The Interrelation Between Morphology, Resistivity, and Flow Properties of Carbon Black–Containing HIPS/EVA Blends

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ABSTRACT: Immiscible polymer blends based on high-impact polystyrene/ethylene vinyl acetate (HIPS/EVA) are interesting host multiphase systems for the incorporation of low concentrations of carbon black (CB). The conductive filler CB tends to accumulate preferentially within the EVA phase, forming segregated structures, and thus conductivity of the blends is only obtained when double percolation is realized. Material properties such as surface tension and crystallinity of the CB-containing polymer are found to influence filler distribution, accordingly affecting the electrical conductivity. A rheological-electrical method is presented, whereupon extrudates of CB-containing binary immiscible polymer blends are produced by a capillary rheometer, and the effect of shear level on the extrudates' structure and resultant resistivity is determined. A descriptive model was derived, illustrating the effect of shear on double percolation at various blend compositions. The flow behavior of the CB-containing compounds was studied in regard to the filler packing factor, ϕ_m , and related to the electrical properties of the extrudates. Blend composition, CB content, and shear level were considered as significant parameters, determining the structure and the resultant electrical properties. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1655-1668, 1999

Key words: conductive plastics; conductive immiscible blends; carbon black

INTRODUCTION

Immiscible polymer blends are interesting host matrices for the incorporation of fillers. The multiphase nature of these systems provides an opportunity for the filler to distribute nonuniformly within the phases, due to the different properties of the blend components. A subtle balance between thermodynamic and kinetic factors, namely, the surface tensions of the constituents and the viscosities and processing parameters, determines the blend morphology and the preferential location of the filler particles within the blend. Thus, unique structures may be formed, with direct implications for the material properties and performance.

This concept has already been applied to electrically conductive polymer blends, containing carbon black (CB).^{1–5} When the CB-containing phase forms continuous structures within the continuous matrix, double percolation may be obtained, forming honeycomb-like structures in which conductive pathways may prevail.¹ It is this exceptional structuring that enhances the electrical conductivity and reduces the critical CB content essential for percolation.

The operative disadvantages of using high CB content are well known. Thus, high CB content

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leads to relatively high costs, processing difficulties, sloughing, and inferior mechanical properties. We introduce an additional difficulty in industrial melt processing of a single polymer matrix with CB when high shear rates are used, resulting in destruction of conductive paths.⁶ Utilizing an immiscible multicomponent matrix in place of a single polymer may offer a practical solution, because lower CB loadings and superior electrical conductivity may be realized. High shear rate processing has been also shown to improve, because the segregated structures not only withstand severe shear conditions, but may also undergo further structuring into more highly segregated structures, further enhancing conductivity.^{7,8}

This study investigates CB-containing multiphase matrices consisting of a high-impact polystyrene (HIPS) blended with an ethylene vinyl acetate (EVA) copolymer, the former constituting the major phase. EVA grades of different vinyl acetate content, varying in polarity and degree of crystallinity,⁹ are used, affecting the blend morphology and resultant conductivity. The effects of shear level on the extrudate electrical properties and the rheological behavior are characterized to interrelate the morphology, resistivity, and flow properties of these compounds.

EXPERIMENTAL

The polymers used in this study were HIPS, Galirene HT-88-5 [melt flow index (MFI = 5 g/10 min; Carmel Olefins, Haifa, Israel)] and the following three grades of EVA random copolymers: Escorene UL-209, Exxon (Houston, TX) [MFI = 2 g/10 min, vinyl acetate VA content = 9%]; Riblene FV2040 (MFI = 2.5 g/10 min; VA content = 19%, Enimont, Milan, Italy); Escorene UL-328, Exxon (MFI = 2 g/10 min, VA content = 30%). These grades are referred to in the text as EVA-9, EVA-19, and EVA-30, respectively. All blend ratios described relate to percentage by weight. The conductive CB used was Ketjenblack EC-300 (Akzo, Netherlands).

