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### FUNCTIONALIZATION OF ETHYLENE-PROPYLENE COPOLYMER (EPR) AND HDPE WITH MONOMETHYL ITACONATE AS POLAR MONOMER AND THEIR APPLICATION IN HDPE/EPR BLENDS

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#### INTRODUCTION

Polyolefins, such as polyethylene (PE), are thermoplastics of high consumption because of their well-balanced physical and mechanical properties, good moisture stability and their easy processability at a relatively low cost, that makes them a versatile material with continuously increasing applications. However, in some cases, not all the characteristics of these materials are suitable for common service conditions. Therefore, one of its major drawbacks is its low impact strength, in particular, at low temperatures<sup>1-4</sup>. In order to overcome these limitations, a great deal of studies have been carried out on blends containing polyolefins and elastomers<sup>1-4</sup>. Among different impact modifiers, ethylene-propylene diene terpolymers (EPDM) and ethylene-propylene copolymers (EPR) are the most commonly and effective ones<sup>5-6</sup> due to their high impact strength over a wide range of temperature. Despite to the similarity of chemical structure of these polymers, the elastomer is not compatible with polyolefins and as a consequence, the elastomeric phase exists as separate domains in the continuous thermoplastic matrix<sup>7</sup>. Unfavorable interactions at the molecular level give rise to high interfacial tension and impede a homogeneous melt mixing of the components. This cause unstable morphology and a poor interfacial adhesion, which are the main causes for poor mechanical properties. In order to improve the compatibility of these systems, functionalization with polar monomers is often used. Several polar monomers, such as oxazoline<sup>8</sup>, mercapto<sup>9</sup>, cyanate ester<sup>10</sup>, maleic anhydride<sup>11</sup>, and alkyl maleates<sup>12-13</sup> have been investigated. Among them, the most studied modifications of polyolefins are those with maleic anhydride and alkyl maleates which are performed either in solution, in the solid state or in the melt phase. Our group has been working on the modification of polyolefins, particularly polypropylene, through free radical grafting of itaconic acid and its derivatives<sup>14-17</sup>. In the present study, both high density polyethylene (HDPE) and EPR were modified with monomethyl itaconate (MMI), in the melt at 190 °C, by using 2,5-dimethyl-2,5-bis(tert-butylperoxy) hexane (Lupersol 101) and dicumyl peroxide respectively, as radical initiators. The aim of this study was to study the functionalization of EPR with a new polar monomer and to determine the effect of using both grafted HDPE and/or EPR with MMI as compatibilizing agents and, consequently, on the properties of HDPE/EPR blends.

#### EXPERIMENTAL

Grafting reaction of HDPE and/or EPR with monomethyl itaconate was carried out in a Brabender Plasticorder internal mixer at 180 °C. The product was dissolved in hot xylene and was precipitated into acetone. The grafted polymer was purified by exhaustive extraction of the sample with methanol in a Soxhlet for 24 hours. The extracted samples were dried under reduced pressure. Evidence of grafting was obtained by FTIR spectroscopy. The extent of grafting was converted into the incorporated weight percent ( $G_{MMI}$  in wt.-%) of the monomer by using a calibration curve obtained from FTIR analysis of physical mixtures obtained by melt mixing of either HDPE or EPR with different amounts of MMI. HDPE/EPR blends were prepared by melt-mixing in a Brabender plasticorder at 190 °C, 60 rpm, 10 min. The materials were compression molded for 15 min at 160

°C into 0.2 mm thick plaques before testing. Thermal analysis experiments were performed using a Mettler Toledo differential scanning calorimeter model DSC 822. Crystallization tests were carried out under isothermal conditions at  $T_c$  123 °C in nitrogen atmosphere, and after the isothermal crystallization, a dynamic scan at 10 °C/min was performed to check the presence of residual crystallinity. Thermal degradation measurements were run from 30 °C to 600 °C at 10 °C/min in a Mettler Toledo SDTA 851 thermogravimetric analyzer (TGA). Nitrogen flow (20 ml/min) was used in order to avoid thermoxidative degradation. Mechanical characterization was carried out by tensile testing at room temperature on a Instron dynamometer, model 4301, according to ASTM D 638M. The blends morphology was characterized by scanning electron microscopy (SEM) in a Tesla BS 343A instrument. Micrographs were obtained from the surface of cryogenically fractured samples after extraction of EPR with toluene at 70 °C/8 h. Impact resistance measurements were carried out according to ASTM D-256 (v-notched) at 20 °C, in an Charpy pendulum Ceast model Resil 25.

## RESULTS AND DISCUSSION

The toughness of many thermoplastics such as HDPE can be improved by incorporation of a low modulus second component. It is assumed that, when the rubbery phase forms highly dispersed small domains, behaves as an effective stress concentrator and enhances resistance to crack propagation in the matrix. In general, polymer blending is an usual practice to produce new materials with desired combination of properties. The compatibility and properties of blends based on HDPE and EPR can be improved by using functionalized polymers with a polar monomer such as MMI as compatibilizers. Grafting reactions performed on EPR produced modified polymer with an optimum degree of grafting of 0.44 %. In the case of HDPE the degree of grafting was 1.56 %. The effect of grating on the processability, morphology, thermal, impact resistance and mechanical properties of HDPE/EPR blends were studied. The results show that the grafting reaction increased the toughness and elongation at break of all tested blends retained their strength and stiffness. Moreover, grafted polymers behave as nucleating agent, accelerating the HDPE crystallization. These results are particularly relevant when both functionalized HDPE and EPR are used as compatibilizers in the blend. Morphological studies are in concordance with the mechanical characterization, showing a reduction of the rubber particle size and a better interfacial adhesion when both polymers are functionalized with monomethyl itaconate as polar monomer.

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