Evaluation of the structural, thermal, rheological and morphological properties of polyethylene functionalized with a maleinized hyperbranched polyester

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Abstract. This experimental study was carried out with the aim of establishing and analyzing the thermal, structural, morphological, and rheological properties of a polyethylene functionalized with a maleinized hyperbranched polyester. This area of study has scarcely been reported. It is important to study the properties of this material, since it can be employed as functionalizing agent in blends of low density polyethylene and hydrophilic polymers. In addition, it also may be used as alternative for replacing the importation of polyethylene functionalized with maleic anhydride in our country. Therefore, in this experimental study, dicumyl peroxide was utilized to catalyze a functionalization reaction between low density polyethylene and maleinized hyperbranched polyester. In the experiment, dicumyl peroxide concentrations were maintained at 0.50 wt%, 1.0 wt%, 1.5 wt%, and 2.0 wt%. The resultant material after of the functionalization was characterized by various analytic methods including infrared analysis, contact angle, thermogravimetric analysis, X ray diffraction, rheological analysis and scanning electronic microscopy. The functionalization degree of the polyethylene functionalized with a maleinized hyperbranched increased with the dicumyl peroxide amount and in all cases it was higher than 8 weight percent.

1. Introduction

Low density polyethylene (LDPE) is a highly hydrophobic polymer; it is cheap, has excellent mechanical properties and is mainly employed in packaging industry [1-5]. This material is usually blended with hydrophilic polymer but the properties of these blends are not satisfactory as phase separation occurs during the process [6]. Therefore, to improve the interaction between hydrophilic polymer with LDPE, LPDE has been used modified with maleic anhydride (LDPE-*g*-MA) as compatibilizer [7,8]. However, the main problem with this is that the LDPE-*g*-MA exhibits low functionalization degree (lower than 3 wt% [7-10]. Therefore, new alternatives of functionalization are employed to obtain LDPE with high functionalization degree (FD) values. Thus, the LDPE has been functionalized with polyacrylic acid [11], maleic acid [12], acrylic acid [13], ethylene glycidyl methacrylate [14], ethylene vinyl acetate (EVA) [15], ethylene-methacrylic acid copolymer partially neutralized with sodium (Na-EMAA) [16]. However, some of these compounds are toxic and have low FD values. We reported in the previous study the functionalization of LDPE with a maleinized hyperbranched polyester (MHBP) [17], but the FD values (determined by infrared (IR) analysis), hydrophilicity (determined by contact angle measurement), the crystallinity (studied by X ray diffraction (DRX) analysis), rheological behavior and fracture mechanism (determined by scanning

electronic microscopy (SEM) analysis) were not evaluated. This is, therefore, the aim of this study as these properties have not been previously reported for LDPE functionalized with MHBP (LDPE-*g*-MHBP). Furthermore, this material may be used as substitution of the LDPE-*g*-MA, which is doing imported in our country.

2. Materials and methods

The LDPE was supplied by PEDEVESA, MHBP was provided by our laboratory (GIMAPOL), and we had reported the properties of this material in a previous study [17]. The dicumyl peroxide (DCP) was supplied by Sigma-Aldrich.

The preparation of the LDPE-*g*-MHBP was carried out in a torque rheometer of Thermo Scientific. In all cases the proportions of LDPE and MHBP were 90 wt% and 10 wt% respectively. In the case of the DCP, these were: 0.50 wt% (LDPE-*g*-MHBP1), 1.0 wt% (LDPE-*g*-MHBP2), 1.5 wt% (LDPE-*g*-MHBP3) and 2.0 wt% (LDPE-*g*-MHBP4) in respect to the amount of LDPE and MHBP. For the preparation of the blends, the respective proportions of the materials were mixed during 15 min. at 50 rpm and 160°C. With the aim of eliminating the residual MHBP from LDPE-*g*-MHBP, all samples were precipitated in methanol and taken to soxhlet extraction during 48 h by using acetone as solvent. Finally, once this process was over, the samples were dried for 72 h at 50°C in an oven. The material obtained looked like powder. Figure 1 shows a schematic representation of a LDPE-*g*-MHBP.

