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William MacKnight, *University of Massachusetts Amherst*

Kuiming Liang

Gyorgy Banhegyi

F. E. Karasz

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Thermal, Dielectric, and Mechanical Relaxation in Poly(benzimidazole)/Poly(etherimide) Blends

KUIMING LIANG, GYÖRGY BÁNHEGYI,* FRANK E. KARASZ, and WILLIAM J. MACKNIGHT

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

SYNOPSIS

Thermal, dielectric, and mechanical relaxation measurements on miscible blends of polybenzimidazole (PBI) and a polyetherimide (PEI, Ultem 1000) prepared by solution casting from dimethylacetamide (DMAc) reveal a number of structurally related features. Annealing below the glass transition temperature induces an enthalpy relaxation process typical of single-phase glasses of nonequilibrium structure. Dielectric relaxation experiments on samples annealed at ambient conditions reveal two relaxation processes below 400°C. At lower temperatures (50–200°C), the desorption of water is observed. Above 200°C in the first run, a composition-dependent relaxation is seen at the highest frequencies (100 kHz) while a relaxation approximately independent of composition appears in the second run. The latter corresponds to the glass transition of the PEI phase. The glass transition of PBI at this frequency is above the degradation temperature. At lower frequencies a strongly dispersive electrode polarization process masks the high-temperature relaxations. Dynamic mechanical results show similar features with respect to phase separation; the main difference is that the $\tan \delta$ curves in the first run are complicated by the desorption of residual solvent.

INTRODUCTION

A new class of polymer blends containing an aromatic polybenzimidazole and an aromatic polyimide has recently been investigated.^{1–6} Measurements have shown that mixtures having single, composition-dependent glass transition temperatures can be obtained, indicating miscibility.¹ However, in many cases, heating above this glass transition temperature causes the system to phase separate; rehomogenization cannot be observed even after careful annealing just below the T_g observed in the first heating. This phenomenon indicates that the observed miscibility is a metastable effect; phase separation during sample preparation is prevented only by the increasing viscosity of the solution upon evaporation of the solvent. It has also been observed that annealing below the glass transition temperature changes the thermal as well as other properties. In

considering these complications, the use and comparison of various characterization methods is helpful. We report on combined calorimetric (DSC), thermogravimetric (TGA), dynamic mechanical (DMTA), and AC dielectric (DETA) studies of blends consisting of poly(benzimidazole) (PBI) and a poly(etherimide) (PEI). Special attention is paid to the questions of residual solvent and of the thermal history in the context of the relaxation properties.

EXPERIMENTAL

Polybenzimidazole, poly(2,2'-(*m*-phenylene)-5,5'-bibenzimidazole), powder with the structure:

was supplied by Hoechst Celanese Corp.

The polyetherimide, poly[2,2'-bis(4-(3,4-dicarboxyphenoxy) phenyl) propane-*m*-phenylenedi-

* Permanent Address: Bio-Pharm, Ltd., Research and Development, Konyves Kalman krt. 76, 1087 Budapest, Hungary.

imine, Ultem 1000, was obtained from General Electric Co. and has the structure:

The reported molecular weight was $M_n = 12,000 \pm 4,000$, $M_w/M_n = 2.5$.

Blends were prepared using dimethylacetamide (DMAc) as cosolvent. PBI (10 g) was dissolved in 100 mL DMAc in a high-pressure vessel at 225°C for 1 h. The solution was filtered and diluted to 3% (w/v) concentration. Ultem 1000 was also dissolved in DMAc under ambient conditions to form a 3% (w/v) solution. Solutions of the blend were obtained by mixing the component solutions in the desired ratios. Films were cast on petri dishes at 80°C under dry nitrogen and were then washed continuously in hot (60–70°C) water for 7 days. The drying schedule was uniform for all samples regardless of composition. The films obtained were yellowish-brown and transparent. Film color darkened on heating in air above 350°C.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) studies were performed using a Perkin-Elmer 7 thermoanalytical system controlled by a Perkin-Elmer 7500 PC. Before DSC runs, samples were dried for 20 min at 150°C in the DSC pan to remove adsorbed water; the heating rate was 25°C/min. To locate the phase boundary, samples were heated to a preselected temperature at a rate of 25°C/min, annealed for 20 min, quenched to 100°C at a rate of about 320°C/min, and scanned (reheated) at a rate of 20°C/min. A nitrogen atmosphere was maintained throughout the experiment. The phase-separation temperature was taken as the lowest annealing temperature for which two DSC transitions appeared after the respective heat treatment.

