

Segregated Structures in Carbon Black-Containing Immiscible Polymer Blends: HIPS/LLDPE Systems

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ABSTRACT: The structure/electrical resistivity relationship in CB-loaded immiscible HIPS/LLDPE blends was studied. Effects of CB content and location, dispersed polymer phase size and shape, dispersed phase viscosity, and processing procedures were examined. The elongated dispersed phase in CB-containing blends is essential for promoting conductivity in formulations prepared by melt mixing and compression molding. However, the same formulations proved highly resistive when injection-molded, due to orientation and excessive shearing. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1097–1106, 1997

INTRODUCTION

Polymer blends assume an important role in CB-filled polymer systems due to the tendency of the filler to accumulate preferentially in certain regions within the multi-phase matrix.¹ This induces the formation of segregated structures whereupon CB may form a network,² enhancing the electrical conductivity and reducing the critical CB content essential for percolation. The practical advantages of low CB loadings in terms of processing, cost, and mechanical properties are apparent^{3,4}; however, the complexity introduced by multi-phase polymer systems, their structure and properties, demands an in-depth understanding of the behavior of such systems and additional caution in material design.

The fact that material properties as well as processing parameters influence the electrical conductivity has already been established in CB-filled one-component matrices. Polymer properties such as surface tension, viscosity, and degree of crystallinity are to be considered in addition to the processing conditions as factors determining the resulting conductivity level.^{5–8}

Some immiscible polymer blend systems have already been studied,^{9–13} yielding the following general results:

- CB locates preferentially within the phase in which it has a higher percolation threshold, being usually the polymer of higher surface tension value. This effect is so significant that occasionally migration of CB from one phase to another may be observed during melt mixing when the filler is initially incorporated within the polymer of lower polarity.
- The phase morphology and CB location determine the blend resistivity level. The double percolation concept, requiring continuity for the CB network, has been introduced and found necessary to obtain conductivity in CB-loaded polymer blends.
- The percolation threshold and resistivity values of the blend are lower than those depicted for the corresponding CB-filled individual polymers.

In this study a high-impact polystyrene/linear low-density polyethylene (HIPS/LLDPE) system was investigated. This constitutes a typical immiscible polymer blend in which the former com-

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ponent is an amorphous matrix and the latter serves as a semicrystalline dispersed phase. An emphasis will be made on effects concerning the dispersed phase viscosity and the processing procedure. The structure/electrical resistivity relationship will be studied with regard to former results obtained for polypropylene/polyamide⁹ and polypropylene/polycarbonate¹⁰ blends.

EXPERIMENTAL

The principal polymers used in this study were HIPS, Galirene HT 88-5 (MFI = 5 g/10 min; Carmel Olefins, Israel) and LLDPE, Dowlex NG 5056 (MFI = 1 g/10 min; Dow). An additional low-viscosity grade of LLDPE, Dowlex 2552E (MFI = 25 g/10 min), was used as well, and referred to in the text as LL25. All blend ratios described relate to percentage by weight. Carbon black (CB) Ketjenblack EC-300, (Akzo), was used in this study.

All polymers and blends were prepared by melt mixing the dry-blended CB and polymer components in a Brabender Plastograph equipped with a 50 cm³ cell at 190°C for ~ 15 min. The resulting blends were subsequently compression molded at 190°C to obtain 3-mm-thick plaques. An alternative processing method used for some selected formulations was injection molding, prepared by an Arburg 220/150 injection molding machine combined with a standard ASTM mold. In order to obtain well-mixed samples, the processing stages were as follows: initially, dry-blending the components in the desired ratios; injection molding; grinding the product, and subsequently remolding it.

The resistivity measuring method of CB-loaded polymers and blends depended on the geometry of the samples produced by the specific processing mode. Compression-molded samples were cut into disks, 5 cm in diameter, and their volume resistivity was measured (DIN 53596) using a Keithley Electrometer 614 and a high 240A voltage supply. For samples with low-level resistivity a Sorensen power supply, model QRD 60-1,5 was used. Injection-molded bars were measured according to ASTM D991, known as the "four point method." Nickel paint was applied to ensure contact between the sample and electrodes.

The blend phase morphology was studied by both optical and electron microscopy. An Olympus optical microscope was used to observe 50- μ m-thick microtomed samples. These samples were

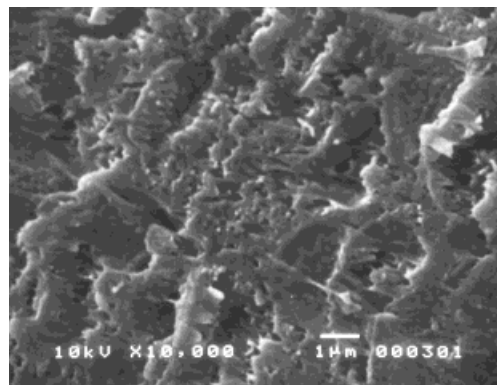


Figure 1 SEM micrograph of microtomed HIPS + 2 phr CB.

studied by regular Nomarsky optics. A Jeol JSM 5400 scanning electron microscope (SEM) was employed for investigating freeze-fractured and microtomed surfaces. All SEM samples were gold sputtered prior to observation.

