Effect of Composition on the Mechanical Properties of Blends of the Copolymer ABS with Polyamides 6 and 12

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Synopsis

Temperature and concentration dependences of the dynamic modulus of blends of an acrylonitrile–butadiene–styrene (ABS) copolymer and polyamides in the range of main transitions of the components were investigated. Small additions of both components displace the transitions temperature into the intermediate region, and additional transitions appear for the acrylonitrile–styrene part of ABS and polyamides. The concentration change of the storage modulus of composites is not monotonic and shows extremes because of miscibility of the components at a low concentration of either component. The system separates into two phases in the range of the intermediate concentrations of components.

INTRODUCTION

The properties of polymer–polymer blends have been studied in many articles, including dynamic methods.[1–5] The mechanical characteristics of polymer blends may be described using mechanical models[6–9] which take into account volume fractions and properties of individual polymers. In real polymer systems, however, the mechanical characteristics depend not only on the phase structure of the blend and the volume ratio of the components, but also on the character of the interaction at the interface.[10] Moreover, for polymer blends an anomalous change of physical properties was observed in the range of small additions of one polymer to the other.[11] In this respect, it is of interest to examine the mechanical properties of polymer–polymer blends, especially in the range of small additions, and to analyze the mutual effect of polymers compared with their individual properties in the mixture.

This investigation is concerned with the temperature and concentration dependence of the dynamic modulus of blends of the copolymer acrylonitrile–butadiene–styrene (ABS) with polyamides–polycaproamide (P6) and polydodecaneamide (P12), viz., systems, where strong interactions between polar groups are expected.

EXPERIMENTAL

Commercial polymers were used in the investigation: polycaproamide (P6)—density 1.124 g/cm^3, melting temperature 225°C; polydodecaneamide (P12)—density 1.02 g/cm^3, melting temperature 180°C; a copolymer of acrylonitrile, butadiene, and styrene (ABS) (28:18:54 by weight)—density 1.032 g/cm^3. The blends were prepared by mixing the melts in a screw plasticator at 230°C during 4 min. Films, 0.3 mm thick, were molded at 140°C from the mixtures thus obtained. Before dynamic tests, the film samples were annealed at 140°C for 60 min and slowly cooled (0.5 K/min) down to room temperature. One part of the samples used in the comparative characterization after annealing was cooled at a rate of about 100 K/min. Dynamic tests used in the determination of the complex Young's modulus (E^*), of its loss (E'') and storage (E') parts, were performed with a Rheovibron dynamometer at 110 Hz with samples $\approx$0.03 $\times$ 0.05 $\times$ 4 cm in size. The experiment was carried out between −120 and +180°C. Stress-at-break σ_b was measured at 25°C with an Instron (type TM-M) apparatus using dumbbell-shaped samples at the rate of deformation 0.9 min^{-1}; the σ_b values were determined as an average from five measurements.

RESULTS

Temperature Dependence of Dynamic Behavior

The ABS sample exhibits two transitions (Fig. 1) (characterized by the temperature of the loss maximum on the plot logE'' vs. T): the low-temperature transition at −67°C corresponds to the glass transition of the butadiene elastomer, and its position on the temperature scale is slightly dependent on the number of polybutadiene blocks in the copolymer.[13] The high-temperature transition at T_α = 127°C owing to the randomness of the AN copolymer[14–16] should be assigned to the main transition of the acrylonitrile–styrene part of ABS. The transition corresponding to the glass transition of the amorphous part of P6 is localized (at the frequency used) near T_α = 67°C (Fig. 1), while for P12 it lies at T_α = 62°C, in accordance with published data.[17] The low-temperature transition of P6 at −55°C is due to the presence of small amounts of water (or monomer) in the polyamide.[18]
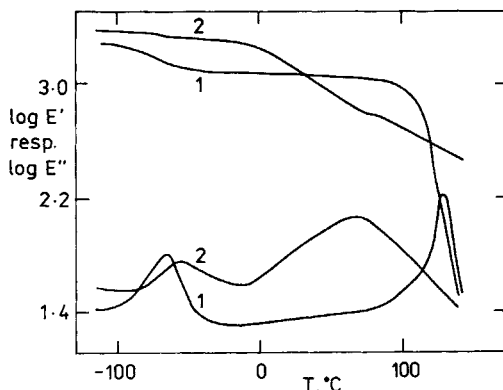

Fig. 1. Temperature dependence of the moduli E' and E'' (MPa) for the copolymer ABS (1) and polyamide P6 (2).

