

Miscible Blends of Poly(butylene terephthalate) and the Polyhydroxyether of Bisphenol A

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Synopsis

Melt blends of poly(butylene terephthalate) (PBT) and the polyhydroxyether of bisphenol A (phenoxy) exhibit excellent transparency above the melting point of PBT as well as for the quenched molded specimens. Dynamic mechanical and calorimetric characterization revealed single and sharp glass transitions intermediate between those for the individual constituents. Increasing phenoxy content in the blends depressed the crystallization rate of PBT due to dilution and viscosity (T_g increase) effects. The apparent miscibility is believed due to the potential specific interactions between phenoxy pendant hydroxyl (proton donor) and the ester carbonyl of PBT (proton acceptor). Heat of fusion results surprisingly show an increase in the degree of PBT crystallinity as the phenoxy content of the blend is increased. No explanation is offered at this point for this unexpected behavior.

INTRODUCTION

Until quite recently, miscible polymer blends have been considered an exceptionally rare and unexpected behavior.^{1,2} This generalization is somewhat less valid now that experimental investigations have recently revealed an exponentially increasing number of miscible blends. This rapid increase in documented miscible blends is undoubtedly due to the increased experimental programs in polymer laboratories investigating potentially miscible blends as well as recent advances in the empirical and theoretical understanding of the nature of miscibility in the polymer blends.³⁻⁵

The importance of specific interactions in yielding a negative heat of mixing ΔH_m is obviously due to the negligible contribution of the entropy of mixing ΔS_m for high molecular weight polymers in the expression

$$\Delta G_m = \Delta H_m - T \Delta S_m$$

The free energy of mixing ΔG_m must be negative for miscibility to result, thereby requiring ΔH_m to be zero or negative. With ionic polymers, anionic and cationic polymer blends form the extreme case of specific interactions resulting in single-phase blend behavior.⁶⁻⁸ It is of interest to point out that many combinations of water-soluble polymers that exhibit acidic or basic characteristics yield miscible blends, e.g., poly(acrylic acid)-poly(ethylene oxide),⁹ poly(methacrylic acid)-poly(ethylene oxide),¹⁰ and poly(methacrylic acid)-poly(vinyl pyrrolidone).¹¹ The specific interactions in these cases are of such strength that mixing water solutions of the respective polymers immediately yields a precipitate exemplifying strong complexation. Miscible polymer blends containing respectively strong electron donor and electron acceptor groups have been described by Sulzberg and Cotter.¹² The unmixed donor or acceptor polymers were characteristically water-white transparent materials. Blends exhibited yellow

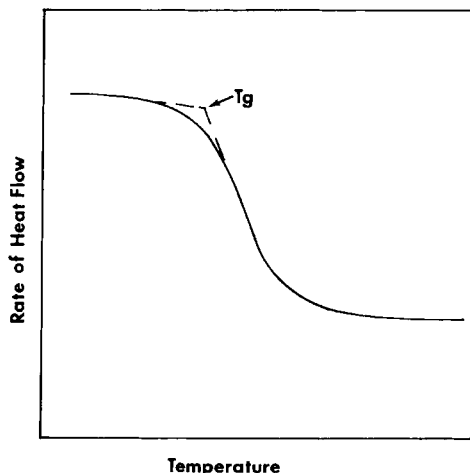


Fig. 1. Determination of T_g from differential scanning calorimetry data.

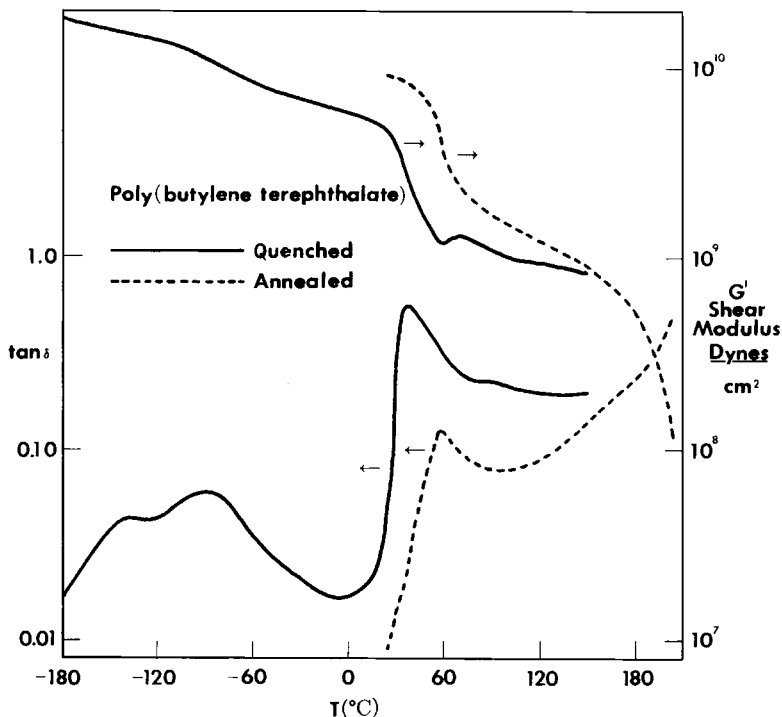


Fig. 2. Mechanical loss and shear modulus for poly(butylene terephthalate) as function of temperature: (—) quenched; (- -) annealed.

