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# Effect of NR and EPDM on the rheology of HDPE/PP blends

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## Summary

We studied melt-rheological properties of ternary blends of polypropylene and high-density polyethylene with an elastomer (natural rubber or ethylene-propylene-diene), at several blending ratios and shear rates. Measurements made on a cone-plate rheometer are presented and discussed as a function of blend composition. The effect of the shear rate on the viscosity and flow curve is discussed in terms of the exponent of the power low for a non-Newtonian liquid. The addition of an elastomer to the polyolefins blends changes the shape of the viscosity-composition curve; this change is discussed in terms of the possible morphology of the blend.

## Introduction

Blending of incompatible polymers for achieving properties suited to particular applications is gaining importance. Performance of such multiphase polymer blends depends mainly upon their morphology that is developed depending upon the properties of the blend components. A knowledge of the rheological properties of the melt, as a well as the blend morphology, is important to control the processing parameters for such multiphase blends and, thus, for making suitable polymer blends for desired end use applications (1-3).

There have been studies of the rheological behavior of polyethylene (PE) and polypropylene (PP) blends, and their incompatibility has been established (4,5). Incorporation of a rubbery phase such as an ethylene-propylene rubber (EPR) improved the compatibility between these polyolefins. It has been observed that the presence of non-compatible elastomers with the polyolefins in proportions of the order of 10wt% increases the impact properties. One of these elastomers is a random ethylene-propylene-diene (EPDM) copolymer (4,6).

This paper presents a rheological study on the effect of an elastomer either EPDM random copolymer or natural rubber (NR) in binary blends composed by high-density polyethylene (HDPE) and PP. Melt-flow data on a cone and plate viscometer are presented. The variation of the melt viscosity with blend composition at different shear rates, and the non-Newtonian nature of the material (plasticity) are studied. The plasticity is studied through the analysis of the log-log plots of shear stress versus shear rate; a power law relation can model these plots, where the exponent gives a quantitative idea of the non-Newtonian behavior.

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## Experimental

The characteristic parameters of the commercial polymers are as follows. High density polyethylene (HDPE) LR7340-00 from Quantum Chemical with a molecular weight $M_w$=1.75 X$10^5$, and polydispersity $M_w/M_N$=14.4. Polypropylene (PP) extruction grade from Petroleos Mexicanos with $M_w$=1.01 X$10^5$, and $M_w/M_N$=3.49. Natural rubber (NR) hevea SMR-5, with $M_w$=1.05 X$10^6$, and $M_w/M_N$=5.9. Ethylene propylene diene (EPDM) Nordel 1040 from DuPon, with $M_w$=4.72 X$10^5$ and $M_w/M_N$=4. The measurements of the melt index (MI) for the four polymers were performed in a Kayeness serial Galaxy model D7053 at the following conditions: temperature 180°C and load 2,160g. The values obtained were $MI_{HDPE}$=0.982, $MI_{PP}$=0.893, $MI_{EPDM}$=0.02300, $MI_{NR}$=0; under these conditions the NR did not flow.

Ternary blends of an elastomer, NR or EPDM, with HDPE and PP were prepared in different weight compositions using a Banbury mixer at 180°C. They were laminated to a thickness of 0.7 mm by compression molding under a pressure of 3.5 MPa, at 180°C with a 5 min residence time in the press. The compression molded plates were quenched in water at room temperature (25°C).

The samples were grouped in five sets. Three sets with constant elastomer content as follows, one with 0 wt% elastomer (HDPE/PP) and two with 10 wt% (HDPE/PP/NR and HDPE/PP/EPDM), where the polyolefins content was varied. The elastomer content in the other two sets (HDPE-PP)/NR and (HDPE-PP)/EPDM was varied up to 30 wt%, but the blends contained the same relative amounts of each polyolefin. Melt-rheological measurements were carried out on a Bohling VOR rheometer with a 300 g-cm transducer and cone-plate geometry at 180°C.

