

EFFECT OF THE PERCOLATION OF NR ON MECHANICAL PROPERTIES OF HDPE/PP/NR BLENDS *

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INTRODUCTION

Polymer blends have been used as a successful cost-effective method to upgrade common polymers [1]. The particular case of polyethylene (PE) and polypropylene (PP) blends has been studied using different techniques; their incompatibility has been established for blends in solution, in melt, and in solid state [2]. Incorporation of a rubbery phase has been used to improve some properties of these blends [3-5], but studies on ternary blends of PE/PP/rubber are relatively few compared to studies on binary blends of PE/PP.

The largest number of works devoted to the study of percolation characteristics of a medium refers to measurements of electrophysical properties of disordered systems [6], although the percolation phenomena are exhibited in other properties, e.g., in the rheological characteristics of microemulsions [7] or in the regularities of their luminescence [8].

As the concentration of rubber particles increases, small particle agglomerates are first formed in the system. At some concentration of the rubber particles, referred to as the percolation threshold, rubber bridges are formed across the clusters. These bridges may be composed of single particles or of their aggregates. Thus, the originally isolated clusters are combined into a large, connecting cluster. At this moment, the nonconnecting system is transformed into a connecting state in a jumpwise manner.

It is well known that the mechanical properties of blends are very sensitive to the morphology. The distribution of an elastomer added to a blend affects these properties. The determination of the elastomer content at which the elastomeric connectivity occurs is of fundamental importance. One way to determine this content is by extraction of the elastomer using good solvents for the rubber but which do not affect the blend components.

The objective of this work was to evaluate the effect of the connectivity of an elastomer in the binary blend composed of high density polyethylene (HDPE) and polypropylene (PP). Natural rubber (NR) was chosen as the elastomer because of its capability to be extracted from the blend. In this way we may get information about the rubber distribution

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in the blend that is related to the mechanical behavior of blends containing NR. We report the NR extraction, and initial and final mechanical properties of HDPE/PP/NR blends.

EXPERIMENTAL

Materials. The characteristic parameters of the commercial polymers are as follows. The HDPE sample was obtained from Quantum Chemical, the PP from Pemex, México, and the natural rubber was hevea SMR-5. The MFI values for HDPE and PP were measured at 180 °C under a load of 2169 g; their average values are 0.982 dg/min for HDPE and 0.89 dg/min for PP. The values of molecular weight and polydispersity for these polymers were reported elsewhere [5]. The polymers were used without any modification.

Sample preparation. Mixing was done using a Brabender Banbury type mixer with a 25 ml chamber. Mixing in the desired weight ratio was made at 180 °C and 30 rpm for 18 minutes. All samples were laminated to a 0.7 mm thickness by compression molding under a pressure of 3.5 MNm⁻² and 180 °C with a 5 min residence time in the press. The compression-molded sheets were quenched in water at room temperature (25 °C). The elastomer content in the samples was varied from 0 up to 30% by weight, but the blends contained equal relative amounts of each polyolefin.

Extraction. All samples containing NR were exposed to solvent to extract the rubber. The extracted weight fraction (NR_{Ex}) is defined as:

$$NR_{Ex} = \frac{W_b - W_a}{W_b}$$

where W_b and W_a are the weight of the sample before and after extraction, respectively. Extraction was done using a Soxhlet system with tetrahydrofuran as solvent and was performed until the asymptotic behavior was obtained. Weights were measured with an Ohaus Analytical Plus balance with a precision of 1×10^{-5} g. Therefore, in the plots of the extracted rubber, the error bars of the experimental values are smaller than the size of the symbols. Rectangular samples with dimensions 15x20 mm were exposed to solvent.

Mechanical testing. Tensile specimens were punched out from the sheets. Tensile tests were carried out up to rupture using an Instron universal testing machine at room temperature and at a crosshead speed of 20 mm/min. From the stress-strain data the Young's modulus (E), and stress at break (σ_B) were obtained. A considerable amount of scatter in the data is inherent in these types of measurements, particularly in the final properties. Therefore, all the reported data represent the average of at least six specimens.

RESULTS AND DISCUSSION

Extraction. The experiments on the kinetics of the NR extraction, performed with blends containing 10% elastomer, show that during the first 24 hours there is a high extraction rate and then the rate is continuously reduced until its asymptotic value. The extraction rate decreases because the extractable NR exposed to the solvent is gradually diminishing until it is completely dissolved and extracted. In the asymptotic region, the NR extracted was close to 60% of the total rubber present in the sample.