All the CB-containing polymers and blends were prepared as follows. The components were initially dry-blended and subsequently melt-mixed at 190°C in a Brabender Plastograph equipped with a 50 cm³ cell for approximately 15 minutes. The resulting blends were then compression molded at 190°C to obtain 3-mm-thick plaques.

Rheological studies of CB-containing polymers and blends were conducted, using an Instron capillary rheometer mounted on an Instron TT-D machine. Samples prepared earlier by melt-mixing in the Brabender Plastograph were extruded in the capillary rheometer at a temperature of 190°C. A capillary of 5 cm (2 min.) length and 0.127 cm (0.05 min.) diameter (L/D = 40) was used. The extrudate output exiting the rheometer was controlled by the crosshead speed, ranging from 0.05 to 50 cm/min, providing an approximate shear rate range of 20–3000 s⁻¹. All samples were collected for electrical resistivity measurements and observation.

The resistivity measuring method of the CBloaded samples depended on the geometry of the samples produced by the specific processing mode. Compression-molded samples were punched into 5 cm-diameter disks, and their volume resistivity was measured (DIN 53596) using a Keithly Electrometer 614 and a 240 A highvoltage supply. For samples with low levels of resistivity, a Sorensen power supply, Model QRD 60-1,5, was used. Nickel paint was applied to minimize contact resistance between the sample and electrodes. Extrudates produced by the capillary rheometer were measured as follows. Silver paint was applied to several areas on the surface of the extrudates, as before, to ensure contact between the sample and electrodes. The resistance between two silver marks along the specimen was measured, and the volume resistivity was calculated in relation to the sample dimensions. Because of the limitations of the electrometer, it was not possible to measure resistivities $> 10^8 \ \Omega \ cm$. Several locations of each extrudate were measured to verify consistency of the results.

The morphology of freeze-fractured samples, gold sputtered before observation, was characterized by a Jeol 5400 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Resistivity-Morphology Relationship

The fact that the percolation behavior of a CBcontaining polymer depends significantly on the type of matrix used has been assessed earlier.¹⁰ It was suggested that the critical content for percolation may relate to the polarity, as the critical content increases with the polarity (or surface



Figure 1 Resistivity of individual polymers versus CB content.

tension) of the polymer.^{11,12} This is due to the fact that matrices of higher surface tension tend to interact better with the dispersed filler of relatively high surface tension, obstructing its ability to cluster and form networks that facilitate electrical conduction.^{2,13} An additional factor to be considered is the degree of crystallinity. As CB tends to accumulate within the amorphous regions of the polymer, the effective CB content within these regions increases, thus reducing the percolation threshold.

As described earlier,¹ HIPS has a low percolation threshold at approximately 2 phr CB content. The EVA grades exhibit percolation (Fig. 1) at higher CB content; EVA-9 at approximately 3 phr CB, and EVA-19 and EVA-30 at above 6 phr CB. The various grades of EVA used in this study vary in both polarity and degree of crystallinity. As the polar VA content within the random copolymer increases, the polarity of the polymer rises, whereas a higher VA content reduces its degree of crystallinity. Thus, as VA content increases from 9 to 19%, the percolation threshold increases as well, as expected. A further increase in VA content to 30% has no effect on electrical resistivity or critical CB content. EVA-9 exhibits a steplike

trend of reduced resistivity as the CB content increases, presumably implying that two different mechanisms are involved. It is suggested that the CB gradually interacts with the polar VA groups in the amorphous regions. Subsequently, it locates in the more hydrophobic paraffinic amorphous regions. At high VA content, such as dual mechanism is expected to diminish, and indeed, when matrices of higher VA content are used (EVA-19 or EVA-30), the dual-stage mechanism is absent. The anomalous behavior of HIPS, an amorphous polymer of high surface tension but low percolation threshold, has been discussed previously.¹ The free radicals active in CB tend to interact with π electrons of double bonds, possibly forming intermediate complexes; thus, CB may structure within HIPS.^{14,15}

