

A Dynamic-Mechanical Study of Polycarbonate-Polyester Blends

YUAN LI* and H. LEVERNE WILLIAMS, *Department of Chemical Engineering and Applied Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A4*

Synopsis

Bisphenol-A polycarbonate and an aromatic linear copolyester were melt blended for dynamic mechanical tests using a Dynastat. Corresponding powders were used in thermal analysis by differential scanning calorimetry. The deduced glass transition temperatures of the pure polymers and blends were compared to estimate the miscibility of the two polymers.

INTRODUCTION

Commercial activity in the field of polymer blends has prompted active investigations for many years in the search for more attractive properties. One essential aspect is that of compatibility or miscibility.¹ Various methods have been used to measure this aspect of which the location of the glass transition temperature has been a major one. If the two polymers are completely immiscible, their respective glass transition temperatures will be found in the blend. If they are completely miscible, then only one transition temperature, between those of the components, will be found. Partial miscibility is also observed.

Two often used techniques for locating the transition temperature are the differential scanning calorimeter and the dynamic mechanical spectrometer which yields the loss factor, storage modulus and loss modulus from which values of the temperature defined as the transition temperature can be deduced.

These techniques were applied to bisphenol-A-polycarbonate (PC) and to an aromatic copolyester (PET) and blends of the two. Similar blends have been studied before. Wahrmond et al.² investigated blends of PC and poly(butylene terephthalate) and Nassar et al.³ made a similar study of PC and PET. They observed one T_g for greater than 60–70% PET but two when the PET content was less than 60–70% in the blend. Murff et al.⁴ concluded that blends of PC and PET yielded two amorphous phases in the PC rich region but one mixed phase in the PET rich region.

It seemed worthwhile to investigate this system by thermal mechanical and dynamic mechanical tests further. The polyester used was described as similar to poly(ethylene terephthalate) but with some modifications of the glycol content to alter the properties somewhat.

* Present address: Department of Chemistry University of Toronto.

EXPERIMENTAL

Equipment

The differential scanning calorimeter unit was attached to a du Pont 990 Thermal Mechanical Analyzer and was operated normally.⁵ The dynamic mechanical measurements were made using a Dynastat from IMASS which has been described both as to construction and operation by Sternstein.⁶ Bar samples were tested by three-point loading in shear.

Materials

The polycarbonate was a commercial product supplied by the Dow Chemical Co. and identified as "Calibre" 300-15. The product was in the form of amorphous pellets. The melt flow by ASTM condition 0 was 13.60 g. The polyester was supplied by Eastman Chemicals and identified as Kodapak PET copolyester 9921. The product was a semicrystalline material in pellet form and the melt index under ASTM condition T was 25.80 g.

Sample Preparation

The pellets were dried at least 24 h at 80°C in a vacuum oven and retained under vacuum thereafter. Blends were made by rolling (tumbling) the correct ratios of pellets in plastic bottles on a laboratory roller. The blend ratios were 80/20, 60/40, 40/60, and 20/80 by weight and with the two pure polymers made a series of six.

Each sample was treated in a C. W. Brabender Twin Screw Extruder with three heating zones. The initial throughput acted as a purge in each case. The three zones were heated to 250–255, 260–265, and 270–275°C respectively. The rotor speed was 20 ± 2 rpm. These conditions were found to be suitable for mixing without degradation. The extrudates were then cut into pieces and cooled for grinding in a C. W. Brabender Granulator Model S 20/9 and the powder stored dry for injection molding.

Bars were molded in a ram jet type injection molding machine, Hillard Industries Ltd. Model P.M. 225 using an ASTM mold with cavities for tensile and impact specimens. The molding pressure was calculated to be 62.4 MPa. The nozzle temperature was controlled at 305°C for PET and the two blends richer in PET and at 310°C for the other three samples. Likewise the mold temperature for PET was 50°C, for the highest PET content blend 80°C, for the second highest PET content blend 90°C, and for the remaining samples of polycarbonate and high polycarbonate content blends 120°C. Dynamic testing of both as-molded and annealed samples (18 h at 120°C) were done as indicated.

Differential Scanning Calorimetry

Measurements were made using the ground powders. Samples were heated at 20°C/min from 0 or 25°C to 240–250°C, then quenched with liquid nitrogen and retested at the same rate. The vertical axis was two mcal/sec/in. The T_g was taken as the temperature of the inflection point and the crystallization and melting temperatures were taken at the peaks of the respective curves. The instrument readings were converted in the usual way to obtain the temperatures.

