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An apparent double glass transition of polyphenylene sulfide in blends with polyarylate

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SUMMARY

Injection molded blends of polyphenylene sulfide (PPS) and polyarylate (PAR) are phase separated as evidenced by transmission electron microscopy (TEM) micrographs and the existence of glass transition temperatures (T_g's) near 100 °C (PPS) and 190 °C (PAR). Upon annealing, blends that contain 15% to 40% by weight PPS exhibited unusual double glass transition temperatures (aside from PAR's T_g at 190 °C) at ca. 88 °C and 110 °C. These transitions coincide, respectively, with the T_g's of amorphous and crystalline PPS homopolymer. PPS crystallinity and average domain size distribution were found to be larger in the skin region than in the core region. It is believed that the double T_g's are brought about by different PPS domains with two types of amorphous material.

INTRODUCTION

Immiscible polymer blends usually exhibit multiple glass transition temperatures (T_g's), each corresponding to a distinct phase in the material. Thus, in a binary blend, each constituent would manifest its specific T_g which can be conveniently observed, for example, by the peak of the loss modulus, G'', in a dynamic mechanical thermal analysis (DMTA). If the dispersed minor phase is a crystallizable polymer, whose T_g increases with the degree of crystallinity, it is possible to imagine the following situation. If a fraction of the crystallizable domains were completely amorphous and the remaining fraction highly crystalline, two G'' peaks may be seen which would correspond, respectively, to the transition of the amorphous and crystalline domains of the crystallizable polymer (A third G'' peak would be found for the transition of the other blend constituent). The two peaks may be observed if the transition temperature of the respective domains are sufficiently separated. Recently, we have observed multiple transitions in blends of polyphenylene sulfide (PPS) with a number of amorphous polymers, namely polyarylate, polycarbonate and polysulfone, which may be brought about by a morphology akin to the situation described above. Annealed blends containing about 15 to 35% by weight PPS exhibited two G'' peaks at ca. 88 °C and 110 °C, which correspond respectively to the T_g's of amorphous and crystalline PPS (1,2), and a third G'' peak at the T_g of the other constituent. In this paper we report the results for PPS and polyarylate (PAR) blends.

EXPERIMENTAL

Polyarylate (PAR) was received from Amoco (Ardel D-100). Its glass transition temperature is 190 °C (1 Hz). Polyphenylene sulfide (PPS) was received from Hoechst Celanese (FORTRON). PPS crystallizes very fast from the melt, and in molded articles its degree of crystallinity is usually around 45% (2). The crystalline melting point (T_m) is 285 °C. The T_g's of amorphous and crystalline (ca. 45%) PPS were determined in our laboratory by DMTA (1 Hz) to be 88 °C and 110 °C, respectively. Blends containing 15 to 65% by weight PPS were compounded at 20 RPM and 300 °C in a Haake extruder Model 245 and subsequently molded into test bars in a BOY Model 50M reciprocating screw injection molding machine. The melt temperature was 350-360 °C and the mold temperature 18 °C. The molded bars were annealed at 160 °C for 4 hours.

Thin sections of PPS/PAR blends for transmission electron microscopy (TEM) were prepared by microtoming at room temperature on either a Sorvall 6000 or Reichert 4D Ultramicrotome using a diamond knife. Sections, approximately 100 nm in thickness, were picked up on an unsupported 200 mesh copper grid and examined in JEOL 100 CX II transmission electron microscope operated at 100 kv.

The dynamic mechanical properties of the blends were measured on a Rheometrics Mechanical Spectrometer Model 800 (RMS-800). Injection molded rectangular specimens were subjected to torsional deformation to measure the dynamic moduli in shear, G' and G''. Sample dimensions were approximately: thickness ≃ 3 mm, width ≃ 12.5 mm, and length ≃ 45 mm. Also determined were the dynamic mechanical responses of the core and skin regions having a thickness of 1.5 mm and 0.7 mm, respectively. These thinner sections were obtained by slow removal of material from the molded bars using water-cooled sand paper wheel. This type of machining was found to have no effect on DMTA and X-ray results of PPS specimens. G' and G'' were measured from 40°C to 200°C at 100 rad/s or 0.1 rad/s. The overall heating rate was 1.3°C/min. The strain amplitude was approximately 0.3%. Preliminary experiments were run for a range of strain amplitudes to insure that G' and G'' were measured in the linear region. More data were collected around the transitions of the respective blend components to clarify the temperature dependence of G' and G'' in these regions.

RESULTS

TEM micrographs of an annealed blend containing 15% PPS are shown in Figures 1 and 2. The former is of the skin area, the latter of the core. A systematic TEM study revealed that PPS is dispersed as long rods in the PAR matrix which are highly oriented in the flow direction. The diameter of the rods at and close to the skin is 10-25 nm. Moving away from the skin towards the core, the rods become much shorter in length and take the shape of elliptical globules with maximum size of about 150 nm x 1.5 μm. The morphology of as-molded specimens (micrograph not shown) is basically the same. There is no evidence for the formation of a PPS rich layer at or close to the skin.