RESULTS AND DISCUSSION

Individual Polymers

Observation of CB dispersion within the polymer matrices was usually conducted through SEM upon cryogenically fractured surfaces. Polystyrene samples are difficult to investigate due to the presence of excessive crazing in the brittle fractured surface, the craze tips hindering recognition of CB particles. A microtomed sample, such as in Figure 1, produces a more coherent picture. HIPS reveals circular regions unoccupied by CB. These areas probably correspond to the cross-linked polybutadiene phase dispersed within polystyrene due to their size (~ 1 μ m) and the fact that CB does not penetrate them. CB particles seem very small within the HIPS matrix, detached from it and nonuniformly dispersed, promoting the formation of a conductive network. LLDPE exhibits a typical ductile fracture surface, of smoother texture in comparison to HIPS. In the 2 phr sample [Fig. 2(a)] CB particles are randomly dispersed in the matrix, too distant for conductive pathways to be formed. The 6 phr CB sample [Fig. 2(b)] shows that CB is usually located in oval cavities larger than the particles themselves. These gaps may be caused by poor adhesion between the filler and the matrix or result from the nonuniform topography obtained upon the fracture surface due to polymer ductility.

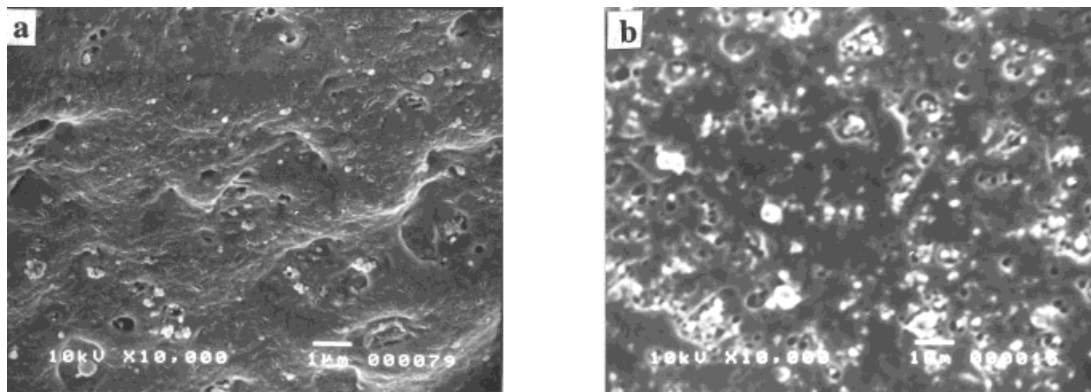


Figure 2 SEM micrographs of freeze-fractured: (a) LLDPE + 2 phr CB; (b) LLDPE + 6 phr CB.

LLDPE of low viscosity, LL25, was studied as well. The fracture surface differs greatly from the smooth texture of the former sample, appearing much more complicated and ductile (Fig. 3), rendering the CB very difficult to distinguish. The addition of CB even in small content results in a more brittle behavior.

The volume resistivity of the HIPS, LLDPE, and LL25 as a function of CB content is depicted in Figure 4. The percolation threshold of HIPS is the lowest of these polymers, at 2 phr CB.

The LL25 percolates at ~ 4 phr CB, whereas the high-viscosity LLDPE threshold is obtained at 6 phr CB. Understandably, polymer viscosity plays an important role in the dispersive mixing process, which consists of particle incorporation within the liquid, deagglomeration, aggregate fracturing, distribution by flow, and flocculation. The viscosity of the suspending liquid undergoing mixing exerts hydrodynamic forces upon the agglomerates, competing with the cohesive forces

within them. Thus, a high-viscosity liquid may induce agglomerate rupture and fracturing of aggregates, whereas the opposed effect of particle flocculation is more pronounced in a low-viscosity medium.¹⁴ Seemingly, the higher-viscosity LLDPE disperses CB more uniformly, reducing particle size and inhibiting floccular configurations. The lower-viscosity LLDPE tends to exert lower shear stresses on the agglomerates, causing less structural degradation, along with reduced resistance to reagglomeration, enabling the CB aggregates to approach one another more easily and form conductive networks.

The effect of surface tension and polarity of polymers on the critical volume fraction in various CB-filled thermoplastics has been well established.^{5,15} An increase in surface tension increases the percolation threshold, favoring CB uniform

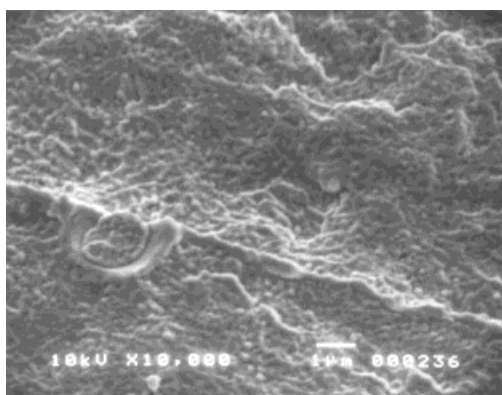


Figure 3 SEM micrograph of freeze-fractured LL25 + 2 phr.

