

Effect of the Percolation of NR on Mechanical Properties of HDPE/PP/NR Blends

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ABSTRACT

The effect of the connectivity of an elastomer in a blend of two polyolefins was studied. Blends of natural rubber (NR) with high density polyethylene (HDPE) and polypropylene (PP) were prepared using a Banbury mixer at 180°C. The samples were laminated by compression molding at 180°C and quenched in water at room temperature. Extraction of the natural rubber was performed for blends containing equal relative amounts of both polyolefins. The percolation of the rubber within the matrix of both polyolefins started to occur at about 20% rubber content. Mechanical properties, such as Young's modulus and stress at break, showed the effect of the percolation phenomenon.

Key Words: Percolation; Natural rubber; HDPE; Polypropylene.

INTRODUCTION

The preparation of polymer blends is used as a successful cost-effective method to upgrade common polymers.^[1–4] The particular case of polyethylene (PE) and polypropylene (PP) blends was studied using different techniques, and their incompatibility has been established for blends in solution, in melt, and in solid state.^[5] Incorporation of a rubbery

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phase has been used to improve some properties of these blends,^[6–8] but there are relatively few studies on ternary blends of PE/PP/rubber compared with studies on binary blends of PE/PP.

The largest number of experimental works devoted to the study of percolation characteristics of a medium refers to measurements of electrophysical properties of disordered systems (see review by Roldughin and Vysotskii),^[9] although the percolation phenomena are exhibited in other properties, e.g., in the rheological characteristics of microemulsions^[10] or in the regularities of their luminescence.^[11]

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. When an elastomer is added to a binary blend, its distribution in the blend affects the mechanical 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 other components in the blend.

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

EXPERIMENTAL

Materials

The characteristic parameters of the commercial polymers used to prepare the blends follow. The high density polyethylene (HDPE) sample was obtained from Quantum Chemical, the PP from Pemex, México, and the natural rubber was hevea SMR-5. The melt flow index (MFI) values for HDPE (marketed under the name LR7340-00) and PP (extrusion grade) were measured at 180°C under a load of 2169 g using a Kayeness instrument (model D7053); 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 have been reported elsewhere.^[8] These 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 done 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 a temperature of 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 varied from 0 up to 30% by weight, but the blends contained equal relative amounts of each polyolefin, i.e., their weight ratio was kept constant in a relation of 1 : 1.

Extraction

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

$$NR_{Ex} = \frac{W_b - W_a}{W_b} \quad (1)$$

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 is the size of the symbols. Rectangular samples with dimensions of $15 \times 20 \times 0.7$ mm were exposed to solvent.

Mechanical Testing

Tensile Specimens were punched out of the compression-molded sheets. Tensile tests were carried out up to rupture using an Instron universal testing machine model 1125 at room temperature and a crosshead speed of 20 mm/min. The Young's modulus (E), and stress at break (σ_B) were obtained from the stress-strain data. 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 results of the experiments on the kinetics of the NR extraction performed with blends containing 10% elastomer are shown in Fig. 1. 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 gradually diminishes 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.

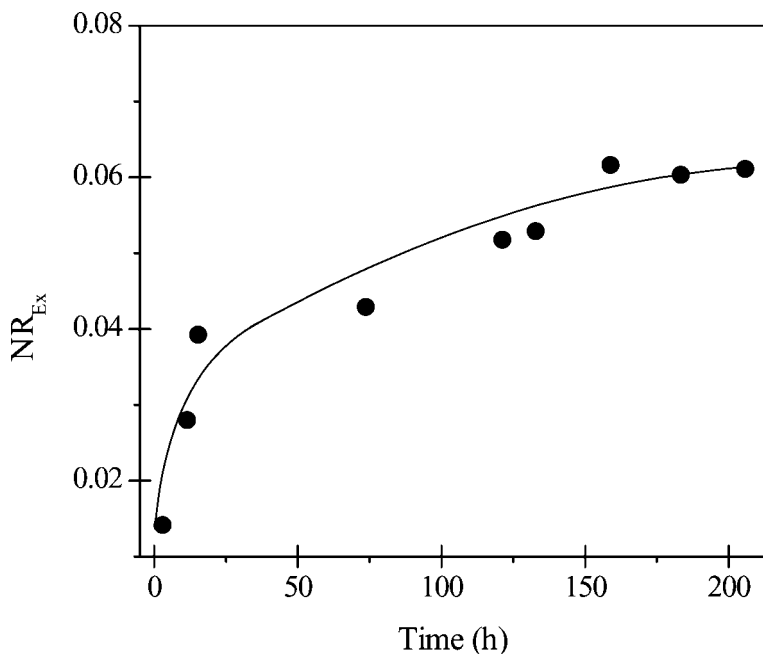


Figure 1. Rubber extraction kinetics for the blend containing 10% of rubber.

The values for extracted rubber as a function of the NR content in the blends are shown in Fig. 2. These 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 as shown in Fig. 1. The straight line corresponds to the ideal situation in which the extracted fraction equals the total NR content in the blends. It was 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 case. This indicates that starting 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 information to be obtained about the connectivity of the rubber phase domains and, consequently, the morphology.