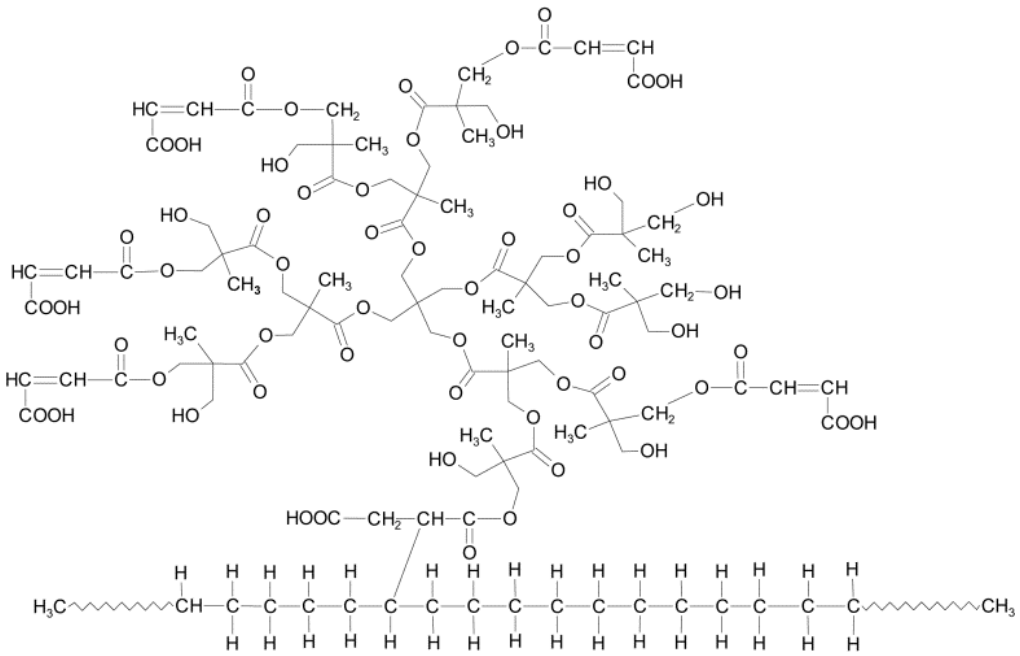

Figure 1. Schematic representation of the LDPE-*g*-MHBP.

With the aim of making the quantitation of the grafted MHBP amount into the LDPE, LDPE/MHBP blends were obtained by using the same conditions employed for the preparation of LDPE-*g*-MHBP. The proportions of MHBP in these blends were as follows: 0.1 (MHBP1), 0.53 (MHBP2), 1.49 (MHBP3), 2.73 (MHBP4), 3.97 (MHBP5), 5.56 (MHBP6), 7.11 (MHBP7), 8.58 (MHBP8) and 11.04 wt% (MHBP9).

The LDPE/MHBP obtained was characterized by IR analysis. For it, films of the LDPE and LDPE-*g*-MHBP with potassium bromide were prepared and then the samples were analyzed in a Perkin Elmer spectrometer model Spectrum One, using 8 scans and a resolution of 4 cm^{-1}. The thermogravimetric analysis (TGA) was done in an equipment of TA Instruments Q-500 by using a heating rate of 10°C/min. from room temperature until 600°C using a nitrogen purge. The DRX analysis was performed in a PANalytical X'Pert PRO MPD diffractometer by employing a radiation of

Cu Kα = 1.5406 A. The voltage and the current were 45 kV y 40 mA respectively. The difractograms were obtained at an interval of Bragg angle (2θ) between 5° and 70°. The rheological analysis was executed in a rotational rheometer of Malvern Kinexus by using a plate-cone geometer of 4°. This analysis was done at 175°C by using a shear rate between 1 s^{-1} and 100 s^{-1}. The contact angle measurement was realized by a static method, using a Rame Hart model 250 goniometer. For it was deposited a water drop on the film surface of the samples at room temperature. Finally, the SEM analysis was performed on the cryofractured surface of the samples. Microscopy trademark Jeol JSM-6490LV was used, using a voltage acceleration of beam between 10 kV and 20 kV.

3. Results and discussion

Figure 2 shows the IR spectra of the LDPE/MHBP blends. The samples exhibited an absorption at 3400 cm^{-1} which is associated with OH bond stretching. The signal at 2960 cm^{-1} and 2871 cm^{-1} correspond to asymmetric and symmetric stretching respectively. At 1720 cm^{-1} appear a signal due to carbonyl group of esters. At 718 cm^{-1}, a signal is observed corresponding to C-CH_2 rock. These signals were previously reported to LDPE-*g*-MHBP1, LDPE-*g*-MHBP2, LDPE-*g*-MHBP3 and LDPE-*g*-MHBP4, which were named as DCP0.5, DCP1.0, DCP1.5 and DCP2.0 respectively [17].

