Study on the Surface Grafting of Polypropylene Fibers

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ABSTRACT: In this article, the surfaces of polypropylene (PP) fibers were grafted by three different grafting systems, of which the initiators belonged to three different types, namely, the water-soluble initiator, the redox initiator, and the oil-soluble initiator, respectively. The grafted products were characterized by FTIR, and the grafting degrees were determined by acid–base titration. In comparison, it was found that the oil-soluble initiator might be more suitable for the surface grafting modification of PP fibers. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 734–737, 2006

Key words: polypropylene; graft; modification

INTRODUCTION

Surface modification of polypropylene (PP) fibers by polar monomers has always been an object of great interest, as it offers an effective route to address such a low cost commodity polymer to higher added value applications, such as applications in concrete,[1–6] applications in medicine,[7] applications in textile industry,[8–9] and so on. However, PP as a saturated hydrocarbon has a low surface energy, which leads to its poor wet ability by water and to very low adsorptive and adhesive properties to polar liquids. Therefore, the modification of PP fibers is very significant.

So far, many methods, including radical,[7,10–16] radiation,[17–19] plasma,[20–24] and UV[25–31] initiating graft polymerization, have been reported to modify or improve the surface properties of PP fibers. Among them, surface modification of PP fibers through free-radical graft polymerization is one of the most commonly useful methods. The free-radical graft polymerization can be initiated by different types of initiators, such as the water-soluble initiator,[16] the redox initiator,[16] and the oil-soluble initiator,[7,14] and so on. However, not all kinds of initiators are effective for the grafting modification of PP fibers. In addition, in some grafting methods, lots of homopolymers formed as side products in the graft polymerization are very troublesome and do not facilitate the grafting process.

In this article, three typical grafting systems were compared and studied. The aim of the study was to find a more effective initiation system for the surface grafting modification of PP fibers and a method in

which little amount of homopolymers were formed in the graft modification of PP fibers. The grafted products were characterized by FTIR, and the grafting degrees were determined by acid–base titration.

EXPERIMENTAL

Materials

PP fibers, purchased from JinShan Chemical Co. Ltd. (China), were used after cutting it to 0.8–1.0 cm length. Acrylic acid was purified by distillation under low pressure. Benzoyl peroxide (BPO) was recrystallized in methanol–chloroform mixture and dried at 60°C under vacuum. Diphenyl (DPh), benzene, and NNO, a dispersing agent, (a mixture of salts of multicore condensat aromatic sulfoacids) were used as received.

Grafting methods

Three different grafting initiation systems and grafting methods[7,14,16] were adopted and compared in our study. They are described in detail as follows:

Method 1 was carried out by the graft polymerization of acrylic acid onto PP fibers, using $KMnO_4/H_2SO_4$ as an initiator (Scheme 1).[16] First, PP fibers of 0.5 g were pretreated at 353 K for 30 min in an aqueous solution of $KMnO_4$ in 5.0×10^{-3} mol/L concentration and acrylic acid in 0.2 mol/L concentration. Then, the PP fibers were preinitiated at 353 K for 30 min after H_2SO_4 was added into the reactive system. H_2SO_4 in 0.2 mol/L concentration was taken for the preinitiation. After the preinitiation, graft polymerization occurred with the addition of acrylic acid. Acrylic acid in 0.8 mol/L concentration was optimum for the graft polymerization. Finally, the grafted PP fibers were

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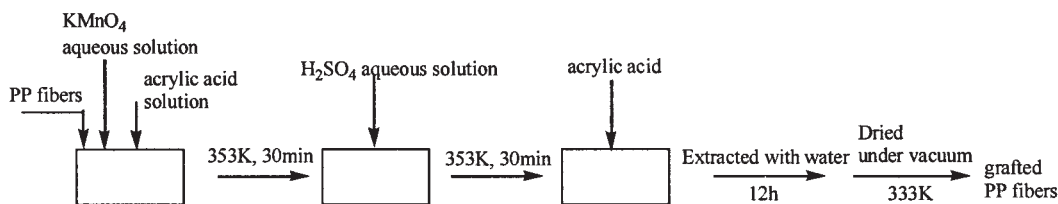
Scheme 1.   The grafting process of Method 1.

extracted with water for 12 h to remove the homopolymer and then dried under vacuum at 333 K to a constant weight.

