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Production of XNBR/PMMA through in Situ Polymerization

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Summary: In this work, acrylonitrile-butadiene rubber / poly(methyl methacrylate) (XNBR/PMMA) blends were obtained through *in situ* polymerization of methyl methacrylate (MMA) monomer in XNBR rubber particles. Firstly, the XNBR rubber was swollen with MMA and then the polymerization was carried out in an aqueous medium, keeping the rubber particles in suspension. The results of the swelling tests indicated that mass transfer of MMA to rubber particles is more efficient in aqueous system. Fourier Transform Infrared (FTIR) analyses revealed the presence of PMMA in the XNBR phase. Thermo-gravimetrical (TG) analyses indicated that as much as 10% of PMMA was present in the blends. Scanning electron microscopy (SEM) analyses revealed that PMMA was dispersed in the XNBR phase, indicating the efficiency of the MMA polymerization inside the XNBR rubber particles.

Keywords: blends; elastomers; PMMA; polymerization; thermoplastic; XNBR

Introduction

The search for new technologies capable of producing new materials based on polymer blends with good properties has been object of concern in many research centers around the world. This is due to the fact that it is normally easier and cheaper to prepare new blends than to synthesize new polymer materials with improved properties. Particularly, the preparation of vulcanized thermoplastics (TVP) may present many advantages, because these materials are relatively inexpensive and can be combined with other materials to improve their performances, while conserving the characteristic good processability of the thermoplastics.[1,2] Several TVPs have been used for preparation of materials with improved performances, such as PP / EPDM.,[3] PP / NR,[4] PVC / SBR,[5] NBR / Nylon[6–8] and NBR/PVC.[9] Therefore, it is possible to design TVPs in order to combine good flexibility with improved impact strength, hardness, among many other properties.[10]

The processes used more often for preparation of TVPs are based on mixers and rotating cylinders, either in solution or emulsion.[3,6,11,12] Over the last years, dynamic vulcanization has also been studied extensively.[12–14] Most processes are characterized by the use of high temperatures and shear stresses, although such conditions can cause premature degradation of the polymer and reduction of its molecular weight, prejudicing the final properties of the blends. Additionally, when the polymer materials are not compatible, final blends can present poor performance due to poor interfacial adhesion and gross phase separation.[15,16]

In practical terms, few elastomer / thermoplastic materials have found real technological applications.[17] Previous studies indicated that the best combinations of elastomer / thermoplastic properties are obtained when the polymer materials have similar surface energies, when the elastomer presents low molecular mass or when

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the crystallinity of the plastic phase is between 15 to 30%.[17] Moreover, stabilization of the blend morphology must also be performed. Finally, enhanced properties can be obtained when the elastomers are finely dispersed into the thermoplastic phase, especially when the rubber phase is reticulated in order to provide the characteristic elastic properties to the mixture.[18]

Based on the previous paragraphs, the main objective of the present work is the development of a method for production of TVPs based on XNBR/PMMA blends. In order to do that, reticulated XNBR was swollen with MMA monomer and the polymerization was carried out in an aqueous medium containing initiator. It is shown that *in-situ* XNBR/PMMA blends with useful properties can be prepared with the help of the proposed technique.

Experimental Part

Material

MMA was supplied by Aldrich S.A. with minimum purity of 99.5 wt%. Reticulated acrylonitrile-butadiene rubber (XNBR), with carboxylated content of 6 wt% and acrylonitrile content of 33 wt% was supplied by Nitriflex S.A. Benzoyl peroxide (BPO) with minimum purity of 95% and methanol P.A were supplied by Vetec Química Fina Ltda. All chemicals were used as received, without further purification.

Swelling Process

Two distinct swelling systems were tested. In the first system, XNBR particles were dispersed in 10ml of H_2O containing 10 ml of MMA monomer. In the second system, XNBR particles were also dispersed in 10 ml of pure MMA. Rubber particles were kept in suspension for specified periods of time, as discussed below. The degree of swelling - amount of monomer inside the rubber particles - was measured gravimetrically by weighing the rubber particles before and after the swelling tests. Samples of swollen particles were vacuum filtered and dried in a Buckner funnel.

Polymerization Reaction

The crosslinked XNBR particles swollen with MMA were transferred into a reaction flask containing distilled water. The system was stirred and kept at 25 °C under nitrogen atmosphere. Specified amounts of initiator, 0.4536g of BPO were added under continuous stirring and the reaction temperature was raised to 75 °C. Reaction conditions were kept constant for 1.5 h. Obtained XNBR/PMMA blends were filtered and washed with distilled water and methanol to remove the residual monomer. In order to ensure that unreacted MMA monomer has been completely removed after the reaction, final XNBR/PMMA blends were additionally dried under vacuum for 1 week at ambient temperature. Reaction tests were performed in triplicate using 2 g of swollen XNBR. An illustrative representation of the swelling and reaction processes is presented in Figure 1.