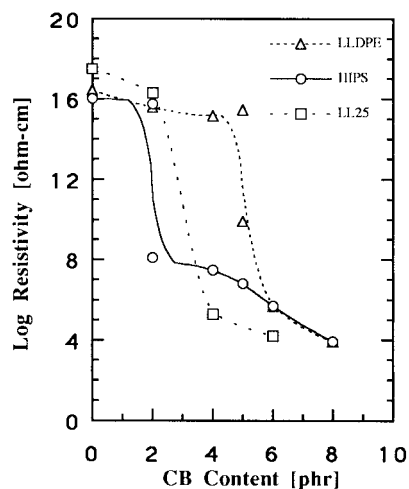


Figure 4 Resistivity of individual polymers versus CB content.

dispersion within the polymeric matrix. Carmona¹⁵ depicts polystyrene (PS) as demanding a higher CB content than polyethylene or polypropylene in order to percolate, inconsistently with observations obtained in this study and previous ones.^{9,10} CB-loaded HIPS has a low percolation threshold, at an approximate loading of 2 phr CB (Fig. 4). This value is especially low in light of the fact that polystyrene has a higher surface tension than either PP or PE ($\sim 41, 30, 36$ dyne/cm at 20°C, respectively).¹⁶ Apart from its higher surface tension, polystyrene also has some extent of polarity (0.168) as opposed to PP and PE (0.0). These facts lead us to expect a higher percolation threshold for PS due to its higher surface tension and polarity.

Apparently PS is a polymer of intermediate surface tension in comparison to PP and LLDPE on one hand, and to polyamide on the other hand. Its slight polar nature differs from that of polar polyamides resulting from aromatic pi-orbitals and polar functional groups, respectively. Polystyrene is also known to be weakly basic (its electron donor parameter, $\gamma^{(-)} = 1.1$ dyne/cm¹⁷), enabling interactions with the CB surface, acidic in nature.¹⁸ Thus, CB in HIPS exhibits a more uniform distribution, compared to the segregated structures viewed in PP and PE. This intermediate nature could enhance some particle breakage, which is sufficient to provide conductive bridges. However, interactions are not strong enough to cause severe agglomerate degradation and disperse CB uniformly within the matrix (as in polyamide-CB systems), which would diminish conductivity. Thus, what seems to be an optimal structure, which produces a conductive network at an extremely low CB content, is formed. The two-phase nature of HIPS, known to have < 10 wt % dispersed crosslinked rubber particles, was found not to have a direct effect on the percolation threshold, as a similar general-purpose polystyrene was measured having the same percolation threshold.

Polymer Blends

The neat blends were studied at proportions of 95/5, 85/15, 70/30, and 55/45 with HIPS serving as the matrix and LLDPE as the dispersed phase. The neat blends exhibit a typical behavior where the dispersed phase is very small for the 95/5 blend (1 μm order of value), slightly larger for the 85/15 blend [Fig. 5(a)] and co-continuous for the 70/30 [Fig. 6(a, b)] and 55/45 blends. Phase

inversion is therefore obtained at about a 70/30 composition, whereupon a co-continuous structure is observed. This does not correlate with the simple model developed by Jordhamo, Manson, and Sperling¹⁹ for predicting phase inversion and the point of co-continuous network formation, according to melt viscosity ratio of the components.

Favis and Chalifoux²⁰ observed a correlation between this prediction and phase viscosity ratio as obtained either by Brabender torque values or viscosities measured by capillary rheometer for the neat polymers at a shear rate corresponding to that within the Brabender mixing chamber. For the present HIPS/LLDPE system, torque values predict phase inversion at approximately 50% (by volume) LLDPE, whereas rheological values of melt viscosity as well as MFI data at 190°C (5 g/10 min for HIPS versus 1 g/10 min for LLDPE) forecast phase inversion at an even higher LLDPE content.

It has already been stated²¹ that the position and shift of the region of dual-phase continuity are not consistent with predictions based exclusively on composition and viscosity ratio. For mobile interfaces in which adhesion between phases is poor, as in the present case, the morphology of immiscible blends appears to be controlled by a series of effects such as interfacial tension, viscosity ratio, and level of shear stress, in this order of significance.

An additional effect may result from the subinclusions of HIPS within LLDPE, when the latter transforms from a spherical dispersed phase at a 85/15 composition to a continuous structure at 70/30. Continuous regions of LLDPE serve as a matrix for HIPS, constituting a type of blend within a blend,²² resulting in an effective higher-volume fraction for LLDPE than the nominal one. This could explain, at least partially, the significant shift in the phase inversion point to a lower minor phase content than the predicted value from the Jordhamo equation.