The distribution of CB within EVA-9 and EVA-30 matrices is shown in Figure 2(a) and (b), respectively. The samples shown contain a relatively high amount of CB (8 phr CB), above the percolation threshold of both polymers. In EVA-9, CB seems to form a network structure (appearing in the micrograph as bright chains), whereas in EVA-30, the filler is more uniformly dispersed, and chainlike structures are more difficult to detect. This is consistent with the higher percolation threshold measured for the latter sample and with the results of previous studies.²

Table I gives the resistivity values of HIPS/ EVA-9 and HIPS/EVA-30 blends as a function of CB content, at two different blend compositions: 85HIPS/15EVA and 55HIPS/45EVA. The blends containing a lower EVA content of 15% appear to undergo percolation at a CB content below 2 phr CB—lower than the values for the neat EVA. The decrease in resistivity is sharper at the critical CB value for the blends in comparison with the individual polymers and is reduced by more than 10 orders of magnitude for blends of both grades of EVA. The blend containing EVA-9 has a resistivity of approximately two orders of magnitude less than the blend containing EVA-30 at a low CB content of 2 phr (only slightly above percolation); however, both show similar resistivities when the CB content is raised to 4 phr. The blends containing 45% EVA have higher resistivities than the blends containing 15% EVA, but show similar trends. Percolation is again obtained below 2 phr CB. The blend containing EVA-9 has a lower resistivity than the EVA-30 blend at 2 phr CB, but values resemble those when 4 phr CB is incorporated.



a.





Figure 2 SEM micrographs of freeze-fractured (a) EVA-9 + 8 phr CB and (b) EVA-30 + 8 phr CB.



Figure 3 SEM micrographs of (a) neat and (b) 4 phr CB-containing 85HIPS/15EVA-9 freeze-fractured blends.

Table I	Resistivity	of HIPS/EVA-9	and HIPS/	EVA-30 Ble	ends, at Two	o Different (Compositions,
as a Fun	iction of CB	6 Content					

	Log-resistivity [Ω cm]							
CB Content (phr)	85HIPS/15EVA-9	85HIPS/15EVA-30	55HIPS/45EVA-9	55HIPS/45EVA-30				
0	16	16	16	16				
2	3.79	5.89	5.07	8.44				
4	3.71	3.75	4.16	5.02				



b.



Figure 4 SEM micrographs of freeze-fractured neat blends of (a) 55HIPS/45EVA-9 and (b) 55HIPS/45EVA-30.

Figure 3 depicts the morphology of 85HIPS/ 15EVA-9 neat and CB-containing blends. The neat blend depicts nonspherical structures of EVA dispersed within HIPS, seemingly approaching the onset of a co-continuous structure. When CB is incorporated, the dispersed phase size is reduced considerably (<1 μ m), and is very difficult to distinguish in the SEM micrograph. The tiny EVA particles appear to contain CB. Figure 4 depicts neat blends of 55HIPS/45EVA for both types of EVA. At this composition, both EVA grades form co-continuous structures within the HIPS matrix; however, EVA-9 forms a much coarser network than does EVA-30. Figure 5 shows the morphology of a 4 phr CB-containing 55HIPS/45EVA-9 blend. On addition of CB, the blend maintains its co-continuous structure as in the neat case, with no apparent reduction in the dispersed phase dimensions due to the presence

a.







Figure 5 SEM micrographs of a freeze-fractured 4 phr CB-containing 55HIPS/45EVA-9 blend, at (a) high and (b) low magnifications.

of CB, as seen in the 85/15 blend. The CB appears to be located mainly within the EVA phase.