Dynamic Mechanical Testing

The testing was done using a bar in three-point bending (flexure) and in the low range displacement control range. The static and dynamic loads were 2 and 1 kg respectively. The frequency was varied from 1 to 50 Hz with five intervals in the logarithmic scale. The temperature was from room temperature (25°C) to 170°C and measurements were made at 5°C intervals. The data for 1 and 10 Hz only are reported here.

RESULTS AND DISCUSSION

Thermal Properties

The thermal test was repeated at least four times and the reproducibility was excellent. The final measurement was preceded by an initial annealing (heating) over the full temperature range as described earlier followed by quenching except for those samples designated unannealed. The thermograms for an annealed and quenched and an unannealed (slow cooled) sample are in Figure 1 as is the set of thermograms for the pure polymers and the blends quenched.

The T_g for PET for the air-cooled semi-crystalline material is 63.5°C and the T_m is 247.3°C. The somewhat lower value of T_g for PET than reported at 67 and 75°C⁷ may be real since the polymer used is a copolyester. On the second heating, i.e., of the quenched sample, the T_g was 84.3°C and the T_m 249.2°C with a crystallization peak at 166.7°C. The increased T_g in the second heating

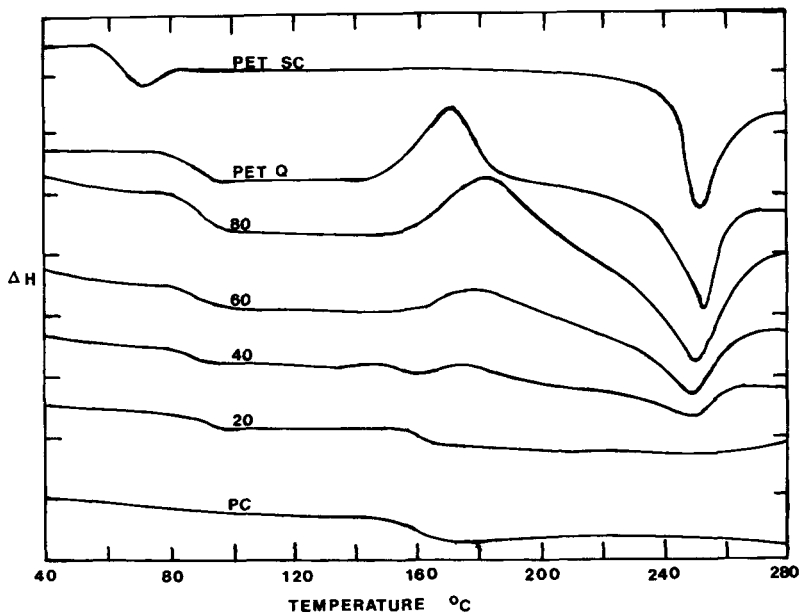


Fig. 1. Thermograms of PET slow cooled, PET quenched, PC quenched, and blends of PC and PET quenched.

is probably explainable on the quenched nature of the sample, i.e., highly amorphous with crystallizable material present increasing the viscosity.

The T_g for the polycarbonate is 154.2°C with no melting point detected. The thermograms for the blends are complex. The 80/20 PC/PET blend shows two transitions corresponding to those of the respective pure polymers. No crystallization peak or melting peak appears because the PET is a minor component. The 60/40 PC/PET blend shows both transitions and the crystallization and melting peaks. However, for 40/60 and 20/80 PC/PET only the one transition can be seen for the PET portion, and also the crystallization and melting peaks. It is suggested that the PC transition is hidden in the PET crystallization peak since the T_g values should lie in the range of 145 to 154°C which is the beginning of the PET crystallization peak. The relevant temperatures of the transitions and peaks are in Table I.

The T_g of the PET phase in a blend is higher than in a pure phase and the crystallization temperatures are also higher. Both these changes are attributed to an increase in the viscosity of the medium caused by the inclusion of some polycarbonate which has the effect of retarding the crystallization and the flow. The crystallization temperature seems to be sensitive to the amount of polycarbonate but no such effect is obvious for the T_g data for the PET. On the other hand the presence of PC lowers the melting point of the PET phase slightly.

It is concluded that the two polymers are quite immiscible but there is a small amount of each in the other component. On balance the blend PC60PET40 would appear to be the most compatible but the criterion of difference between the two values of T_g has little value for so few data.

Dynamic Mechanical Properties

The study of the PET is complicated by a crystallization and melting stage of the crystallites. Preliminary data on the comparison of annealed and as-molded sample on the dynamic mechanical properties were collected for PET.