When comparing the dispersed-phase size and distribution of the blend containing high- and low-viscosity LLDPE [Fig. 7(a, b)], it is apparent that the former is of smaller droplet size, while the latter has larger droplets and is of wider distribution. Two opposing processes taking place throughout the blending should be considered: mixing (involving continuous breakdown of the dispersed particles) versus coalescence (upon which dispersed particles approach one another and eventually collide, the matrix material between them being removed).^{21,23} Coalescence time

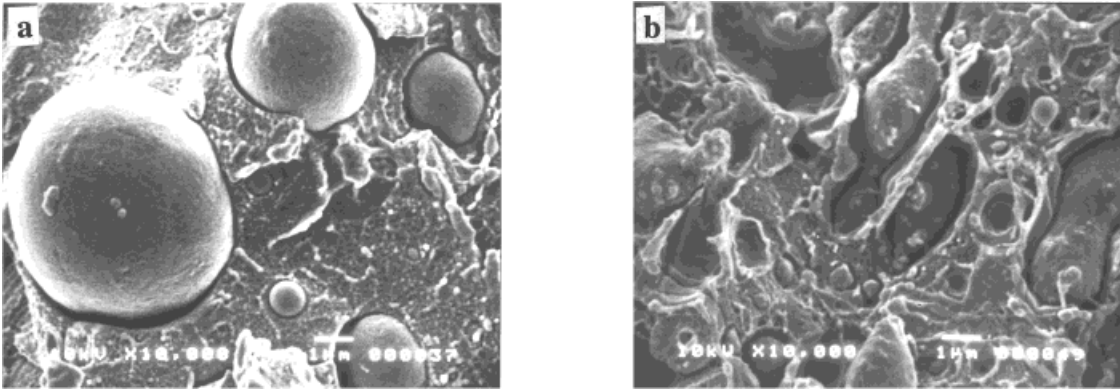


Figure 5 SEM micrographs of freeze-fractured 85HIPS/15LLDPE: (a) Neat blend; (b) 2 phr CB-loaded blend.

is highly dependent on the dispersed-phase viscosity, which implies rapid fusion of particles of low viscosity.¹⁴ The final morphology of a blend is a result of the dynamic processes of break-up of

large droplets and coalescence of the smaller ones during mixing. Apparently, in blends with low-viscosity LLDPE, both processes of droplet breakup and coalescence occur more rapidly,

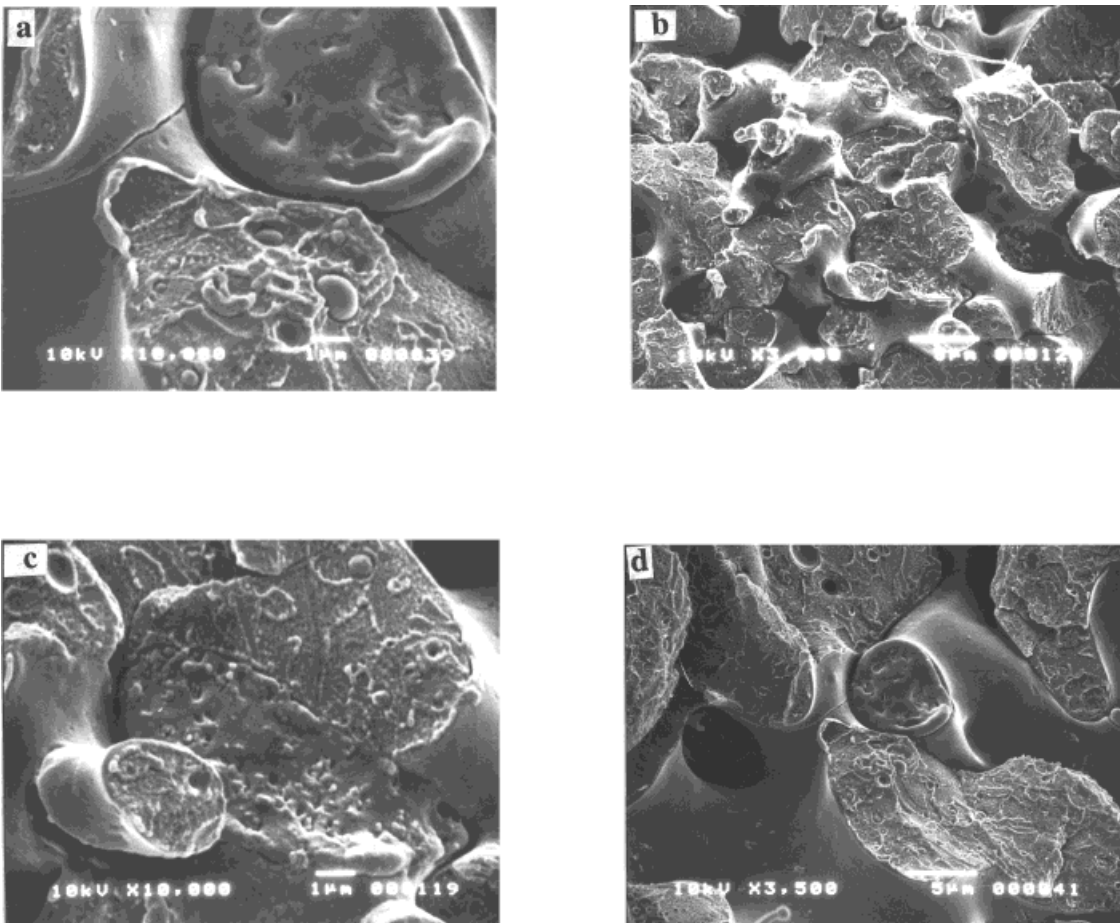


Figure 6 SEM micrographs of freeze-fractured 70HIPS/30LLDPE blend: (a, b) Neat blend at 2 \times ; (c, d) 2 phr CB-loaded blend at 2 \times .

