

# A Dynamic-Mechanical Study of Polycarbonate-Polystyrene 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 (PC) and polystyrene (PS) were melt-blended and molded for dynamic mechanical tests on a Dynastat. Corresponding powders were submitted to thermal analysis using the differential scanning calorimeter. The deduced glass transition temperatures of the blends and those of the pure polymers were compared to estimate the miscibility of the two polymers.

## INTRODUCTION

Studies of blends of polymers have been made for a long time. The field remains very active, driven by attractive commercial applications. One aspect of the blends is that of compatibility or miscibility<sup>1</sup> and, in turn, one measure of compatibility is the glass transition temperature obtained by dynamic mechanical measurements or by calorimetric measurements. If the two polymers are completely immiscible the two individual glass transition temperatures will be found in the blend, whereas if the two polymers are miscible one new glass transition temperature will be found between those of the pure components. Intermediate cases of partial miscibility are also of interest.

Two techniques were used to determine the glass transition temperature, the differential scanning calorimeter and the Dynastat mechanical spectrometer which yields the anelastic spectrum, the loss factor, storage modulus and loss modulus, from which values defined as the glass transition temperature are deduced.

These techniques were applied to bisphenol-A polycarbonate (PC) and to polystyrene (PS) and blends of the two. Blends of polycarbonate and polystyrene have been studied before.

Blends of polycarbonate (PC) and polystyrene (PS) are claimed in a patent assigned to the Dow Chemical Co.<sup>2</sup> Krause<sup>3</sup> in a review quoted a study that reported that PC/PS blends yielded phase separation in cyclohexanone solution, interpreted to show incompatibility.

Groeninckx et al.<sup>4</sup> studied the morphology of PC/PS blends as well as their mechanical properties from which they concluded that the PS inclusion in a 75/25 PC/PS blend was particularly helpful in enhancing the properties between the two glass transition temperatures of the two pure components. Kunori

\* Present address: Department of Chemistry, University of Toronto.

and Geil<sup>5</sup> concluded from dynamic mechanical and thermomechanical studies that PC and PS were somewhat bonded in blends by low mutual solubility in these essentially incompatible blends. Lipatov et al.<sup>6</sup> studied the viscoelastic properties of blends in the melt and noted greater changes at low concentrations of one component in the other. Rudin and Brathwaite<sup>7</sup> noted that the closeness of the refractive indices resulted in transparent blends but that actually up to about 15% PS was probably "dissolved" in the PC, a concentration which corresponded well with a change in the die swell of the molten extrudates and the onset of brittleness in the tensile test. Wisniewski et al.<sup>8</sup> also concluded that a limited miscibility existed at each end of the blending range from viscoelastic data. Bye and Miles<sup>9</sup> reported viscosity data in agreement with the foregoing for polystyrene containing up to 10% polycarbonate. Kim and Burns<sup>10</sup> concluded from thermomechanical data that the  $T_g$  of the PC phase decreased as the PS in the blend increased but the  $T_g$  of PS increased with increasing PC. PS seemed to dissolve more in the PC phase than the reverse.

It seemed to be worthwhile to investigate the blends by dynamic mechanical methods further and to repeat the thermomechanical studies to enable correlation with the previous studies of the thermal and viscoelastic properties.

## EXPERIMENTAL

### Equipment

The differential scanning calorimeter unit attached to a du Pont 990 Thermal Mechanical Analyzer was operated in the normal way.<sup>11</sup> The dynamic mechanical measurements were made using a Dynastat from IMASS which has been described both as to construction and operation by Sternstein.<sup>12</sup> The bar samples were tested by three-point bending.

### Materials

The polycarbonate (PC) was a commercial grade of "Calibre" kindly supplied by the Dow Chemical Co. and identified as 300-15. It was composed of amorphous pellets. The melt flow by ASTM condition 0 was 13.60 g.

The polystyrene (PS) Styron, also supplied by Dow Chemical Co. was labeled 678 C 26 and was also in the form of amorphous pellets. The melt flow index by ASTM condition G was 11.25 g.

### Sample Preparation

The pellets were dried at least 24 h at 80°C under vacuum and stored in a dry atmosphere 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 samples.