## Model

The rheological behavior of the blends can be analyzed from the shear stress versus shear rate plots. These plots obey a power law relation. Thus:

$$\sigma = K\gamma^{n} \qquad 1$$

where $\sigma$ is shear stress; $\gamma$, the shear rate; K, the proportionality constant and *n* the power law exponent. When *n*=1 the fluid behavior is Newtonian, but when it is not so, the exponent can be used as a quantification of the plasticity of the blend. The blends rheological behavior may be analyzed by the change of exponent as a function of the composition. The exponent values were obtained from the slope of the logarithmic plots of relation 1.

## Results and discussion

### *HDPE/PP set*

The viscosity as a function of HDPE content at different shear rates is shown in Figure 1-A. The viscosity in all these blends is lower than it would be expected if a linear blending rule was followed. This is because both phases (discrete and continuous) have an elastic response, and therefore each of them can store a part of the elastic energy supplied to them by the cone and plate viscometer, a fact that has been reported before in the literature (8, 9). However, it is reasonable to expect that the discrete domains would dissipate less energy while flowing in the viscometer than the continuous phase that wets the cone and plate walls. In turn, they will oppose less resistance to flow and hence lower viscosity, and will be much lower if the disperse phase may be deformed by the flow. For the central zone none of the two phases is discrete so the viscosity gets closer to the linear blending rule. After the 50/50 composition, the viscosity increases with HDPE content. This could be attributed to the higher viscosity of the new continuous phase (HDPE) and the fact that the PP phase is now discrete.

The viscosity of the blends becomes more sensitive to the variation of shear rate as the HDPE content increases. The viscosity of PP does not change considerably with the shear rates reported here. However, the HDPE shows a large decrease in viscosity with increasing shear rates. The behavior of these changes in the viscosity at the rich-polyolefin blends is dominated by the phase with the higher composition. This behavior is reflected quantitatively in Figure 2 where the power law exponent is plotted as a function of the composition. Thus, discrete domains of the HDPE do not affect the pseudo-plasticity of PP.

HDPE has a lower exponent value than that presented by PP as shown in Figure 2. In the 25/75 blend, the power law exponent does not change respect to that of PP. The same behavior is observed in the HDPE-rich blends, since the 75/25 blend presents a value of power law exponent similar to that of the HDPE. In the 50/50 blend, the morphological effect would dominate the behavior of the power law exponent. In this blend the two polymers present continuous phases (10), then the exponent takes an intermediate value between those of the two polymers. The general behavior of the power law exponent is consistent with the behavior of the viscosity as a function of the shear rate, in the sense that the 50/50 point presents an especial behavior since it is the only point with two continuous phases.