to amber coloration with retention of transparency indicative of strong specific interactions. Glass transitions of these blends were intermediate between the constituents' T_g 's, and the maximum absorption of the blends in the visible spectra exhibited values quite different from either component. Specific interactions have also been credited to yield miscibility in blends of nylon 6/ethylene-acrylic acid copolymers,¹³ poly(vinyl chloride)/ethylene-ethyl acrylate-carbon monoxide terpolymers,¹⁴ poly(vinyl chloride)/poly- ϵ -caprolactone,¹⁵ and poly(vinyl chloride)/ethylene-vinyl acetate-SO₂ terpolymers.¹⁶ This paper

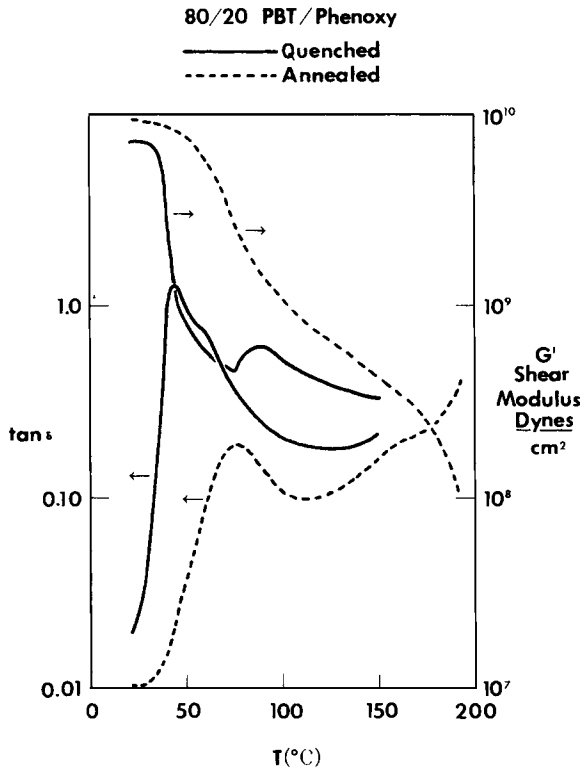
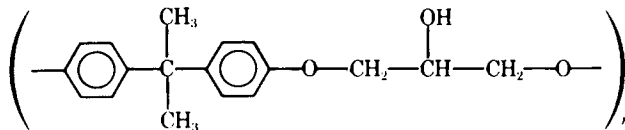


Fig. 3. Mechanical loss and shear modulus data for the 80/20 (by wt) poly(butylene terephthalate)/phenoxy blend as a function of temperature: (—) quenched; (- - -) annealed.

describes the miscible blend of two polymers which have the potential for specific interactions through hydrogen bonding.

EXPERIMENTAL

The primary blend studied in this investigation is that of poly(butylene terephthalate) (PBT) and the condensation polymer resulting from the reaction of epichlorohydrin and bisphenol A commonly referred to as the polyhydroxy-ether of bisphenol A,¹⁷ or phenoxy:



The specific polymers chosen for this study were poly(butylene terephthalate) (6 PRO from Tennessee Eastman, $T_g = 34^\circ\text{C}$, $T_m = 221^\circ\text{C}$) and phenoxy (PKHH from Union Carbide Corporation, $T_g = 96^\circ\text{C}$). The blends of these two polymers were prepared (after proper drying to prevent hydrolysis of PBT) via melt extrusion in a 1-in.-diameter single-screw extruder ($L/D = 36$) with two fluted Maddox mixing elements to assure a high degree of mixing. The temperature range chosen was $230\text{--}235^\circ\text{C}$ with a residence time of approximately 4 min at those temperatures. The time-temperature history of this blend is quite relevant

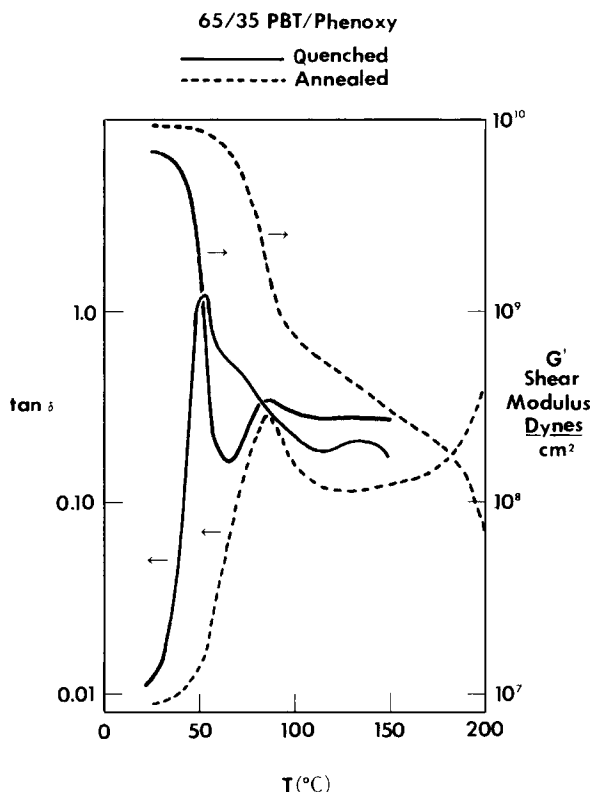


Fig. 4. Mechanical loss and shear modulus data for the 65/35 (by wt) poly(butylene terephthalate)/phenoxy blend as function of temperature: (—) quenched; (- - -) annealed.

because of the potential transesterification reactions between the blend constituents which would yield graft and/or crosslinked polymers under proper conditions.