Method 2 was carried out by the graft polymerization of acrylic acid onto PP fibers, using BPO as an initiator (Scheme 2).[14] The experimental details could be described as follows: First, the PP fibers were washed with acetone, two washes 3 min each, and dried in a vacuum oven at room temperature for 24 h, before initial mass was determined. Monomer solution of acrylic acid, with various concentrations (from 10 to 70 wt %), and BPO (0.5 mol % of acrylic acid) in 50 mL toluene were mixed together after dissolving the initiator in a small amount of toluene. The mixture solution was purged by nitrogen gas for 5 min and dropped into a glass flask in nitrogen atmosphere, in which the PP fibers (0.4 g) were added at the bottom. Then, the flask was placed in an oil bath at a temperature of 333–348 K and was shaken for 4 h with a shaking speed of 150 rpm. Then, the AA-grafted PP fibers were removed from the reaction flask and washed in 5% NaOH

water/ethanol (50/50 v/v) solution and extracted with methanol for 24 h to remove any residual monomer and polymer. The PP fibers were then washed with a large amount of water and dried under vacuum and weighed.[14]

Method 3 is done[7] for the grafting of poly (acrylic acid) on PP fibers, using DPh and NNO in the grafting bath as additives, to facilitate the grafting process (Scheme 3). In the grafting process, first, 2.0 g sample of PP fibers were kept in 40-cm^3 benzene solution (1.25% w/v BPO contained) for 0.5 h at varied temperatures from 323 to 363 K. Then, the excess of the BPO solution was squeezed out and traces of benzene were removed by evaporation for 15 min at 368 K. The PP fibers were placed into a 250-cm^3 reactor, equipped with a mechanical stirrer, a thermometer, a reflux condenser, and nitrogen supply. Grafting was carried out in acrylic acid solution, DPh, and NNO (0.4 wt % each). The resultant product was extracted with water to remove the homopolymer and then dried under vacuum to a constant weight.[7]
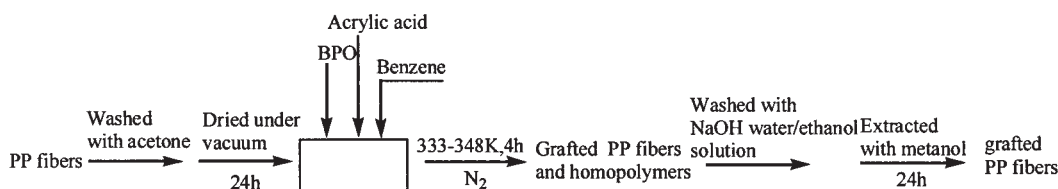
Scheme 2.   The grafting process of Method 2.
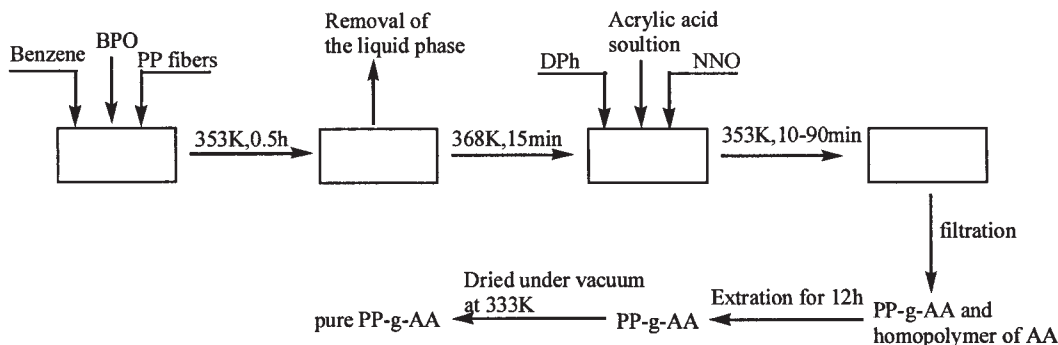
Scheme 3.   The grafting process of Method 3.
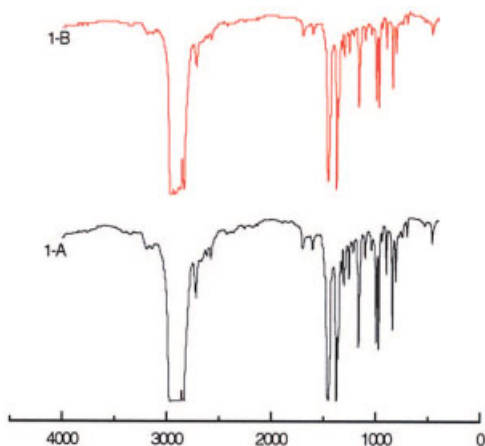
Figure 1 FTIR spectra of PP fibers and the grafted PP fibers produced by Method 1. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