The electrical resistivity results obtained for the blends coincide with the observed morphology for the single-phase matrices. In the individual CB-loaded polymers, percolation was found to take place at relatively low CB content for HIPS, higher values for EVA-9, and even more so for EVA-30. This implies stronger interactions between CB and EVA than with HIPS, in particular for EVA-30, which has the highest VA content studied and thus is the most polar one. This relatively strong interaction is manifested in the fact that the CB preferentially locates within the EVA phase in the blends. The percolation threshold of the blends is lower than that of the individual polymers, due to the higher effective content of CB in the EVA phase. This also leads to lower resistivity values above percolation. As the EVA content increases, the effective CB content within the dispersed phase is reduced at a given CB content in the blend, thereby increasing the resistivity. Double percolation is obtained already at an EVA content of 15%, and thus any increase in EVA content only increases the resistivity. Both 85/15 and 55/45 blends containing 2 phr CB have higher resistivity values when EVA-30 is used, due to the fact that interactions between CB and this polymer detain the formation of the conducting network as opposed to EVA-9, in which CB tends to network at lower concentrations. When 4 phr CB is incorporated, the blends obtain similar resistivity values, because the effective CB content in both grades of EVA significantly exceeds the percolation threshold. These results coincide with the former reported data relating the polarity of the polymers to the CB distribution in them and its partitioning within the multiphase matrix.

Reduction in size of the CB-containing dispersed phase comes into effect in the 15% EVA blend presented in Figure 3, as observed previously for the CB containing high-impact polystyrene and linear low-density polyethylene (HIPS/ LLDPE) system.¹ This phenomenon has been noted previously in terms of blend compatibilization and discussed in relation to both the interfacial thermodynamics^{14–17} and the mixing kinetics of the system.¹ In some cases, fillers have been shown to play an actual role in raising the thermodynamic stability of blends, by decreasing the interaction parameter.¹⁶ Del Rio and Acosta¹⁷ reported a significant decrease in the interaction parameter of poly(vinylidene difluoride) polystyrene (PVDF/PS) systems, on addition of low CB content into the blend, from a positive value in the case of the neat system to negative values for the CB-containing blends. This corresponds to compatibilization of the latter. An additional approach attributes the reduction in dispersed phase size to friction between the CB and the polymer in the system.¹ The presence of CB may abrade the dispersed particles, induce droplet breakup, and inhibit coalescence. The friction may also generate droplet elongation, resulting in rodlike structures of reduced diameter, as seen formerly.¹

It thus is clear that CB contributes to more than just the conductivity when incorporated in multiphase matrices. Apparently, CB also plays a role in enhancing the electrical conductivity of polymer blends, by locating selectively within the blend, forming conductive networks, and modifying the blend's rheology and the associated morphology to form fine, continuous structures, essential for double percolation.

Resistivity of Extrudates

CB-containing extrudates were produced by a capillary rheometer at various shear rates, and their resistivity values measured. Figure 6 depicts the resistivity versus extrusion shear rate of



Figure 6 Resistivity versus extrusion shear rate of CB-containing EVA-9 and EVA-30. Points of resistivity above $1E + 8 \Omega$ cm exceed the range of the measuring equipment and are depicted for illustration purposes only.

individual CB-containing EVA extrudates for EVA-9 and EVA-30. Polymers with CB content of 4 phr have high resistivity values in the entire shear rate range of extrusion. When 8 phr CB is incorporated, resistivity is significantly reduced, as shown in the figure. For both EVA grades, a similar trend is seen, whereupon the resistivity increases with extrusion shear rate. This effect is more significant for the EVA-30 matrix.