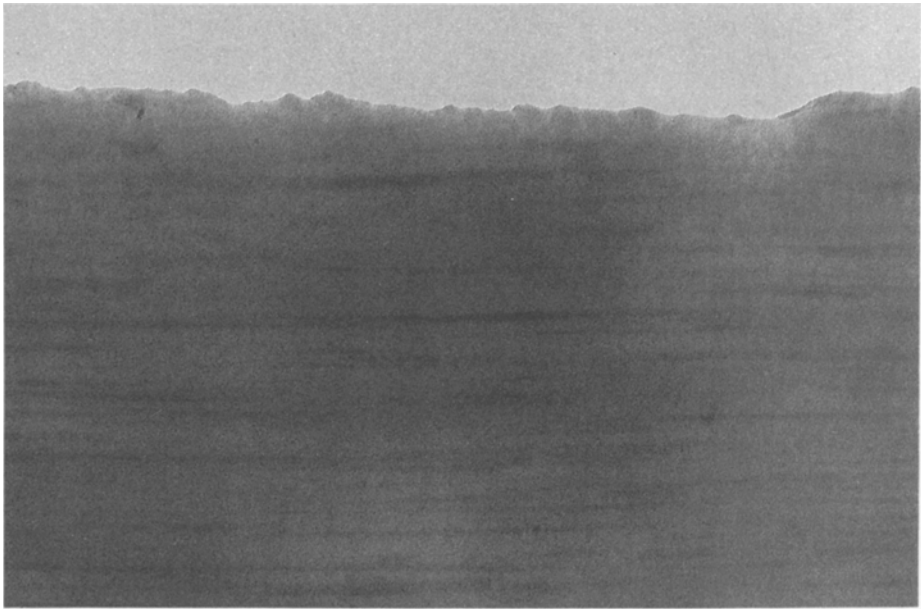

Figure 1 TEM micrograph (parallel to flow) of annealed 15% PPS blend showing stratified morphology near the surface. Dark streaks are PPS domains (87,000X).

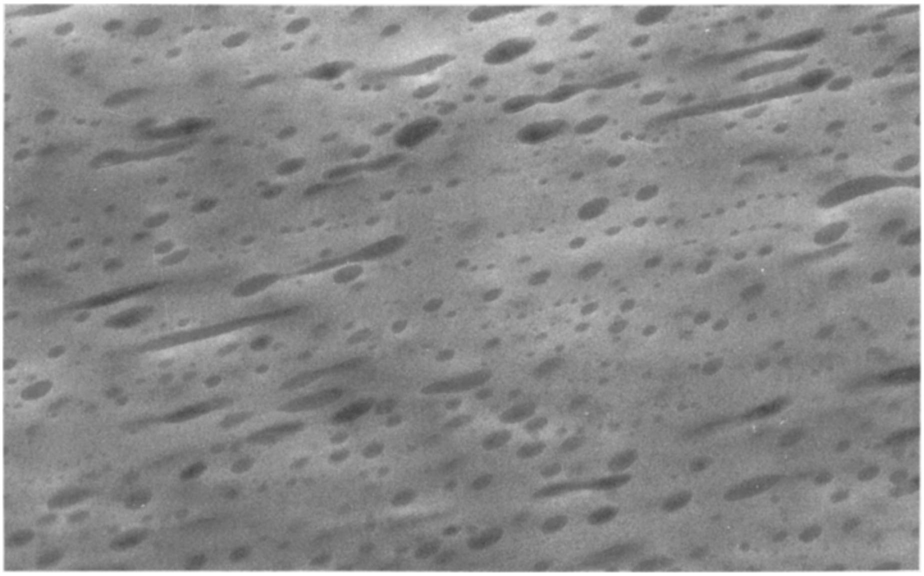

Figure 2 TEM micrograph (parallel to flow) of annealed 15% PPS blend showing core morphology. Dark globules are PPS domains (21,600X).

Figure 3 shows G' and G'' at 0.1 rad/s for a 15% PPS blend. The G'' peak in region I is at 87 °C. Also observed is the emergence of a second peak at about 105 °C (region II). These peaks are at the T_g's (0.1 rad/s) of amorphous and crystalline PPS, respectively. The third G'' peak (region III) at ca. 180 °C is the T_g of the polyarylate phase. Figure 4 shows DMTA data (100 rad/s) for 30% PPS blend. Because TEM revealed a skin-core morphology in PPS/PAR blends, both core (1.5 mm thick) and surface (0.7 mm thick) sections were tested, as shown on the Figure. The G'' trace of a whole specimen (3 mm thick) was found to lie between the traces of the core and surface sections. Table 1 lists the G'' peaks of the three regions at 0.1 and 100 rad/s.

