Rheological and Morphological Properties of High-Density Polyethylene and Poly(ethylene–octene) Blends

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ABSTRACT: The rheological and morphological properties of blends based on high-density polyethylene (HDPE) and a commercial ethylene–octene copolymer (EOC) produced by metallocene technology were investigated. The rheological properties were evaluated in steady and dynamic shear experiments at 190°C in shear rates ranging from 90 s^{-1} to 1500 s^{-1} and frequency range between 10^{-1} rad/s and 10^2 rad/s, respectively. These blends presented a high level of homogeneity in the molten state and rheological behavior was generally intermediate to those of the pure components. Scanning electron microscopy (SEM) showed that the blends exhibit dispersed morphologies with EOC domains distributed homogeneously and with particle size inferior to 2 μm. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 86: 2240–2246, 2002

Key words: morphology; rheology; polyethylene; electron microscopy; polyolefins

INTRODUCTION

The polyethylenes are the plastic materials with more uses in the industry. The members of polyethylene family offer a broad spectrum of structures, properties, processability, and applications. Their blends are also of commercial interest and both theoretical research and practical development are currently very active.[1,2] The newest members of this family are the ethylene–octene copolymers produced by metallocene technology.[3,4] This new class of polyethylene modified by the nature of long chain branching and the arrangement of short chain branching in the macromolecule, if used in blends with polyolefins like polypropylene, PP, and other polyethylenes, PE, produce materials easily processable and with tailored properties for specific purposes.[5–10]

Polymers produced by metallocene technology generally exhibit a molecular structure with narrow molecular weight distributions. The shear sensitivity of these polymers can be controlled to the desirable level through selective incorporation of long chain branchings.[11]

Several researchers have studied the rheological properties of metallocene polymers.[12–19] However, very little is known regarding the rheological properties of blends based on polyolefin (PP and PEs) and metallocene polymers.[10,20] Therefore, in this work, a systematic study has been carried out to investigate HDPE-based blends containing a commercial metallocene poly(ethylene-co-1 octene) as a second component. The influence of the blends composition on their rheological and morphological properties were evaluated.

EXPERIMENTAL

Material and blend preparation

High-density polyethylene (HDPE) (M_w = 285,700 ; MFI = 0.93 g/10min) and poly(ethylene/1 octene) (EOC) (ENGAGE 8100, with 24 wt % of octene; M_w = 323,000; MFI = 1.0 g/10min) were donated by Polialden/BR and Dow Chemical/USA, respectively. A Wortex single screw extruder, model H210, was used to prepare the binary HDPE/EOC blends by melt blending. The screw speed was set at 50 rpm, and the temperature profile in the extruder from the feed to the metering zone was set at 230°C. The extrudate in form of narrow sheets was quenched in a cold water bath. The volume fraction of EOC was varied in a large range from 5 to 80%.

Rheological behavior

The steady shear experiments were carried out in an Instron capillary rheometer, model 4204 using a cap-

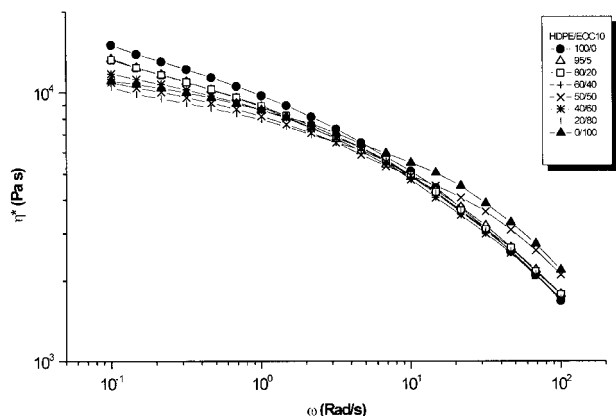**Figure 1** Complex viscosity of HDPE, EOC, and HDPE/EOC blends.

Figure 3 Loss modulus of HDPE, EOC, and HDPE/EOC blends.

illary of L/D = 70 at 190°C over shear rates ranging from 90 to 1500 s^{-1}. The shear stress (τ_W), the shear rate (γ) and the viscosity (η) were calculated using standard procedures. Due to the high L/D ratio of the capillary, Bagley correction for elasticity was not necessary. Rabinowitsch correction for non-Newtonian behavior was made. The flow behavior index (n) was determined by regression analysis of the values of τ_w and γ_w obtained from the experimental data. The dymanic viscoelastic properties were determined in a Rheometrics dynamic rheometer SR200 in a cone-plate geometry at 190°C. The complex viscosity (η^*), the storage modulus (G'), the loss modulus (G''), the relaxation modulus [$G(t)$] and the relaxation spectrum [H(λ)] were determined in frequencies ranging from 10^{-1} rad/s to 10^2 rad/s under nitrogen atmosphere. All rheological measurements were carried out in the linear viscoelastic region.