Thermogravimetric analysis was used to monitor the residual solvent content in the samples. Weight changes were usually followed from room temperature up to 700°C under N₂. The heating rate used was 25°C/min.

Dielectric studies were performed using a Polymer Laboratories DETA apparatus that consists of a General Radio 1689M digital RLC bridge, a thermostatted dielectric cell with a temperature controller unit and a Hewlett-Packard 9816 computer with peripheral units. Measurements were made at a heating rate of 5°C/min between room tempera-

ture and 400°C. Measuring frequencies were 100, 10, 1, and 100 and 20 Hz.

Dynamic mechanical measurements were carried out using a Polymer Laboratories DMTA system with a Hewlett Packard 9816 computer. Measurements were made in the single cantilever mode. Heating rate was 4°C/min and measuring frequency was 1 Hz.

RESULTS

Differential Scanning Calorimetry

The thermal stability of the pure components of the PBI/polyimide blends was studied previously by repeated thermal cycling above the respective blend glass transition temperatures.^{1,5,6} It was observed that after the first run, the T_g of Ultem 1000 was practically constant (225°C) upon repeated cycling between 100 and 400°C. It was found also that aging at 400°C for 20 min did not shift the T_g value. T_g values for pure PBI remained practically constant (around 400°C) provided that the heat treatment was performed below 380°C.⁶ With annealing at temperatures above 400°C, however, the T_g increased abruptly and, in fact, combined DSC, solubility, and dynamic mechanical measurements show that PBI began to crosslink at these higher temperatures.^{7,8}

The effect of thermal history on the thermal behavior of the blends was studied over the whole composition range. In the initial DSC runs, samples exhibited a complex thermal transition in the neighborhood of the T_g expected from an approximate linear mixing rule, in agreement with previous results.⁵ Additionally, small endotherms were observed at lower temperatures. This complexity compromises the interpretation of the phase structure in these blends. For a better understanding of the thermal behavior, a series of annealing experiments were performed. Figure 1 shows a series of thermograms obtained using 60/40 wt % PBI/PEI blends annealed under different conditions. The most important feature of the thermograms is the appearance of an endotherm below the glass transition, which at first appears as a weak transition about halfway between the annealing temperature (T_a) and T_g . With increasing T_a , the peak temperature shifts toward T_g and finally overlaps the glass transition. When T_a equals T_g the endotherm disappears and the DSC trace shows a single, smooth glass transition characteristic of single-

Figure 1. DSC traces of 60/40 wt % PBI/PEI blends annealed for 20 min at selected temperatures.

phase glasses. A further increase of the annealing temperature broadens the glass transition and shifts the T_g toward higher temperatures, leading finally to phase separation, as has been previously observed.^{1,5} Figure 2 shows a second series of DSC traces of the same 60/40 wt % PBI/Ultem 1000 blend. In this set of measurements, the annealing temperature was held constant (220°C) and annealing time was changed systematically. The effect of annealing time is similar to that of increasing temperature below T_g ; longer annealing, however (at least in the time range studied) does not lead to phase separation.

Thermogravimetry

Thermogravimetric analysis was used to assess thermal stability and to determine the amount of adsorbed residual solvent (DMAc) in the samples over the whole range of blend compositions.