Samples for dynamic mechanical and calorimetric testing were prepared by compression molding in a 20-mil cavity mold at 230°C. Quenched specimens were prepared by removing the molten sample held between aluminum sheets with immediate quenching in ice water. All quenched specimens were transparent, thus providing a strong possibility (but not sufficient evidence) of miscibility. Specimens were prepared under normal molding conditions in which the cooling water circulating through the mold yielded an approximate cooling rate of 20°C/min. Samples were also annealed at 150°C for 30 min. The specimens prepared under normal molding as well as annealing conditions were opaque (except for 100% phenoxy) due to the resultant crystallization of PBT.

Dynamic mechanical testing on the quenched and annealed specimens was conducted with a torsion pendulum similar to the design reported by Nielsen.¹⁸ Sample dimensions were chosen to give a nominal frequency of 1 Hz in the glassy state.

The glass transition, crystallization temperature T_c , and melting temperature T_m for the above-mentioned blends and individual components were measured with a Perkin-Elmer DSC-2 differential scanning calorimeter.

Calorimetric data were determined from room temperature to $T_m + 10^\circ\text{C}$ at

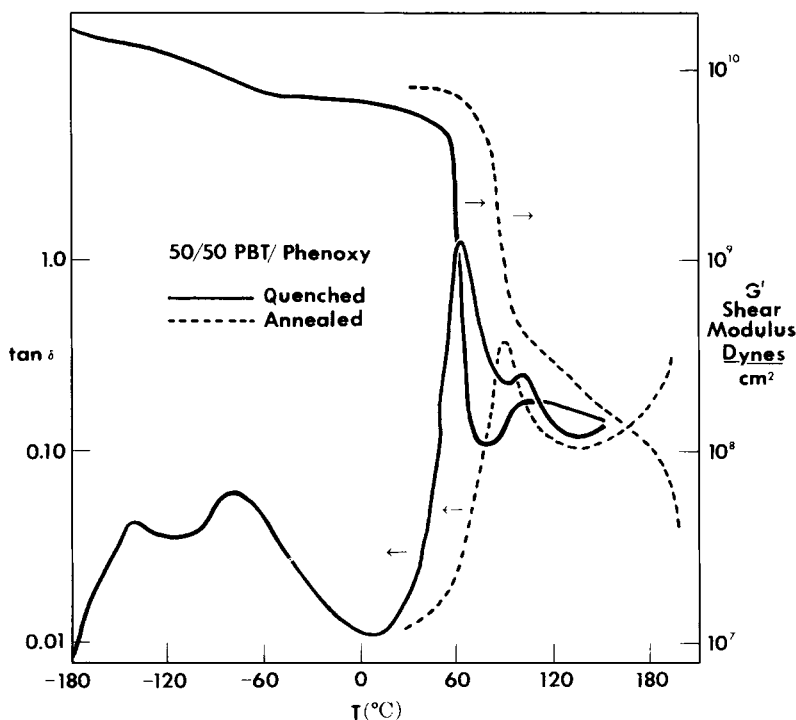


Fig. 5. Mechanical loss and shear modulus data for the 50/50 (by wt) poly(butylene terephthalate)/phenoxy blend as function of temperature: (—) quenched; (---) annealed.

a heating rate of $10^{\circ}\text{C}/\text{min}$. The T_g was determined as the intersection of the lower temperature specific heat component data and the transition region, as shown in Figure 1. T_c and T_m were determined from the peaks of the crystallization exotherm and the melting endotherm, respectively. Heats of crystallization ΔH_c and heats of fusion ΔH_f were determined from the areas below the respective curves. For quenched samples containing higher levels of PBT, crystallization occurred immediately after the rising temperature exceeded the glass transition, and accurate measurements of ΔH_c were not possible due to the inability to determine baseline positions for area measurements due to baseline shifts resulting from the glass transition.

The rate of transesterification reactions between phenoxy and PBT was measured qualitatively by following relative viscosity changes in a Brabender mixer. Torque-time measurements were determined at 250°C to a point where a powder-like substance indicative of a high level of crosslinking was formed.

EXPERIMENTAL RESULTS

The dynamic mechanical characterization of the blends and the individual components was conducted on quenched and annealed specimens (nominal frequency = 1 Hz in the glassy state). The mechanical loss $\tan \delta$ and the shear modulus G' temperature dependence are illustrated in Figures 2 to 8 for 100/0, 80/20, 65/35, 50/50, 35/65, 25/75, and 0/100 weight ratios of PBT/phenoxy blends. For all blends, single and sharp $\tan \delta$ peaks corresponding to the glass transition are observed intermediate between the corresponding component values, thus