Figure 2 shows the plot of the log tan δ versus temperature for PET at one Hz. The nonannealed sample (as molded) yielded a sharp peak attributable to the glass transition at 84.9°C. The annealed sample on the other hand yielded a broader and lower peak with a probable glass transition of 99.6°C. This latter curve also shows a shoulder on the high temperature side of the peak which is absent in the nonannealed sample.

TABLE I
Glass Transitions from DSC Curves

Composition	PET T_g (°C)	PC T_g (°C)	Crystallization T_c (°C)	Melt T_m (°C)
PC100PET0	—	154.2	—	—
PC80PET20	88	154.7	—	—
PC60PET40	88	148.7	171.7	245.3
PC40PET60	88	—	174.7	245.3
PC20PET80	88	—	178.7	247.3
PC0PET100	84.3	—	166.7	249.2

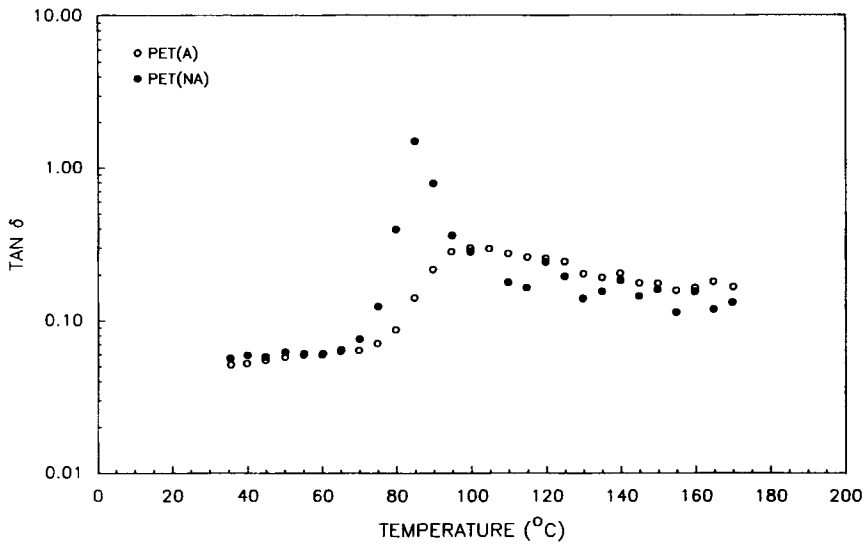


Fig. 2. $\text{Tan } \delta$ versus temperature for the PET slow cooled and annealed, at 1 Hz.

Annealing raises the glass transition temperature perhaps due to increased restrictions on the motions imposed by the crystallites. An increase with increasing crystallinity has been reported.⁸ Figure 3 shows similar data for 10 Hz with the glass transition for nonannealed (as molded) and annealed samples being 89.8 and 104.7°C respectively, some 5°C higher than for 1 Hz. The T_g values are 15–20°C higher by dynamic mechanical tests than for the DSC determination.

The plot of the storage modulus (M') versus temperature for PET at 1 Hz is in Figure 4. Below 70°C the values for the quenched and annealed sample

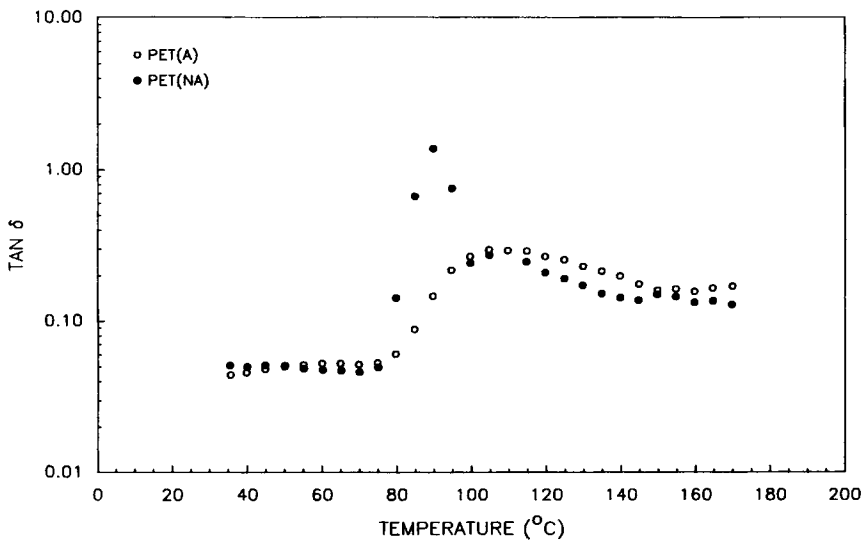


Fig. 3. $\text{Tan } \delta$ versus temperature for the PET slow cooled and annealed, at 10 Hz.