Under relatively mild drying conditions (80–90°C under vacuum for one week), a small amount of residual solvent remains in the blend samples. This solvent can be removed by heating above 50 and below 250°C; above 250°C the pure components, PBI and Ultem 1000, exhibit weight loss only above 500°C; the respective blends show a 1–5 wt % drop

between 250 and 400°C. The onset temperature of the latter process is a function of composition: it increases with increasing PBI content.

Dielectric Relaxation

For the dielectric measurements the samples were stored under ambient conditions to observe the effect of adsorbed water on the dielectric behavior.

Figures 3 and 4 show as an example the temperature dependence of the real part (E') of the complex permittivity and of the loss tangent ($\tan \delta$), respectively at five frequencies after different heat treatments for the 50/50 wt % blend. Drying at 150°C (curves b) removes the dispersion and loss features observed below 200°C on curves a. As was found in the case of the TGA data, this heat treatment is not sufficient to completely remove DMAc, but it removes adsorbed water. Thus the dispersion process observed below 200°C for samples stored under ambient conditions is due to adsorbed water. This has been shown by re-equilibrating samples previously dried at 150°C in ambient air for a few days: the original dielectric behavior is restored. The 150°C drying protocol does not alter the dielectric properties above 200°C. The second dispersion process, attributable to the glass transition in the blend, can be observed at higher frequencies only, because at lower frequencies a strongly dispersive transport

Figure 2. DSC traces of 60/40 wt % PBI/PEI blend samples annealed for selected times at 220°C.

Figure 3. Temperature dependence of the real part of the complex permittivity in 50/50 wt % PBI/PEI blends after different pretreatments: (a) stored under ambient conditions, (b) dried at 150°C for 1 week under vacuum, (c) annealed at 380°C for 10 min.

process (discussed below) masks the relaxation. If the sample is annealed above the relaxation temperature observed in the first run (as in the case of curves c), the relaxation shifts toward lower temperatures and the loss peak is better resolved from the increasing background loss.

The 100 kHz loss curves of blends of varying composition in the first run and after annealing the samples above the relaxation temperature observed in the first run were compared. In the first run the main feature observed is a shoulderlike relaxation at temperatures varying smoothly with composition. In the second run, after annealing, a relaxation below 250°C is always observed, the intensity of which decreases with increasing PBI content. We have also observed that the magnitude of the dispersive transport process observed at high temperatures and low frequencies is reduced by annealing the samples above the relaxation temperature.

Mechanical Relaxation

The mechanical loss tangents observed at 1 Hz in the first and second heating runs of the pure components and of some of the blends are shown in Figures 5 and 6, respectively. Two or three maxima can be observed in the $\tan \delta$ curves in the first run. The temperature of the first transition increases slowly with increasing PBI content. The second run shows two transitions in the $\tan \delta$ curves, one between 180 and 230°C and another around 430°C with intensities varying with composition. The latter behavior is typical for phase-separated polymeric glasses. There is also a characteristic difference between the temperature-dependent moduli E' in the first and second runs (see Fig. 7 which shows the E' and $\tan \delta$ curves for the 30/70 wt % PBI/PEI system as an example). The appearance of an apparent doublet in the first transition peak in the first run is caused by the anomalous behavior of the $E'(T)$ curve; above the first transition peak, E' begins to increase with increasing temperature, reaches a local maximum, then decreases again. This feature of the modulus curve can be easily observed for samples containing 10/90, 20/80, 30/70, 40/60, and 50/50

Figure 4. Temperature dependence of the dielectric loss tangent in 50/50 wt % PBI/PEI blends after different pretreatments. For explanations of a, b, c see Fig. 3.

Figure 5. Temperature dependence of the 1 Hz mechanical loss tangents of PBI/PEI blends of selected compositions in the first heating run.

wt % PBI/PEI. At higher PBI contents the doublet in the $\tan \delta$ curves is less visible, and the E' (T) curves exhibit a smoother temperature dependence. In the second run the E' (T) curve decreases monotonically with temperature in all cases.

