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Development of reinforced hydrogels — I. Radiation induced graft copolymerization of methylmethacrylate on non-woven polypropylene fabric

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Abstract

Polypropylene (PP) fibers were grafted with methylmethacrylate. Effects of direct and pre-irradiation method and monomer concentration on the degree of grafting were investigated. The grafted PP fibers were characterized by swelling measurements, IR spectroscopy and by its mechanical and thermal properties. It was found that the direct method was more efficient than the indirect or pre-irradiation method and the monomer concentration for highest degree of grafting was 40% of MMA. Mechanical properties (tensile strength) and thermal stability decrease with grafting yield. Those changes were related to degradation of tie molecules between crystals and formation of rigid branches of PMMA on PP amorphous phase.

Keywords: Polypropylene; Methyl methacrylate; Mechanical properties; Electron beam

1. Introduction

Polymeric hydrogels are an important class of materials used in many medical applications, for instance: contact lens, wound dressings and slow release devices. However, due to the hydrophilic nature of its polymeric chains, they lose mechanical properties as they absorb water (Rosiak et al., 1995; Lugão et al., 1998). The reinforcement of its polymeric structure with hydrophobic fibers is an usual attempt to overcome this drawback. PP fibers have excellent mechanical properties and are extremely cheap. Nevertheless, the lack of compatibility between the phases can be a weakening factor. The hydrocarbon nature of PP and the absence of any reactive site are limitations for various applications. One solution to improve PP hydrophilicity is by its grafting with suitable monomers. Some typical examples are methylacrylic acid, methyl and ethyl acrylate, *N*-vinylpyrrolidone, and others (Mukherjee and Gupta, 1985; Mehta et al., 1994; El-Nesr, 1997; El-Salmawi et al., 1997). El-Nesr (1997) grafted methylmethacrylate on polypropylene films using gamma radiation. The maximum value for the highest grafting yield was obtained by using the solvent mixture decalin/methanol in the ratio 2:3 wt and the grafting had practically no effect on the crystallinity of PP. El-Salmawi et al. (1997) investigated the radiation graft copolymerization of comonomer mixtures of acrylic acid (AAc) and styrene (S) on PP films by the direct method. The highest degree of grafting was obtained at a solvent composition of 20% H_2O: 80% MeOH and a comonomer mixture of 20% AAc:

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80%S. The purpose of this work was to perform a preliminary assessment on the preparation and characterization of non-woven PP fabric grafted by irradiation with MMA for hydrogel reinforcement. It was studied the best method of preparation to accomplish the highest degree of grafting. The mechanical and thermal properties, as well as, swelling ratio were evaluated and related to the morphological changes under irradiation.

2. Experimental

The polypropylene fiber was an isotatic polymer supplied by Fitesa S/A, Rio Grande do Sul, Brazil. The fibers were washed with acetone and dried in vacuum at 60°C before use. Methylmethacrylate, methanol (Merck, Germany), Decalin (Reagente, Brazil) and Ferric Chloride (Carlo Erba, Italy) were of pure grade and were used without further purification.

2.1. Graft copolymerization by direct irradiation

Methylmethacrylate dissolved in 2:3 methanol/decalin was put in glass ampoule together with the PP fibers and Ferric chloride (0.05%). The reactor was deaerated by bubbling nitrogen for 10 min. After, it was immediately subjected to electron beam with dose 20 kGy (dose rate 11.3 kGy/s).

2.2. Graft copolymerization by pre-irradiation

Polypropylene fibers were subject to electron beam with dose of 50 kGy in the absence of air (dose rate 11.3 kGy/s). The irradiated fibers were weighted and immersed into glass ampoule containing MMA solutions at different concentrations (10–50%). The solution was purged with N_2 for 5 min to ensure an oxygen-free solution.

2.3. Characterization

The grafted fibers treated by both methods were thoroughly washed with warm water and extracted with hot benzene at 70°C to remove any residual homopolymer. Then, they were dried under vacuum at 60°C for 24 h to a constant weight. The degree of grafting was calculated as follows:

$$\mathrm{DG}(\%) = \left[\frac{W_g - W_0}{W_0}\right] \times 100$$

where: DG = degree of grafting; W_g = weight of grafted fibers; W_0 = initial weight.

The grafted PP fibers were immersed in distilled water for 48 h at ambient temperature. Then the grafted PP fibers were removed from the water, dried quickly with filter paper to remove water attached to the surface and weighted. The swelling percent (S%) was calculated as follows:

$$S(\%) = \left[\frac{W_S - W_0}{W_0}\right] \times 100$$

where: W_s = weight of swelled fibers; W_0 = initial weight.

The infrared spectroscopy analyses were carried out using a Perkin–Elmer FTIR spectrophotometer model Paragon 1000PC. An INSTRON equipment model 5567 using at a crosshead speed of 25 mm/min measured the tensile strength (T_b) and percentage elongation at break (E_b). The samples were prepared according to ABNT NBR 6241/80 type I. Thermogravimetric analyses (TGA) were performed using a Shimadzu TGA-50H analyzer with a heating rate of 10°C/min under nitrogen atmosphere.

3. Results and discussion

3.1. Effect of monomer concentration

As may be observed, in Fig. 1, in both methods the grafting yields increase with monomer concentration to a maximum around 40% of MMA when it starts decreasing.