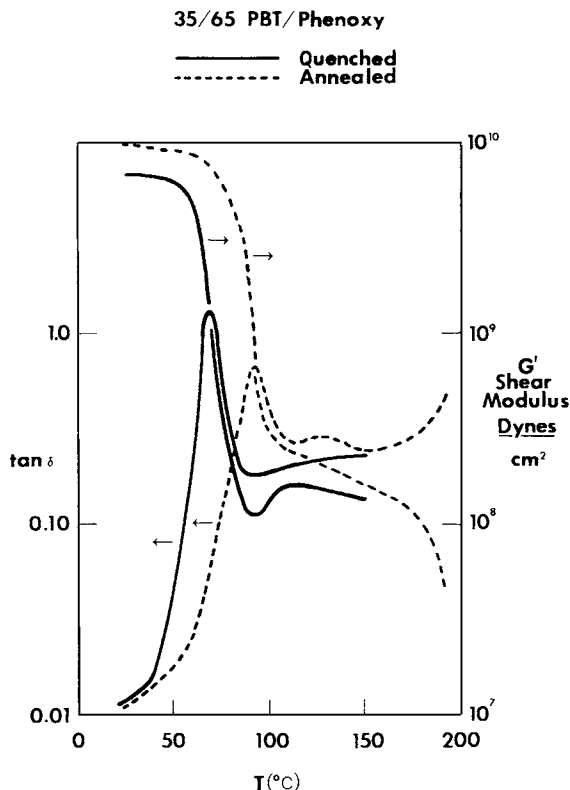


Fig. 6. Mechanical loss and shear modulus data for the 35/65 (by wt) poly(butylene terephthalate)/phenoxy blend as function of temperature: (—) quenched; (- - -) annealed.

providing experimental evidence of miscibility. The T_g is increased and the $\tan \delta$ peak height is decreased with annealing in the blends as well as for the 100% PBT sample. The modulus for the quenched blends as well as for 100% PBT initially decreases at the T_g to a point where an increase in temperature yields an increase in modulus due to the increasing level of crystallization occurring above the T_g . The modulus change is also accompanied by a loss in transparency for the sample.

The calorimetric data are tabulated in Table I for PBT and the PBT/phenoxy blends for samples prepared under quenched and normal molding conditions. The quenched samples all exhibited crystallization exotherms with ΔH_c values somewhat lower than ΔH_f , implying that the quenched specimens were not wholly amorphous. The specimens prepared under normal molding procedure did not yield crystallization exotherms. It is interesting that the quenched specimens, after crystallization, gave higher ΔH_f values than the samples prepared under normal molding conditions. ΔH_f values corrected for PBT content ($\Delta H_f/\text{PBT wt-\%}$) yielded a surprising increase over that which would be normally expected (namely, constant value or lower value due to dilution and kinetic effects).

As with the dynamic mechanical characterization, calorimetric T_g values intermediate between the individual components were observed, thus providing further evidence of miscibility in the amorphous phase of the blend. An increase in $T_c - T_g$ was observed with increasing phenoxy concentration, thus implying

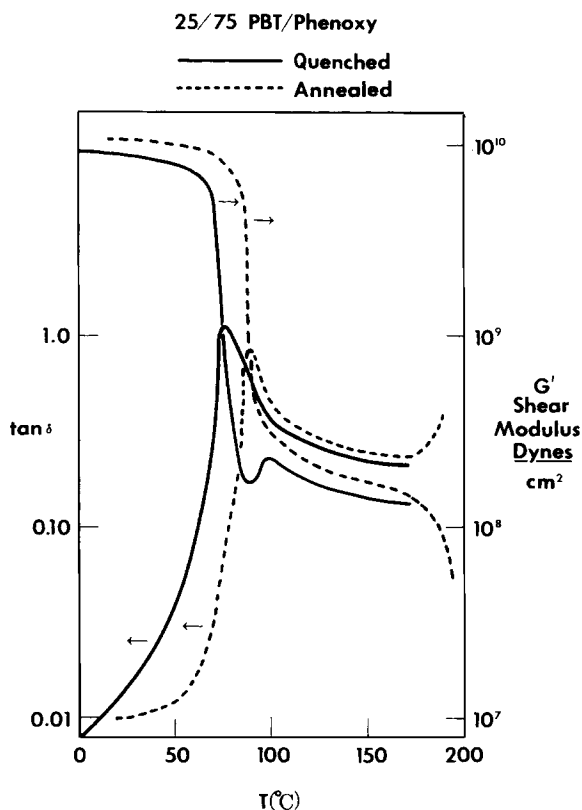


Fig. 7. Mechanical loss and shear modulus data for the 25/75 (by wt) poly(butylene terephthalate)/phenoxy blend as function of temperature: (—) quenched; (- - -) annealed.

a reduction in the crystallization rate. With 100% PBT and 80% PBT samples, accurate measurements of ΔH_c were not possible due to indeterminate baseline values resulting from the proximity of the T_g . At higher phenoxy content, accurate values of ΔH_c were possible, and ΔH_c /PBT wt-% increased with Phenoxy content, thus implying a lower relative degree of crystallization of PBT in the quenched blends. This provides additional evidence of the reduction in the

TABLE I
Calorimetric Data on Poly(butylene Terephthalate)/Phenoxy Blends

Blend description	Preparation	T_g , °C	T_m , °C	Heat of fusion ΔH_f , cal/g	T_c , °C	Heat of crystallization ΔH_c , cal/g
100% PBT	quenched	32	219	10.9	43	—
80/20 PBT/phenoxy	quenched	38	220	10.2	59	—
65/35 PBT/phenoxy	quenched	45	220	8.5	77	4.1
50/50 PBT/phenoxy	quenched	59	219	7.0	97	4.0
35/65 PBT/phenoxy	quenched	65	219	5.5	113	3.2
100% PBT	normal molding	39	221	8.0	—	—
80/20 PBT/phenoxy	normal molding	49	221	7.3	—	—
65/35 PBT/phenoxy	normal molding	49	220	7.0	—	—
50/50 PBT/phenoxy	normal modling	—	220	5.8	—	—
35/65 phenoxy	normal molding	—	218	4.7	—	—