Morphological characterization

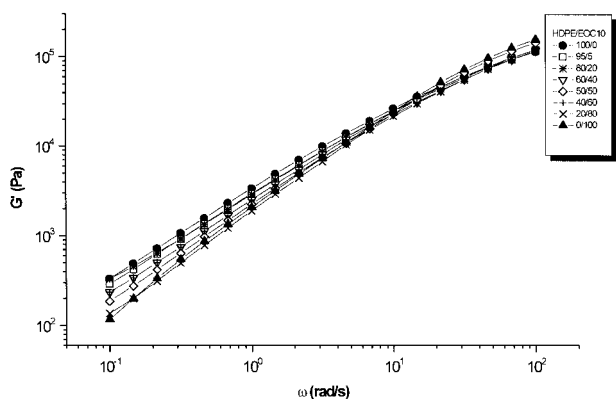The morphologies of the blends were examined in a DSM-960 digital scanning electron microscope (SEM),

at operating voltage of 15 kV. The samples were cryogenically fractured in liquid nitrogen in perpendicular way to the extrusion direction and etched with xylene at 60°C for 30 s to extract the EOC phase, dried at 30°C for 2 days, and finally coated with gold prior to their SEM examinations.

RESULTS AND DISCUSSION

Dynamic rheological properties

The melt flow index similarity of HDPE and EOC makes the influence of blend composition on the rheological properties little significant. As shown in Figures 1–5, the rheological curves present crossover, superposition, and inversion behavior regions.

The measurements of complex viscosity at low and intermediate frequencies in blends allows to study interactions between phases, because the morphology, in most of the cases, is undisturbed by the flow deformation. The dependence of complex viscosity on the shear rate at 190°C for HDPE, EOC, and their blends is shown in Figure 1. The pure components and blends
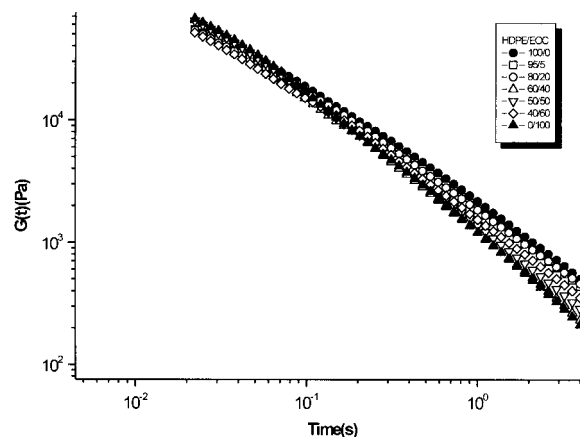

Figure 2 Storage modulus of HDPE, EOC, and HDPE/EOC blends.

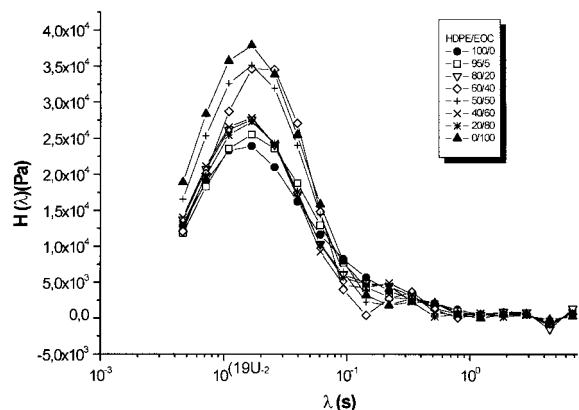**Figure 4** Relaxation modulus of HDPE, EOC, and HDPE/EOC blends.