Annealing below the lowest transition temperature affects the mechanical behavior. Figure 8 shows the temperature-dependent moduli in a 50/50 wt % blend after different heat treatments. In the lower part of the figure the two curves compare the moduli of a sample dried under vacuum at 150°C for one week and of a second annealed at 260°C for 10 min, which is just below the lowest transition peak observed for the first sample. The upper curve shows the modulus of the sample in the second run heated previously to 400°C. After annealing, the temperature of the first transition drifts upward but the local maximum of E' is still visible although it is of lower intensity. If the E'' curves are compared with the $\tan \delta$ curves of the annealed and unannealed samples (Fig. 9) in the first runs, it can be seen that while the E'' peaks correspond to the decreasing portions of the $\log E'$ curves, the second of the $\tan \delta$ peaks

Figure 6. Temperature dependence of the 1 Hz mechanical loss tangent of PBI/PEI blends of selected compositions in the second heating run.

Figure 7. A comparison of 1 Hz dynamic mechanical loss tangents and storage moduli of a 30/70 wt % PBI/PEI blend in the first (a) and second (b) runs. Note the local maximum on the upper E' curve above the second $\tan \delta$ peak.

Figure 8. Temperature dependence of the 1 Hz storage moduli of 50/50 wt % PBI/PEI blend samples after different heat treatments: (a) dried at 150°C under vacuum for 1 week, first heating run, (b) annealed for 10 min at 260°C, first heating run, (c) second heating run after heating to 400°C.

appears at temperatures where $\log E'$ shows a minimum and begins to increase again. The local maximum of E' disappears if the sample is annealed above the lowest transition temperature observed in the first run.

DISCUSSION

Blends composed of polybenzimidazoles and polyimides exhibit complex relaxation behavior depending on the thermal treatment; the behavior can be understood in terms of physical aging, solvent removal, possible crosslinking, and phase separation.

We discuss first the DSC and TGA data. The first DSC runs are less informative and phase behavior must be studied by performing a series of annealing experiments at each composition. It might, at first, be concluded from the DSC traces in Figures 1 and 2 that the system is phase separated, but the experimental findings are not compatible with this hypothesis. If the system is truly phase separated then two distinct ΔC_p steps should be observed in the vicinity of the glass transitions of the pure components (see the uppermost curve of Fig.

1) and the positions of these steps should not depend on the annealing temperature.⁹ The observed phenomena, however, can be understood in terms of a physical aging process¹⁰ involving volume and enthalpy relaxation in the glass. On annealing, a gradual equilibration of the glassy structure occurs, which can be understood, for example, in terms of free volume theory. According to the effective temperature concept¹¹⁻¹⁵ the appearance of an endotherm upon annealing is a consequence of structural equilibration. It has been observed that the endothermal peak appears significantly below the glass transition temperature and with relatively high intensity in pressure-densified glasses,¹⁶⁻¹⁹ in glasses deformed or distorted below their glass temperatures,^{19,20} and in glasses prepared by freeze drying from solution.²¹ This last process essentially parallels the solution casting of high T_g polymers or their blends.

Enthalpy relaxation measurements on polymer blends have been reported.^{22,23} If the blend is miscible, the enthalpy relaxation process is similar to that observed for pure polymeric glasses. In fact, because it is easier to detect the appearance of enthalpy relaxation endotherms just below the glass transition than to detect the ΔC_p step itself, annealing studies have aided in detecting miscibility in blends consisting of components with similar T_g values.²⁴ In the present case, however, the T_g s of the blend constituents are widely separated, so that if the system were phase separated, annealing would lead to *two* endotherms below the glass transition temperatures of the respective components, depending on the annealing temperature. Instead one observes the usual broad ΔC_p step with slowly varying position and a superimposed endotherm that

Figure 9. Comparison of the temperature-dependent loss moduli (left) and loss tangents (right) of a 50/50 wt % PBI/PEI blend after different heat treatments (for a, b see Fig. 7).

shifts more rapidly with increasing annealing temperature and, eventually, disappears. The relatively large temperature difference between the T_g (identified as the center of the ΔC_p step neglecting the endotherm) and the endothermal peak position at low annealing temperatures can be understood as a consequence of the strained, nonequilibrium glassy structure formed during the casting process. However, the enthalpy relaxation is complicated by the presence of strongly bound residual solvent molecules as indicated by thermogravimetric analysis.