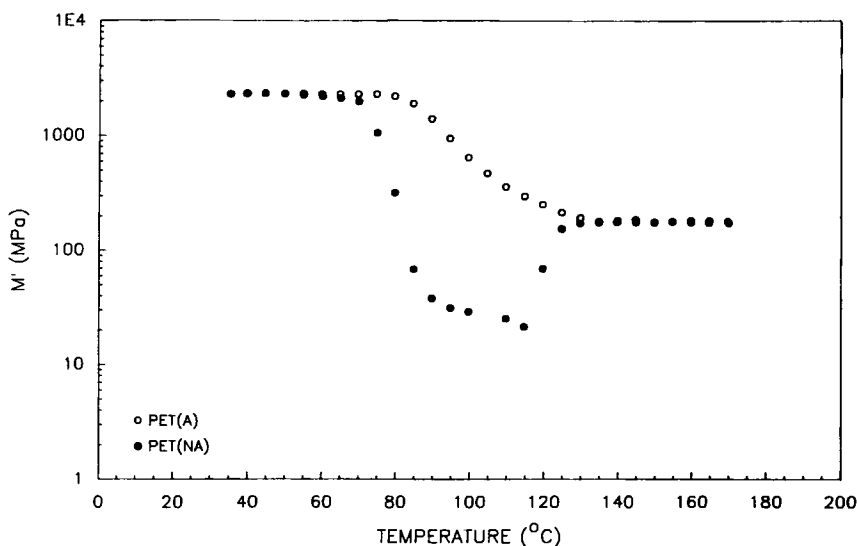


Fig. 4. Dynamic modulus versus temperature for PET slow cooled and annealed, at 1 Hz.

are the same and constant down to 35°C. The storage modulus of the quenched sample decreases above 70°C to 110°C and then increases to 130°C with an inflection point at 84.9°C, the T_g . These data are similar to those reported.³ The storage modulus of annealed PET decreases between 80 and 130°C with an inflection point at 99.6°C, the T_g . The two samples again yield the same values above 130°C up to 165°C.

The data obtained at 10 Hz are very similar, yielding T_g values of 89.8°C and 104.7°C for the quenched and annealed samples respectively, some 5°C higher than the temperatures obtained at 1 Hz (Fig. 5).

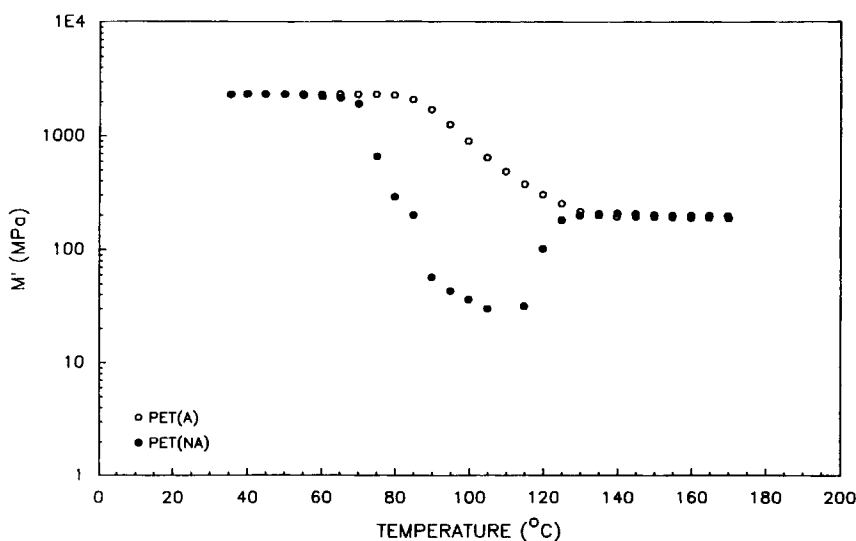


Fig. 5. Dynamic moduli versus temperature for PET slow cooled and annealed, at 10 Hz.