The viscoelastic properties of polymers depend on the thermal history of the samples,[19] because of the difference in their morphology. It is shown (Fig. 2) that the temperature dependence of log E^* is determined by the regime of cooling. In order to rule out the deviation of the properties of composites caused by this effect, all the samples were annealed and slowly cooled simultaneously in the same regime, after which the properties of the samples were stable and reproducible.

On the temperature dependence of log E'', the high-temperature transition of ABS is localized in a comparatively narrow temperature range (Fig. 3). After the incorporation of polyamides, into ABS the transition becomes broader, and an additional maximum appears at a temperature T'. It should be stressed that the additional maximum does not appear at low concentrations of polyamide P12. At first, only a displacement by 10–11 K of the high-temperature maximum of ABS towards lower temperatures can be seen. At a concentration of P12 near 5%, the maximum is split into two, and the main maximum (at higher temperature) is situated close to the original position. There is no difference between the effect of the additions of P6 and P12 on the temperature dependence of log E'', but the additional maximum already appears with 1% P6.

An additional transition appears at a temperature T'' which is close to the main transition of the polyamide component (Fig. 4). It can be observed only within the concentration range 10–20% P6 and 5–50% P12. It seems of interest that the additional maximum of polyamide is located at a temperature higher than that corresponding to the main transition.
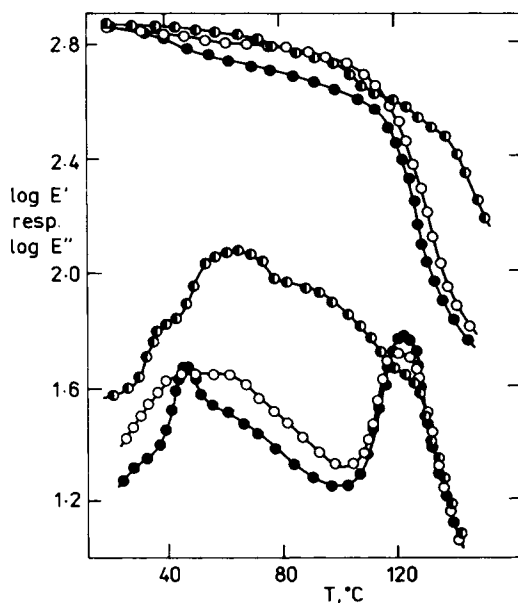

Fig. 2. Temperature dependence of the moduli E' and E'' (MPa) blend 50% ABS–50% P6 with various thermal history (◖) annealed at 140°C for 60 min and rate of cooling 100 K/min; (○) annealed at 100°C for 30 min and rate of cooling 0.5 K/min; (●) annealed at 140°C for 60 min and rate of cooling 0.5 K/min.
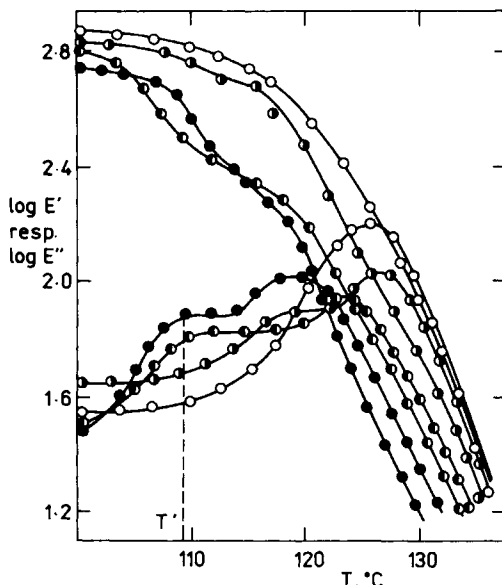
Fig. 3. Temperature dependence of the moduli E' and E'' (MPa) in the high-temperature transition region of copolymer ABS (O) ABS; (◑) 2% P6; (◓) 5% P12; (●) 5% P12 rate of cooling 100 K/min.