When constructing the phase diagram of the system, composition-dependent T_g values were chosen as the midpoints of the ΔC_p steps for those annealing temperatures in which the enthalpy relaxation peak practically disappears and the residual solvent content is lowest. The phase separation temperature is identified as the lowest annealing temperature where two, composition-independent, transitions appear in the DSC traces. The phase diagram constructed on these principles is shown in Figure 10, where it can be seen that phase separation occurs just above T_g , indicating the instability of the single phase mixture if the molecules possess sufficient mobility. The nonequilibrium nature of single-phase blends also is evidenced by the fact that no remixing occurs upon annealing the blends below the glass transition temperature observed in the first run. It is assumed that the lower critical solution temperature (if present) is located below the T_g composition curve; phase separation at these temperatures is prevented only by the low mobility of the chain segments. The T_g composition curve is slightly different from that reported earlier,¹⁻⁵ which may be due to small differences in sample preparation and residual solvent content.

The dielectric and mechanical data are compatible with and provide further support for the mechanisms indicated by DSC and TGA analysis. The dielectric data reflect the desorption of water, phase separation, and solvent loss above the glass transition temperature. The water effect is illustrated in Figures 3 and 4, which show the dielectric parameters of the 50/50 wt % blend after different heat treatments. The differences between the samples stored under ambient conditions and those dried at 150°C appear mainly in the 50–200°C temperature range. The dried samples show much less frequency dependence of ϵ' in this region and the dielectric loss is also considerably reduced. Water can influence the dielectric relaxation of polymers in various ways.²⁵ It usually enhances the local relaxation processes by dipole-dipole coupling and it can act as an effective plasticizer in polar polymers. If water

Figure 10. Glass transition temperatures and apparent phase boundary obtained from DSC data together with calculated glass transitions based on linear ($T = w_1T_{g1} + w_2T_{g2}$) and inverse ($1/T = w_1/T_{g1} + w_2/T_{g2}$) mixture rules, where T_g and w_i are the glass transition temperature and the weight fraction of the i^{th} component, respectively).

can form a hydrogen-bonded superstructure, it produces a very specific dielectric response, often termed "an anomalous low frequency dispersion."²⁶ This type of response appears typically if water is adsorbed in a porous structure²⁷ or at the matrix-filler interface in composites,²⁸ but it can also be observed in proteins such as keratin.²⁹ The essence of this kind of response is that both ϵ'' and $\epsilon' - \epsilon_\infty$ increase with decreasing frequencies according to a fractional power law (ω^{n-1} ; $0 < n < 1$). If the temperature changes, there is a double effect; the mobility of the protons increases, shifting the response toward higher frequencies (i.e., at a given frequency the intensity increases) and the amount of the adsorbed water decreases because of desorption and diffusion. Of these two competitive effects the first prevails at lower temperatures, the latter at higher temperatures. As a result, both $\epsilon' - \epsilon_\infty$ and ϵ'' go through a maximum and the maximum increases with lower measuring frequency. It is precisely this kind of response that is observed for the PBI/PEI blends between 50 and 200°C. As noted above, the original response can be restored after drying at 150°C if the sample is again equilibrated under ambient conditions for a few days. The magnitude of the loss between 100 and 150°C in the first run is

higher with higher PBI content in the blend, again in accordance with the hypothesis of water adsorption, as the water uptake of the pure PEI component is negligible compared to that of PBI.