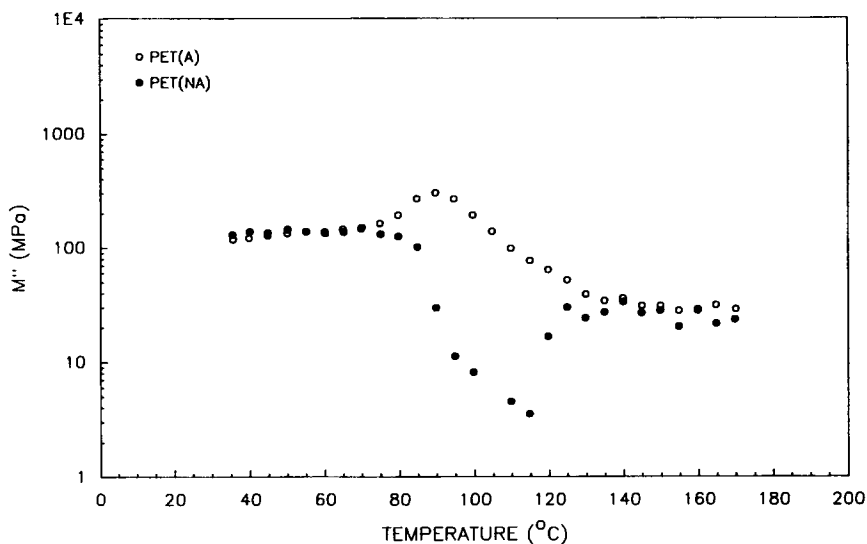


Fig. 6. Loss modulus versus temperature for PET slow cooled and annealed, at 1 Hz.

The data for the loss modulus are in Figures 6 and 7 for 1 Hz and 10 Hz respectively. The data resemble those in Figures 2 and 3 for the $\log \tan \delta$ except that the peaks interpreted as measures of T_g occur at a lower temperature.

The samples of PC/PET blends were all annealed before testing so the appropriate curves for PC and PET are included with those for the blends in Figure 8 for the $\log \tan \delta$ measured at 1 Hz. For pure PC the maximum for the peaks lies at 154.7°C, the T_g for the PC, and for PET the maximum lies at 99.6°C, the T_g of the PET. For the blends there are two peaks. The peak cor-

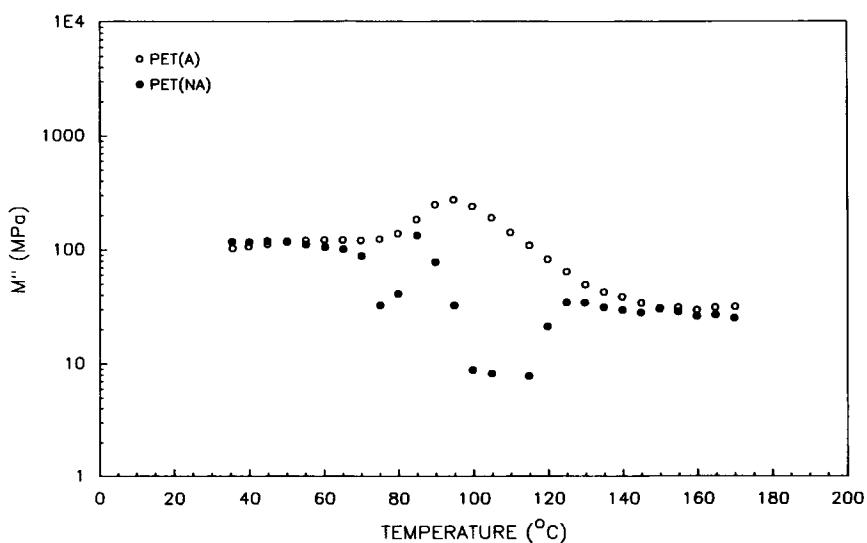


Fig. 7. Loss modulus versus temperature for PET slow cooled and annealed, at 10 Hz.

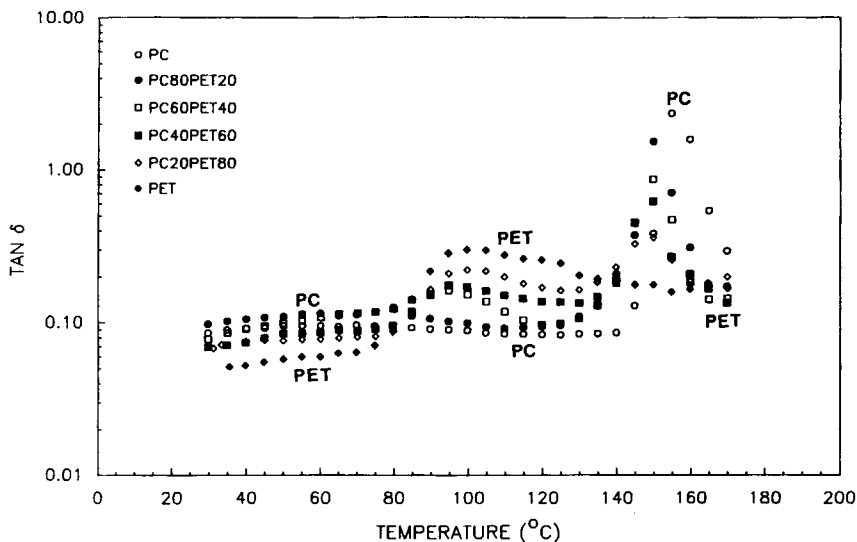


Fig. 8. $\text{Tan } \delta$ versus temperature for PC, PET, and their blends annealed, at 1 Hz.