TABLE 1: G'' Peak Temperatures (°C) vs. Frequency (30% PPS)

Frequency, rad/s	Region: I	II	III
0.1	87 (86)*	104 (104)	176
100	97 (95)	115 (114)	194

*Values in parentheses are for amorphous (region I) and crystalline (region II) PPS homopolymer.

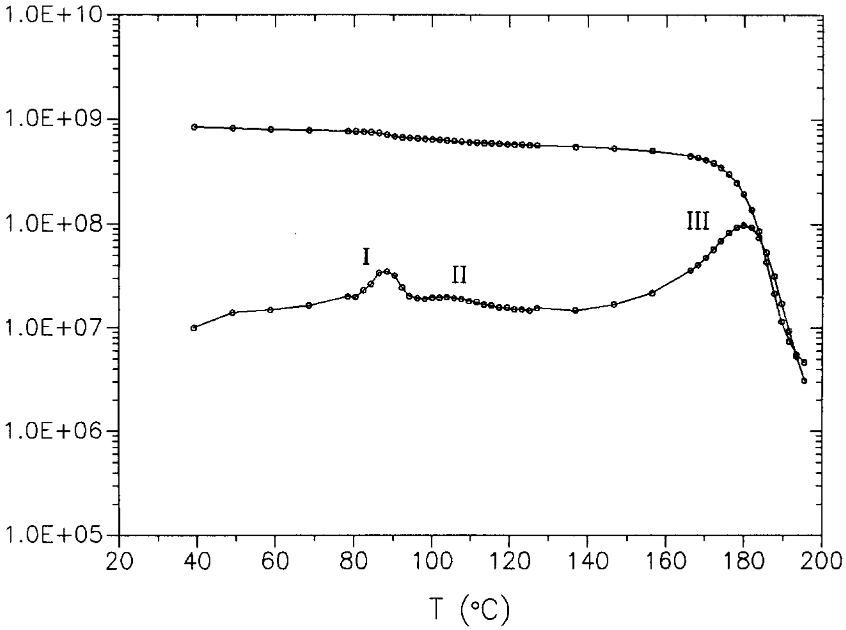

Figure 3 DMTA results (0.1 rad/s) of annealed 15% PPS blend. Region I is the T_g of amorphous PPS and region III of PAR. Note the emergence of a secondary T_g of PPS (crystalline) in region II.

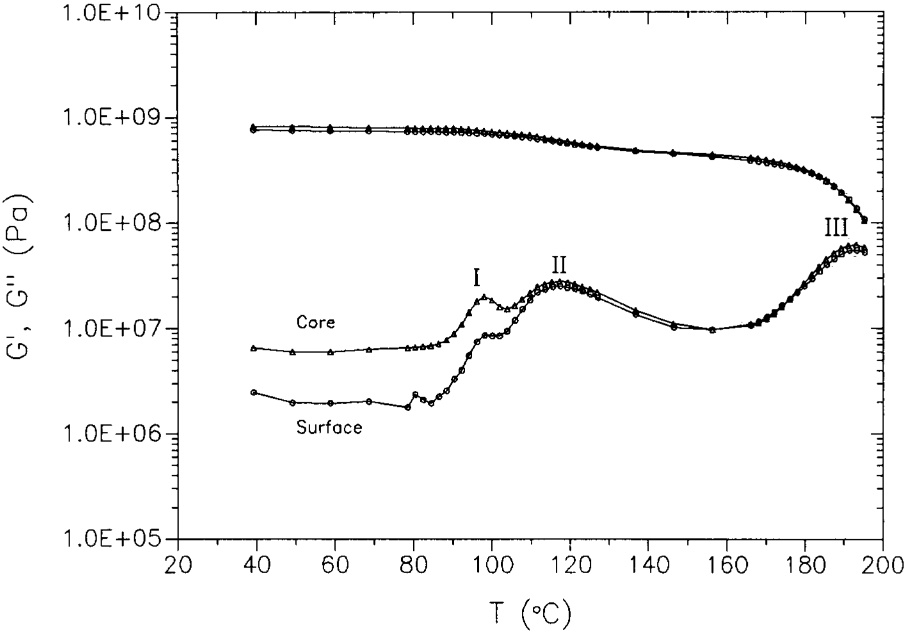

Figure 4 DMTA results (100 rad/s) of skin and core sections of annealed 30% PPS blend. Note the difference in G'' peak height in region I between the core and surface sections.