Figure 5 Relaxation spectrum of HDPE, EOC, and HDPE/EOC blends.

present typical pseudoplastic behaviors. At low shear rates , the viscosity of HDPE is higher than EOC, while an inverse behavior is observed at high shear rates. The complex viscosities of the blends vary in a non-linear mode in relation to the pure components. As can be seen in Figure 1, the curves show a tendency to converge and later split out. This feature was also observed in other polyethylene and polypropylene blends.[10,21–25] The presence of long chain branching in the EOC copolymer affect significantly the rheological behavior of HDPE/EOC blends. Entanglements between branches and chain segment of EOC and HDPE may occur randomly, modifying the entanglement density of these blends under shear flow. Consequently, a nonlinear rheological behavior is observed. A different behavior was verified when a different grade of EOC (ENGAGE 8200) with high MFI and low long chain branching proportion was used in blending with HDPE.[44,45] In this case a linear rheological behavior was found corroborating the importance of long chain branching proportion on the shear sensitivity of these metallocene copolymers and their blends.[11,21]

The Figures 2 and 3 show the dependence of storage and loss moduli with frequency, respectively. The storage modulus increases with increasing frequency. At low frequencies HDPE presents the highest G' values and this behavior changes as the frequency increases. The storage modulus of the blends are intermediate to those of the pure components. The curves also show a tendency to converge and separate out similarly to what was observed in the complex viscosity plot. The loss modulus of the pure polymers and blends increases with increasing frequency and is practically about the same for all blends. At high shear rates (>2 rad/s) the loss modulus of all samples tend to a converging value of about 150,000 Pa.

In the region of low frequencies the chain entanglements are more pronounced for HDPE, making it more viscous than EOC and the blends. This effect is

reflected directly on its higher G' values. The presence of long chain branching in EOC structure unables the polymer to retain its unstressed initial state completely under shear flow.[18] Long chain branchings (LCB) and molecular weight distributions (MWD) are parameters that affect the shear sensitivity of metallocene ethylene copolymers. In the region of high frequencies , EOC is more viscous than HDPE and this behavior may be attributed to either its narrow MWD or the presence of long chain branchings.[16,15,21,25] The blends can exhibit complex rheological behaviors, presenting deviations from linearity also caused by different morphological states that may undergo flow induced changes under shear experiments.[23]

The relaxation processes of HDPE, EOC, and their blends are depicted in Figures 4 and 5. The relaxation modulus for the pure components (Fig. 4) presents a crosspoint of about 24,000 Pa and 0.071 s. At shorter times ($<10^{-1}$ s) EOC presents the highest modulus and at longer times ($>10^{-1}$ s) its modulus is one of the lowest. The relaxation modulus in most of blends are intermediate to the pure components and the curves of the all samples, in a general way, become more separated as the relaxation time increases. The relaxation spectra (Fig. 5) of all samples are alike, and tend to exhibit a same value at relaxation time (λ) around 0.017 s. In the region of 10^{-3} s to 10^{-1} s, the spectra present different magnitudes indicating that for the same time scale, the samples pass by different numbers of deformational states.[26–30] EOC presents the highest magnitude of relaxation and HDPE the lowest one. At relaxation times higher than 10^{-1} s, the magnitudes of relaxations decrease continously and tend to a constant value.

The relaxation time of polymer blends may be used to analyze the interfacial properties and the miscibility behavior.[26,31–35] All blends compositions studied in this work present the same relaxation time (0.017 s), indicating that in the molten state there is a certain degree of homogeneity and/or very low interfacial
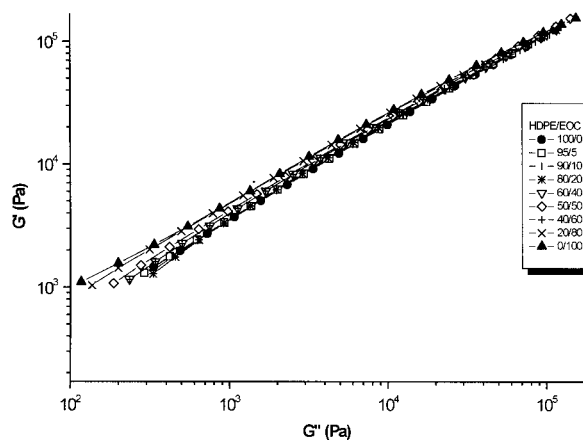