This behavior could be explained by the favorable kinetics of synthesis of the insoluble homopolymer, PMMA, at high concentrations of MMA, competing with the grafting reaction (Tabata et al., 1991). Additionally, Fig. 1 clearly shows that direct irradiation method is more efficient than the pre-irradiation method. This was a result of the higher radical availability by the direct method where both components were irradiated simultaneously. On the other hand, the lower availability of pre-irradiated radicals was a result of the very short lifetime of PP

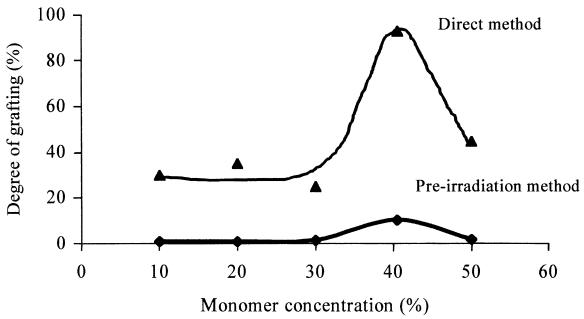

Fig. 1. Effect of monomer concentration on the grafting yield by direct and pre-irradiation method in PP fibers.

macroradicals in the amorphous phase. Probably, all reacting radicals in the pre-irradiation method were the trapped radicals from the crystals, moving to the interface of the amorphous phase.

3.2. Swelling of measurements

Fig. 2 shows the increase in the amount of absorbed water with the degree of grafting. At 100% grafting the amount of adsorbed water is twice the initial amount. The increase in the swelling of the fibers mesh is proportional to the amount of grafted material. Since no clear porous structure was observed by photomicrographs on these fibers, we believe that this swelling is mainly due capillary effect. Therefore, the enhancement of PP surface compatibility with water should increase capillarity and, hence, swelling. However, care should be taken in analyzing these data, since not only grafting is occurring. Degradation, physical and chemical crosslinking are always major processes in any PP irradiation.

3.3. Spectroscopy analysis

The IR spectra of the ungrafted and grafted samples of PP fibers having different grafting yields. The characteristic bands for non-irradiated PP fibers appear at 841 and 1167 cm^{-1} due to (~$HC(CH_3)$—C~). In ungrafted PP fibers irradiated with a 20 kGy dose occurs an increase of the bands at 1738 cm^{-1} corresponding to C═O stretching. As may be seen, the grafting process produces new bands appearing at 1738 and 1268 cm^{-1} corresponding to C═O and C—O—C groups from the acrylate group. The intensity of these bands increases with increasing the grafting yield.

3.4. Mechanical properties

It is presumed that the crosslinking and branching of PP grafted molecules should increase tensile strength. However, this trend was not detected. The results in Fig. 3 show a marked decreased with the degree of grafting. The decrease of the tensile strength for the grafted fibers could be explained by the degradation of PP tie molecules at the initial stages of irradiation, since it was not verified any major change in the crystallinity by DSC. Also, it was observed that the elongation decreased with the degree of grafting. The grafted fibers became more brittle than the ungrafted ones. The decrease in elongation and brittleness of the sample were explained by the rigidity of the modified amorphous phase caused by PMMA branches.

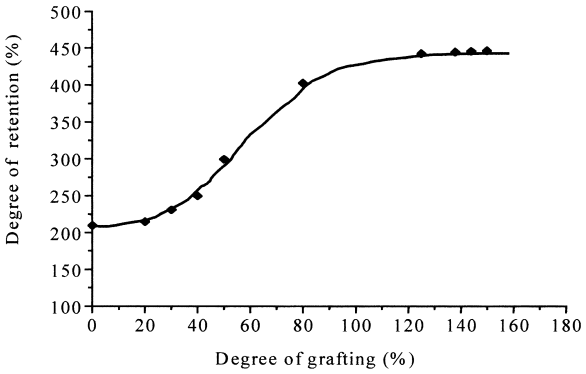

Fig. 2. Change of retained water with degree of grafting.

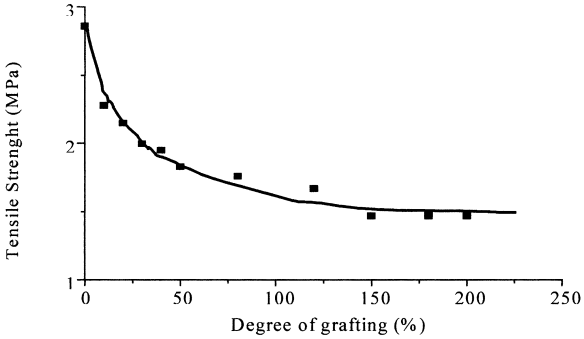

Fig. 3. Tensile strength for the grafted fibers vs degree of grafting.

3.5. Thermal analysis

As may be seen in Fig. 4, the thermal stability of PP was higher than that of PMMA. One could expect that the introduction of the MMA into PP fibers would decrease the thermal stability of the PP fibers. The onset of thermal degradation for the branched PP started at much lower temperature. There were two basic possibilities to explain it: the short chain branches of PMMA have lower degradation tempera-

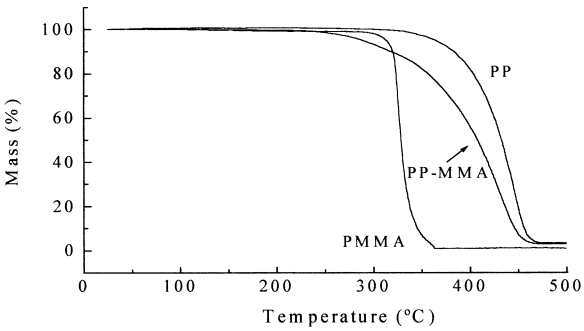

Fig. 4. Thermogravimetric analysis of the ungrafted PP, PMMA and PP-MMA 50%.

ture than the homopolymer and/or PP with was heavily oxidized during the irradiation process (Jaffe, 1981).

4. Conclusion

PP fibers became highly hydrophilic by MMA grafting, improving its compatibility with hydrogels. The direct method showed much higher efficiency over the pre-irradiation one. The obtained product is expected to serve as mechanical support for hydrogels.

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