Each sample was treated in a C. W. Brabender Twin Screw Extruder with three heating zones. The initial throughput was a purge in each case. The three zones were heated to 255, 265, and 275°C for polycarbonate and to 200, 215, and 225°C for the polystyrene. For the blends the first and second zones were

heated to 200 and 215°C, but the third zone was heated to 235, 230, 230, and 225°C as the amount of polycarbonate in the blend was reduced.

Bars were molded in a ram type injection molding instrument, 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 and mold temperature for the polycarbonate were 310°C and 120°C and for the polystyrene and the blends they were 250°C and room temperature.

The samples for dynamic mechanical testing were cut from the tensile bar to a length of about 60 mm and annealed for 18 h at 120°C.

### Differential Scanning Calorimeter Procedure

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 scale was one 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 (mv) were converted in the usual way to obtain the temperature.

### Dynamic Mechanical Procedure

The testing was done using three-point bending (flexure) and in the low range displacement control mode. The static and dynamic loads were 2 and 1 kg. The frequency was varied from one to 50 Hz with five intervals in the logarithmic scale. The temperature was from room temperature to 125–170°C depending on the polymer or blend and measurements were made at 5°C intervals. The data reported here are for 1 and 10 Hz only.

## RESULTS AND DISCUSSION

### Thermal Properties

All samples were measured at least four times and the reproducibility was excellent. The measurements were always preceded by an initial heating over the full range as mentioned earlier. The thermograms for PC, PS, and the blends are in Figure 1. For the pure polymers the glass transition temperatures are 92°C for polystyrene and 154.7°C for the polycarbonate.

For the blends there are always two peaks, i.e., glass transitions, corresponding to the two components. As the PC in the blend increased, the  $T_g$  of the PS phase, the lower peak, increased from 99.5°C to 106.3°C. The presence of some PC in, or around, the PS phase raised its measured  $T_g$ .

Conversely the glass transition of the PC phase diminished to range from 148.7 to 144.7°C as the PS phase increased. Thus the two components appear to have some mutual solubility, there being somewhat more effect of PC raising the  $T_g$  of PS than of PS lowering the  $T_g$  of PC. These data agree with previous observations. (The data are summarized in Table I.)<sup>5,7,8,10</sup>

It is apparent from Table I that the  $T_g$  of the PS phase passes through a maximum for the PC60PS40 blend and the  $T_g$  of the PC phase passes through

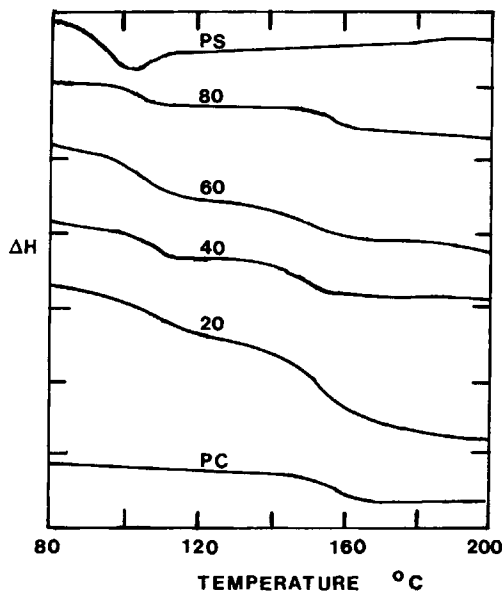


Fig. 1. DSC curves for polycarbonate, polystyrene, and their blends.

a minimum for the same blend suggesting that at or near that ratio there is a maximal mutual solubility or interpenetration.

### Dynamic Mechanical Properties

The plots of  $\tan \delta$  versus temperature for PC, PS, and their blends are in Figure 2. Taking the maximum of the peak as the measure of  $T_g$  then the  $T_g$  for PC is 154.7°C and for polystyrene is 99.7°C at 1 Hz. The blends show two peaks, the peak corresponding to the PS component ranges from 99.7 to 114.8°C while the peak for the PC rich phase ranges from 139.7 to 149.7°C. These data show that the two components are slightly compatible as indicated earlier by the DSC measurements and in confirmation of the earlier literature.<sup>5,7,8,10</sup> The measured  $T_g$  values and the differences are in Table II.