The calibration curve (Figure 3) was done by using the area ratio of the absorptions at 3400 cm^{-1} (A_{3400}) and at 718 cm^{-1} (A_{718}). It can be observed that the calibration curve displays an excellent linearity and the correlation factor is the highest (0.9996), it indicates that the quantitation done by using this calibration curve offers the highest reliability. The FD values of the LDPE-*g*-MHBPs were obtained from calibration curve by interpolation of A_{3400}/A_{718}. These values were found from IR spectra of the LDPE-*g*-MHBPs [17].

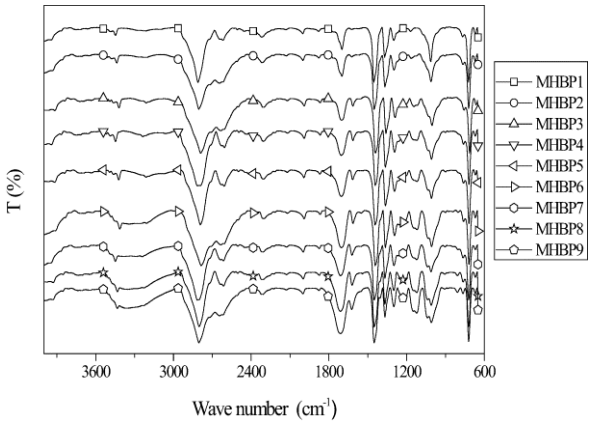

Figure 2. IR Spectra of the LDPE/MHBP Blends.

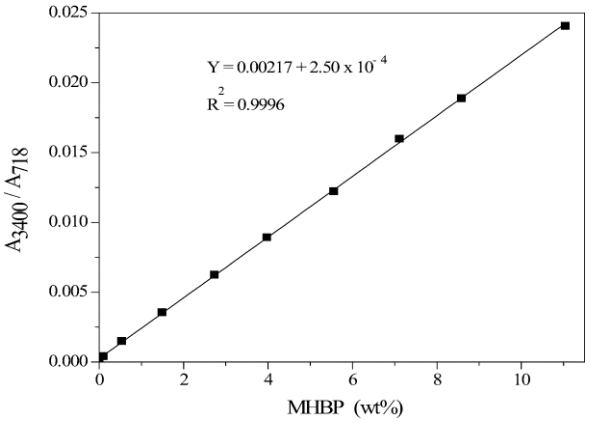

Figure 3. Calibration curve.

The LDPE-*g*-MHBPs presented the following FD values: LDPE-*g*-MHBP1:8.14, LDPE-*g*-MHBP2: 9.44, LDPE-*g*-MHBP3:9.18 and LDPE-*g*-MHBP4:9.65 wt%. The FD increased with the DCP content. This was due to high probability of the occurrence of the reaction, due to the high number of free radicals. The FD values are higher than those obtained by other authors for functionalized LDPE [7-16], whose values are lower than 7 wt%. The FD values obtained for LDPE-*g*-MHBPs are lower than those obtained by gravimetric analysis for these same materials, which were previously reported by us [17]. This may be attributed to errors produced by the weighted or losses during the extraction process.

Figure 4 shows the TGA thermograms of the LDPE and LDPE-*g*-MHBP. The decomposition temperatures of the samples were the followings: LDPE, 380°C; LDPE-*g*-MHBP1, 393°C; LDPE-*g*-MHBP2, 395°C; LDPE-*g*-MHBP3, 395°C and LDPE-*g*-MHBP4, 397°C. The thermal decomposition of the LDPE was lower than those of the samples LDPE-*g*-MHBP, this behavior was possibly due to the functionalization process and some crosslinking degree trough LDPE chains or grafted MHBP.

The same behavior has been observed by other authors in the functionalization of LDPE with MA [18]. The thermal behavior of the LDPE-*g*-MHBP was very comparable and it did not show a dependence with the DCP content nor FD values, which is probably due to competition of the grafting process with the crosslinking reaction.

Figure 5 exhibits the DRX difractograms of the samples. LDPE presents a peak at 2θ=21.5°, which is attributed to crystalline region associated to an orthorhombic unitary cell (100) [19,20]. In the LDPE-*g*-MHBP, the intensity of this peak decreased with the DCP amount and FD values; it indicates that the crystallinity of LDPE was diminished in the same sense. The reduction on crystallinity exhibited by the samples LDPE-*g*-MHBP in regards to that of the LDPE may be assigned to several factors such as: a) LDPE was functionalized with MHBP and this material is amorphous [17] and b) crosslinking process, which was mentioned before. Furthermore, it has been reported to the LDPE [10] and PP functionalized with a MHBP [21]. At 2θ=23.95 another signal appears in the LDPE, which is shifted in the samples LDPE-*g*-MHBP due to the grafting of the MHBP. This signal has been observed in the LDPE and is associated with the arrange (200) [20].