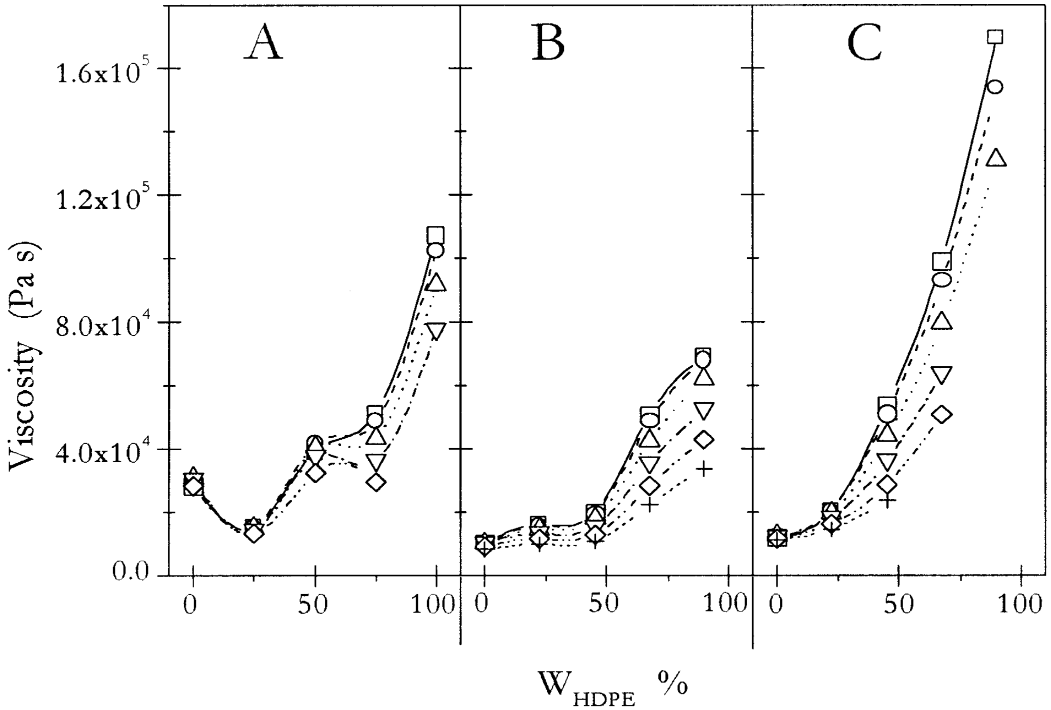

Figure 1 Viscosity behavior as a function of blending ratio for blends of: (A); HDPE/PP, (B); HDPE/PP/NR, (C); HDPE/PP/EPDM at 180°C, at various shear rates ($s^{-1}$): 0.0058 (□); 0.0093 (0); 0.0147 (Δ); 0.0233 (∇); 0.0369 (◊); 0.0585 (+).

### *HDPE/PP/NR set*

The behavior of the viscosity curve for this set (Figure 1-B) is simpler as compared to that for the HDPE/PP set. There are two zones in which the points obey almost linear relations; the blend with equal proportions of both polyolefins marks the limit of the zones, i.e. $0 \leq W_{HDPE} \leq 45$ and $45 \leq W_{HDPE} \leq 90$. Much of the structure observed in the HDPE/PP blends disappears with the presence of NR, since the elastomer forms a discrete phase on the polyolefins. The domains of NR produce a decrease on the viscosity on the samples that did not have a discrete phase, changing the shape of the curve especially in the central zone. The presence of the NR discrete domains makes a larger contribution to reduce the viscosity in the middle point, this is in accordance with extraction experiments reported (11), that suggest a size distribution that has a maximum at central zone. The large domains are easier to deform than the small ones; therefore, they have more capacity of storing elastic energy; thus, the viscosity of the blends decreases (8,9).

The viscosity of each blend decreases as shear rate increases. One of the differences as compared with the blend whiteout rubber is that in the PP-rich blends the viscosity decrements are higher than the ones observed in this zone. This is attributed to the discrete domains of NR in these blends, which are deformed and aligned in the direction of the rotation as the shear rate increases, giving as a result a decrement of viscosity. In the HDPE-rich blends, the presence of the PP discrete phase shows the same effect that the NR phase, namely deformation and alignment of discrete domains as shear rate increases.

The shape of the curve of the power law exponent as a function of the HDPE content is different with the presence of 10 wt% of NR in the PP-rich zone, Figure 2. When there are discrete domains of NR in the PP, a small decrease of the power law exponent of the 0/90/10 blend occurs. The power law exponent of the 22.5/67.5/10 blend (PP continuous phase) decreases due to the combination of discrete domains of HDPE and NR. When the polyolefins are found as continuous phases and the NR is found in discrete domains (45/45/10 blend), the exponent value is almost the same as the previous point. In both cases the value of the exponent shows the sensitivity of the rubber phase to the shear rate. For the HDPE-rich blends the PP is in discrete domains and the exponents are pretty close to the ones of the blends without elastomer. As in the viscosity behavior the discrete domains of PP are the ones that play the main role in the behavior of the blend.

### *HDPE/PP/EPDM set.*

In this set the viscosity behavior as a function of HDPE composition is shown in Figure 1-C. The form of the viscosity curve is simpler as compared to that one for the HDPE/PP set (Figure 1-A). For the 0/90/10 blend, the discrete domains of EPDM cause a decrease in viscosity, respect to the viscosity of the PP. In the case of the 90/0/10 blend, the discrete domains of EPDM cause an increase in its viscosity, respect to the viscosity of HDPE. This means that the discrete domains of the EPDM interact differently with each polyolefin, since in the first case there is almost no interaction and the deformation of the discrete domains decreases the viscosity, while in the second case the interaction causes an increase on the viscosity. The viscosity of 22.5/67.5/10 blend is practically the same that the 25/75 blend; therefore, the EPDM discrete domains do not affect its viscosity value. For the points where the HDPE forms a continuous phase the effect is always to increase the viscosity.

