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Radiation grafting of N,N′-dimethylacrylamide and 2-hydroxyethylmethacrylate onto polypropylene films by one step method

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ABSTRACT

The work presented herein reports on polypropylene films grafted with N,N′-dimethylacrylamide and 2-hydroxyethylmethacrylate. The grafted films were obtained by an oxidative pre-irradiation method in one step using a gamma source of ^{60}Co. The optimal conditions such as reaction time, monomer concentrations and radiation doses were investigated. Characterization of the grafted polymers was carried out through FTIR-ATR, TGA, DSC, and swelling. Grafts onto polymeric films between 10 and 850% were obtained at doses from 20 to 150 kGy and a dose rate of 8.3 kGy/h.

1. Introduction

Sensitive hydrogels have been extensively investigated because of their potential applications in the biomedical and pharmaceutical industries (Deligkaris et al., 2010). These hydrogels are termed sensitive or smart polymers because they are responsive to external physical or chemical stimuli, such as changes in temperature, pH, light and mechanical variations (Kumar et al., 2007). In the last decades, several systems combining two or more polymers that respond to different external stimuli have been developed, such as the system vinyl pyridine and N-isopropylacrylamide onto polypropylene, (PP-g-VP)-g-NIPAAm, which is responsive to variations of temperature and pH (Meléndez-Ortiz and Bucio, 2009).

The hydrogel obtained from the polymerization of 2-hydroxyethyl methacrylate (HEMA) is well known for its biocompatibility (Wichterle and Lim, 1960; Hoffman, 2006), its hydrophilic character (Gregonis et al., 1978; Verhoeven et al., 1989), and its antimicrobial properties (Tomic et al., 2010). Thus, 2-hydroxyethyl methacrylate is considered to have great potential in biotechnological applications. However, its mechanical properties are poor and the hydrogel is usually grafted onto a material with superior mechanical properties, such as PP. Furthermore, PP is frequently used in several biomedical applications and its use is increasing due to its low elastic modulus, superior biocompatibility and enhanced corrosion resistance when compared to currently used materials (Silva et al., 2004). PP is also frequently used due to its antimicrobial properties and its resistance to changes in the environment (pH and temperature). In order to achieve the grafting of N,N′-dimethylacrylamide and 2-hydroxyethylmethacrylate onto PP films, oxidative pre-irradiation utilizing a ^{60}Co γ-source was employed. This technique promotes the formation of peroxides and hydro-peroxides on the film; once these peroxides and hydro-peroxides are exposed to heat, free radicals are formed and initiate the grafting of the monomers onto the PP film (Bucio and Burillo, 2009; Contreras-García et al. 2008; Ramírez-Fuentes et al. 2008).

The copolymer synthesized by this methodology was characterized by attenuated total reflectance-infrared spectroscopy (FTIR-ATR), thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and swelling tests.

2. Experimental

2.1. Materials

Polypropylene films (PP) from PEMEX (Mexico), 60 μm thickness and 1×5 cm^2 in size were washed in methanol for 1 h and dried under vacuum until constant weight was obtained. N,N'-dimethylacrylamide (DMAAm, 99%) and 2-hydroxyethylmethacrylate (HEMA, 97%) were acquired from Aldrich Chemical Co., USA, and purified by vacuum distillation

2.2. Grafting

PP films were exposed to ^{60}Co γ-source (Gammabeam 651 PT, MDS Nordion) in the presence of air at room temperature, and a

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dose rate of 8.3 kGy h^{-1} and doses between 20 to 150 kGy. The irradiated films were placed in glass ampoules which contained an aqueous solution of DMAAm/HEMA (50:50) and water. These ampoules were filled with argon to remove air and sealed. The ampoules were heated at 50 °C at different reaction times (from 1 to 18 h). In order to extract the residual monomer and homopolymer that could be formed and occluded in the films during the grafting, the samples were soaked in water for 24 h and dried under vacuum until these reached a constant weight. The grafting yield (Y_g) was calculated by the equation: $Y_g\ (\%) = 100[(W_g - W_o)/W_o]$, where W_o and W_g are weights of the initial and grafted films, respectively.

2.3. Characterization

FTIR-ATR spectra were taken using a Perkin–Elmer Spectrum 100 spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT) with 16 scans. Thermal decomposition of samples was determined in a nitrogen atmosphere between 25 and 800 °C at a heating rate of 10 °C min^{-1} using a TGA Q50 (TA Instruments, New Castle, DE). Differential scanning calorimetry (DSC) studies for the determination of thermodynamic transitions were carried out under a nitrogen atmosphere using a DSC 2010 calorimeter (TA Instruments, USA) from 25 to 250 °C at a heating rate of 10 °C min^{-1}. To determine the water absorbency equilibrium, the samples were immersed into distilled water for different periods of time (from 15 to 90 min). The excess of water on the copolymer films was removed with filter paper, and the swollen samples were weighed. The swelling percentage was determined by the equation: Swelling $(\%) = [(W_s - W_d)/W_d]100$; where W_s and W_d are weights of the swollen and initial films respectively.

3. Results and discussions

The grafting percentage of HEMA (●) and HEMA/DMAAm (▲) onto PP films as a function of reaction time was plotted in Fig. 1. An increase in grafting yield was observed as a function of reaction time, but no plateau was reached in the range of time studied. Under these conditions, HEMA grafting was between 10 to 850% graft in 1–6 h, while HEMA/DMAAm solutions yielded grafts from 3 to 1400% in 2–18 h.

