into the mixed phase. Upon annealing, the shoulder at 45 °C disappears into a broad transition and a very small shoulder at ~8.5 °C (which might not be easily seen from Figure 5b) appears to be superimposed upon the very broad transition with a maximum at 72 °C. This small peak could be attributed to the EAVP phase being enriched in EAVP upon annealing and thus becoming discernible from the broad transition. However, the reason for the disappearance of the shoulder at 45 °C is not well understood.

Determination of Phase Compositions. Phase compositions in all blends were calculated from both DSC and DMTA data according to the Fox equation:

$$\frac{1}{T_g} = \frac{W_1}{T_{g1}} + \frac{W_2}{T_{g2}}$$

where T_g is the glass transition temperature of the phase, T_{g1} and T_{g2} are the glass transition temperatures of the individual pure components, and W_1 and W_2 are the weight fractions of each individual component in that phase. Results calculated are summarized in Tables 4 and 5.

On the basis of the results calculated with the DSC data, both unmodified blends, quenched and annealed samples, show essentially pure phases. For EAVP/PET-SO_3Zn-25/75, both quenched and annealed samples, it is shown that the two polymers are significantly mixed in the "mixed phase" and also in the PET-SO_3Zn-rich phase, but to a much lesser extent. For EAVP/PET-SO_3Zn-58/42, both quenched and annealed samples, moderate mixing is observed in both EAVP- and PET-SO_3Zn-rich phases. This level of mixing as shown from the phase compositions, however, is less than that of EAVP/PET-SO_3Zn-25/75.

The phase compositions calculated from the DMTA data differ from those determined from the DSC results. For EAVP/PET-SO_3Zn-25/75, the quenched sample shows a similar phase mixing pattern as observed from that based on the DSC data with significant mixing in the "mixed phase" and some mixing in the PET-SO_3Zn-rich phase. However, the DMTA technique is sensitive enough to probe the EAVP-rich phase in the annealed sample which cannot be detected by DSC. The "mixed phase" in the annealed sample could not be resolved by DMTA as its peak is probably undetectable under the broadened PET-SO_3Zn-rich phase peak as shown in Figure 5b. For EAVP/PET-SO_3Zn-58/42, both quenched and annealed samples apparently show better phase mixing based on the DMTA results as compared to the DSC results. However, with the higher sensitivity and resolving power of DMTA, the phase compositions calculated should reflect more closely the actual phase compositions in the blends. Nevertheless, the degree of mixing is considered moderate as compared to that of the 25/75 blend.

Interestingly, it is observed that there is a general phase composition shift in all blends upon crystallization of the PET-SO_3Zn component as shown in Tables 4 and 5. This positive shift in the EAVP composition could be rationalized in part by the relative enrichment of the EAVP components as a result of the crystallization of the amorphous PET-SO_3Zn in the respective phases.

It should be noted that the phase compositions calculated for the blends did not match with the overall bulk compositions as shown in Table 1. Apart from experimental error, one of the major reasons is that the calculations based on the Fox equation failed to take into account the effect of specific interactions on the composition-dependent glass transition temperature. The calculated results are by no means absolute; however, they serve as a guide for quantifying the degree of mixing in the two modified blends in comparison to the unmodified counterparts.

Conclusion

With the incorporation of a small amount of interacting groups in both poly(ethyl acrylate) and PET, the blend is made partially compatible as demonstrated by DSC and DMTA. The intermolecular interactions between the otherwise immiscible polymer pair through a zinc transition metal coordination complex between the interacting pairs along the chain backbone were successfully probed with infrared spectroscopy. It is found that the specific interactions are more complete in EAVP/PET-SO_3Zn-25/75 than those found in the 58/42 blend. With DSC, the relative extent of compatibility of the two modified blends is readily rationalized. The modified blend of EAVP/PET-SO_3Zn-25/75 is found to be significantly compatibilized as revealed by DSC with a T_g representative of the mixed phase. However, the EAVP/PET-SO_3Zn-58/42 blend is only partially compatibilized as shown by the merging of the two T_g's, representative of its component polymers. Thus, on the basis of the FTIR and DSC findings, it is shown clearly that more favorable specific interactions between polymer chains indeed give rise to better mixing between the otherwise immiscible polymer pair. More detailed phase behavior of the modified blends is further invstigated using DMTA due to its higher sensitivity in detecting the glass transition. It is found that both modified blends show partial compatibilization as indicated by the merging of the two tan δ peaks. Furthermore, it is interesting to investigate the different phase behaviors between the quenched and annealed blends. The results reveal that the PET-SO_3Zn-rich phase, behaving in a similar manner to pure PET, is "stiffened" upon crystallization as shown by an increase in T_g's, whereas the EAVP-rich phase is becoming richer in EAVP component upon crystallization of the PET-SO_3Zn in that phase, thereby resulting in a decrease in T_g. The degree of mixing in both modified blends is further quantified with a series of phase composition calculations using the Fox equation.

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