DISCUSSION

In the pursuant discussion, the glass transition temperature of PAR (region III) will not be addressed. The observed G'' peaks at regions I and II coincide in shape (i.e. sharp peak in region I, broad peak in region II) and position with those of an amorphous and crystalline PPS homopolymer. With the dynamic mechanical technique employed here the appearance of the peaks in regions I and II was seen in a limited composition range (Note: The same results were also seen in a Polymer Laboratory D.M.T.A. instrument as well as another Rheometrics machine). Below about 15% and above 40% by weight PPS, a single G'' was seen at region I or region II, respectively.

A single, broad G'' peak between region I and II was usually observed in the 15-40% PPS prior to annealing. Also, in the as-molded 20-30% PPS blends (i.e. before annealing) a small shoulder (region I) was seen as well. After annealing, the broad G'' peak between regions I and II resolved into two distinct peaks whose position did not seem to depend on blend composition between 15% and 40% PPS. The frequency dependence of the G'' peaks was the same as that of pure PPS (Table 1). It is, therefore, believed that the G'' peaks in regions I and II are manifestations of two types of PPS domains. One type crystallizes upon annealing and exhibits a glass transition temperature in region II. The other type remains amorphous and exhibits the T_g in region I.

The concept of double glass transition temperatures related to crystallinity and morphology in semicrystalline homopolymers has been reviewed by Boyer (3). A lower, $T_g(L)$, and upper, $T_g(U)$, glass transition temperature was proposed for semicrystalline polymers in that review (3). $T_g(L)$ is relatively independent of crystallinity and, in completely amorphous polymers, is the classical glass transition temperature. $T_g(U)$ increases with crystallinity and should disappear as crystallinity approaches zero. It is not clear, however, if the appearance of the two transitions in PPS/PAR blends fits the concept proposed by Boyer (3), since Boyer's idea is based on various morphological features of chain folded crystals in homopolymers. For several polymers, the ratio of $T_g(U)$ to $T_g(L)$ was calculated by Boyer (3) to be between about 1.1 and 1.4, centering around 1.2. In the PPS/PAR blend this ratio is only 1.05. Moreover, in the PPS homopolymer and in PPS/PAR blends outside 15% to 40% PPS concentration, we did not observe double glass transitions. Rather, a single T_g was seen at 88 °C (amorphous PPS) or 110 °C (annealed PPS).

In a private communication to Boyer, Illers suggested (see Ref. 3, page 535) that the two types of amorphous material in semicrystalline polymers must be physically separated to obtain two distinct T_g's. In semicrystalline homopolymers it is apparently difficult to realize a sufficient physical separation and, hence, usually a single, broad T_g is observed. The immiscible blends of PPS and PAR (as well as polycarbonate and polysulfone, Ref. 6) appear to provide the requisite conditions for the double glass transition when PPS is between about 15% and 40% by weight. The results of this study show double T_g's of PPS and suggest that this phenomenon is brought about by different PPS domains with two types of amorphous material. Hence, PPS/PAR blends may fit the Illers criterion of physical separation.

The amorphous material distribution in injection molded specimens does not appear to be uniform. TEM micrographs show different morphology and different PPS domain size distribution in the skin and in the core. The TEM micrographs, however, show no evidence for the formation of a PPS rich layer at or close to the skin. We have also conducted X-ray photoelectron spectroscopy analysis (XPS) of the surface and core of a 15% PPS. Because Si was present on the surface (mold release agent), it was not possible to determine atomic composition (i.e. carbon/sulfur) of the surface. In the core, XPS measured an atomic composition close to that expected for a 15% PPS, indicating a fairly uniform distribution of PPS. In addition, we have measured the crystallinity using wide angle X-ray diffraction. In the 30% PPS, X-ray results showed that the surface crystallinity of an annealed specimen was three times higher than in the core. In the 15% PPS, some crystallinity was seen at the surface of an annealed bar but none in the core. The dynamic mechanical data of the skin and core sections (Fig. 4) also suggest that the crystallinity in these sections is different. Looking at the relative peak heights it appears that the amount of region I type amorphous material is larger in the core, in agreement with the X-ray data.

If the crystallization of PPS in the blends is based on heterogenous nucleation it would depend on the domains size (4). The TEM data show that the size distribution and shape of the PPS domains in the skin are different from the core, i.e. elongated rods vs. small globules. Qualitatively, it appears that the average domain size distribution is larger in the skin zone than in the core zone.

Wahrmund, et al. (5) studied the dynamic mechanical properties of poly(butylene terephthalate) (PBT)/ polycarbonate blends and reported the appearance of an intermediate peak between the peak loss modulus of PBT and PC. Since the position of this intermediate peak varied with composition, Wahrmund, et al. concluded that it indicated an amorphous phase of PC and PBT in proportions that depended on overall blend composition. Thus, the phenomenon observed by Wahrmund, et al. seems to be different from ours.

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