The viscosity decreases as a function of the shear rate. The change of viscosity in the first two points (PP-rich zone) is similar to that observed in the corresponding blends of HDPE/PP/NR. From then on, to the HDPE-rich zone, the viscosity change is higher than

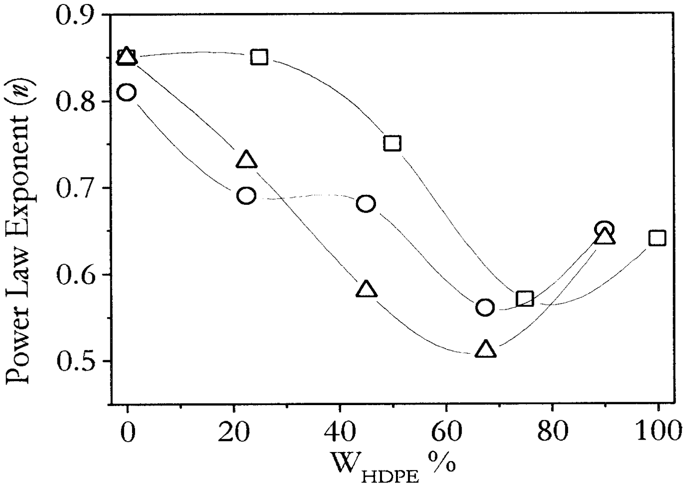

**Figure 2** Power law exponent versus blending ratio for blends of: (□); HDPE/PP, (O); HDPE/PP/NR, (Δ); HDPE/PP/EPDM.

that observed in the corresponding blends of the other two sets. The presence of the EPDM domains has larger influence in this zone since it increases viscosity and shear thinning, therefore the interaction of the EPDM with the HDPE is large and it allows for an easier orientation of the domains with the shear rate giving a reduction in the viscosity.

The power law exponent behavior just confirms the last discussion (Figure 2), since it decreases continuously as the HDPE content increases, this is different from the other two sets. Only the last point shows a deviation, but in all the sets the last point is affected by the limitations of the equipment since the exponent was calculated with fewer points, since the torque was saturated in the measurement, and it was not possible to get higher shear rates. The fact that the blend is more shear rate sensitive confirms that the EPDM domains should be easier to deform in the HDPE continuous domain. Also that the morphology should be different to the NR case since the EPDM blends viscosity is higher but with a higher shear rate sensitivity. This could be due to the EPDM domains migrating to the interface. This migration causes that the behavior of the blend changes by the presence of HDPE domains (discrete or continuos).

### *(HDPE-PP)/NR set*

The variation of viscosity as a function of rubber content for this set is shown in Figure 3-A at different shear rates. Initially, the viscosity decreases as the NR content in the blend increases up to 10 wt% NR. The viscosity presents small changes around 15 and 25 wt% of NR at low shear rates. It was found in experiments of NR extraction performed elsewhere (11) for this set, that around 20 wt% of NR, this elastomer starts to percolate. The behavior of the viscosity shows a dependence on the size of the NR domains until 10 wt%, after this point there are small fluctuations but it does not have a major effect at percolation, and when the shear rate increases even the small fluctuations disappear. The rheology of the rubber phase is the main influence and the sensibility to percolation is small in the viscosity value.

Figure 4 shows the behavior of the power law exponent for these blends, which decreases up to 15wt% NR. Between 15 and 30 wt% of NR content, there are changes in the curvature showing a sharp inflexion point around 15 wt%. This change in the shape is attributed to the percolation of the NR domains within the matrix formed by the polyolefins, the percolation should take place between 15 and 20 wt%. As the content of NR increases from 0 to 15 wt%, the discrete domains of NR increase in size and number (extraction experiments); therefore, the power law exponent of the blend decreases. In the NR percolation zone, the majority of the NR discrete domains form a continuous phase within the blend, causing a change in the power law exponent behavior.