Figure 3 shows the scanning electron microscopy (SEM) images of the extracted samples for several concentrations of NR; the first image is with 5% wt of NR and shows dispersed bowl-shaped surface depressions where the rubber was extracted. The following micrographs are of 20, 25, and 30% wt NR; images c and d, after the percolation threshold, show cavities and connected regions, where a large amount of the NR was extracted. In contrast, Fig. 4 shows two micrographs of unextracted samples of 5% and 25% wt, they show a smooth surface, with protuberances in the case of the 25% wt;

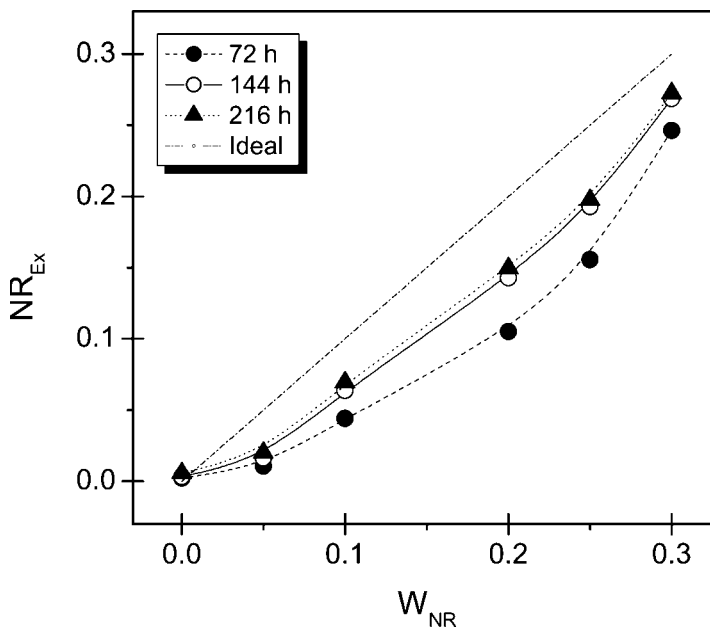


Figure 2. Rubber extraction as a function of rubber content, at three different times.

these protuberances, mainly occur where the natural rubber is present, as the extracted samples show.

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. Figure 5 shows the elastic modulus and the stress at break as a function of the weight fraction of the rubber. The error bars are included to emphasize that the decrement is nonlinear. 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 with 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 within experimental error. This concentration value also corresponds to the percolation threshold of the elastomer within the matrix.

Ha and Kim^[12] studied a similar system (HDPE/PP) 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 and Williams^[13] 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.

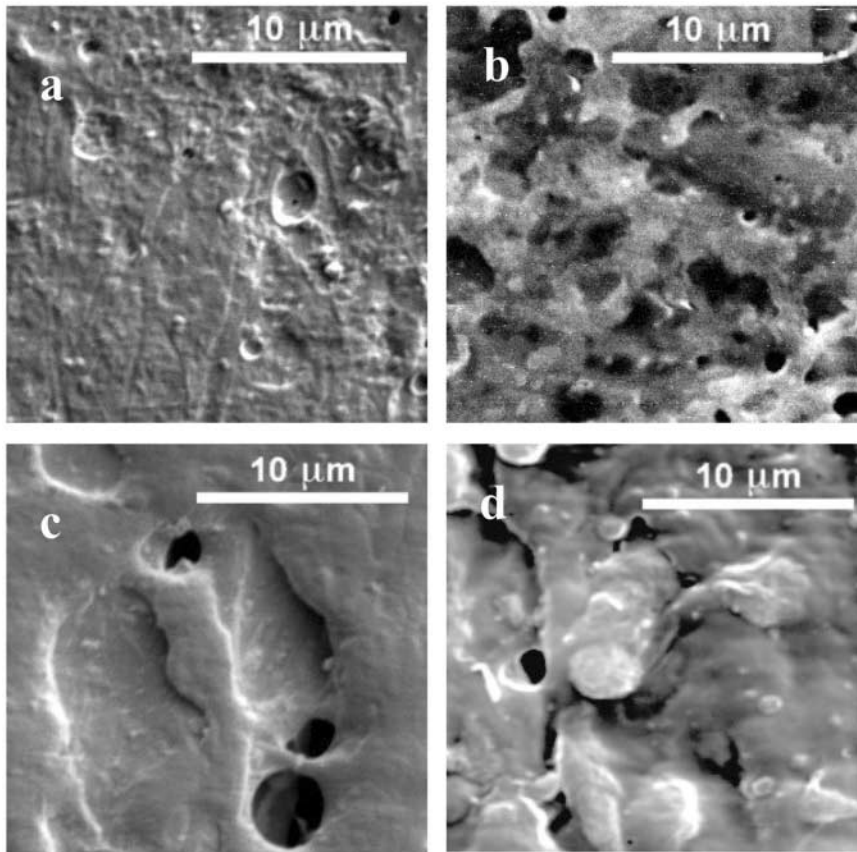


Figure 3. SEM micrographs for extracted NR samples. a: 47.5/47.5/5, b: 40/40/20, c: 37.5/37.5/25, d: 35/35/30.