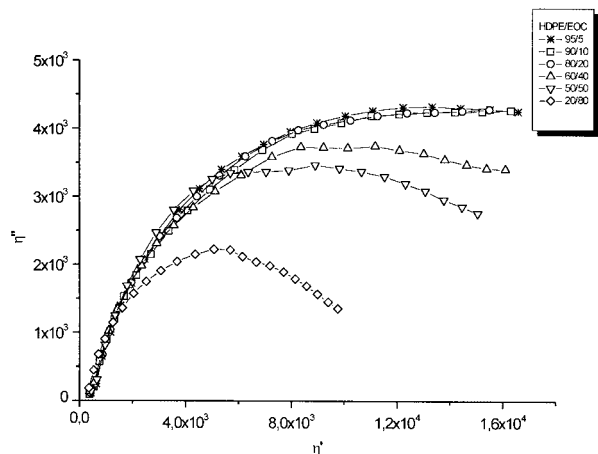**Figure 6** Plot of log G' vs. log G'' for HDPE/EOC blends.

Figure 7 Cole–Cole plot for HDPE/EOC blends.

TABLE I
Flow Behavior Index (n) of HDPE/EOC Blends at 190°C

EOC (%)	n
0	0.538
5	0.672
20	0.624
40	0.619
80	0.647
100	0.703

miscibility is indicated by the appearance of the curves with semicircle shapes. In Figure 7 is shown that for all blend compositions semicircles were obtained. Thus, we may also conclude that all blends present the same relaxation mechanism.

Steady shear rheology

The steady state shear viscosity, as a function of the shear rate, is a dominating parameter in the processing behavior of polymer melts. Thus, the ability to predict the viscosity from molecular parameters is of general interest.[20,42]

Figure 8 shows a 3D surface plot of the dependence of blend composition and shear rate on the shear viscosity. In the shear rates range studied in this work, all samples presented pseudoplasticity, with EOC exhibiting the highest viscosities. The blends viscosity, like their complex viscosity, shows a nonlinear change between the characteristics of the pure components HDPE and EOC. The effect of blend composition on the viscosity displays positive and negative deviations from linearity provoked by induced changes in the entanglement densities under shear flow.

The 3D plot was built using a mathematical model that employs rational functions together with a classical rheological model.

tension. Our previous work[36,37] about mechanical and thermal properties of these blends, showed that a certain level of interdiffusion of domains may occur in solid state favoring good mechanical properties.

The polymer–polymer miscibility has been evaluated by using dynamic rheological properties such as G', G'', η', and η''.[1,14,38–41] Han and coworkers[40] established a thermorheological criterion to determine copolymers and blends homogeneity in the melt state. A linear correlation in the plot of G' vs. G'' in logarithmic scale indicates that there is a high level of homogeneity and compatibility in the system.

Figure 6 displays the plot of log G' vs. log G'' for the pure polymers and their blends. It can be seen that the data fit well to a single linear correlation with very close slope values, suggesting that the blends have certain degree of homogeneity in the melt. This result may be confirmed by the analysis of a Cole–Cole plot (Fig. 7), in which the data of storage viscosity (η') are plotted against the data of loss viscosity (η'').[39] The
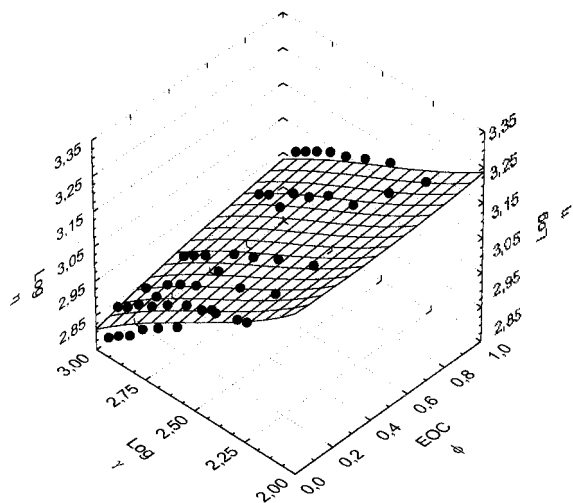

Figure 8 3D surface plot of the dependence of composition and shear rate on the viscosity of HDPE/EOC blends.
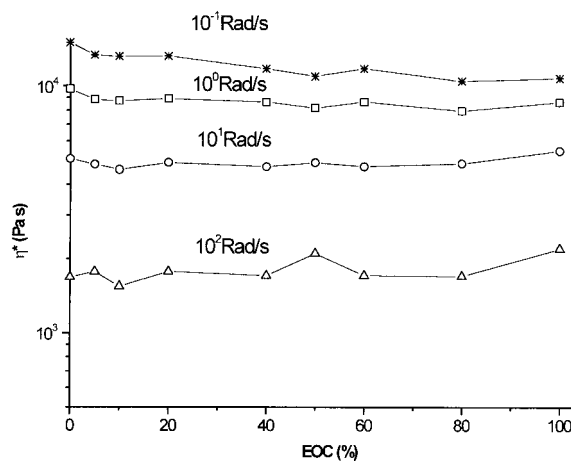