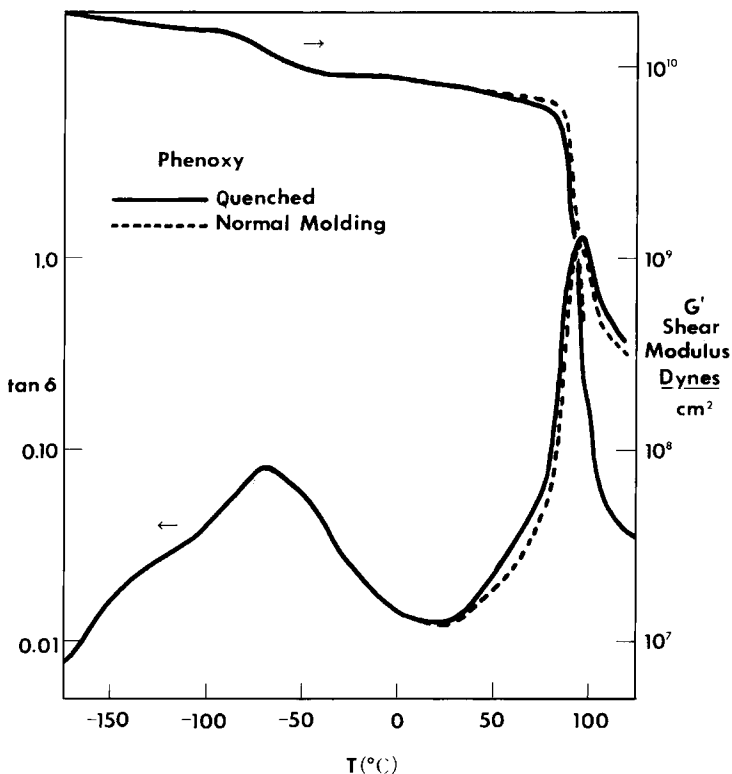


Fig. 8. Mechanical loss and shear modulus for phenoxy as function of temperature: (—) quenched; (---) normal molding.

crystallization rate with increasing phenoxy content. The crystalline melting point is somewhat invariant with phenoxy content. For the samples prepared under normal molding conditions, a slight melting point depression occurs, but the magnitude is much lower than that reported for the poly(vinylidene fluoride) in miscible blends with poly(methylmethacrylate).¹⁹

The melt viscosity–time measurements conducted in a Brabender at 250°C are illustrated in Figure 9. An initial drop in viscosity is due to the melt plasticization of the sample followed by a constant viscosity to the position where a viscosity increase due to transesterification reactions is occurring. With the increase in viscosity a temperature increase was also observed. At the peaks in the viscosity–time curve, melt fracture occurred followed by a rapid decrease in viscosity with a resultant nonfusible crosslinked product. This clearly establishes the potential for transesterification to occur in this blend. The induction time is concentration dependent and maximum reaction appears to occur near 35% phenoxy. At 230°C, the viscosity was constant up to 45 min, at which time the measurements were stopped as this time is approximately ten times the contact time occurring during blend preparation extrusion.

The crosslinking behavior is depicted in Figure 10 for a modulus–temperature curve of a sample (50/50 phenoxy/PBT) molded at 230°C for approximately 2 min and a sample molded at 275°C for 20 min. The severe molding conditions yield a specimen with a residual modulus above the melting point for PBT due to the crosslinking. A depressed T_m is also observed due to the high level of grafting and crosslinking. These results imply that under the conditions of specimen blending and normal molding, transesterification was quite low.

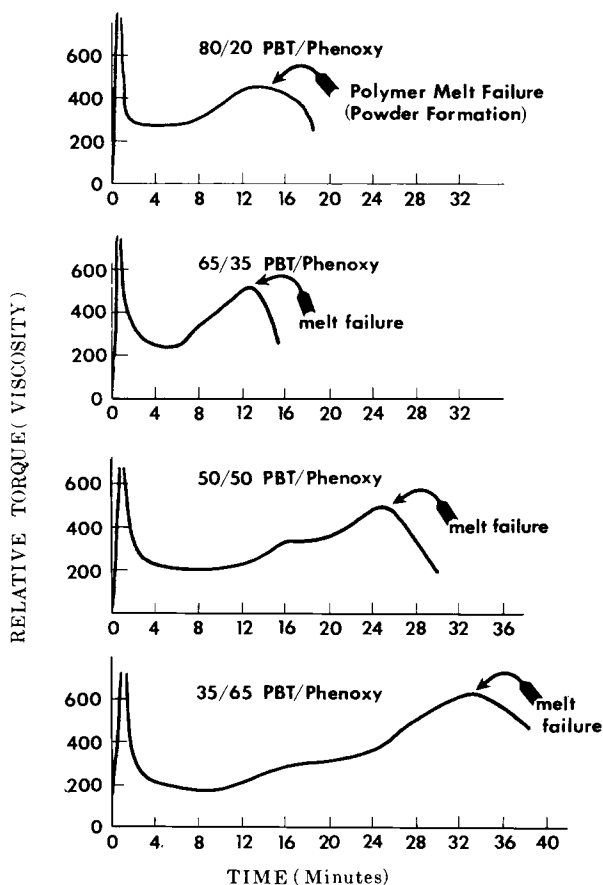


Fig. 9. Relative viscosity-time measurements for poly(butylene terephthalate)/phenoxy blends at 250°C (determined in a Brabender mixer).