The resistivity of samples based on a single polymer matrix is high when the CB content ≤ 4 phr CB; it is beyond the capability of the measuring system.⁸ For the EVA-30 sample, this is indeed understandable, because of the high percolation threshold of the compression-molded sample (>6phr CB). For the EVA-9 compression-molded sample, percolation occurs at approximately 3 phr CB (Fig. 1); however, because intermediate levels of resistivity are involved, the resistivity of the 4 phr CB-containing EVA-9 extrudate is unmeasurable. At 8 phr CB content, both the EVA-9 and EVA-30 compression-molded systems exceed their percolation thresholds and have similar resistivity values; however, their extrudates exhibit a slightly different behavior. EVA-9 at 8 phr CB (Fig. 6) exhibits a general trend of resistivity increase with extrusion shear rate. However, when shear rates higher than 10 s^{-1} are used, an oscillatory behavior is seen, whereupon some of the extrudates produced in the higher shear rate range have lower resistivities. This may be attributed to the inclination of CB networks to undergo simultaneous opposing processes of rupture and reagglomeration under shear flow. EVA-30 attains a slightly higher resistivity value at low extrusion shear rates than EVA-9, maintaining a relatively constant resistivity as shear rate of extrusion increases, with no oscillations. At all extrusion shear rates, EVA-30 has higher resistivity values than EVA-9, moreso at the higher extrusion shear rates. The fact that EVA-30 has higher resistivities throughout the entire extrusion shear rate range again demonstrates the fact that it is more difficult for CB to form a segregated conducting network within a matrix of higher polarity, as has already been seen for the compression-molded samples (Fig. 1). In the case of extrudates, both EVA grades are sensitive to shearing, exhibiting increased resistivity when high shear rates are imposed, due to enhanced wetting of CB by this matrix. Apparently, effects of CB agglomerate rupture and dispersion undermine tendencies of reagglomeration and network formation. The resistivity-shear rate relationship for CB-containing HIPS has been described previously.⁸



Figure 7 Resistivity versus extrusion shear rate of 4 phr CB-containing HIPS/EVA-30 blends. Points of resistivity above $1E + 8 \Omega$ cm exceed the range of the measuring equipment, and are depicted for illustration purposes only.

Figure 7 depicts resistivity-extrusion shear rate relationships for 4 phr CB-containing HIPS/ EVA-30 blends. The 2 phr containing blends, at both compositions (not presented here), have high resistivities throughout the entire shear rate range. When 4 phr CB is incorporated, the blend resistivity is relatively low for extrudates produced at low shear rates, but increases when higher shear rates are used. A similar behavior, with lower resistivity values, has been observed for blends containing the less polar EVA-9 (not presented here).

As shown in Figure 7, the 55HIPS/45EVA-30 + 4 phr CB blend is the most sensitive to shear, with resistivity rising sharply at relatively low shear rates. The 85HIPS/15EVA-30 + 4 phr CB composition demonstrates a more gradual increase in resistivity with shear rate, whereas the 70HIPS/30EVA-30 + 4 phr CB blend exhibits the lowest resistivities in the intermediate shear rate range. The resistivities obtained at low shear rates correspond approximately to the values observed for the compression molded samples (Table I).

A schematic model (Fig. 8) has been derived in an attempt to describe the behavior of these 4 phr CB-containing systems, on the basis of the resistivity-extrusion shear rate data and morphological observations by SEM. It has already been

Low shear rate

Intermediate shear rate



Figure 8 A schematic model describing the structure of 4 phr CB-containing HIPS/ EVA-30 blends of various compositions, at low and intermediate shear rates.

established that an essential condition for the conductivity of CB-containing blends is double percolation¹⁻⁵; that is, the CB must surmount its percolation threshold within the polymer in which it is located (first percolation), and the CBcontaining polymer must undergo percolation in the matrix, maintaining connectivity within the blend (second percolation). In the 85HIPS/ 15EVA-30 blend, the dispersed phase assumes a cylindrical form. As the CB is located mostly in the EVA-30, rather than in the HIPS matrix and at the interface, it has an extremely high effective content, and thus the first percolation is indeed attained. When the extrudates are produced at low shear rates, the CB-containing component assumes random positions, enabling contact between them, so the second percolation is realized as well. As shear rates increase, the dispersed phase gradually becomes oriented and more susceptible to breakup, eventually destroying the second percolation, as demonstrated in Figure 8. It is believed that in this case, the high effective filler content produces such a dense CB network that the first percolation is preserved. The 55HIPS/45EVA-30 blend is thought to depict an opposing trend; the low effective CB content in EVA, only slightly above the percolation threshold, renders the network sensitive to shear, obstructing the first percolation as the shear rate increases, but the second percolation is maintained, due to the coarse nature of the continuous EVA phase. The 70HIPS/30EVA-30 composition constitutes an intermediate case, in which both the first and the second percolations remain relatively intact as shear rate increases. This is due to the combination of high effective CB content within the dispersed phase and the continuous structure of the EVA within HIPS.