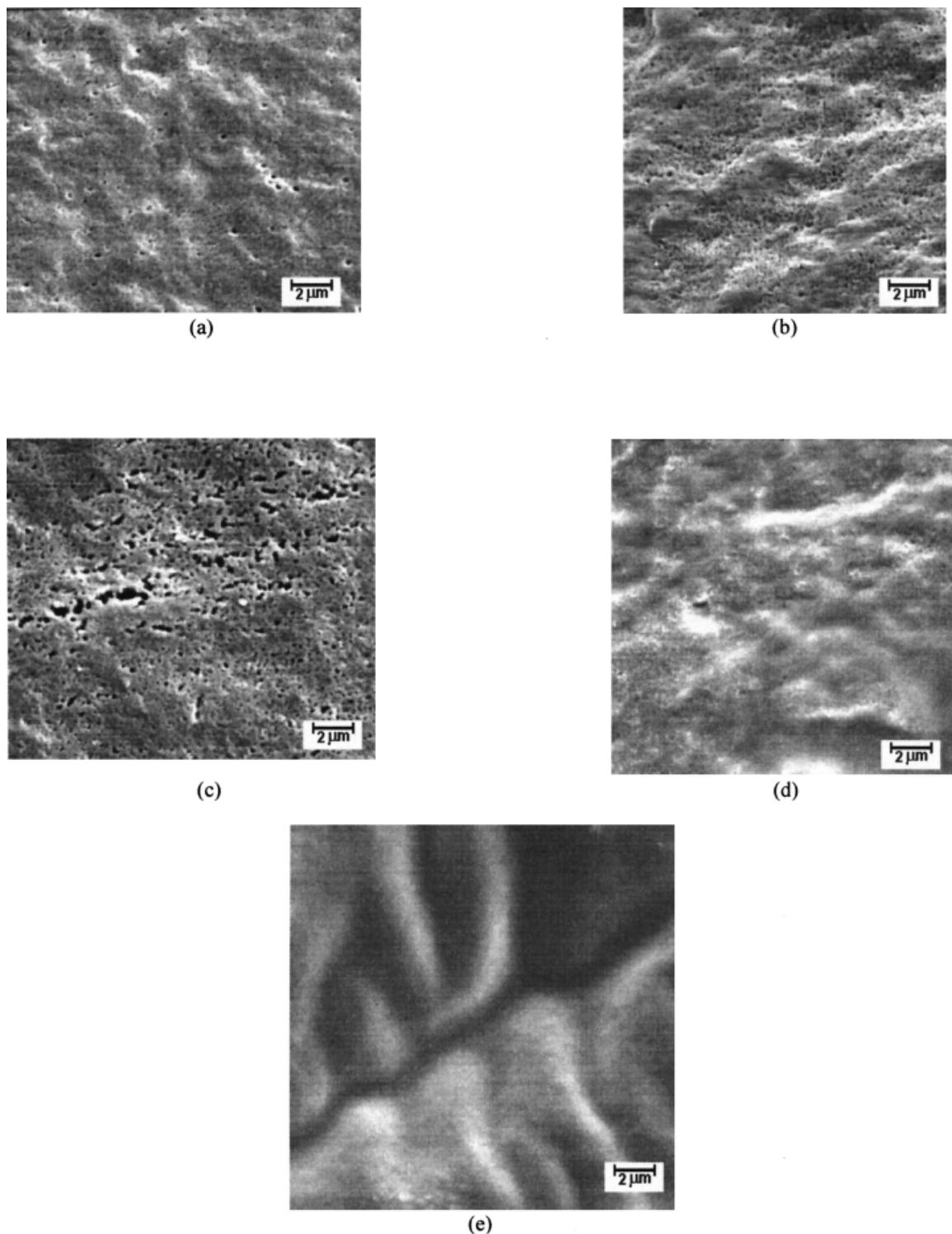**Figure 9** Viscosity vs. blend composition plot for HDPE/EOC blends.