DISCUSSION OF RESULTS

All PBT/phenoxy blends exhibited transparency in the melt ($>220^{\circ}\text{C}$) as well as for quenched compression-molded films. With annealing, normal molding, or increasing the quenched blend temperature above the T_g , opacity occurred, indicating crystallization of PBT from the polymer mixture. Phase separation which would also account for opacity has been ruled out due to single T_g determination on opaque samples. While transparency per se is not adequate justification for establishing polymer-polymer miscibility, the single and sharp mechanical loss peaks observed for all blends (transparent and opaque) illustrate that phenoxy and PBT do indeed constitute a miscible polymer blend. Additional confirmation of the single T_g values intermediate between those of the components was shown with calorimetric data.

Annealing the initial quenched blends at 150°C resulted in an increase in the T_g , but a single sharp $\tan \delta$ peak was retained indicating the miscibility of the amorphous phase. Note that peak heights for the quenched specimens ($\tan \delta \approx 1.2$) are in the range of single-component amorphous polymers (e.g., as illustrated for phenoxy in this study). The lowering of the peak's height with annealing is expected due to the presence of PBT crystallinity. A monotonic decrease in the $\tan \delta$ peak height is observed with increasing PBT content.

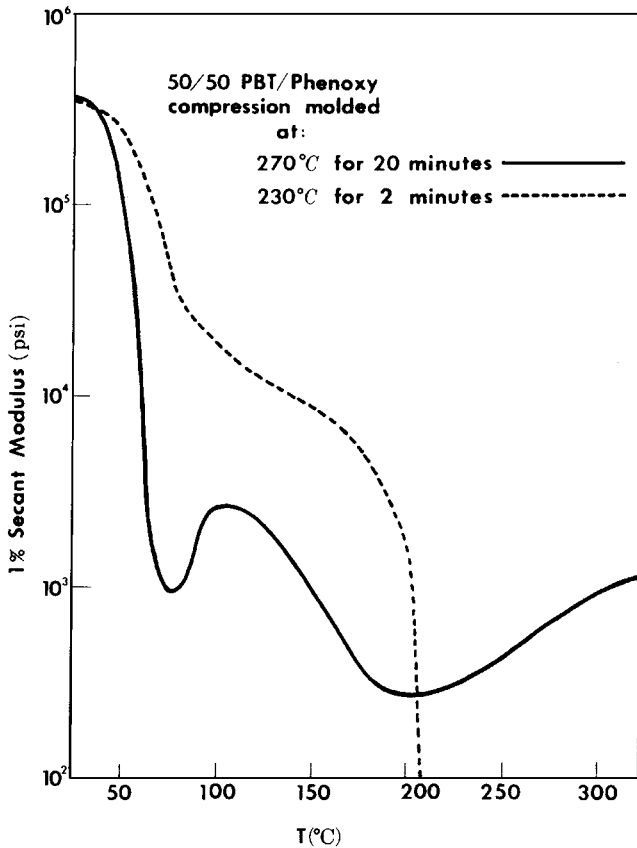


Fig. 10. Modulus-temperature data for 50/50 poly(butylene terephthalate)/phenoxy blend: comparison of molding conditions.

The dynamic mechanical determined T_g values for quenched and annealed specimens are illustrated in Figure 11. The quenched specimens follow the T_g relationship predicted by the Fox equation:

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

where

$$T_{g1} (\text{PBT}) = 307^\circ\text{K}$$

$$T_{g2} (\text{phenoxy}) = 369^\circ\text{K}$$

$$W_i = \text{weight fraction}$$

The annealed specimens yield a trend opposite to what the Fox equation predicts due to the resultant effect of PBT crystallization. With the crystallization of PBT, the PBT concentration in the amorphous phase of the blend is depleted, thus yielding the observed position deviation over that expected from either the Fox equation or a linear extrapolation of the individual component T_g values. Previous studies involving poly(vinyl chloride) and poly- ϵ -caprolactone had shown that T_g data on annealed and quenched (amorphous) blends combined with calorimetry data allowed for a direct calculation of the degree of crystallinity

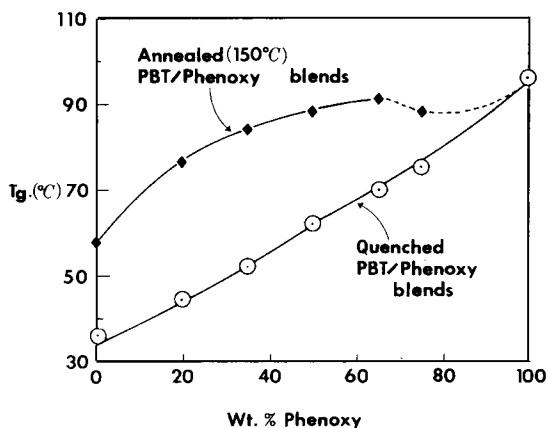


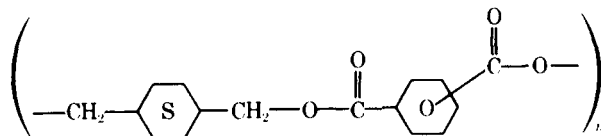
Fig. 11. Glass transition data for poly(butylene terephthalate)/phenoxy blends (dynamic mechanical results).