responding to PC is unchanged at $149.75^\circ\text{C} \pm 0.05^\circ\text{C}$, somewhat lower than that of the pure PC. For the 20/80 PC/PET blend the PET rich region transition is 99.7°C , the same as for pure PET. The transitions for 40/60 and 60/40 PC/PET blends are at 94.7°C and when the ratio is 80/20 the temperature at the peak is reduced to 79.8°C . The reason for the reduced T_g may be that the lower PET content reduces the effect of annealing so that the T_g is tending towards the quenched values. The presence of some PC in the PET may well restrict crystallization, an effect which increases with reduced PET in the blend.

The data are consistent with the suggestion that the two polymers are essentially incompatible, very little PET enters the PC phase and only enough PC enters the PET phase to restrict crystallization on annealing. It has been suggested³ that PC/PET blends are incompatible with less than 50% PET and (slightly) compatible at and over 60% PET in the blend. Differences between the two sets of data may well be related to the use of the copolyester in this study.

Very similar data were obtained (Fig. 9) for the same samples at 10 Hz. The T_g values were for PET 79.8°C , for PC 154.7°C , for 80/20 PC/PET 79.8°C and 154.7°C , for 60/40 PC/PET 97.7°C , and 154.8°C , for 40/60 PC/PET 104.7°C and 149.7°C , and for 20/80 PC/PET 104.7°C and 149.8°C .

The corresponding plots of the dynamic modulus (Fig. 10 and 11) for 1 Hz and 10 Hz respectively show values which are independent of blend ratio and are constant from 30° to 80 – 85°C . The inflection point for pure PET is 99.6°C and for pure PC is 154.7°C . The blends show two inflection points associated with the glass transitions of the respective phases. The storage modulus increases with increasing PC content in the blend between 155 and 165°C . As previously, the increase in frequency from 1 to 10 Hz raises the glass transition, as measured, by about 5°C .

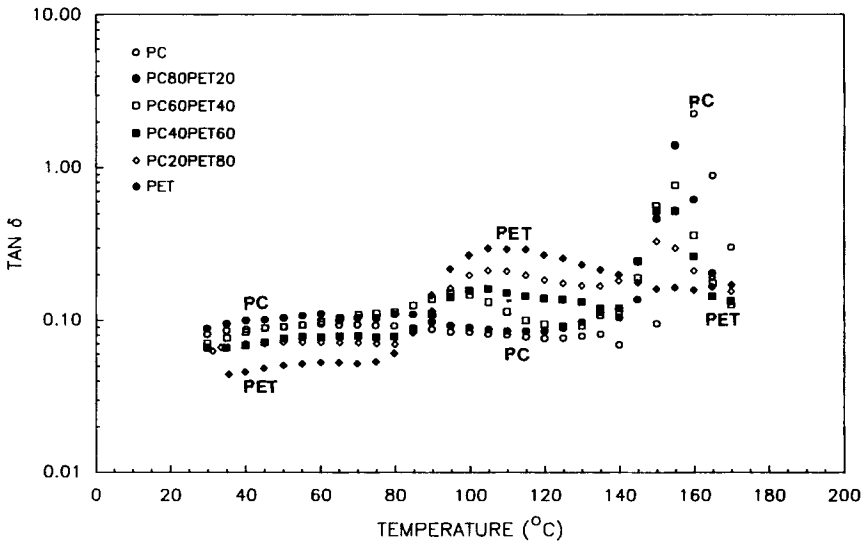


Fig. 9. $\tan \delta$ versus temperature for PC, PET, and their blends annealed, at 10 Hz.

The plots of loss moduli are in Figures 12 and 13 for 1 and 10 Hz respectively. As expected, the curves are very similar to those for $\log \tan \delta$ (Figs. 8 and 9) and show the same trends.

