Electrical conductivity in carbon black-loaded polystyrene-polyisoprene blends.
Selective localization of carbon black at the interface

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Summary

The electrical conductivity of carbon-black loaded polystyrene-polyisoprene blends has been studied. In this ternary system, the filler is at the interface of co-continuous polyblends as confirmed by the very low value of the filler percolation threshold (0.2 vol % for blends compression molded at 250°C) and by optical microscopy. As a result of the selective localization of carbon black at the interface, the percolation threshold is very sensitive to the compression molding temperature.

Introduction

Conducting polymer composites are prepared by dispersing a conducting filler within a polymer matrix, in such a way that the individual particles contact each other. Among the available fillers, carbon black (CB) is well known for its ability in imparting conductive or semi-conductive properties to insulating polymeric materials (1-3). Futhermore, it is extensively studied as a reinforcing filler in elastomers.

A polymer composite can change from an insulator to a (semi) conductor over a very narrow range of CB concentration. This sharp discontinuity in the relationship between the filler content and conductivity of composites, often called percolation threshold point, C*, is a well documented phenomenon for several CB-polymer systems, that implies some sudden change in the dispersion state of CB. This critical point depends primarily on the shape of the filler particles and their distribution throughout the polymer matrix (3). Using a binary polymer-CB composite, distribution of CB in an amorphous matrix is uniform, so that the necessary amount of CB to reach the desired level of conductivity may be large, depending on the interplay of interactions between the components of the binary system (1).

The use of multiphase polymer blends is a good way to reduce C*. Indeed, there may be an uneven distribution of the fillers in polymer blends provided that the filler selectively interacts with one constitutive phase of the polyblend (4-6). This heterogeneous distribution should concentrate the filler inside one continuous phase or at the interface of two co-continuous phases, promoting an earlier interparticle contact at a constant loading (14,15).

This paper deals with the localization of CB at the interface of polystyrene-polyisoprene blends of a co-continuous phase morphology and the effect on electrical conductivity.

Experimental part

Polystyrene (PS : BASF 158K) and polyisoprene (PIP : Good Year NAT 2200) were used as polymer samples. Two types of CB were employed in this work : BP2000 supplied by CABOT (surface area : 1435 m^2/g; pore volume DBP : 330 cm^3/100g; average particle size : 15nm) and XE2 supplied by DEGUSSA (surface area : 1000 m^2/g; pore volume DBP : 400 cm^3/100g). Polymers were first blended with a Brabender Plasticorder, under nitrogen

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atmosphere, at 160°C for 2 min at 20 rpm. Then, the CB was added at 20 rpm, mixed during 2 min and finally dispersed for 8 min at 64 rpm. The mixtures were compression-molded under 250 Kg/cm^2, in a 0.2 cm thick mold for 10 min. Sample preparation and electrical conductivity measurements were performed as described in a previous paper by one of the authors (7).