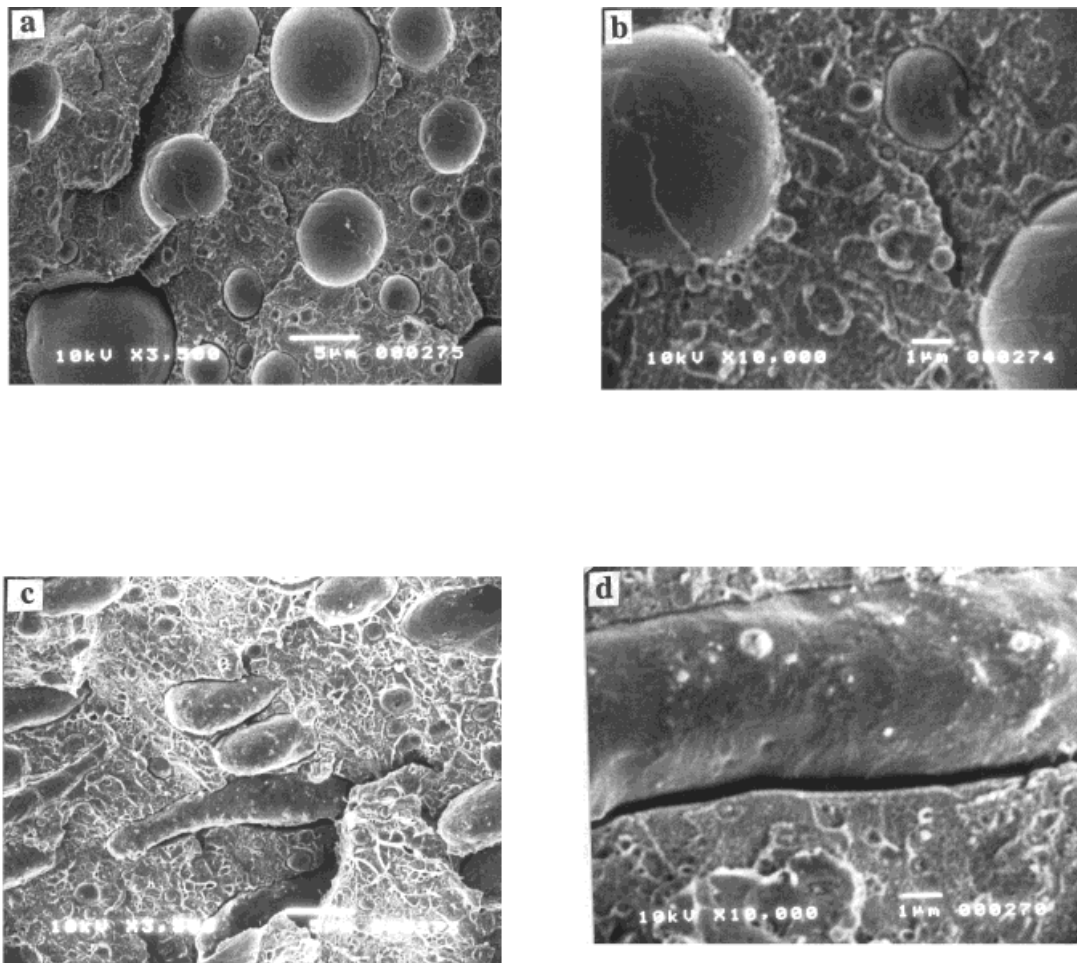


Figure 7 SEM micrographs of freeze-fractured 85HIPS/15LL25: (a, b) Neat blends at 2 \times ; (c, d) 1 phr CB-loaded blend, at 2 \times .

which may explain the wide distribution of particle size depicted in the 85/15 blends of HIPS with low-viscosity LLDPE.

Addition of CB to the HIPS/LLDPE systems is accompanied by its preferential location in the LLDPE, as depicted in Figures 5(b) and 6(c, d). SEM micrographs reveal that CB is usually positioned upon the surface of the LLDPE dispersed phase, and less incorporated within it. The CB particles are clearly seen on the surface, and tiny cavities corresponding to them are stationed upon the HIPS surface. The higher percolation threshold of the individual LLDPE in comparison to HIPS implies the tendency of CB to locate preferentially within LLDPE, as observed previously.^{9,10} Interaction of CB with both polymers, of intermediate nature in the case of HIPS and weak for LLDPE, may promote CB location in the interfacial region. When utilizing LL25, the low viscosity

enables CB penetration within the dispersed phase, so that mixing dynamics comes into effect.