A comparison between the resistivity-extrusion shear rate behavior of CB-containing EVA-30 as opposed to the blends indicates that the blend extrudates require lower CB contents to obtain measurable resistivity values. This is attributed to the higher effective CB content within the dispersed EVA particles. The CB-containing EVA phase within the blends behaves in a manner roughly similar to its behavior when it constitutes a single matrix subjected to shear. The resistivity of blend extrudates has been found to be somewhat higher than that of the individual EVA-30 of identical effective CB content, due to deficiencies in the second percolation, or possibly to loss of some of the CB to the HIPS matrix.



Figure 9 Apparent viscosity versus shear rate of neat and CB-containing HIPS.

This system differs from the CB-containing HIPS/LLDPE blends.^{1,8} The HIPS/LLDPE blends exhibit enhanced conductivity for most compositions at low CB content at high shear rates; however, CB is located mainly at the interface and generates highly segregated structures on shear rate increase. Conversely, for HIPS/EVA, the CB filler is located mostly within the polar phase rather than on its surface, and is well dispersed within it. Therefore, the major benefit from using HIPS/EVA blends rather than the individual polymers is obtained by increasing the effective CB content within EVA, as opposed to the enhanced structuring in the HIPS/LLDPE systems.

Rheological Properties

Figures 9 and 10 depict the apparent viscosity of the CB-containing individual polymers, HIPS and EVA-30, respectively. Data regarding EVA-9 are not displayed, due to their similarity to EVA-30. All compounds exhibit a typical pseudoplastic behavior, where HIPS has a higher apparent viscosity than EVA-30, both neat and containing CB. In both polymers, the apparent viscosity increases with CB content, moreso for HIPS. The presence of CB affects the apparent viscosity of HIPS throughout the entire range of shear rates, whereas in the case of EVA-30, only the low shear rate viscosity increases with CB content. At high shear rates, all EVA-30 samples assume similar viscosity values, regardless of CB content.



Figure 10 Apparent viscosity versus shear rate of neat and CB-containing EVA-30.

The effect of the presence of fillers on the rheological properties of polymers has previously been discussed.^{18–25} For CB, the phenomena usually discussed relate to the role of large contents of CB in altering the viscosity of polymeric systems. Usually, an increase in viscosity is observed, pertaining either to interactions occurring between the filler and the matrix or to the formation of gellike structures when high filler contents are incorporated. Opposing effects have been reported as well, whereupon the viscosity decreases with CB content, especially in the high shear rate $range^{19-21}$; nevertheless, these are not detected here. The systems studied here contain much lower CB concentrations than are usually utilized; however, the effects of CB content on the melt rheology may still be detected.

The difference in rheological behavior between CB-containing HIPS as opposed to EVA may provide some insight regarding distribution of CB within the polymeric matrix. The observed increase in polymer viscosity with CB content, even at low CB concentrations, is expected.²² In the EVA-30/CB, both SEM micrographs (Fig. 2) and flow curves (Fig. 10) reveal a different state of distribution, different from HIPS/CB systems. The interactions between CB and EVA-30 are preserved when low shear rates are applied; however, as the shear rate increases, increasing chain slippage occurs across the interface, resulting in similar behavior of all compounds, regardless of CB content. CB-containing HIPS has already

been shown to be a unique system, with a surprisingly low percolation threshold and finely dispersed CB.¹ The increase in apparent viscosity of this system, even when high shear rates are used, may indicate the existence of tiny CB particles dispersed within the matrix. It is possible that these particles are produced by erosion of CB agglomerates during the dispersive mixing process.²³ Due to their large surface area, the apparent viscosity is affected, even at low CB content. This could explain the onset of percolation, obtained at approximately 2 phr CB, and the fact that the conductive network is indistinguishable by SEM.¹