of the blends as well as for poly- ϵ -caprolactone by a simple material balance.²⁰ Adaptation of this procedure to the PBT/phenoxy blend was not possible due to the inadequacy of the quenching technique employed to yield wholly amorphous samples. However, it was observed that the level of crystallinity of PBT was decidedly depressed as the concentration of phenoxy was increased in the blends. This is expected due to a dilution effect as well as the increase in T_g (over that for PBT) which will noticeably depress the crystallization rate. This is predicted by the spherulitic growth rate equation²¹ which contains the T_g dependence in the form of the WLF equation.²² This has been experimentally verified for the blend of poly(vinyl chloride) and poly- ϵ -caprolactone.^{23,24}

As the structures of PBT and phenoxy imply the definite potential of transesterification leading to branching and then crosslinking, viscosity measurements as a function of time were determined. This is an important point in order to determine if the miscibility observed for this blend is due to the formation of a graft polymer of the constituents which would be expected to exhibit better miscibility than the nonreacted components based on theoretical as well as experimental results concerning block copolymers.²⁵⁻²⁷ Viscosity consistency for the blends at 230°C up to ten times the residence time employed during blend preparation indicated negligible transesterification. At 250°C, viscosity changes were observed at mixing times (concentration dependent) as low as 6 min of residence time. The rapid increase in viscosity and temperature, due to viscous heating, was followed by a rapid drop in torque after melt fracture occurred. The final product was a nonfusible powder characteristic of a crosslinked material. This observation was verified by modulus-temperature data on a specimen subjected to severe molding conditions which clearly showed a significant modulus plateau above the melting point of PBT. While transesterification reactions are indeed possible with this blend, the negligible extent of the reaction (as judged by viscosity changes) for samples prepared for characterization in this study leads to the conclusion that this blend is miscible in the nonreacted state.

In order to explain the observed miscibility, we propose that the specific interaction between the ester carbonyl of PBT (proton acceptor) and the hydroxyl of phenoxy (proton donor) is of sufficient magnitude to yield a negative heat of mixing thus satisfying the thermodynamic criteria for miscibility. It is of interest

to note that a similar interaction may exist with phenoxy and poly- ϵ -caprolactone which has previously been reported to yield miscible blends.²⁸ To further investigate this potential interaction, blends of phenoxy and poly(cyclohexylenedimethylene tere/isophthalate) blends were prepared.



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Modulus and resilience temperature data on the resultant clear films (Fig. 12) showed the existence of a single T_g for the blend intermediate between the component values, thus illustrating an additional miscible blend.

Based on the proposed specific interaction of the ester carbonyl of the previously mentioned polyesters with the hydroxyl of phenoxy, phenoxy-poly(ethylene terephthalate) blends were an obvious choice for further investigation. Blends of phenoxy and poly(ethylene terephthalate) (VFR-2527B) were prepared in the extruder described previously at 265°C. Quenched specimens exhibited ductility with dynamic mechanical results shown in Figure 13. Due to the proximity of the T_g values of the components, unambiguous resolution of the

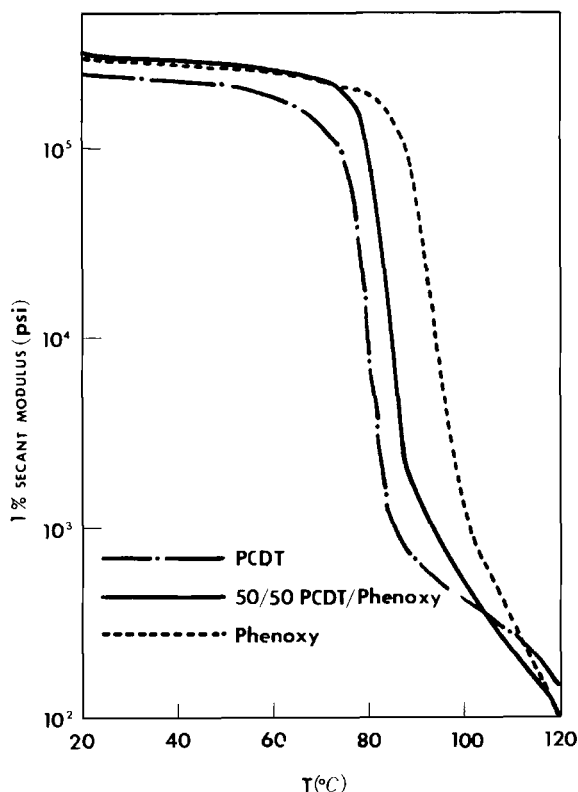


Fig. 12. Modulus-temperature data for poly(1,4-cyclohexylenedimethylene tere/isophthalate) (PCDT) (—), phenoxy (---), and a 50/50 PCDT/phenoxy blend (---).