Sample Characterization

The qualitative characterization of the obtained XNBR/PMMA blends was performed through FTIR, using the Perkin Elmer FT-GO 1600 equipment and the KBr tablet method. TG analyses were carried out under nitrogen atmosphere from 0 °C to 800 °C, using a Shimadzu TGA-50 equipment and heating rates of 10 °C/min. The morphology of the XNBR/PMMA blends was characterized with help of SEM, using the Stereoscan 200 equipment provided by Cambridge Instruments.

Results and Discussion

Firstly, the swelling conditions were investigated and adjusted. Figure 2 illustrates important aspects related to the swelling process. It is interesting to note that the rate of swelling was higher in the water/MMA system. It can be assumed that mass transfer is enhanced because of the ionic nature of water, which shifts the partitioning of the

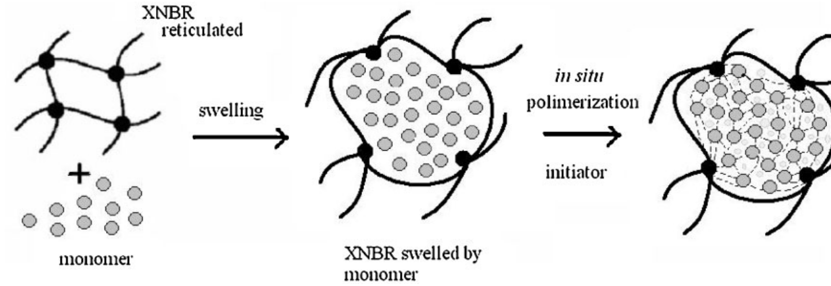

Figure 1.
Swelling of XNBR rubber by monomer.

MMA molecules towards the organic XNBR phase.

Polymerization Reaction

The polymerization of MMA has been extensively investigated in the literature in emulsion, suspension and bulk processes.[19] Assuming that the swollen XNBR rubber particles only contain monomer and initiator, as water is not absorbed by XNBR, MMA polymerization proceeds in the XNBR particles as a typical bulk or solution polymerization. Besides, the preferential polymerization of monomer on the external particle surfaces, due to resistance to transfer BPO molecules into the rubber particles, could reduce the polymerization rates inside the XNBR rubber particles and lead to formation of a core-shell structure and to MMA polymerization in water.

After the end of the reaction, XNBR particles were withdrawn from the reactor and washed with water. The presence of PMMA in the XNBR was confirmed by infrared spectroscopy, as shown in Figure 3. The characteristic carbonyl groups of the ester could be observed at 1735,6 cm^{-1} and nitrilic groups at 2237,5 cm^{-1}, suggesting the occurrence of the polymerization inside the XNBR particle.

As mentioned previously, samples of XNBR/PMMA were washed with methanol and completely dried under vacuum for 1 week to ensure the complete removal of residual MMA. Therefore, it can be ensured that the absorption bands observed in the FTIR spectrum refer to the polymer PMMA and not to residual MMA monomer.

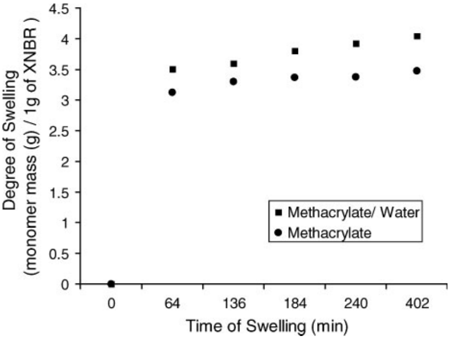

Figure 2.
Degree of Swelling of XNBR mass (g) of MMA/ 1g of XNBR; ● = swelling with monomer (10 ml of methacrylate); ■ = swelling with monomer in aqueous medium (10 ml of methacrylate/10 ml of water).

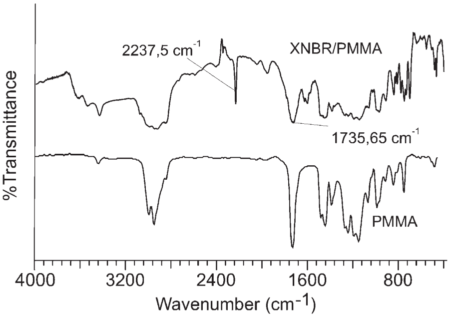

Figure 3.
FTIR spectra of XNBR/PMMA blend and thermoplastic PMMA.