TABLE I  
Glass Transition Temperature from DSC Curves

Composition	PS Phase $T_g$ (°C)	PC Phase $T_g$ (°C)	Difference (°C)
PC0PS100	92.0	—	—
PC20PS80	99.5	148.7	49.2
PC40PS60	103.5	146.7	43.2
PC60PS40	106.3	144.7	38.4
PC80PS20	105.3	148.7	43.4
PC100PS0	—	154.7	—

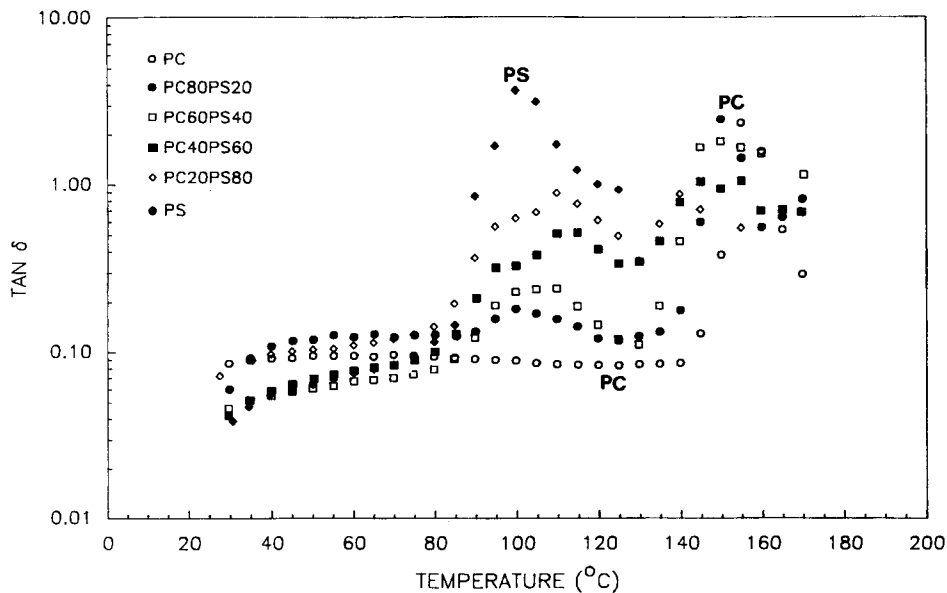


Fig. 2.  $\tan \delta$  curves for polycarbonate, polystyrene, and their blends at 1 Hz.

The compatibility is higher at the high styrene range of the blends, probably maximal when the blend is about 60% PS. Figure 3 shows comparable data at 10 Hz. There is a general shift to higher temperatures for the peak  $\tan \delta$  and some evidence of greater effective compatibility. The  $T_g$  values, as above, are listed in Table III.

A difference from the DSC data is that the maximal increase in the  $T_g$  of PS and the maximal decrease in the  $T_g$  of the polycarbonate rich phase are for the 40/60 polycarbonate/polystyrene blend.

The plot of storage modulus ( $M'$ ) versus temperature is in Figure 4. The storage moduli are the same for all of the polymers and blends up to 80°C. For the pure polymers there are inflections at their respective glass transitions and for the blends there are two inflections, corresponding to the two components but displaced as described above for the  $\tan \delta$  plots. Above 80°C the storage moduli are higher the higher the PC content of the blend.

TABLE II  
Glass Transition Temperatures from  $\tan \delta$  Curves at 1 Hz

Composition	PS Phase $T_g$ (°C)	PC Phase $T_g$ (°C)	Difference (°C)
PC0PS100	99.7	—	—
PC20PS80	109.7	139.7	30
PC40PS60	114.8	144.8	30
PC60PS40	109.7	149.7	40
PC80PS20	99.7	149.7	50
PC100PS0	—	154.7	—