The values for extracted rubber as a function of the NR content in the blends and as a function of time were calculated; the samples were in contact with the solvent during 72, 144 and 216 hours. For 144 and 216 hours there is practically no difference in the amount extracted since these times are in the asymptotic region. A plot of extracted NR vs. NR content, a straight line to 45°, would correspond to the ideal situation in which the extracted fraction equals the total NR content in the blends. It is observed that as the rubber content increases, the curves of extraction diverge from the ideal case from the beginning up to the weight fraction of 0.2; from this fraction on, the tendency of the curves becomes convergent to the ideal situation. This indicates that starting up from a fraction of about 0.2 the NR percolates in the matrix formed by the polyolefins. It is not possible to extract all the rubber in the blends since there would be domains that remain isolated in the matrix even though the percolation phenomenon occurs. As the rubber content increases, fewer domains remain isolated and the extracted fraction approaches the total content in the blends, thus going towards the ideal case line. These results on the kinetics of extraction and the amount of extracted rubber allow to obtain information about the connectivity of the rubber phase domains and, consequently, the morphology.

The SEM images, for the extracted samples for several concentrations of NR, show that the sample with 5% wt of NR has dispersed bowl-shaped surface depressions where the rubber was extracted. The samples for 20, 25 and 30% wt NR, after the percolation threshold, show cavities and connected regions, where a large amount of the NR was extracted. In contrast, the unextracted NR samples for 5 and 25% wt show a smooth surface, with protuberances in the case of the 25%; these are mainly where the natural rubber is present, as the extracted samples showed.

Mechanical properties. The effect of the rubber on the tensile properties of the binary blend HDPE/PP containing equal relative amounts of each polyolefin was also investigated. Since the response of the material to the applied stress depends on the morphology, from the behavior of these properties we can infer that the morphology of these blends is not simple. A change is shown in the behavior of the elastic modulus around 20%. This change is associated to the onset of percolation of the elastomer. The stress at break also decreases for values of w_{NR} between 0% and 20%. For higher NR content it is almost constant. This concentration value also corresponds to the percolation threshold of the elastomer.

Ha et al. [9] studied HDPE/PP blends and according to the SEM micrographs in the polyolefin-rich zones one component is continuous and the other one dispersed. They found that the blend with equal content of each material has interconnected phases. However, Lovering et al. [10] reported that the 50/50 blend shows a two-phase structure; islands of HDPE are dispersed within the continuous matrix of PP. These different morphologies may be ascribed to the different relative molecular weights. The freeze-fracture micrographs of

our system showed no clear morphology. The morphology observed by Ha et al. for the 1:1 binary blend is proposed here since it is also in accordance with the rheology of these blends [5]. Since crystalline polymers are essentially composite materials with alternating crystalline and amorphous regions, it is reasonable to expect the incorporation of the NR predominantly in the bulk amorphous phase surrounding the crystalline regions [11].

D'Orazio, et al. [3] studied the influence of the addition of rubbery ethylene-propylene copolymer (Dutral) on the morphology and mechanical tensile properties of binary HDPE/PP (1:1) blends; the curve for the Young's modulus as a function of rubber content as well as that for the ratio between modulus and overall crystallinity exhibited a change of slope at about 25%; we suggest that the appearance of this change is due to percolation.

Broadly speaking, with the increment of the rubber content there are 2 competing factors expected to reduce E and σ_B : (1) incompatibility of the polymers and (2) overall crystallinity and rubber phase domain size. The deterioration of ultimate strength as a result of incompatibility of the polymers is due to poor interphase adhesion. This explanation was proposed for blends of different composition of NR in PE/PS at 1:1 ratio [12]. Decreases in overall crystallinity of the blend, caused by the addition of rubber to the HDPE/PP blend, result in decrement of E and σ_B , as well. The deterioration of these mechanical properties with increase in rubber concentration is also associated with the increment of the rubber phase domain size. The amorphous phase of the ternary blend becomes softer and consequently its ability to transmit the applied stress to the crystalline regions weakens. The results here obtained for the extraction, elastic modulus, and stress at break show that the change observed at 20% of NR content undoubtedly is due to the percolation effect.

CONCLUSION

The effect of the incorporation of natural rubber (up to 30% content) on the blend HDPE/PP, with equal proportions of both polymers, was studied. The ability of the rubber to be extracted, without affecting the polyolefins, allowed to detect the percolation phenomenon of the rubber around 20% of its content. The addition of the rubber phase caused decrements of the initial and final mechanical properties because the total crystallinity of the binary blend is reduced. Additionally, because the bulk amorphous phase increases with the rubber, the whole amorphous phase of the system becomes softer and reduces its capability to transmit the applied stress to the crystalline regions. The sensitivity of these mechanical properties also allowed to detect the percolation of the rubber at about 20% of the rubber content.

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