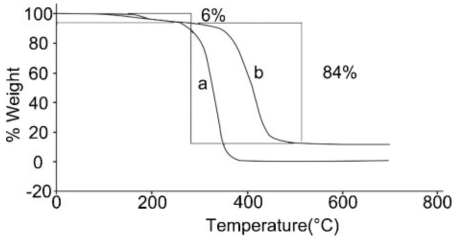

Figure 4.
TGA curves of (a) PMMA pure and (b) XNBR/ PMMA blend.

Thermogravimetric analyses

TG analyses of the obtained XNBR/PMMA blends are shown in Figure 4. The first degradation step was initiated at 130°C. The mass loss corresponding to 6 wt% was attributed to the acrylate decomposition. This corresponds to 10 wt% of PMMA in the XNBR/PMMA blends. The second degradation step was initiated at 350°C, and was attributed to XNBR and PMMA chain backbone degradation. The presence of XNBR shifts the TG curve towards higher temperatures, indicating that XNBR/PMMA blends exhibit better resistance to thermal degradation.

Blend Morphology

Figure 5 a-d present the SEM micrographs of the XNBR/PMMA blends. All micrographs indicate the presence of two phases, XNBR and PMMA, confirming the MMA monomer polymerization. The darker regions are related to the XNBR phase, while the clearer regions indicate the presence of the PMMA phase.

Conclusion

The obtained results showed that the XNBR/PMMA blends can be produced *in situ* in swollen XNBR particles. The proposed technique presents some advantages: organic solvents are not used,

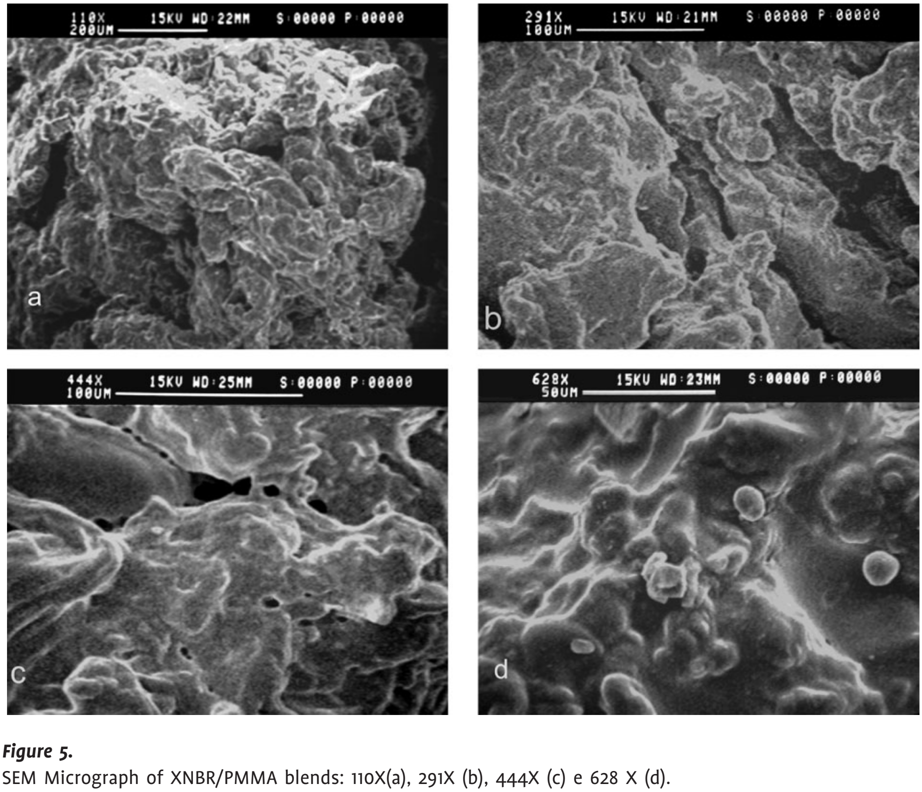

Figure 5.
SEM Micrograph of XNBR/PMMA blends: 110X(a), 291X (b), 444X (c) e 628 X (d).

purification is easy and the end product in obtained in pellets. The use of mild temperatures and shear rates constitutes additional advantage. Obtained results also showed that mass transfer of MMA into the XNBR particles is enhanced in the aqueous medium. FTIR analyses confirmed the occurrence of polymerization inside cross-linked XNBR particles, while SEM analyses indicated that the PMMA phase is dispersed in the XNBR matrix. This is in agreement with obtained TG results, which indicated a blend composition of 90:10 wt% with respect to XNBR and PMMA, respectively.

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