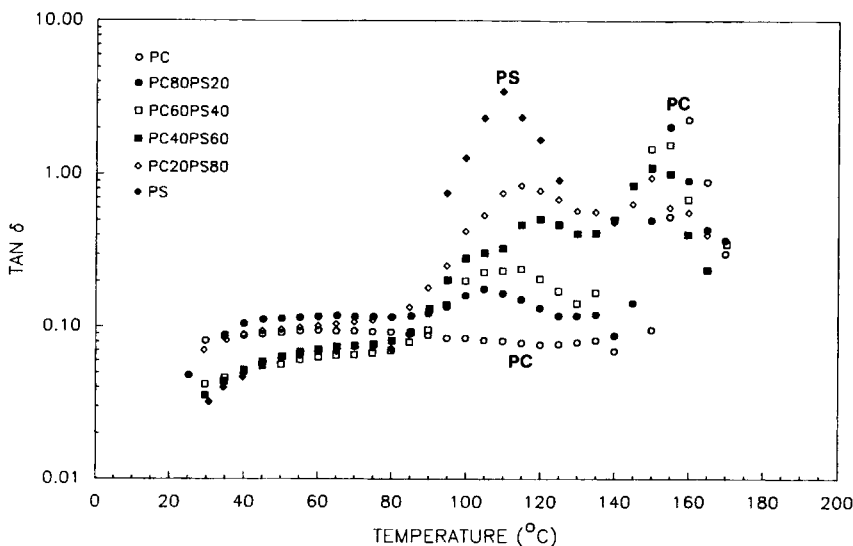


Fig. 3.  $\tan \delta$  curves for polycarbonate, polystyrene, and their blends at 10 Hz.

Very similar data are observed for the storage moduli tests at 10 Hz, Figure 5. The inflection points are at slightly higher temperatures and the storage moduli are slightly higher at 10 Hz than at 1 Hz.

Figure 6 is the plot of the loss moduli ( $M''$ ) versus temperature at one Hz. In general the curves are similar to the log  $\tan \delta$  plot Figure 2, but the peaks of the curves occur at lower temperatures. The same is true for the loss moduli ( $M''$ ) at 10 Hz (Fig. 7). The loss moduli differ below 80°C, those of 60% PC being the lowest, then PS and PC40PS60, then PC, followed by PC20PS80 and highest for PC80PS20. Above 80°C the curves lie in the order PC highest to PS lowest.

An extension to the dynamic mechanical plots was made by Han and coworkers<sup>13-15</sup> who noted that when the dynamic modulus was plotted against the loss modulus for molten polymers on log scales a curve was obtained which was often independent of temperature and frequency, i.e., these measurements appear on two additional dimensions or axes at an angle to the log-log plot.

TABLE III  
Glass Transition Temperatures from  $\tan \delta$  Curves at 10 Hz

Composition	PS Phase $T_g$ (°C)	PC Phase $T_g$ (°C)	Difference (°C)
PC0PS100	109.7	—	—
PC20PS80	114.7	149.7	35
PC40PS60	119.8	149.8	30
PC60PS40	114.7	154.7	40
PC80PS20	104.7	154.8	50
PC100PS0	—	159.7	—

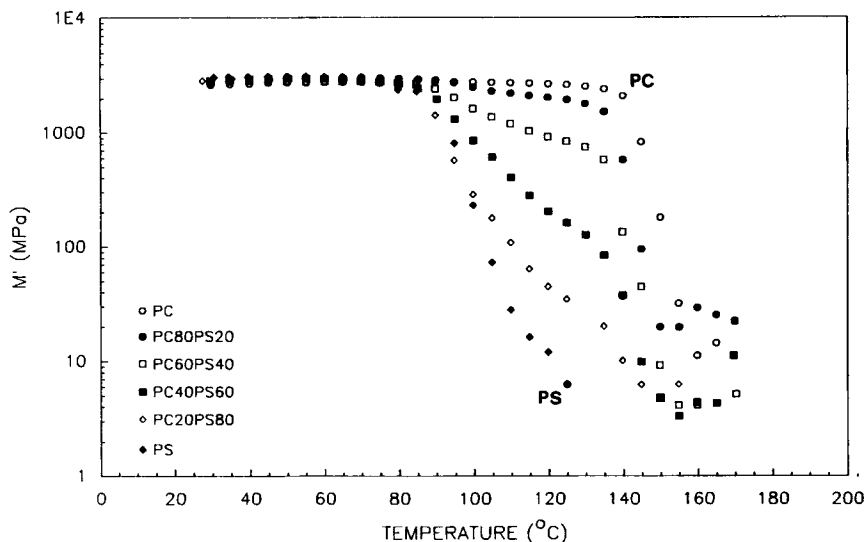


Fig. 4. Dynamic moduli for polycarbonate, polystyrene, and their blends at 1 Hz.