Results and discussion

It is known that electrical conductivity in CB-loaded polymer blends is governed by two levels of percolation. The first one concerns the critical CB content in the phase enriched in filler. The other one is related to the blend ratio at which the phase co-continuity is achieved (4). Before studying the effect of CB concentration on electrical resistivity, it is worth establishing the conditions for a morphology with a dual phase continuity. Therefore, a study dealing with phase morphology as associated to polymer composition in compression-molded PS/PIP blends has been performed. The PIP phase has been selectively extracted by n-heptane from blends molded at 250°C. Figure 1 shows the dependence of the degree of co-continuity on the volume fraction of PIP in blends with PS.
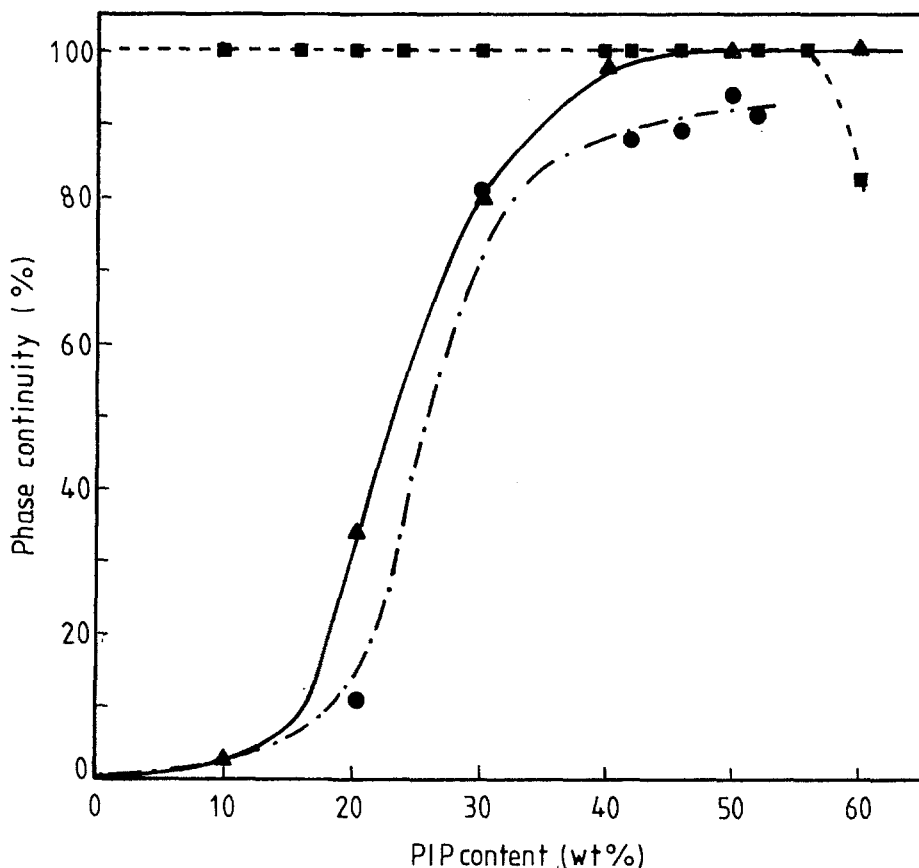

Figure 1 : Degree of phase continuity in PS/PIP blends compression-molded at 250°C. PIP continuity without (▲) and with 2 wt % CB (●). PS continuity (■).

These curves have been built up by plotting the experimental extracted weight fraction of PIP against the blend composition, as described in the literature (8). Extraction of PIP is close to completion in blends containing ca. 45 vol % PIP and more. Addition of 2 wt % carbon black (BP 2000) shifts the experimental curve towards blends of a higher PIP content and prevents more than 90 % PIP to be extracted. This observation might indicate the occurrence of a bound rubber phenomenon (9). The PIP extraction experiments show that PS forms a continuous phase in blends containing up to 55 % PIP. Above this concentration, it starts to be fragmented. It is thus clear that a dual phase continuity occurs in a composition range from 45 to 55 % PIP.