CB usually alters the morphology significantly, depending on the initial blend structure. The 95/5 blend loaded with 2 phr CB has a dispersed LLDPE phase of tiny dimensions, resulting in difficulty to recognize the CB within it. CB is distributed throughout the matrix in this case, and the dispersed LLDPE phase consists of tiny particles which have no significant effect on the CB location. The 85/15 blend, composed of spherical dispersed LLDPE particles in the neat case (Fig. 7), exhibits a change both in size and in shape, developing an elongated dispersed-phase structure upon CB addition [Fig. 5(b)]. The dispersed phase becomes smaller, but as the dimensions are reduced the number of particles increases, creating numerous CB-coated LLDPE cylinders, as depicted in Figures 5 and 7. The reduction in dis-

persed phase size and its change in shape has been previously reported^{9,10} and has been attributed to friction between CB and the dispersed polymer. The higher viscosity of the dispersed droplets upon CB addition is expected to affect the resulting morphology; according to Min, White, and Fellers,²⁴ deformation should be less pronounced. In practice, since CB tends to locate more on the dispersed particle surface than within it, the interface between the dispersed and continuous phases may become less mobile. Friction between the CB-coated dispersed particles and the matrix may cause deformation leading to elongated structures, contrary to the description by Min. These maintain their rodlike structure with no apparent droplet breakup as obtained in the neat case. This phenomenon occurs in both types of LLDPE. As to the 70/30 and 55/45 blends, co-continuity prevails, as in the neat case. The co-continuous structure of the CB-loaded blends is finer than that of the unloaded ones, resulting in an enhanced network (Fig. 6). The 55/45 composition is of coarser structure than the 70/30 one.

The resistivity curves of the CB-loaded blends are depicted in Figures 8 and 9. The 95/5 blend (Fig. 9) percolates at ~ 1 phr CB, slightly less than the individual HIPS, which percolates at 2 phr. The dispersed LLDPE particles are very small and of minor quantity, so that this blend acts similarly to the individual HIPS. The dispersed LLDPE phase is not necessarily penetrated by CB and conductivity in this case results from the effective CB content in HIPS. The 85/15 blend demonstrates a percolation threshold at

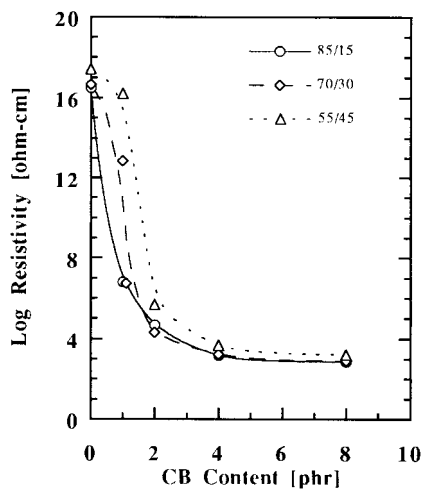


Figure 8 Resistivity versus CB content of various HIPS/LLDPE blends.

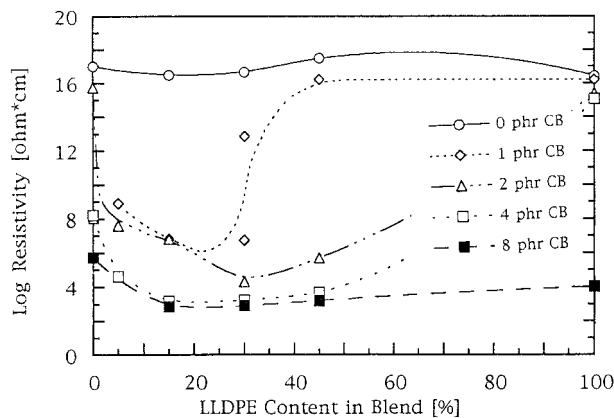


Figure 9 Resistivity as a function of LLDPE content in HIPS/LLDPE blends, for various CB loadings.

< 1 phr CB (Fig. 8), due to the tendency of CB to locate itself in the LLDPE phase, and the elongated dispersed phase structure obtained in this case. Thus, CB is concentrated in the LLDPE (mainly upon its interface) in an effective content highly above the polymer's percolation point, and the elongated configuration creates loci of contact between the dispersed domains, leading to the observed conductivity. The 70/30 composition has a slightly higher percolation threshold (Fig. 8) and is slightly less conductive (Fig. 9), although co-continuous. Due to the higher LLDPE content than in the former case, it has a smaller effective CB loading in it and thus conductivity is slightly diminished, as seen in Fig. 9. This demonstrates that extended configurations that contact each other enhance the formation of a network and double percolation may be realized, leading to a reduced percolation threshold. This takes place for the 55/45 blend as well, which has a percolation point similar to the individual HIPS at 2 phr CB. For most blend compositions, the percolation point is not greatly reduced in comparison to the individual HIPS matrix, perhaps due to the fact that HIPS alone percolates at a low CB content. However, the magnitude of the resistivity is decreased by approximately four orders of magnitude, which is indeed a significant enhancement. This may be attributed to the unique morphology obtained in the blend systems, in which the CB is preferentially placed upon the LLDPE phase surface. Thus, the concentration of CB particles upon the interface greatly promotes conductivity, in comparison to conductivity values typical of CB dispersed within a single matrix, even above the percolation point.