Attempts were made to fit the rheological data obtained for CB-containing EVA-30 to models describing the behavior of dilute suspensions of rigid particles. Several models were used; however, satisfactory results were obtained only by applying the modified Roscoe equation²⁶:

$$\frac{\eta}{\eta_1} = \left(1 - \frac{\phi_v}{\phi_m}\right)^{-2.5} \tag{1}$$

where η is the apparent viscosity of the fillercontaining melt, η_1 is the apparent viscosity of the neat melt, ϕ_v is the volume fraction of the filler, and ϕ_m is the packing factor of the filler.

Figure 11 shows the correlation between the experimental data and the curve predicted by the Roscoe equation for two CB contents. A value of



Figure 11 Roscoe equation fit to the apparent viscosity of CB-containing EVA-30, as a function of shear rate.

 $\phi_m = 0.2$ has been found to be suitable for use in the Roscoe equation prediction for 2 phr CB-containing EVA-30, as well as in the lower range of shear rates for 8 phr CB-containing EVA-30. A higher value of $\phi_m = 0.3$ coincides with the high shear behavior of 8 phr CB-containing EVA-30.

The packing factor ϕ_m is defined as the ratio of the true volume of the filler to the apparent volume that it occupies. It usually reflects the filler geometry, which determines its ability to pack. Nielsen²⁶ suggested a value of 0.37 for aggregated systems in which the initial particles pack randomly into loose agglomerates to form larger, nonagglomerating particles that also pack randomly. An alternative value of 0.11 was proposed by Lee,²⁷ specifically for Ketjenblack CB. In the presently studied system, ϕ_m seems to increase at high shear rates for the 8 phr CB-containing EVA-30. It thus is suggested that ϕ_m is a factor reflecting the state of dispersion of the filler in the polymeric matrix, rather than just the particle shape. The increased value of ϕ_m at high shear rates may reflect structural changes of the CB from a highly structured, branched particle morphology to a more linear form.

The same considerations are taken into account regarding the percolation behavior of CBcontaining polymers. Comparison of the flow curves of 8 phr CB-containing EVA-30 with the resistivity-extrusion shear rate data depicts parallel trends in behavior as shear rate increases; that is, viscosity is reduced and resistivity is increased. Both effects are attributed to the change in CB cluster structure and dispersion.

Use of the packing factor or equivalent parameters relating to filler structure has been made for establishing the percolation threshold of various conductive filler-polymer systems. This has been done, for example, in the classical statistical percolation model of Kirkpatrick and Zallen²⁸ and the equation derived by Janzen.²⁷ However, no model has yet been able to account for the extensive influence of different processing methods on the percolation process, because of inhomogeneity in the distribution of the conductive phase and changes in its structure.

Figure 12 displays the viscosity data for HIPS/ EVA-30 blends. The following compositions were studied: 85HIPS/15EVA-30 and 55HIPS/45EVA-30, containing 0, 2, and 4 phr CB. Both blend compositions depict a rise in viscosity with CB content. The 85HIPS/15EVA blend, rich in HIPS, has higher viscosity values than the latter at all CB contents, at low to intermediate shear rates, and is more affected by the presence of the CB. At high shear rates, the viscosity values of both blend compositions at all CB contents converge to relatively similar values.

At low shear rates, the apparent melt viscosities of both neat and CB-containing blends decrease as the EVA content increases, as expected, but generally exhibit negative deviations from the inverse rule of mixtures²⁹ (not shown). This is probably due to the mobile interface, typical of immiscible blends, in which slippage occurs between the phases. The effect is more significant for the neat blend; for the HIPS/EVA-30/CB compositions, the negative deviation is smaller. This may result from the lower deformability of the EVA CB-containing phase, and the possibility that CB raises the thermodynamic stability of the blend,^{14–17} consequently diminishing the interface mobility.