Figure 2 shows plots of the resistivity versus PIP concentration for PS/PIP blends containing 1.0 vol % of CB BP2000. For this system, the maximum of conductivity is observed for PIP composition in the 45-50 vol % range, which agrees with the extraction experiments. The conductivity values increase with compression molding temperature. This behavior might indicate that CB is localized at the polyblend interface. It has been reported in the scientific literature that compression molding of polyblends is responsible for an increase in the average domain size (10). The decrease in viscosity caused by an increasing molding temperature should result in an increased phase size and consequently in a decrease in the interfacial area. This change in morphology can affect the conductivity particularly if the conducting particles are localized at the interface. In this case, the filler concentration at the interface increases, which increases the probability for individual particles to contact each other. Additional and more conclusive evidence for CB location at the interface have been found in the dependence of the electrical resistivity on CB concentration and from optical microscopy.
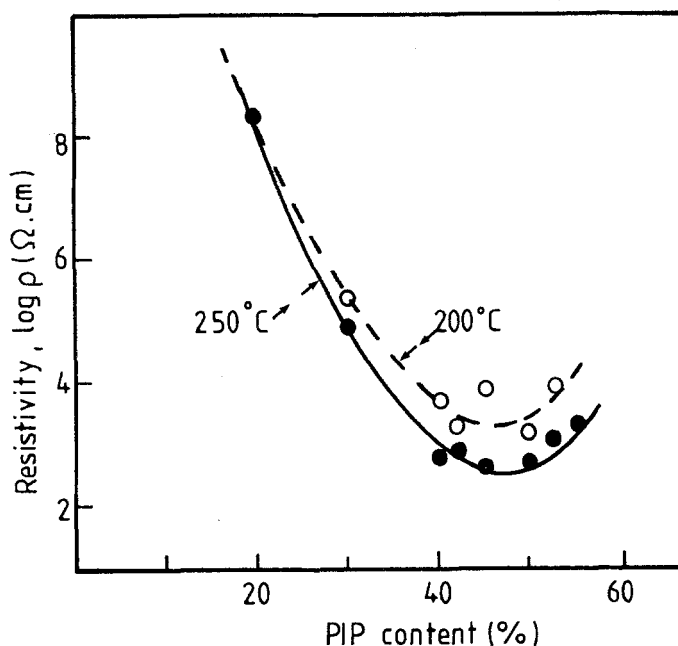

Figure 2 : Effect of the PS/PIP blend composition on resistivity in the presence of 1.0 vol % of CB at different compression molding temperatures.

Figure 3 shows the electrical resistivity of 45/55 vol % PS/PIP blends in relation to CB content and structure. Both BP2000 and XE2 type CB give similar values for the percolation threshold point. When samples are compression-molded at 200°C, this point is observed at around 0.8 vol % of CB. At 250°C, this value drops to nearly 0.2 vol %. These values are much smaller than the values found for PS-CB composites prepared under the same experimental conditions. Indeed, the percolation threshold in PS-CB composites compression molded at 200°C and 250°C is approximately 3.6 vol % and 1.3 vol %, respectively.

In PS/PIP blends, CB is expected to interact more favorably with PS because of π interactions, as suggested by Donnet and coworkers (11). Therefore, if CB is selectively localized in PS, the calculated critical CB content, C*, for the 45/55 vol % PS/PIP composite should correspond to 1.6 vol % (when molded at 200°C) or 0.6 vol % (when molded at 250°C). Actually, C* in the PS/PIP composites with BP2000 and XE2 is two times lower than the calculated value for blends molded at 200°C and three times lower for blends molded at 250°C. These results are a strong evidence for CB localization at the interface, which is supported by optical microscopy of ultrathin sections of blends compressed at 250°C (Figure 4). The average size of the phases is increased by a factor 4 when the molding temperature is increased from 200°C to 250°C, which gives credit to the explanation proposed for the temperature effect on resistivity of polyblends as observed in fig. 2.