Concentration Dependence of Transition Temperatures and of Storage Modulus

From Figures 5 and 6 it follows that up to a certain concentration (10% P6 or 5% P12 in ABS and 5% ABS in P6), the main transitions of the minority components do not appear. One can also observe a sharp change in the main transition temperature T_α of the prevailing component with the exception of the addition of ABS to P12. The high-temperature transition of ABS appears in
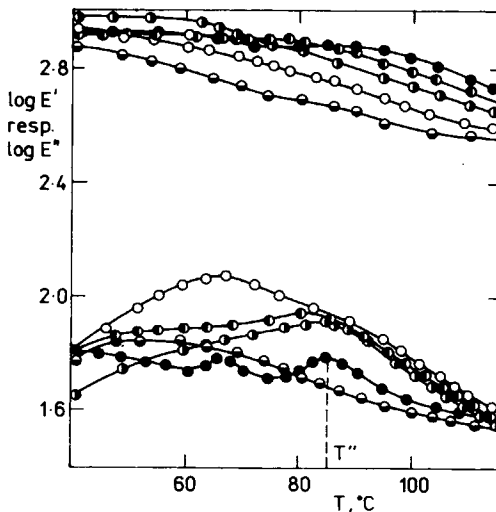

Fig. 4. Temperature dependence of the moduli E' and E'' (MPa) blends of ABS-P6 in the main transition region of P6 (O) P6; (◐) 1% ABS; (◑) 2% ABS; (◒) 5% ABS; (●) 80% ABS.
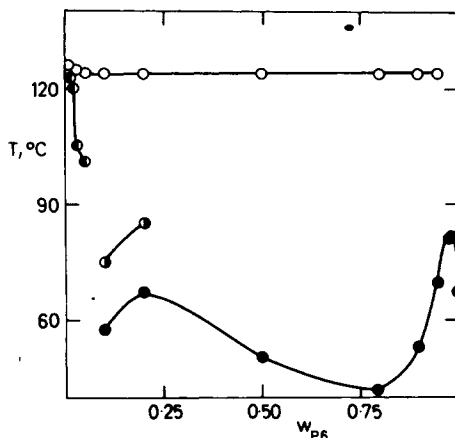
Fig. 5. Dependence of the main (T_α) and the additional (T' and T'') transition temperatures on weight fraction of P6, w_{P6}, in the blend. (O) T_α (ABS); (●) T_α (P6); (◑) T'; (◐) T''.

the blend with P12 within the whole range of compositions, including 1% ABS.

The transition temperature T_α of ABS in blends with P6 and P12 are not identical (Figs. 5 and 6). The difference consists of T_α passing through a minimum in the range of 0–5% P12 followed by its gradual increase. The dependences of T_α of ABS and P12 on composition have virtually the same shape. In the blends of ABS with P6, T_α of ABS is lowered by 4–5 K within the concentration range of 0–5% P6 and remains at this level at higher concentrations. On the contrary, the position of T_α of P6 varies with composition not monotonically and within a broad range (about 40 K) which suggests a considerable influence of ABS on the amorphous phase of P6.

The dependence of log E' on the composition of the ABS-P6 blends (Fig. 7) is not monotonic either. It may be divided into three sections: the first and the third sections are the regions of extremes, the second section is the region of
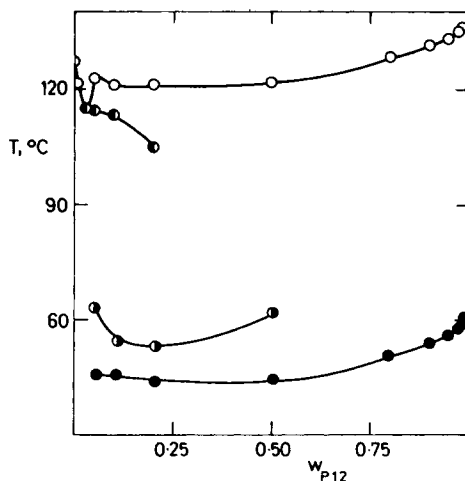

Fig. 6. Dependence of the main (T_α) and the additional (T' and T'') transition temperatures on the weight fraction of P12, w_{P12}, in the blend. (O) T_α (ABS); (●) T_α (P6); (◑) T'; (◐) T''.
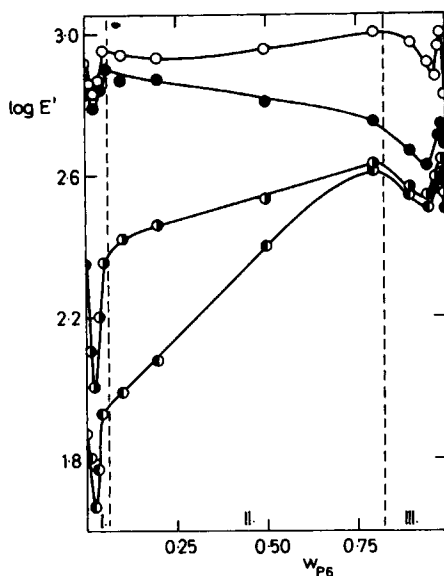
Fig. 7. Dependence of the storage modulus E' (MPa) read off at various constant temperatures on the weight fraction of P6 in the blend. (O) $T = 20°C$; (●) $T = 90°C$; (◐) $T = 125°C$; (◓) $T = 130°C$.