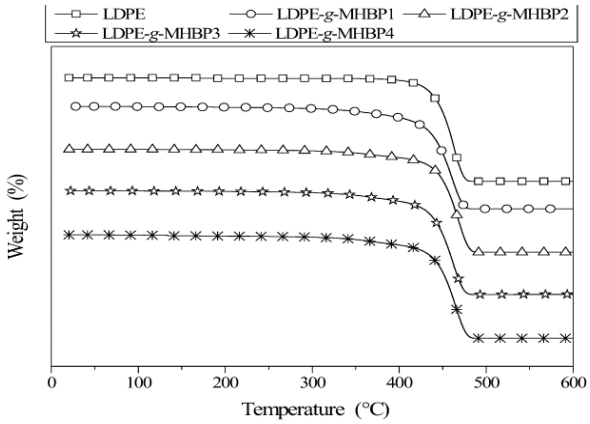

Figure 4. TGA thermograms of the LDPE and LDPE-*g*-MHBP.

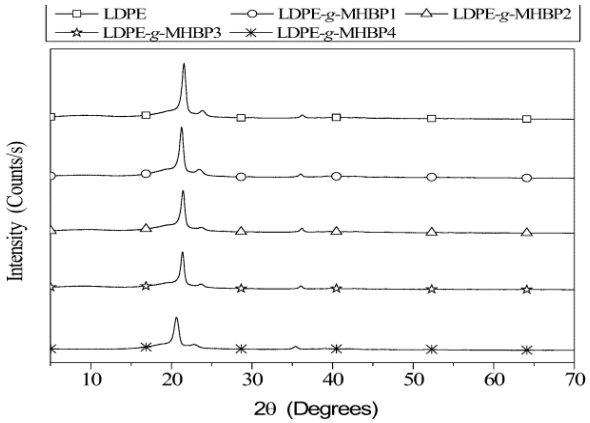

Figure 5. Difractograms of the LDPE and the LDPE-*g*-MHBP.

All samples exhibited a pseudoplastic rheological behavior (Figure 6), this may be interpreted as a disentanglement of the chains. In the range of the shear rate studied, the LDPE presented a lower viscosity (η) than the samples LDPE-*g*-MHBP. This means that these samples increased the molecular weight due to functionalization or crosslinking processes. The η value of the samples LDPE-*g*-MHBP at shear rate of 1 s^{-1} increased with the FD value and DCP content. This behavior has been observed to LDPE-*g*-MA [7]. The samples LDPE-*g*-MHBP2, LDPE-*g*-MHBP3 and LDPE-*g*-MHBP4 presented an abrupt drop in the viscosity at shear rate of 40.53 s^{-1}. This behavior is associated with the dissociation of the interactions (hydrogen bonds) between grafted MHBP macromolecules. The absence of this behavior in the sample LDPE-*g*-MHBP1 possibly is due to lowest FD and interactions degree, and different arrange of the grafted MHBP into the LDPE.

Figure 7 shows the contact angle values. The contact angle value of the LDPE was lower than that of the samples LDPE-*g*-MHBP, this indicates that the LDPE was functionalized with the MHBP (hydrophilic material). It was expected that the contact angle values of the samples LDPE-*g*-MHBP decreased with the FD values, but it did not happen to the sample LDPE-*g*-MHBP4, since the angle contact to this sample was higher than that of the sample LDPE-*g*-MHBP3. This behavior was due to the highest crosslinking degree of this sample since it was obtained with the highest DCP content and the probability of the crosslinking reaction is greatest when enhancing the free radicals. Furthermore, the crosslinking reaction increases the hydrophobicity.

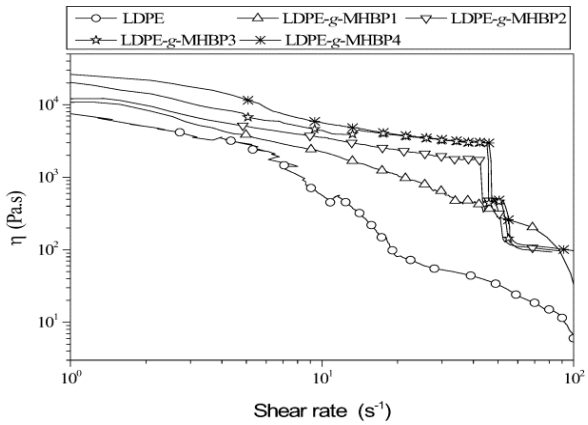

Figure 6. Flow curve of the LDPE and LDPE-*g*-MHBP.