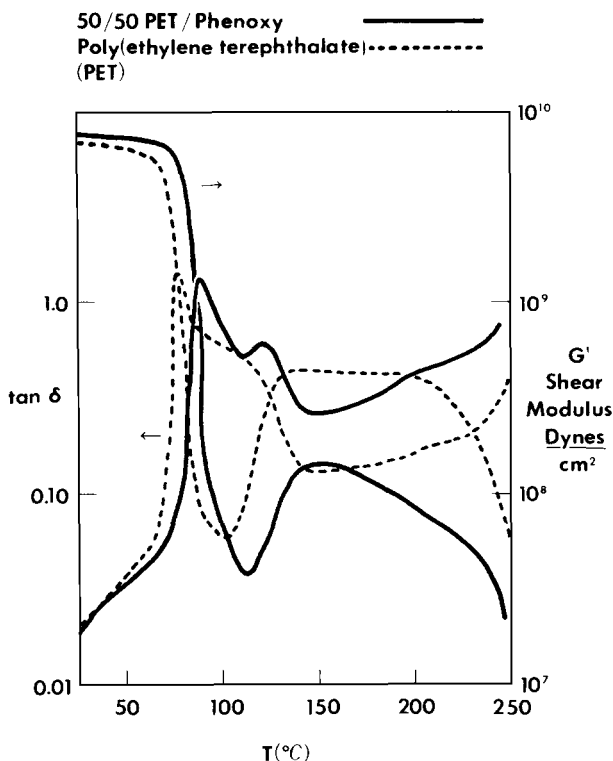


Fig. 13. Mechanical loss and shear modulus data for poly(ethylene terephthalate) (---) and a 50/50 poly(ethylene terephthalate)/phenoxy blend (—) as function of temperature (both samples quenched).

blend behavior is not possible, as is also the case with phenoxy and poly(cyclohexylenedimethylene tere/isophthalate). Note that the single and sharp transition for the blend does imply single phase behavior, as one would expect a broader transition for a two-phase mixture of polymers with T_g 's separated by $\sim 20^\circ\text{C}$.

Certain analogies between phenoxy and poly(vinyl chloride) can be drawn in that both have the potential of acting as proton donors [α -hydrogen of poly(vinyl chloride)]. Poly- ϵ -caprolactone has been reported to be miscible with both phenoxy and poly(vinyl chloride).²⁸ Blends of poly(cyclohexylenedimethylene tere/isophthalate) and PVC exhibit sparkling clarity with averaged mechanical properties. Due to the equivalent T_g 's for both polymers, T_g determinations cannot be utilized to establish miscibility. Blends of phenoxy and PVC exhibit two-phase behavior presumably due to the absence of specific interactions.

The observation based on ΔH_f results (Fig. 14), namely, the apparent level of PBT crystallinity is increased with phenoxy addition, is quite unexpected, particularly in view of the depression of the crystallization rate with increasing phenoxy concentration. At present, no hypothesis is forthcoming to explain the observation. In order to check this observation experimentally, densities of the annealed samples were determined using the gradient column density technique. The results shown in Figure 15 indicate linearity of specific volume versus composition for the annealed blends and the individual components. With an increase in crystallinity of PBT with addition of phenoxy, one would

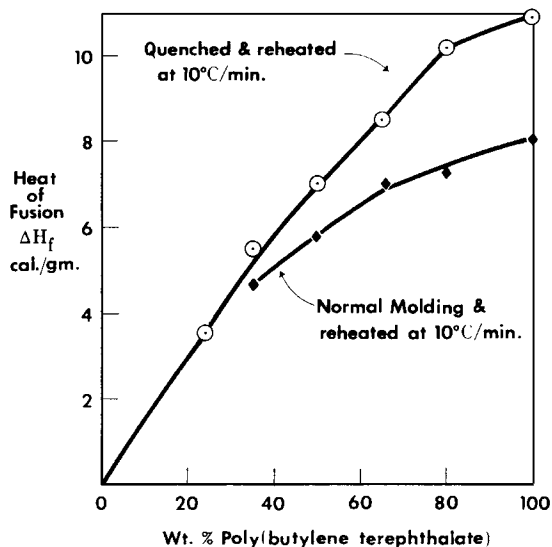


Fig. 14. Heat of fusion of poly(butylene terephthalate) in poly(butylene terephthalate)/phenoxy blends.

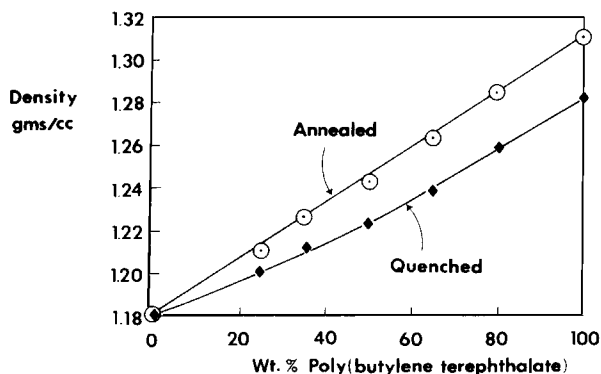


Fig. 15. Density data for poly(butylene terephthalate)/phenoxy blends.

expect a nonlinearity of specific volume versus composition. Quenched sample specific volume dependence on composition exhibits some deviation from linearity due to the increasing level of PBT crystallinity with increasing PBT due to the kinetics of crystallization.

Low-temperature mechanical relaxations for PBT were observed at -140° and -90°C (Fig. 2). The -140°C transition is typical for polymers containing $(\text{CH}_2)_n$ ($n \geq 4$) groups such as PBT. The -90°C transition is possibly due to a rotation around the $\text{O}-\text{CH}_2$ bond. For phenoxy (Fig. 8), a prominent transition is observed at -70°C with the origin of the transition ascribed to a rotation around the $\text{O}-\text{CH}_2$ bond. The 50/50 phenoxy/PBT blend (Fig. 5) exhibits the -140°C transition and a peak at -80°C which can be ascribed to a composite relaxation spectrum of the individual components.

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