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POLYPROPYLENE GRAFTED WITH GLYCIDYL METHACRYLATE USING SUPERCRITICAL CO_2 MEDIUM

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Abstract – Films of polypropylene (PP) were grafted with glycidil methacrylate (GMA) using supercritical CO_2 as swelling agent and solvent. Different pressures and temperatures were used to study their effects on the soaking and grafting process. FTIR results showed signals at 1726 and 1640 cm^{-1}, assigned to C=O and C=C (after the soaking process), and a decreased signal at 1640 cm^{-1} (after the grafting procedure), suggesting the effective grafting of GMA. For the grafted material immersed in ethylenediamine, peaks in the 3600 to 3250 cm^{-1} range (N-H stretching) were evident. Contact angle measurements showed an increasingly hydrophilic nature in the direction from pure PP to grafted PP/GMA (PP-*g*-GMA) to PP-*g*-GMA immersed in ethylenediamine (PP-*g*-GMA/En). X-ray photoelectron spectroscopy provided evidenced of the effective incorporation of ethylenediamine in the grafted material.

Keywords: Polypropylene; Glycidil methacrylate; Grafting; Supercritical CO_2 medium.

INTRODUCTION

Polypropylene (PP) has been used in many applications but, in general, its use is limited by its lack of functional groups. Thus, functionalization reactions have been used to increase its interfacial interactions (Zhang et al., 2002). The grafting process is one of the methods most frequently used to modify PP. Graft polymerization by hydrogen abstraction from tertiary carbon offers an effective approach to introducing some desirable properties into the polymer, thus expanding its applications without adversely affecting the backbone architecture (Allmér et al., 1989). Using benzoyl peroxide (BPO) as initiator and GMA as monomer, the copolymerization process occurs via a free-radical mechanism, through the scission of the double bond in the GMA (Espinosa et al., 2001). The detailed mechanism of GMA grafting in a saturated polymer using BPO as initiator was described elsewhere (Huang and Liu, 1998). It was observed that grafting does not modify the epoxy ring of the GMA, maintaining its reactivity in the final product (Huang et al., 1998; Zhang et al., 1995). Some authors have used this reactivity to attach molecules with specified properties. Martel et al. (2000) used an epoxy ring of grafted PP/GMA to anchor cyclodextrins, which kept their complexing ability. Allmér et al. (1989) grafted glycidil methacrylate onto polypropylene, polystyrene and polyethylene to improve the interactions with stabilizers such as 2,4-dihydroxy benzophenone, phenyl 4-aminosalycilate, and 4-amine-2,2,6,6-tetramethyl piperidine. These stabilizers were attached to the GMA epoxy groups protecting the polymer from most of the

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UV irradiation (improving degradation stability). In similar work, Liu et al. (2002) prepared isotactic PP grafted with methylmethacrylate using supercritical CO_2 and observed a decrease in crystallinity with an increase in degree of grafting, thus indicating the optimal conditions for the grafting.

The use of supercritical fluid to prepare new materials is an interesting method, especially for supercritical carbon dioxide (SC CO_2), which has many unique properties (Liu et al., 2003) compared to conventional solvents. One of its important contributions has come from the continuing environmental pressures on industry to move away from volatile organic compounds (Taylor, L. T., 1996) and ozone-depleting substances as processing solvents, resulting in a "green" alternative for industry; this feature that was recently reviewed for supercritical carbon dioxide in the processing of polymers (Tomasko et al., 2003).

The aim of this work was the functionalization of polypropylene by a process of free radical grafting with glycidil methacrylate using benzoyl peroxide as initiator and supercritical CO_2. Moreover, we studied the main factors involved in the grafting process and evaluated the reactivity of the GMA epoxy group after its grafting onto PP films.

MATERIALS AND METHODS

Materials

Thin films of PP (50 µm, supplied by Poliolefinas Co., Brazil) were cut into 3 x 4 cm pieces, extensively washed with acetone (Merck) for 12 h (Soxhlet), dried at 80 °C for 4 hours and kept in vacuum. Glycidil methacrylate (GMA, Aldrich) and the initiator benzoyl peroxide (BPO, Riedel-de-Häen) were used as received.