Figure 10 SEM micrographs of HDPE/EOC blends: (a) 80/20; (b) 60/40; (c) 50/50; (d) 40/60; (e) 20/80.

$$Z = (a + b\phi_{EOC} + c\phi^2_{EOC} + dy + ey^2 + fy^3)$$
$$\div (1 + g\phi_{EOC} + h\phi^2_{EOC} + iy + jy^2) \quad (1)$$

where Z = log viscosity (η); y = log shear rate (γ) and ϕ = mass fraction of EOC and a,b,c,d,e,f,g,h,i,j are the coefficients of the polynomium.

This model was tested by Schellenberg to study the steady rheological properties of blends based on HDPE and ethylene–octene copolymer with low proportion of octene (ρ = 0.909 g/cm^3) and high content of long chain branching.[20] The model 1 fits well our data with a correlation coefficient (R = 0.98) slightly

inferior to that one found by Schellenberg ($R = 0.99$). The values of eq. (1) coefficients determined are: $a = 12{,}6$; $b = 4.5$; $c = -1.5$; $d = -5.6$; $e = 2{,}7$; $f = -0.5$; $g = 1.4$; $h = -0.5$; $i = 1.1$; $j = -0.2$, respectively.

The effect of blend composition on the flow behavior index (n) is listed in Table I. HDPE exhibits the lowest flow behavior index and EOC the highest one. In the whole shear rates range studied in this work, EOC was less sensible to the shear than HDPE and the blends. The n values did not show a regular variation with the blend composition. These results show again the complexity of the rheological behavior of these systems that is influenced by the structural characteristics of the pure components, such as molecular weight, molecular weight distribution and, more specifically, by the proportion of short chain and long chain branchings in the metallocene copolymer (EOC).

Relation of morphology to the rheological properties

The shape of curves of rheological properties vs. composition with their maxima and minima, are related to the morphology of the materials, at different blend compositions, stress field, and temperature, which in turn, depend on the components viscosity, elasticity ratio, phase interaction as well as interfacial tension and hydrodynamic effects.[27,30] The method of blend preparation is an other parameter that controls the observed interrelations between melt or solid state morphology and rheology.[42] Phase inversion, particle size, and shape, cocontinuity and conversion of drops into fibrils with different degree of alignment, depending on the stress level, are all parameters that have been suggested to be responsible for the shape of rheological curves.

The dispersion state in polymer blends may be evaluated by the relation between the melt viscosity and blend composition.[23,41,43] The cocontinuity is determined applying the criterion for phase inversion that relates the viscosity of pure components with their volume fraction [eq. (2).

$$\eta_1 / \eta_2 = \phi_1 / \phi_2 \tag{2}$$

Figure 9 shows the dependence of blend composition on the complex viscosity. The curves at different shear rates exhibit positive and negative deviations that become more pronounced with increasing shear rate due to higher level of deformation and the entanglements of the materials. Applying the criterion of phase inversion for HDPE/EOC blends with data of viscosity of the pure components at the shear rate of 10^{-1} s ($\eta_{\text{HDPE}} = 15{,}024$ Pa s and $\eta_{\text{EOC}} = 1075$ Pa s) the cocontinuity would be expected to occur in the vicinity of 50/50 blend composition.

The SEM micrographs of HDPE/EOC blends with different volume fraction of EOC are displayd in Figure 10. Small EOC domains (size < 2 μm) are dispersed homogenously in the HDPE matrix for materials containing up to 40% of EOC. The cocontinuity seems to have occurred in the vicinity of 50/50 composition, in agreement with the data obtained from rheological measurements. After the cocontinuity point a gradual phase inversion can be observed, with the blends exhibiting large HDPE domains dispersed in the EOC matrix.

CONCLUSIONS

The rheological properties of HDPE/EOC blends present complex behaviors, in general, intermediate to those of the pure components. The presence of high long chain branching concentration in the EOC structure contributes significantly to the nonlinear rheological behavior observed for these blends. These systems exhibit homogeneity in the molten state and good interfacial adhesion, which is extended, to a certain degree, to the solid state favoring the production of engineering materials with good mechanical properties. The morphological characterization of these blends is difficult, due to chemical and melt flow index similarity. Processes of interdiffusion of phases make the complete removal of EOC without affecting the HDPE phase almost impossible. The very small particle size of the EOC dispersed phase is also one of the factors that contributes for good compatibility of these blends in melt or solid state.

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