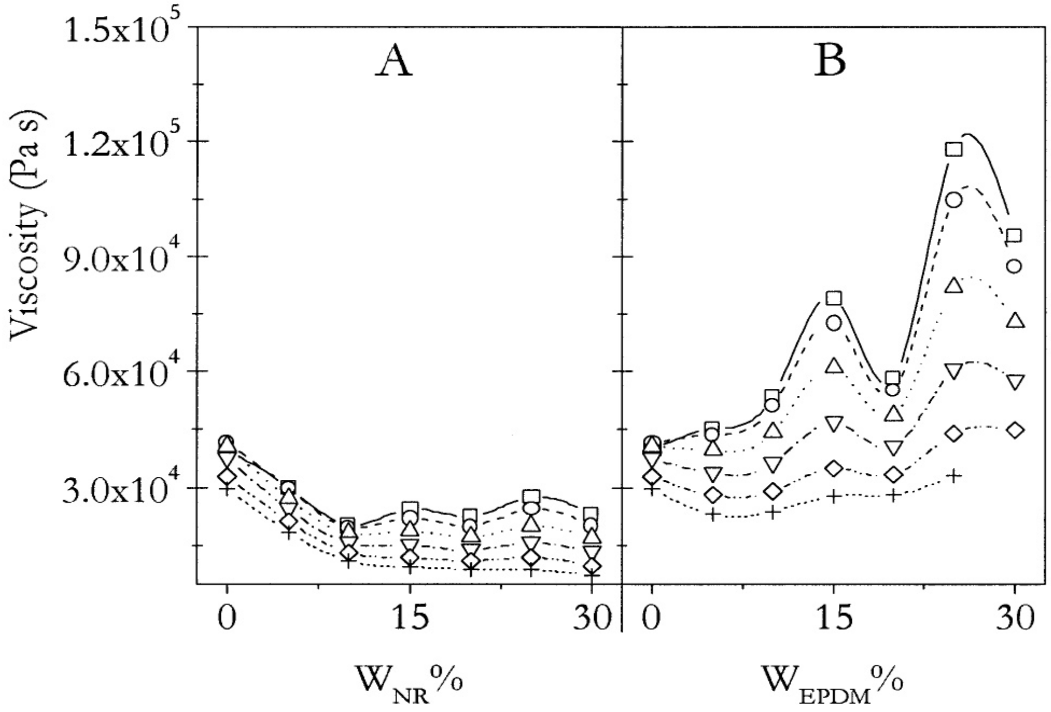

Figure 3 Viscosity versus blending ratio for blends of: (A); (HDPE-PP)/NR, (B); (HDPE-PP)/EPDM at 180°C, at various shear rates ($s^{-1}$): 0.0058 (□); 0.0093 (0); 0.0147 (Δ); 0.0233 (∇); 0.0369 (◊); 0.0585 (+).

*(HDPE-PP)/EPDM set.*

Figure 3-B shows viscosity versus blending ratio for this set at several shear rates. In these plots there is an increment in the viscosity with an increase of EPDM composition up to 10 wt% EPDM and at 15 wt% the increment is larger. As in the NR set, this point gives a different behavior but in contrast to that set, now from this point on the rheology has large fluctuation. That could be interpreted as a percolation zone but the complex morphology of the EPDM domains is not easy to follow since as it was established that the EPDM may go to the interface. The proposed interaction between the EPDM and HDPE domains may be the cause of the large viscosity changes, but again, as the shear rate increases the morphological effects almost disappear. The blend should go to a morphology that avoids or diminish the EPDM-HDPE contacts.

When there is an increase of EPDM content in the set, the value of the power law exponent decreases continuously up to 15wt% (Figure 4). The behavior is very close to the one shown by the (HDPE-PP)/NR set. The shape of the power law exponent curve is different between 15 and 30 wt% of EPDM content, as in the NR set, but in this case it shows large fluctuations. This change on the behavior between 15 and 30 wt% is related to the difference in morphology of the EPDM domains, they must be close to the interface between the two polyolefins and this gives higher interaction and therefore large fluctuations. As it was pointed out by the analogy to the NR set there could be a percolation zone also between 15 and 20 wt%, but the complex morphology makes it hard to visualize.