Grafting Process

The glycidil methacrylate was incorporated onto the PP in two steps: soaking and thermal treatment. In the first step, the PP films, GMA monomer and BPO free radical initiator were fed into a supercritical fluid vessel. The conditions studied in this step were i) a time of 4 hours; ii) a temperature of 50 °C and iii) a pressure of 110 bar. After the soaking time, the CO_2 was released and the PP films with impregnated GMA/BPO were washed with acetone to remove the unreacted GMA. In the second step, the PP films impregnated with GMA/BPO were added to an other supercritical vessel and pressurized with N_2. The system was heated and the conditions for this grafting process were the following: a) a temperature of 115 °C; b) a time of 4 hours and c) a pressure of 50 bar. At the end of the thermal treatment the PP films were extracted in a Soxhlet using acetone for 12 hours to remove the unreacted monomer and homopolymers (Zhang et al., 1995). Soon afterwards, the samples were stored in vacuum.

To check the reactivity of the epoxy ring the samples of polypropylene-grafted-glycidil methacrylate (PP-g-GMA) were immersed in a bath of ethylenediamine and stirred for 4 hours at 50 °C.

Instrumentation

The grafting process was carried out using Thar equipment, model SFE 500. Carbon dioxide (White Martins) 99.95% pure was used. FTIR spectra were obtained using a Bomem spectrophotometer, model MB100. The grafting reaction was monitored by Fourier Transformed IR spectroscopy (FTIR) with a BOMEM-MB100 spectrophotometer. Contact angle was measured with a TANTEC model CAM-Micro meter. X-ray photoelectron spectroscopy (XPS) measurements were obtained in a Perkin-Elmer Phi Model 5400 ESCA system with a magnesium anode ($K\alpha$ = 1253.6 eV) operating at 400W.

RESULTS AND DISCUSSION

Figure 1 displays the FTIR spectra of pure and treated PP films. Spectrum (B) shows peaks at *ca.* 1726 and 1640 cm^{-1} (assigned to C=O and C=C, respectively) (Pavia, D. L. 1996), which confirms the incorporation of GMA. The GMA grafting on the polymeric matrix can be observed by the decreased intensity of the peak at 1640 cm^{-1} (C=C) (spectrum (C)). After immersion in ethylenediamine, spectrum (D), we observed a broad band in the 3600-3250 cm^{-1} range assigned to the reaction between GMA and ethylenediamine (*cf.* Figure 2), which is supported by data reported by Allmér et al. (1989).

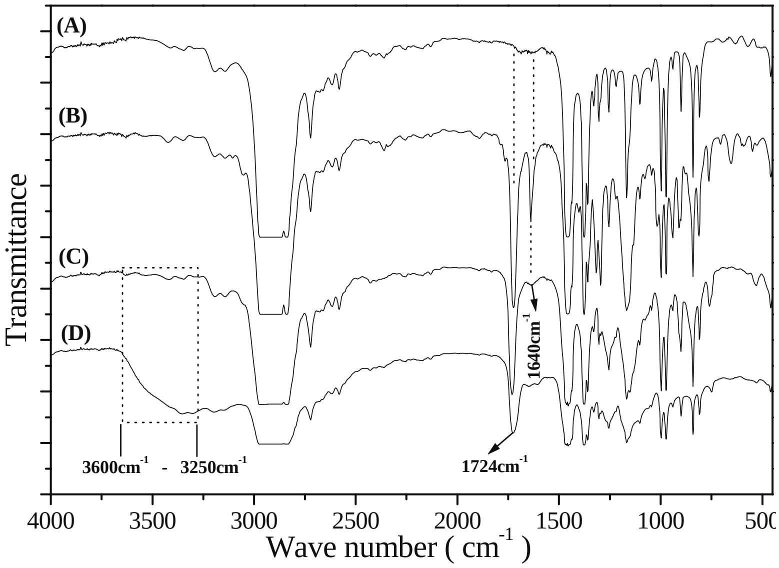

Figure 1: FTIR spectra of (A) pure PP; (B) impregnated GMA PP film in supercritical CO_2; (C) impregnated GMA PP film in supercritical CO_2, submitted to the grafting process and (D) after immersion in ethylenediamine for 4 hours at 50 °C.