The grafting yield of HEMA (●) and HEMA/DMAAm (▲) onto PP films as a function of irradiation dose, at dose rate of 8.3 kGy h^{-1}, is shown in Fig. 2. Higher grafting yields were obtained as radiation dose increased. Further, it was observed that grafting

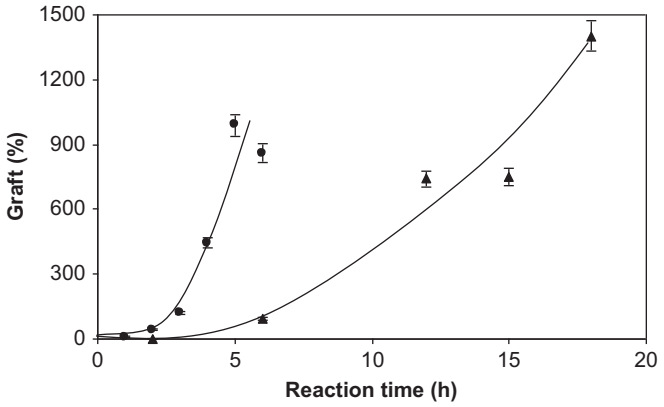

Fig. 1. Effect of reaction time on grafting yield of HEMA (●) and HEMA/DMAAm (▲) onto pre-irradiated PP for increasing reaction times at 50 °C, absorbed dose 75 kGy, and monomer concentration of 50%.

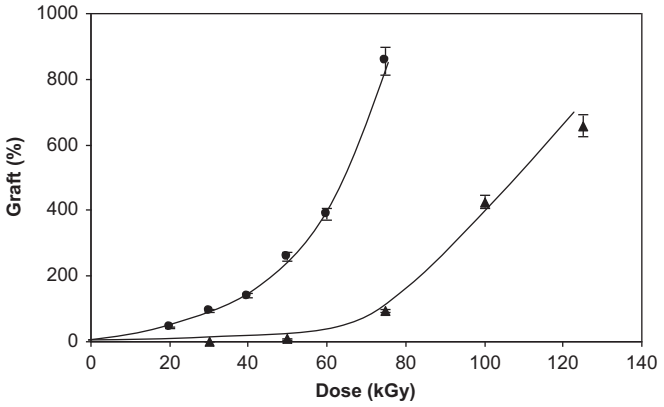

Fig. 2. Effect of irradiation dose on the grafting yield of HEMA (●) and HEMA/DMAAm (▲) onto pre-irradiated PP as a function of pre-irradiation dose. Reaction time 6 h, and temperature 50 °C, and monomer concentration of 50%.

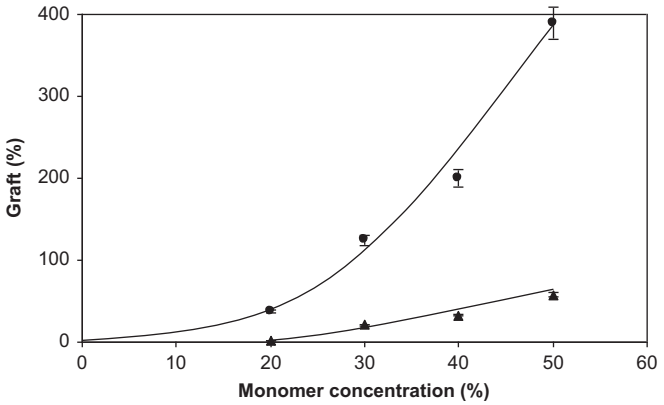

Fig. 3. Dependence of the grafting yield of HEMA (●) and HEMA/DMAAm (▲) onto pre-irradiated PP as a function of monomer concentration. Absorbed dose 60 kGy, reaction time 6 h, and reaction temperature 50 °C.

pure HEMA monomer resulted in homopolymerization and high yields.

The effect of monomer concentration (between 20 and 50%) on the grafting yield of HEMA (●) and HEMA/DMAAm (▲) was examined in Fig. 3. The data shows that higher monomer concentrations promoted higher grafting yields onto PP films. Further, while HEMA/DMAAm was grafted in a linear behavior, HEMA polymerized in an exponential manner, suggesting homopolymerization. Experimentally, it was observed that it was difficult to remove the homopolymer.

The swelling behavior of PP-g-HEMA and PP-g-HEMA/DMAAm as a function of time was studied between 15 and 90 min (Fig. 4). Grafted PP films were immersed in water at 25 °C and followed by gravimetry. The water uptake was high during the first 15 min, but leveled off regardless of the particular system, clearly indicating that equilibrium was reached at 15 min. It was also observed that swelling increases with higher grafting percentage, which in turn depends on monomer concentration, reaction time and radiation dose. Therefore, the hydrophilic character of the graft copolymer is higher when there is a longer pendant chain of HEMA and HEMA/DMAAm onto the PP films, thus increasing the swelling capability of the graft copolymer.

The FTIR-ATR spectra presented in Fig. 5 show that graft polymerization occurred successfully, as explained underneath. Spectrum (a) demonstrates the absorption bands characteristic of CH_2 (2919 and 1461 cm^{-1}), and CH_3 (1376 cm^{-1}) in PP films. Spectrum (b) shows the homopolymer of poly(DMAAm) with bands around 2938 and 1619 cm^{-1} corresponding to C–H and