monotonic changes. In the range of small concentrations, one can see a pronounced drop in log E' for ABS and its rise for P6. The overall change in log E' (20°C) at intermediate concentrations (Section II) is insignificant, although its value is perceptibly higher than for the pure components. In Section II, log E' at 90°C decreases with increasing fraction of P6, while at 125 and 130°C it increases. This is because the P6 component is above its T_α at 90°C and the modulus of the blend decreases with increasing concentration of P6. On the contrary, amorphous ABS is in the rubberlike state at 125–130°C and then P6 has a reinforcing effect because of its semicrystalline structure.

DISCUSSION

The results may be given a qualitative interpretation bearing in mind the partial miscibility of the components. The dissolved minority component accounts for a displacement of T_α of the prevailing component towards T_α of the minority component. Moreover, a "rigid" additive causes a rise in E', while an "elastic" one leads to a decrease in E' of the prevailing component. Above the "critical" concentration of a polymer, the separation sets in and the system becomes heterogeneous. Basing on the absence of the main transitions of the minority components, it is possible to estimate "critical" concentrations (Figs. 5 and 6): 10% P6 or 5% P12 in ABS and 5% ABS in P6. Partial miscibility also causes a significant change in the stress-at-break values σ_b of the blends (Fig. 8). Qualitatively, addition of polyamides has the same effect on the position of the transition in ABS. However, the effect of ABS on polyamides is not equal: T_α varies for P6 more than for P12, which may be explained by a different concentration of polar groups in P6 and P12.

It also seems evident that the miscibility and the appearance of additional
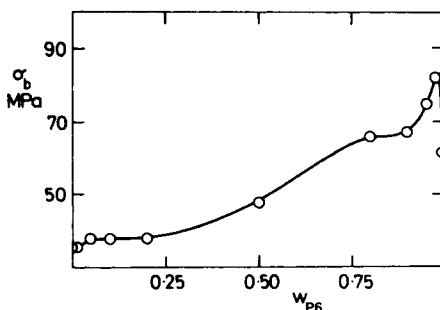
Fig. 8. Dependence of the stress-at-break σ_b (MPa) on the weight fraction of P6 in the blend.

transitions depend on the regime of cooling of the composites. The rapidly cooled sample (Fig. 2) retains the structure of an undercooled melt. As a consequence, the dependence of $\log E''$ on temperature exhibits one large maximum at intermediate temperature, indicating a very good mixing of the components. With decreasing cooling rate the intermediate maximum diminishes, while the intensity of maxima of the components increases. This suggests a gradual phase separation in the system in the process of heat treatment. This finding also allows us to explain the existence of additional transitions (Figs. 3 and 4) and their position in the intermediate range of temperatures (Figs. 5 and 6) as a consequence of the incomplete phase separation in the system as well as the existence of an interfacial layer.

Such a conclusion is also corroborated by the electron-microscopic investigation of some samples. The disperse phase of polyamide P6 in ABS could not be detected in the concentration range 0–5%. At the same time, the disperse phase of ABS in polyamide P6 could be detected already at the lowest concentrations of ABS. However, a statistical treatment of microphotographs and the calculated volume content of ABS particles in P6 revealed that in the range of small additions the volume fraction of the ABS phase was smaller than the volume of ABS added. The respective contents of the disperse phase of ABS for 99% P6–1% ABS and 98% P6–2% ABS are 0.58 and 1.2%, respectively. Also, the x-ray analysis of blends at large angles failed to reveal the crystalline phase of polyamide P6 at its concentrations lower than 10%. Consequently, in the range of small concentrations a considerable part of the added polymer remains in the dissolved state. The results clearly demonstrate that the mechanical behavior of blends of ABS with polyamides is so complicated that it cannot be described by known mechanical models of two-phase mixtures.

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