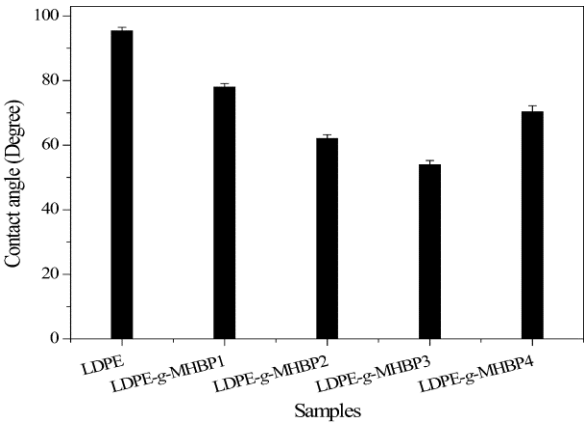

Figure 7. Behavior of contact angle of the samples.

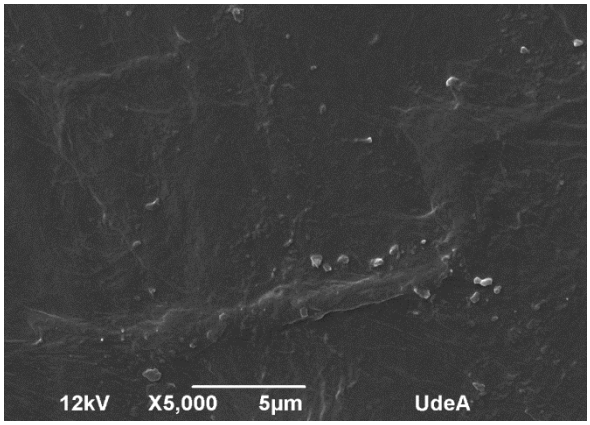

Figure 8. Micrographs of the LDPE.

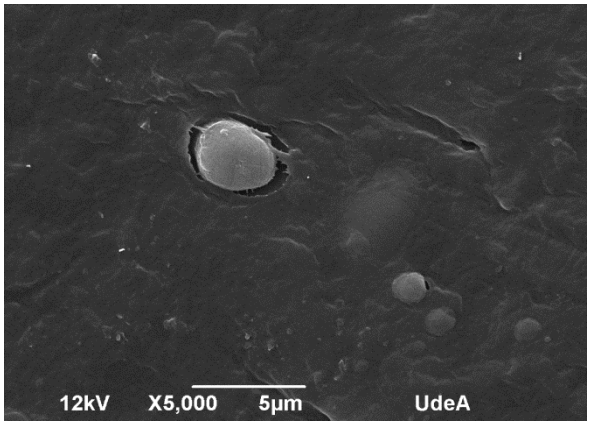

Figure 9. Micrographs of the LDPE-*g*-MHBP4.

The micrographs obtained by SEM analysis of the LDPE and LDPE-*g*-MHBP4 are presented in Figure 8 and Figure 9 respectively. No sample exhibited cavities, since all surfaces are smooth. This therefore means that the fracture is ductile. This is related with the elastic characteristic of the LDPE. On the other hand, the sample LDPE-*g*-MHBP4 showed the presence of a material that appears forming another phase. Since this material was not observed in the sample LDPE, it indicates that it was possibly formed during the processing as a result of the crosslinking reaction, which forms a gel. This is according to the results obtained by contact angle analysis.

4. Conclusion

In this study LDPE-*g*-MHBP was obtained. These materials may be an alternative as compatibilizing agent for blends of hydrophilic polymers and LDPE since they exhibit FD values higher than those reported in the literature. The FD of the LDPE-*g*-MHBP increased with the DCP amount. Neither thermal stability nor contact angle show dependence with the DCP amount and the FD. By DRX analysis it was observed that the samples LDPE-*g*-MHBPs exhibited lower crystallinity than the LDPE, but in the case of the rheological behavior it was the opposite, due to crosslinking reactions. The η value of the samples LDPE-*g*-MHBP at shear rate of 1 s^{-1} increased with the FD value and DCP content. Results showed that LDPE's contact angle was upper than the sample LDPE-*g*-MHBP. The thermal stability of the samples LDPE-*g*-MHBP was greater than that of LDPE. The LDPE and the samples LDPE-*g*-MHBP presented a pseudoplastic rheological behavior. By SEM analysis found that the fracture type of the samples LDPE-*g*-MHBP was fragile. This research expands the knowledge

base about the thermal, structural, morphological, and rheological properties of LDPE, functionalized with a MHBP.

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