The morphology observed by Ha and Kim^[12] for the 1 : 1 binary blend is proposed here since it is also in accordance with the rheology of these blends.^[8] Since crystalline polymers are essentially composite materials with alternating crystalline and noncrystalline regions, it is reasonable to expect the incorporation of the natural rubber predominantly in the bulk amorphous phase surrounding the crystalline regions, as suggested elsewhere.^[14]

D’Orazio et al.^[6] 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 the percolation phenomenon.

Broadly speaking, with the increment of the rubber content there are two competing factors expected to reduce the initial modulus and ultimate strength: 1) incompatibility of the polymers and 2) overall crystallinity and rubber phase domain size. The deterioration

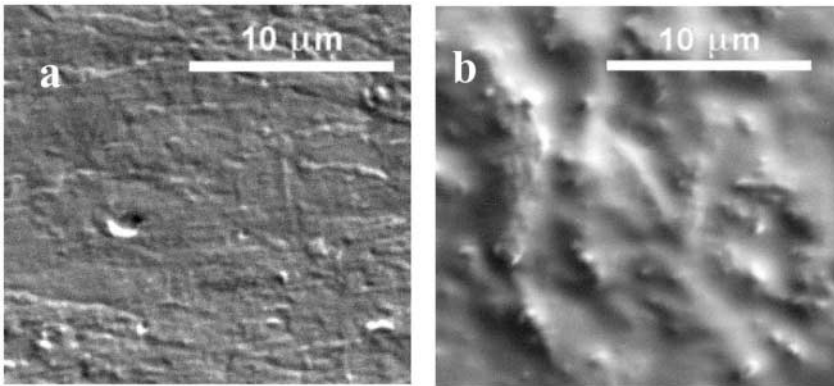


Figure 4. SEM micrographs for unextracted NR samples. a: 47.5/47.5/5, b: 37.5/37.5/25.

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.^[15] Decreases in overall crystallinity of the blend, caused by the addition of rubber to the HDPE/PP blend, result in decrement of modulus^[14,16] and of strength, as well. The deterioration of these mechanical properties seen with an increase

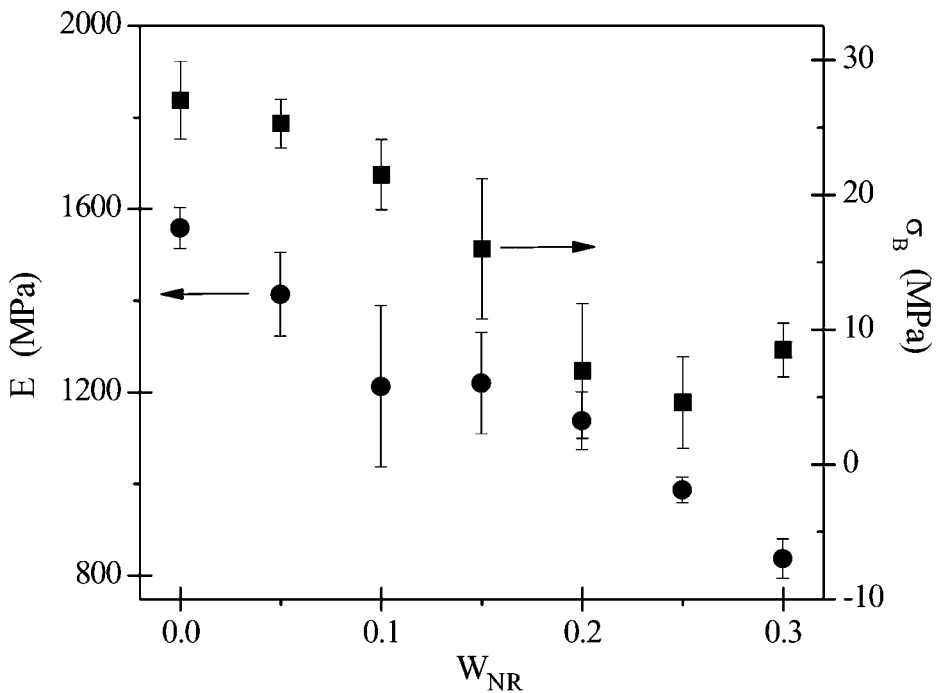


Figure 5. Elastomer dependence of the elastic modulus and stress at break for blends with equal content of HDPE and PP.

in rubber phase concentration is also associated with the increment of the rubber phase domain size.^[15] 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 contained in Figs. 2 and 5 show that the change observed at 20% of rubber content undoubtedly is due to the percolation effect.

CONCLUSION

The effect of the incorporation of natural rubber (up to 30% content) on the binary blend HDPE/PP, with equal proportions of both polyolefins, was studied. The ability to extract the rubber, without affecting the polyolefins, allowed detection of the percolation phenomenon of the rubber at around 20% of its content.

The addition of the elastomeric 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 detection of the percolation of the rubber at about 20% of the rubber content.

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