An extension of the dynamic mechanical plots was made similarly to Han et al.⁹⁻¹¹ who noted that when the dynamic modulus was plotted against the loss modulus for polymer melts on a log scale a curve was obtained which was independent of temperature and frequency, i.e., these measurements appear on

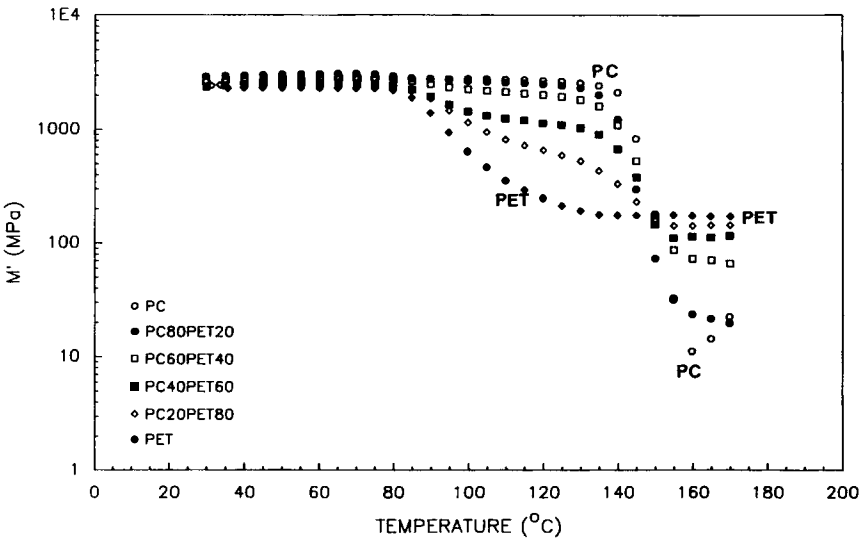


Fig. 10. Dynamic moduli versus temperature for PC and PET, and their blends annealed, at 1 Hz.

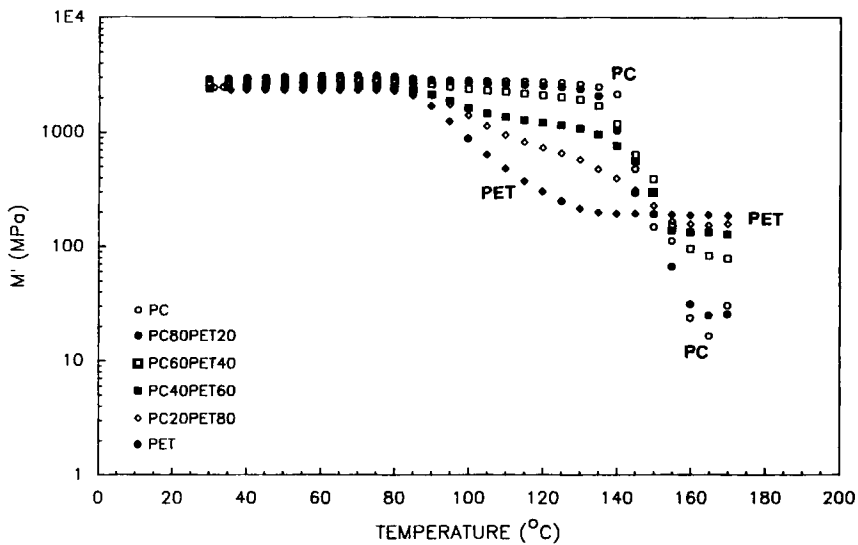


Fig. 11. Dynamic moduli versus temperature for PC and PET, and their blends annealed, at 10 Hz.

two additional dimensions at 45° to the log-log plot. The plots were extended by Rong and Chaffey¹² through the glass transition of titanium dioxide filled polystyrene. Similar plots were attempted for the PC/PET polymers and copolymers. They did not reveal any new data but reflected the changes in the loss factor, dynamic modulus, and loss modulus as expected.

The M'' curves show peaks which may be used to estimate a glass transition temperature. However, the curves are flat and do not yield values of sufficient