However, the adsorption and desorption of water does not influence the dielectric response observed at high temperatures. In the case of the 50/50 wt % blend in the first run, no distinct loss peak can be distinguished above 200°C, only a step-like change in the $\log(\tan \delta)$ curves. In the second run, however, a clearly defined loss peak appears at lower temperatures than in the first run. Measurement at lower frequencies is hampered by the presence of a strong dispersion process. The latter cannot be of dipolar origin as the low-frequency apparent permittivities may reach values as high as 10^4 . This type of response is frequently observed in ionic conductors,³⁰⁻³² and is interpreted as a consequence of electrode polarization. Because of the high T_g s of the components in this study, the mobility of impure ions above T_g is sufficient to produce such electrode polarizing effects. It has been observed that in the second heating the low frequency permittivities are significantly lower than in the first run, but still are high enough to obscure low-frequency dipolar relaxations above 250°C. This decrease of ϵ' is a consequence of the desorption of the residual solvent observed in TGA, resulting in lower ionic mobility. For monitoring of the phase separation process, the highest frequency (100 kHz) data are the most useful. Loss curves in the first run indicate a composition-dependent relaxation temperature. At higher PBI contents the relaxation shifts to very high temperatures, so only the onset of the relaxation process can be detected, associated with an ohmic conduction process and probably with electrode polarization. In the second run in all cases, a loss peak appears below 250°C; its intensity decreases with increasing PBI content. This relaxation corresponds to the glass transition of the separated PEI phase, which in a simple system should be independent of composition. This is not the case here, indicating incomplete phase separation and some residual interaction between the separated phases.

The mechanical $\tan \delta$ curves obtained in the first run show a complicated structure (see Fig. 5), again because of the superposition of various processes: the glass transition of the nonequilibrium single-phase blend, the desorption of the residual solvent (1–5 wt %, from TGA) above T_g , and finally phase separation. The $\tan \delta$ representation overemphasizes the doublet appearance of the lower temperature transition peak in the first run. The second peak observed within this doublet at compositions be-

tween 10/90 and 50/50 wt % is clearly due to the fact that when the residual solvent begins to volatilize above the glass transition temperature, E' begins to increase owing to the plasticizer loss (see Fig. 7). Above this temperature the mechanical properties do not correspond to those of a single-phase glass; the highest temperature-loss peak in the first run above 350°C is the glass transition of the separated PBI phase. The effect of annealing on the dynamic mechanical properties (see Figs. 8 and 9) is also consistent with the picture presented. If the blends are annealed close to, but still below, the glass transition temperature observed in the first run, then the glass transition shifts toward higher temperatures, but solvent removal is not complete; there is still a local maximum on the $E'(T)$ curve above the glass transition. The mechanical losses observed in the second heating run (see Fig. 6) are typical for phase-separated glasses, that is, two transitions with varying magnitudes, depending on the actual composition. Here, as in the dielectric experiments, the transition temperatures are not absolutely independent of the composition, indicating minor interactions between the separated phases.

CONCLUSIONS

A study of the complex relaxation behavior of solvent-cast films of poly(benzimidazole)/poly(etherimide) blends has shown that

- Transparent films associated with single-phase glasses can be obtained by casting at 80°C under N_2 .
- When annealed below their composition-dependent glass transition temperatures the blends will exhibit well-defined enthalpy relaxations, characteristic of glasses with mechanically strained structure.
- Above their glass transition temperatures the blends undergo rapid phase separation that cannot be reversed by any annealing protocol.
- Above the glass transition a further small amount (1–5 wt %) of residual solvent is removed from the samples simultaneously with phase separation.

The conclusion from these observations is that this binary polymer mixture forms homogeneous dilute solutions in DMAc, and on the removal of the solvent, a nonequilibrium, single-phase structure remains. Phase separation is prevented by kinetic

factors (by low segmental mobility in the glassy state) but occurs above the glass transition, that is, as soon as the mobility is high enough. Thus, preparation conditions (especially solvent removal, drying, and annealing regimes) play an important role in determining the properties of the solvent-cast films; these factors must be taken into account in future processing protocols.

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