Figure 2 FTIR spectra of PP fibers and the grafted PP fibers produced by Method 2. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]
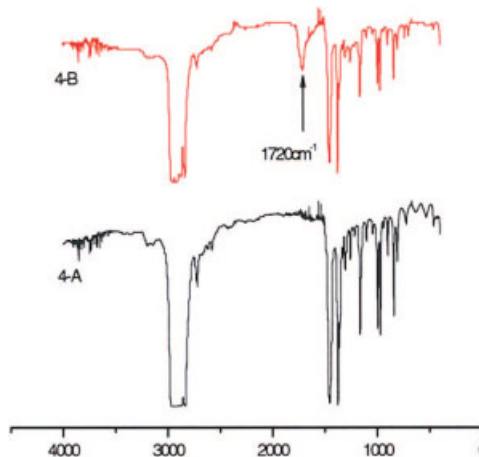
FTIR characterization

FTIR spectra of the ungrafted PP fibers and the grafted PP fibers were recorded at a Nexus 670 FTIR spectrophotometer (Nicolet, Waltham, MA). The ungrafted PP fibers and the grafted PP fibers were pressed into films at 413 K, before FTIR characterization.

RESULTS AND DISCUSSION

Analysis of the FTIR spectra

Figures 1–3 are the FTIR spectra of the ungrafted PP fibers and the grafted PP fibers produced by Method 1–3, respectively. Spectrum A and Spectrum B in each figure represent the spectra of ungrafted PP fibers and the grafted PP fibers, respectively.

The spectra of ungrafted PP fibers (Spectrum 1A, Fig. 1) and the grafted PP fibers (Spectrum 1B, Fig. 1) are almost identical and no additional absorption bands for carboxyl groups can be detected in the spectrum of the grafted PP fibers. This could possibly be due to the very small concentration of carboxyl groups compared with the bulk PP matrix, which may be related to the following two reasons. One may be in accordance with the difference between the stereospecificity of the PP fibers used in our study and that of the PP fibers used in the article.[16] At the same reaction conditions, PP fibers of lower stereospecificity are easier to be grafted than those of higher stereospecificity.[32–34] May be the stereospecificity of the PP fibers used in our study is higher than that of the PP fibers used in that article.[16] Another is that $KMnO_4/H_2SO_4$ is not an effective initiator for the grafting polymerization of PP fibers. So far, few articles have reported that $KMnO_4/H_2SO_4$ is used as an effective initiator for the grafting polymerization of PP fibers.

Comparing with Method 1, Methods 2 and 3 are more effective for the grafting polymerization of PP fibers. An absorption band at 1720 cm^{-1} appears in the spectra of the grafted products (Spectrum 2B, Fig. 2; Spectrum 3B, Fig. 3).

As for Method 2, during the grafting polymerization, the decomposition speed of BPO and the reactive speed become faster with an increase of the reaction temperature. Because the grafting polymerization is exothermic, enough heat generated in the reaction system may result in a violent polymerization. Therefore, the control of the reaction temperature is a key issue and troublesome. And also due to plenty of homopolymers formed in the reaction system, the grafted degree is always rather low.
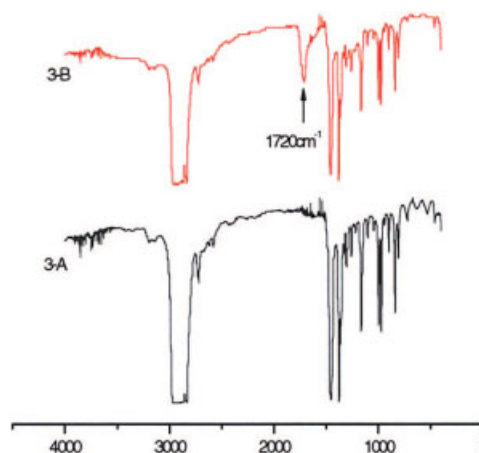
Figure 3 FTIR spectra of PP fibers and the grafted PP fibers produced by Method 3. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]

In contrast, the grafting degrees of the grafted PP fibers produced by Method 3 are higher than those of the grafted PP fibers produced by Method 2, in which there is no excess of initiators during the grafting polymerization in Method 3, namely, after the active sites are introduced onto the PP backbone through initiation the excess of initiators was squeezed out of the reaction system. Therefore, the homopolymerization of monomers was confined to a certain degree to facilitate the grafting polymerization.[7]

The grafted degrees of Methods 2 and 3 are both within the scope of 17.0–20.0 wt %, according to our experimental data. However, Method 3 is more effective in the surface grafting of PP fibers than Method 2. The reason is that the reaction conditions in Method 2, such as the reaction temperature, are harder to control than those in Method 3. And also plenty of homopolymers formed in Method 2 is also troublesome.

CONCLUSIONS

In this article, three different grafting methods were compared and selected to modify the PP fibers. It was found that the oil-soluble initiation systems are more effective in the surface grafting of PP fibers. The comparison of Methods 2 and 3 indicates that, if the excess initiators are squeezed out of the reaction system after the active sites have formed in PP fibers, the possibility of the homopolymerization of monomers can be greatly reduced which in turn facilitate the grafting process.

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