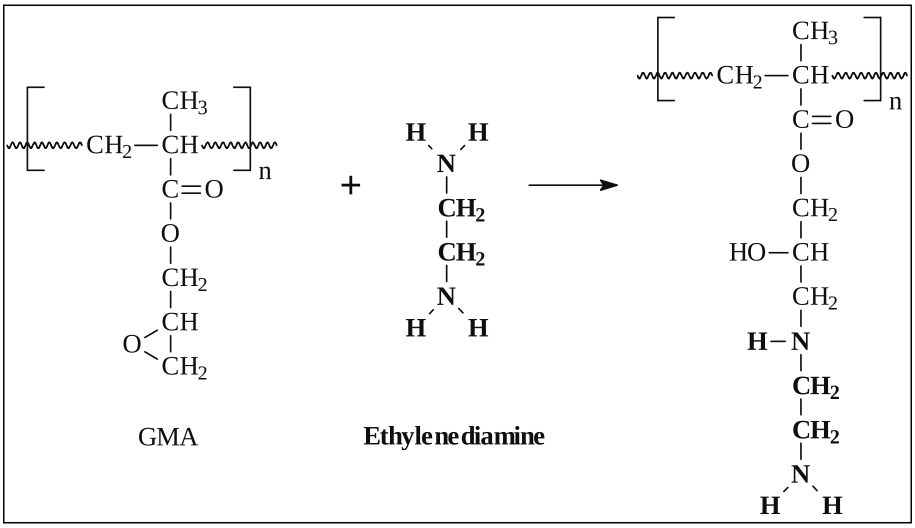

Figure 2: Proposed reaction between GMA and ethylenediamine.

The contact angle measurements for pure PP and modified PP-*g*-GMA films shows a decrease from 92°±2 to 87°±1. After immersion in ethylenediamine the angle was 76°±1. These results provide evidence of the increasingly hydrophilic nature of grafted PP films.

Figure 3 shows the XPS spectra for the different samples. The results reveal subtle variations in surface composition according to the grafting process. Figure 3(B) shows an increased oxygen peak due to the incorporation of GMA. A nitrogen peak is observed in Figure 3(C) after immersion of the grafted polymer in ethylenediamine, which evinces the incorporation of amine.

The atomic concentrations on the PP surface as a function of the treatment are presented in Table 1. There is a decrease of *ca.* 4% in the relative amount of carbon in the PP-*g*-GMA compared to that in pure PP. A relative amount of 1.8% can be observed on the surface of the PP-*g*-GMA immersed in ethylenediamine (PP-*g*-GMA/En). Considering that this percentage of nitrogen is provided by the reaction of ethylenediamine with oxygen (in the epoxy ring), it represents approximately 64% of the epoxy group that reacts with ethylenediamine (in accordance with Figure 2). In addition, the lower percentage on the O1s signal (Fig. 3(B) to 3(C)) agrees with the proposed reaction.

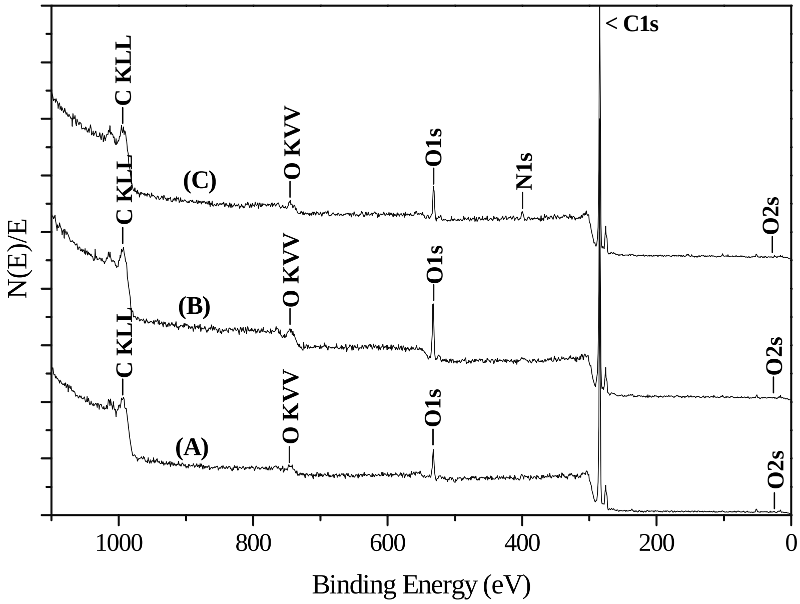

Figure 3: XPS spectra of (A) pure PP; (B) PP submitted to GMA grafting in supercritical fluid and (C) PP-g-GMA immersed in ethylenediamine for 4 hours at 50 °C.

Table 1: Atomic concentration on the virgin modified surfaces of PP.

Element	PP	PP-g-GMA	PP-g-GMA/En
C1s	94.8	90.6	92.7
O1s	5.2	9.4	5.5
N1s	-	-	1.8

CONCLUSIONS

The PP-g-GMA graft copolymer could be prepared by free radical polymerization in the PP matrix with the aid of supercritical CO_2 (SC CO_2) as solvent for GMA/BPO and as swelling agent for the PP matrix. FTIR and XPS results provided evidenced of the modification of the PP surface. PP grafted with GMA is more hydrophilic than unmodified PP. Thus, this method can be used to obtain physicochemically altered PP surfaces. Moreover, the modified material can be used to prepare composites with polymeric matrixes containing reactive groups such as amines.

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