An additional parameter of interest is the point of phase inversion. A relatively simple prediction of the point of phase inversion may be obtained by the following equation, generated by Jordhamo, Manson, and Sperling³⁰:

$$\frac{\eta_1}{\eta_2} \times \frac{\phi_1}{\phi_2} \approx 1 \tag{2}$$

When applying this equation to the neat blend, a value of 70HIPS/30EVA-30 has been predicted as the phase inversion point. When considering a 4 phr CB-containing blend, and utilizing viscosity values that relate to CB-containing EVA-30, the point of phase inversion is shifted to a higher EVA content, corresponding approximately to 55HIPS/ 45EVA-30. This coincides with SEM observations; the presence of CB alters the shape of the dispersed phase, causing its elongation and reducing its size. There is a relatively wide range of dual phase continuity, in which CB-containing EVA forms a continuous phase within HIPS; however, the midpoint for phase inversion occurs only at an approximate 1 : 1 HIPS/EVA composition. The model predicts that the phase with the lower viscosity or higher volume fraction will form the continuous phase; therefore, when the viscosity of EVA-30 is increased by addition of CB, a higher CB content is required to obtain phase inversion.

CONCLUSIONS

In view of the electrical, rheological, and morphological properties of CB-containing HIPS/EVA blends, the following conclusions are generated



Figure 12 Apparent viscosity versus shear rate of neat and CB-containing blends (a) 85HIPS/15EVA-30 and (b) 55HIPS/45EVA-30.

• The polarity and degree of crystallinity of the EVA-containing CB has a significant influence on the distribution of the latter within

the polymer, and on the resultant resistivity. High polarity induces polymer-filler interactions, hindering the formation of a segregated conductive network and thus increasing the percolation threshold; conversely, a semicrystalline polymer promotes the formation of conductive structures, reducing the percolation point.

- The double-percolation concept is once more assessed for these blend systems, in which percolation of the CB within the EVA as well as structural connectivity of the EVA-dispersed phase are necessary to realize conductivity of the blends. The presence of CB in the system modifies the morphology in a complex manner. By locating preferentially within the blend, and altering the flow properties and interfacial thermodynamics of the blend components, various structures are obtained. These in turn determine the electrical properties. Differences in blend structure and electrical conductivity in relation to the EVA grade, were detected.
- The resistivity of capillary rheometer extrudates as a function of extrusion shear rate was studied. A descriptive model was derived to illustrate the effect of shear rate on the structure and the resultant resistivity. The 4 phr CB-containing 70HIPS/30EVA-30 blend extrudates were found to withstand shear fields better than the other compositions, maintaining both first and second percolations as shear rates increase to intermediate values. The major benefit obtained by using HIPS/EVA blends rather than the individual polymers is increasing the effective CB content within EVA, as opposed to the enhanced structuring that occurs in the previously described CB-containing HIPS/LLDPE systems.
- All compounds containing EVA-9 (of lower polarity) exhibit lower resistivities than those with EVA-30.
- The presence of CB in the individual polymers and the blends affects the rheological properties of the compounds, despite the low contents utilized. Some parallel features were observed between the rheological behavior and extrudate resistivity values. The importance of structures obtained or degraded by flow was assessed in relation to the electrical properties of the extrudates.
- The blend viscosity depends greatly on composition. When CB is incorporated, the morphology is altered, depicting a positive-negative deviation from the inverse rule of mix-

tures, as opposed to the negative deviation behavior of the neat blends.

Thus it is evident that the nature of the blend components, the blend composition, CB content, and shear level are significant parameters, determining the structure and the resultant electrical properties. The formation of conductive structures is a dynamic process in which the CB not only constitutes a conductive filler, but also modifies the mixing kinetics and the interaction parameter between the components. This induces structuring, which in turn affects the electrical properties. The interrelation among the morphology, resistivity, and flow properties of these blends demonstrates a synergistic cycle in which conductivity may be enhanced. From a practical point of view, conductive blends may be engineered and their properties tailored according to these considerations.

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