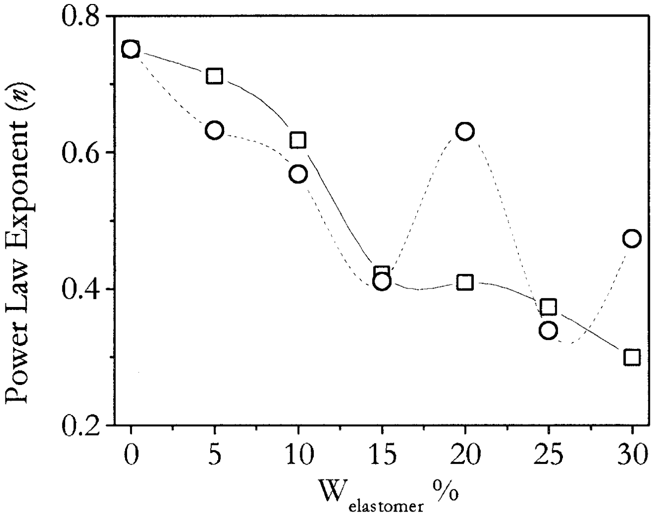

**Figure 4** Power law exponent versus blending ratio for blends of: (□); (HDPE-PP)/NR, (O); (HDPE-PP)/EPDM.

## Conclusion

1. The viscosity presents a maximum on the 50/50 composition for the blends without rubber, which was interpreted as a behavior that supports the proposition that the two polymers are in continuous phases. Also, the power law exponent is consistent with the proposition since it has one value for the PP-rich zone and changes for the 50/50 composition taking a final value for the HDPE-rich zone. Therefore the continuous phase defines the power law exponent and in the central point some kind of average exponent is obtained.
2. The viscosity of the blends with NR is affected by the presence of the rubber discrete phase in all the samples, but especially on the ones that did not have a discrete phase before. The shape of the curve of viscosity against composition shows this effect and it is the responsible for the rheological behavior of these blends.
3. The EPDM discrete domains have different effect on each polyolefin when 10% of this rubber is added to the blends. At high HDPE content the rubber integrates to the blend and produces an increment on the viscosity and a higher sensitivity to shear rate. Meanwhile on the PP-rich blends the rubber segregates and produces a decrement in viscosity and small changes with the shear rate.
4. For compositions between 15 and 20 wt% of elastomer (NR or EPDM) the viscosity behavior suffers a change. This change is associate to a percolation effect of the elastomer within the matrix formed by the polyolefins. Noteworthy in the case of EPDM the complexity of the morphology gives a fluctuating rheology.
5. The power law exponent is clearly affected by the percolation effect, since the shape of the curve shows a deviation in the tendency of the points at this region. It also shows the effect of the complex morphology of the EPDM domains.

## References

1. Ultracki LA (1982) Polym Eng Sci 22:96
2. Ultracki LA (1983) Polym Eng Sci 23:602
3. Ultracki LA (1990) Polymer Alloys and Blends, Thermodynamics and Rheology. Hanser Publishers, New York
4. Teh J, Rudin A, and Keung J (1994) Advances in Polymer Technology 13:1
5. Krause S (1978), Polymer Blends Vol. 1, D.R. Paul and S. Newman (Eds.), Academic Press, New York
6. L. D'Orazio, R. Greco, E. Martuscelli and G. Ragosta. (1983) Polym Eng Sci 23:9
7. Bhattacharya AK, Santra RN, Tikku VK, Nando GB (1995) J Appl Polym Sci 55:1747
8. Han CD (1976) Rhelogy in Polymer Processing. Academic Press, New York
9. Han CD (1981) Multiphase Flow in Polymer Processing. Academic Press, New York
10. Ha CS and Kim SC (1989) J. Appl Polym Sci 37:317
11. Hernández-Sánchez F, Manzur A, Olayo R (1994) Influence of NR on the Mechanical and Thermal Properties of HDPE/PP Blends. Gramado, Brazil (4th Latin-American Polymer Simposium -SLAP, pp 900-902)