Blending the ingredients by a different mixing

sequence does not practically produce different resistivity values or morphology, as described elsewhere.^{9–11} Upon incorporating CB into HIPS prior to LLDPE addition, results were indistinguishable from the standard method used.

HIPS/LLDPE blends in which low-viscosity LLDPE is used generally exhibit a behavior similar to the one described above (Fig. 10). CB tends to penetrate the LLDPE phase more in this case, due to its lower viscosity. The lower percolation values exhibited for all blend ratios stems from the lower percolation point of the lower-viscosity LLDPE. No unique morphology was obtained, however, coarsening of the dispersed phase due to the accelerated coalescence has led to a more gradual formation of a co-continuous structure. Thus, a higher dispersed-phase content resulting in a 70/30 composition is necessary to obtain lower resistivity in this case (Fig. 11).

Processing Effects

Injection-molded samples were tested for morphology and resistivity data. The samples consisted of HIPS + 8 phr CB, 85 HIPS/15 LLDPE + 4 phr CB, and 70 HIPS/30 LLDPE + 4 phr CB. The electrical resistivity of these samples was measured by the four point method (specified above) and was proved to be relatively high (above 10^8 ohm/cm) even for samples that were of low resistivity by the former compression-molding processing method.

SEM micrographs of HIPS/LLDPE + CB blends depict, as expected, significant differences

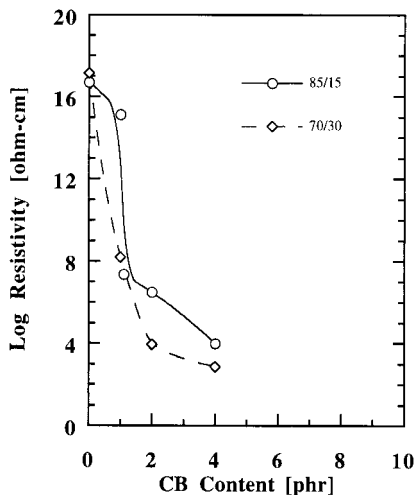


Figure 10 Resistivity versus CB content of various HIPS/LLDPE blends.

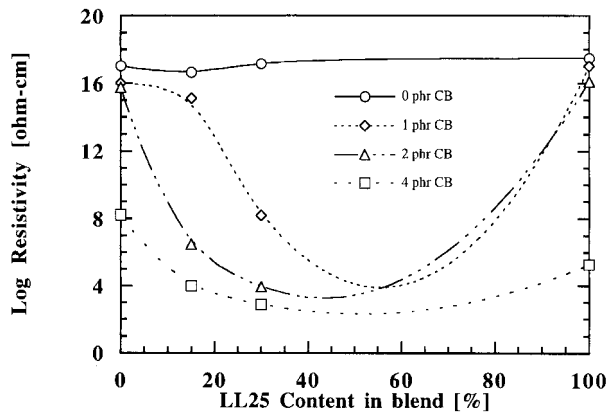


Figure 11 Resistivity as a function of LL25 content in HIPS/LL25 blends, for various CB loadings.

between the directions parallel and transverse to flow. Within the CB-loaded 85/15 HIPS/LLDPE blend [Fig. 12(a, b)], the dispersed PE phase becomes highly extended, obtaining cylindrical structures of relatively low diameter ($\sim 1 \mu\text{m}$) and widely distributed lengths of a few microns. CB is located within the dispersed phase, more so than for the former processing method, in which CB was upon the interface. The 70/30 formulations are relatively similar (Fig. 13); however, structures are more co-continuous in the direction parallel to flow and the dispersed phase is of irregular, rather than circular, cross-section.

Morphological observations provide some insight as to why injection-molded samples are insulative. The high orientation of the dispersed phase within the matrix causes an orderly sequence of cylindrical structures; however, these hardly come into contact. In the case of Brabender mixing, extended structures were observed as well, but these were randomly oriented, overlapping to provide a well-established conductive network. Even the 70/30 blend, with a slight tendency toward co-continuity in the direction parallel to flow, is insufficiently continuous. CB penetrates the dispersed phase in injection-molded samples more thoroughly than in the Brabender mixed ones, presumably due to the significantly high shear rates involved in the injection molding process followed by rapid solidification in the mold. This may constitute an additional reason for the higher CB contents required for percolation, and the corresponding higher resistivity values.