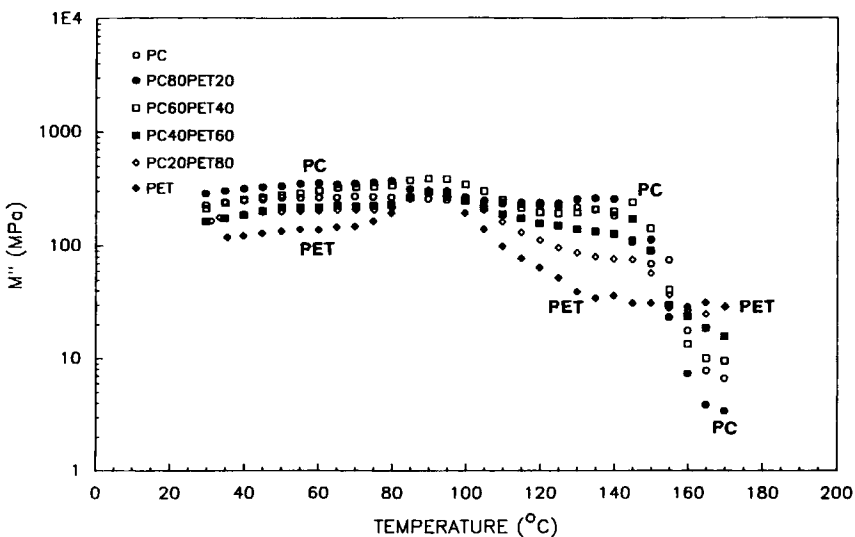


Fig. 12. Loss moduli versus temperature for PC, PET and their blends, annealed, at 1 Hz.

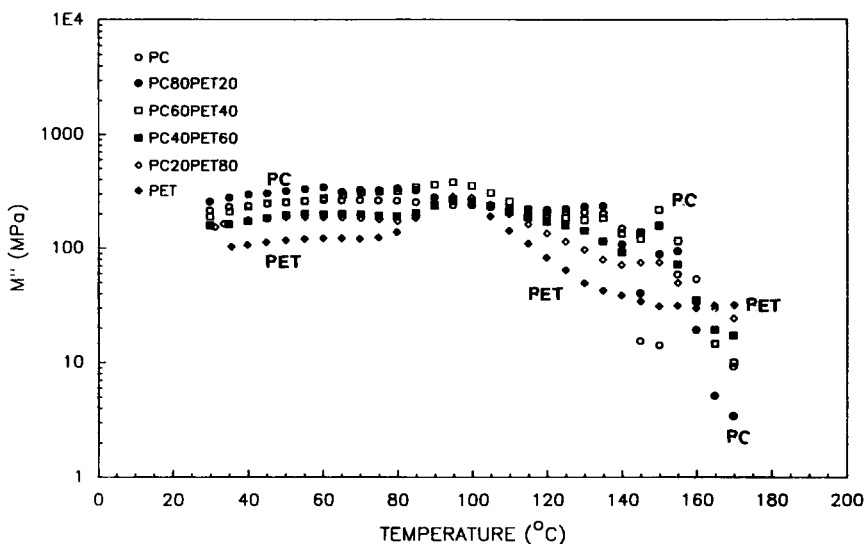


Fig. 13. Loss moduli versus temperature for PC, PET, and their blends, annealed, at 10 Hz.

accuracy for internal comparisons from which to deduce something about compatibility although the glass transition temperatures so obtained would lie closer to those obtained by DSC than do those derived from the $\tan \delta$ curves.

In practice, such blends would be used, for example, to make articles by injection molding. Under such conditions the blend would be quenched. Subsequently with time and particularly with heating the PET portions would crystallize changing the properties. This possibility would have to be considered and the time effects eliminated by annealing at a temperature somewhat above the glass transition temperature and below the melting point of PET.

CONCLUSIONS

Polycarbonate-polyester blends have limited miscibility at 20 and 40% PET as indicated by DSC measurements and at 80% PET as indicated by dynamic mechanical measurements. The glass transition attributable to the PET-rich phase is insensitive to blend ratio according to the DSC measurements but somewhat concentration dependent according to the dynamic mechanical tests. The crystallization temperatures and melting points of the PET phase depend on the concentration in the blend at least from 40 to 80% PET. There is no crystallization or melting peak in the DSC measurement for 20% PET in the blend.

Slowly cooled PET clearly shows a glass and a melting transition (T_m). A quenched sample yields a higher glass transition temperature, then shows a crystallization peak followed by a melting transition which closely reproduces that of the slowly cooled PET. The crystallizable material appears to raise the glass transition temperature and yields the crystallization peak, but the size of the subsequent melting peak is not changed substantially whether the sample has been slow cooled or quenched previously.

DSC data show that the T_g of PET is slightly increased and remains constant. The crystallization temperature (T_c) increases slightly with increasing PET and obscures the T_g of the PC-rich phase above about 50% PET. The T_m also decreases slightly, probably indicative of some PC in the PET.

Dynamic mechanical tests of slow-cooled and annealed PET showed that the latter had a glass transition only whereas the former had both a T_g and a T_c . The annealed blends below 80°C yielded constant values for M' but composition dependent values for M'' and $\tan \delta$. Above 80°C the blend values lay between those of PC and PET, the values being highest for PET at its expected T_g and highest for PC at its expected T_g for $\tan \delta$ and the reverse for M' and M'' , i.e., lowest.

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