Extension of these plots to titanium dioxide filled polystyrene below  $T_g$  was made by Rong and Chaffey<sup>16</sup> who noted the effect of passing through the glass transition.

Thus these plots were attempted for the polycarbonate-polystyrene system. However, the plots did not seem to add any new dimension to the data. The humps expected for the loss factor appear on an axis at  $45^\circ$  to the main plot.

There is sufficient interpenetration or mutual miscibility that the blends adhere firmly<sup>5</sup> and they would not need a compatibilizer, adhesive interlayer, or toughener.

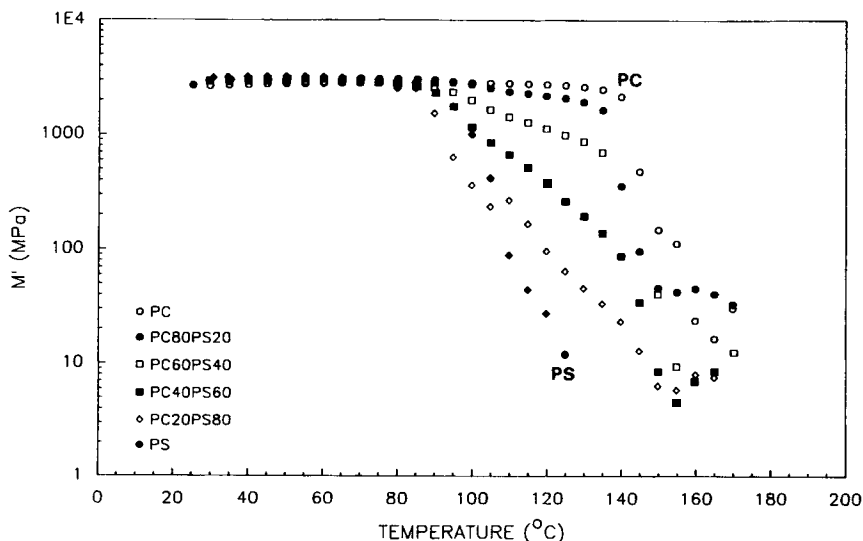


Fig. 5. Dynamic moduli for polycarbonate, polystyrene, and their blends at 10 Hz.

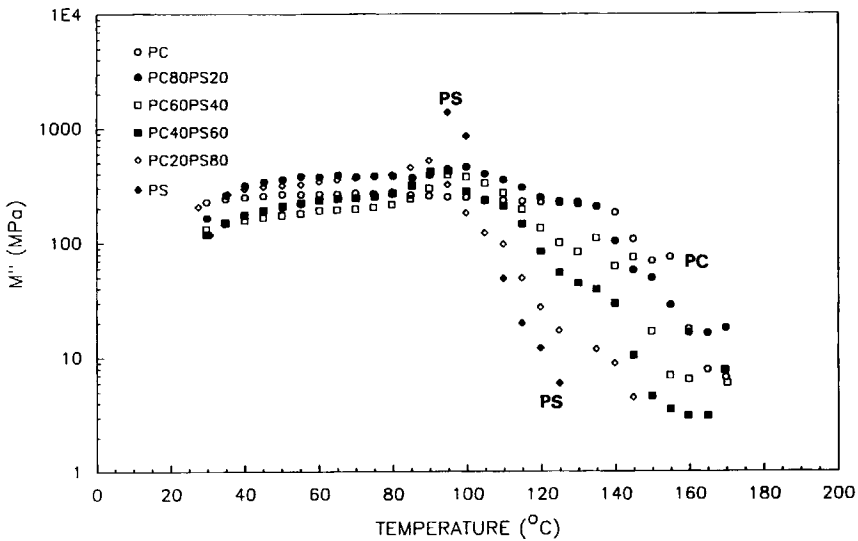


Fig. 6. Loss moduli for polycarbonate, polystyrene, and their blends at 1 Hz.