In a previous paper by these authors (15), localization of CB at the interface of PS/PE blends was reported as a result of a kinetic control. Indeed, CB was first dispersed in the PS phase and let to migrate toward the thermodynamically preferred PE phase at a high temperature. It was observed that CB rapidly accumulated at the polyblend interface before being dispersed in the PE phase. It is thus possible to freeze in CB at the interface by cooling the polymer composite down to room temperature. In this paper, the selective localization of CB at the interface of a co-continuous PS/PIP blend is no longer kinetically controlled but it results from the thermodynamics of the PS/PIP/CB ternary system. Donnet et al. (11) have suggested that π interactions might occur between PS and CB. Actually, the same type of interactions might occur between PIP and CB. Would it be so, the CB particles should be distributed throughout the two phases, which is not observed. Thus CB does not interact favorably with unsaturated polymers, such as PS and PIP, which results in the selective localization of CB in the PE phase of PS/PE blends (15).
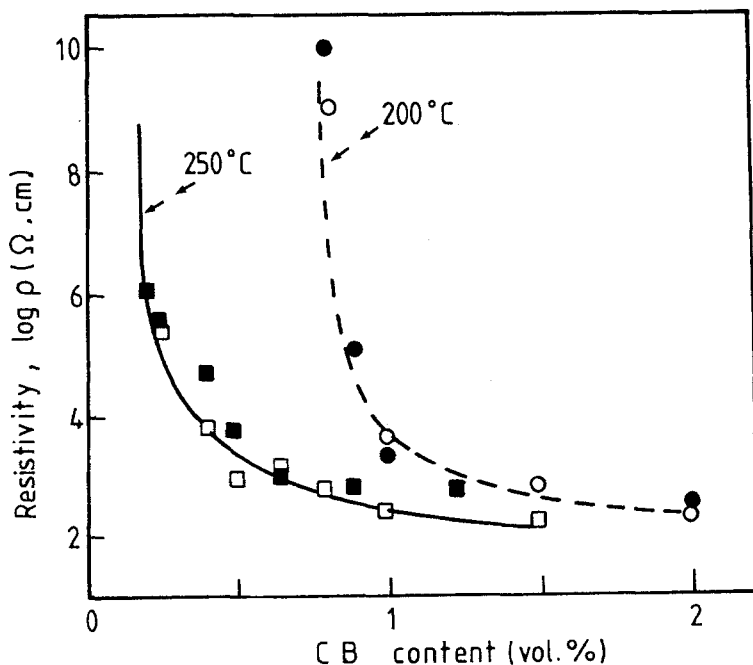

Figure 3 : Effect of CB concentration on resistivity of 45/55 vol % PS/PIP composites, using (●, ■) BP2000 type CB and (○, ❑) XE2 type CB; (●, ○) molded at 200°C and (■, ❑) molded at 250°C.
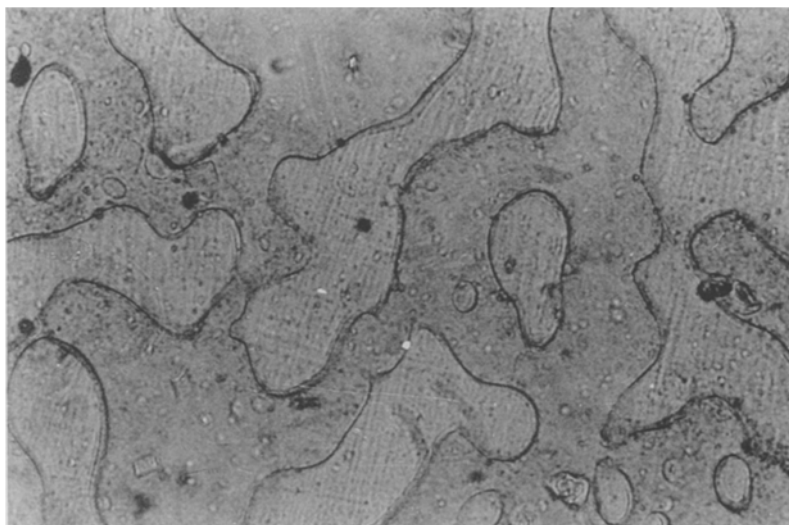
Figure 4 : Optical micrograph of 45/55 vol % PS/PIP composites containing 1.0 vol % of XE2 type CB, molded at 250°C.

Conclusions

The critical CB content at the percolation threshold point, C^*, for PS/PIP conductive composites is significantly smaller than the value calculated for the selective localization in one phase. It also depends on the compression molding temperature. There is no difference in the electrical behavior when different electrically conductive CB are used, such as BP2000 and XE2. Nevertheless, XE2 is expected to provide a given level of conductivity at a smaller content than other conventional electroconductive furnace blacks, because of a higher porosity, as stated by Donnet and co-workers (12). However, the three-dimensional structure of CB is less critical for conductivity when the particles are localized in a two-dimensional space such as a binary blend interface.

Finally, a percolation treshold of 0.2 vol % of CB, as found in this system, can only be accounted for by formation of a chain-like structure or a two-dimensional structure, as pointed out in a review on this subject (3). Similar values have been reported for composites with conducting fibers (3,13).

Acknowledgments

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