The higher shear rate exercised in injection molding definitely has an effect on agglomerate degradation and destruction of chainlike tendencies—this is apparent by the fact that the 8 phr

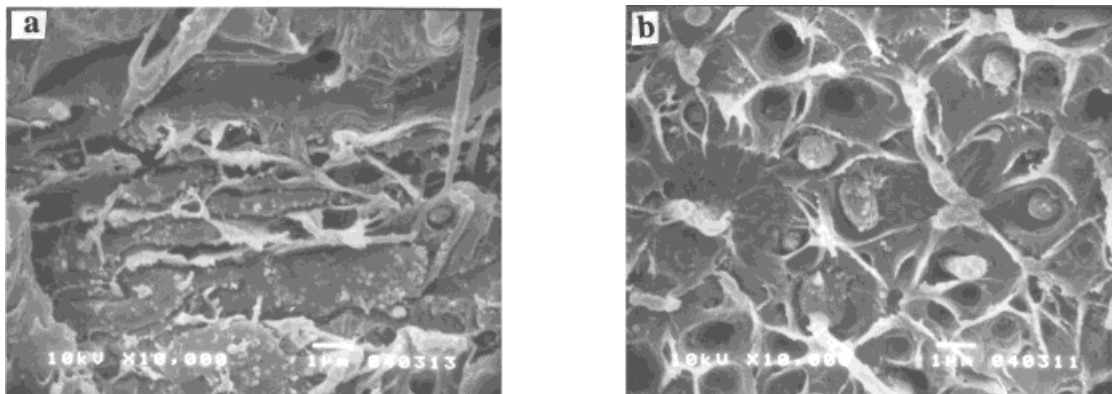


Figure 12 SEM micrographs of microtomed samples of injection molded 85HIPS/15LLDPE+ 4 phr CB: (a) parallel to flow; (b) transverse to flow.

loaded HIPS is insulative when injection molded. However, SEM micrographs are insufficient to depict this clearly, due to the very small CB agglomerate size involved.

Several authors have related to the increased resistivity of CB-loaded injection-molded polymer systems^{4,25,26} due to orientation and degradation of agglomerates by shearing. Webling²⁷ attributed this to kinetic effects, whereupon thermodynamically stable cohesive structures of CB chains cannot be restored within the time scale of the injection molding process.

It is therefore clear that two competitive processes are implemented during injection molding, when deformation comes into effect: the destruction of CB structures formed during the compounding step versus their tendency to reconstruct by shearing. In this case, the former effect prevails, due to the rapid rate of the injection molding process. Thus, this procedure results in highly deformed structures in the high-resistivity

injection-molded samples, in comparison to Bra-bender mixing combined with compression molding, where much lower resistivities are obtained.

CONCLUSIONS

As was previously shown^{9,10} the CB percolation thresholds in the individual polymers vary from one matrix to another, based on effects of surface tension, polarity, and viscosity. An emphasis has been placed on HIPS, unique in its combination of a relatively high surface tension and low percolation threshold, yielding an optimal network structure at low CB contents. CB percolates in LLDPE at a higher content than in HIPS, and locates preferentially in LLDPE (or upon its surface) in HIPS/LLDPE systems. The location depends upon a balance between CB-polymer interactions, mixing kinetics and viscosity effects. Blends exhibit lower percolation thresholds and

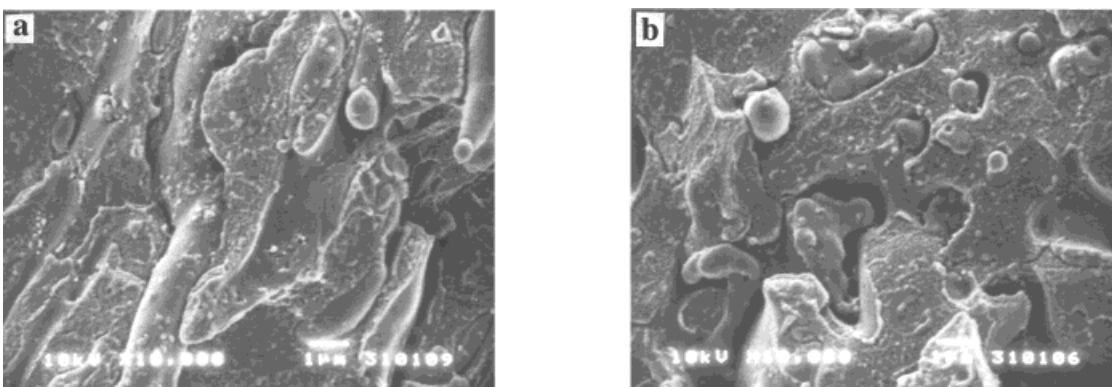


Figure 13 SEM micrographs of freeze-fractured samples of injection-molded 70HIPS/30LLDPE+ 4 phr CB: (a) parallel to flow; (b) transverse to flow.

lower resistivity values than those depicted for the individual polymers.

Double percolation is implemented in these systems through formation of overlapping extended structures of the dispersed LLDPE phase in which CB is located primarily on its surface. In HIPS/LL25 a higher dispersed phase content is needed to provide a more well-developed co-continuous network, as blend structure is coarser. CB enhances the networking effect by reducing the dispersed phase size and elongating it, generating a fine honeycomb-like structure.

Injection molding severely diminishes conductivity compared to conductive blends processed by Brabender mixing followed by compression molding. This is attributed to high shear rates, orientation, and rapid kinetics involved in injection molding, which induce the formation of noncontinuous highly deformed dispersed-phase structures in which CB agglomerates disintegrate and only partially reagglomerate.

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