The data compare well with those of Kunori and Geil<sup>5</sup> in respect to the dynamic properties and thermograms. Their data, obtained at 110 Hz with a Rheovibron, yielded similar patterns for  $M'$  and  $M''$ .

Values of the estimated glass transition temperature can be made also from the plots of  $M'$  and  $M''$  versus temperature. The values from the plots of  $M'$  would be quite close to those obtained from the data for the  $\tan \delta$  versus temperature. On the other hand, those from the plots of  $M''$  would be at a lower

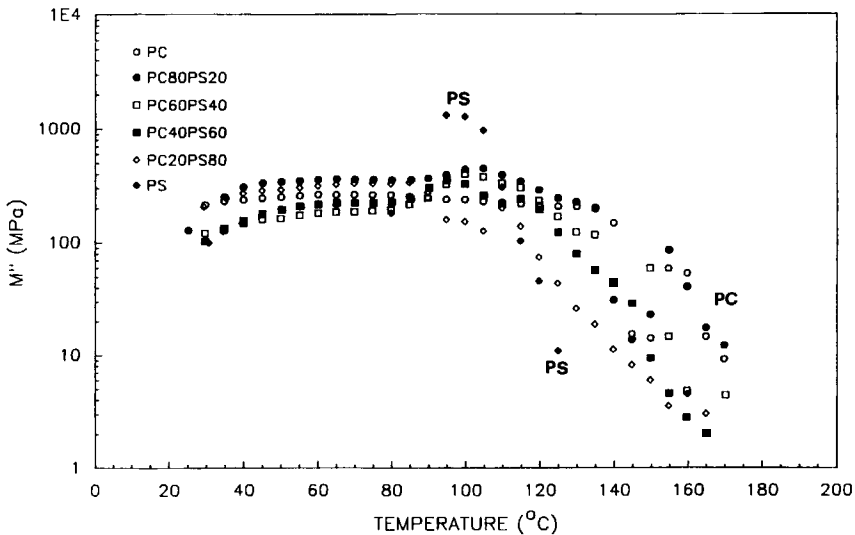


Fig. 7. Loss moduli for polycarbonate, polystyrene, and their blends at 10 Hz.



temperature and thus they would lie nearer to the values obtained by the DSC technique. These values were not used since the peaks of the  $M''$  curves tend to be flat and to yield numbers which are less helpful for comparing the blends for evidence of miscibility.

It should be noted that the effect of test frequency on the glass transition temperature is dependent on the polymer. For PS the values obtained by DSC and at 1 Hz and 10 Hz are 92, 99.7, and 109.7°C respectively from the  $\tan \delta$  curves and 92, 94, and 97°C when the  $M''$  curves are used. The corresponding changes in the glass transition temperature values of PC are much less: very little at 1 Hz and about 5°C at 10 Hz. This suggests that the stiff polycarbonate chain is less influenced by frequency in the dynamic test and that the polystyrene phase shows a disproportionately large response to frequency. It is tempting to suggest that PS plasticized the PC very little and that the stiffening effect of the PC on the PS is more marked.

## CONCLUSIONS

Polycarbonate-polystyrene blends are partially compatible. The location of the  $T_g$  attributed to the PC phase or the PS phase is concentration dependent by both thermal and dynamic mechanical analysis.

The  $T_g$  by DSC measurements of the polystyrene-rich phase increased to a maximum for the 60/40 PC/PS blend whereas the  $T_g$  of the polycarbonate-rich phase decreased to a minimum for the same ratio in thermal tests.

By dynamic mechanical tests a similar phenomenon was observed but the maximum and minimum were obtained with the 40/60 PC/PS blend at both 1 and 10 Hz. The  $\tan \delta$  peaks diminished in height and broadened as the percentage of a particular polymer in the blend diminished.

The dynamic moduli are constant for all polymers and blends below about 80°C but thereafter lie between the high values for PC and the low values of PS at least up to 170°C.

The loss moduli below about 80°C are above those for PC for 80/20 and 20/80 blends but above PS and below PC for 60/40 and 40/60 blends. Above about 80°C the loss moduli lie between the high values for PC and the low values of PS up to at least 170°C.

The data at 10 Hz were shifted generally to about 5°C higher temperature than observed at 1 Hz.

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