

Studies on Preparation and Ion-Exchange Properties of Weakly Acidic Cation Exchange Fiber by Preirradiation-Induced Graft Copolymerization with Electron Beam

LU YUN, ZHANG ZHU, and ZENG HANMIN

Materials Science Institute, Zhongshan University Guangzhou, 510275, People's Republic of China

SYNOPSIS

Weak acidic cation exchange fibers were obtained by means of preirradiation-induced graft copolymerization of methacrylic acid, acrylic acid, and acrylic acid and diglycol acrylate onto polypropylene nonwoven fabric with electron beam. Effects that influence grafting and the exchange adsorptive property of the ion-exchange fibers obtained toward transition and rare-earth metal ions have been investigated. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Ion-exchange fiber as a fibrous adsorbing material possesses a highly developed specific surface area. Therefore, if its exchange capacity is suitably large, adsorption and desorption speeds are faster than that of a granular exchanger. It can be used in various forms, such as yarn, fabrics, nonwoven fabrics, and yurt for satisfying the needs of various exchange adsorption processes. For this reason, since the 1970s, great attention has paid to it.¹ Recently, we have obtained strongly and weakly acidic cation exchange fibers by chemically induced grafting.^{2,3} In this study we present the results of preparation and ion-exchange properties of weakly acidic cation exchange fiber based on polypropylene (PP) nonwoven fabric by preirradiation-induced graft copolymerization of methacrylic acid (MAA), acrylic acid (AA), and AA diglycidyl acrylate (DGA) onto PP nonwoven fabric, respectively, with an electron beam.

EXPERIMENTAL

Materials

PP nonwoven fabric was produced by Guangzhou Second Chemical Fiber Factory. Standard on fabric

is 40 g/m². Fabric was extracted with acetone and then dried under vacuum before irradiation.

Monomers MAA and AA are chemical reagents. They were purified by vacuum distillation before use. Crosslinking agent DGA was synthesized following our method:³ $\eta = 1.4640$.

(NH₄)₂Fe(SO₄)₂ (Mor's salt), transition metal salts (chlorides and sulfates), and rare-earth oxides are AR grades, being used without purification.

Preirradiation of PP Nonwoven Fabric

The PP fabric with an area of 20 × 26 cm² was preirradiated with an electron beam (electron static accelerator model JJ-2 made in China) with 1.5 meV, 30. μ A at room temperature (25°C) in air. The scanning width was 26 cm and the speed of parallel motion of the sample table was 1 cm/s. The irradiation dose was 2.5 × 10⁵ GY. After irradiation the sample packet was melt sealed and stored in the dark, dry and cool (below 0°C).

Graft Copolymerization and Treatment of Products

The aqueous solution of monomer with requisite concentration was added into a three-neck flask (ratio of bath 1 : 150 w/v). After air was exhausted with highly pure N₂, the preirradiated PP nonwoven fabric, sheared into strips, was put into the flask under a plus pressure of N₂. The reaction was per-

formed under N_2 with a magnetic stirrer and in a thermostated bath. After reaction the graft copolymer was immersed in dilute HCl solution overnight, and then washed with deionized water to neutrality. The sample was dried at 60°C under vacuum to constant weight (W_1) and then extracted with methanol in a Soxhlet extractor for 24 h. The extracted product was dried at 60°C under vacuum to constant weight (W_2). The graft percentage ($G\%$) and efficiency of grafting ($E\%$) are calculated as follows²:

$$G\% = \frac{W_2 - W_0}{W_0} \times 100 \quad E\% = \frac{W_2 - W_0}{W_1 - W_0} \times 100$$

where W_0 is original weight of fabric.

Characterization of Graft Copolymers

1. IR analytical: The IR spectra of fabrics before and after grafting were recorded with an attenuated IR attachment on a Nicolet 50-DX spectrometer.

2. Differential scanning calorimetry (DSC) spectra: The DSC spectra of samples were recorded with a differential scanning calorimeter made in Shanghai.

3. Determination of ion-exchange capacity.²

4. Determination of exchange adsorptive amount of graft fiber toward transition and rare-earth metal ions. 0.050 g graft fiber transmuted into Na^+ or NH_4^+ type was added to the 0.05 mol/L metal ion solution in an iodometric flask, which was placed in the thermostatic vibrator. The flask was shaken for a certain time at the required temperature. Concentration of metal ion solution before and after ex-

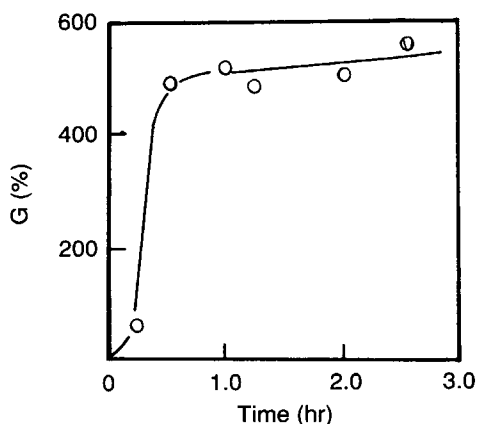


Figure 1 Relationship between grafting percentage and reaction time. $[\text{Fe}^{2+}]$ is 0.4 wt %; $[\text{MAA}]$ is 10 vol %; reaction temperature is 70°C .

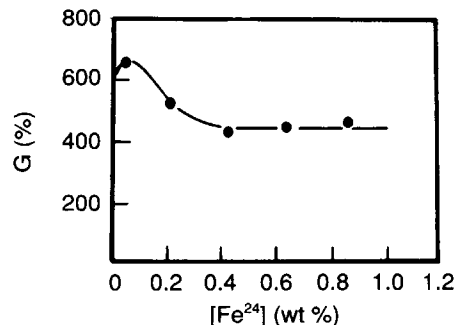


Figure 2 Relationship between grafting percentage and amount of the Mor's salt used. $[\text{MAA}]$ is 8 vol %; temperature is 70°C ; time is 0.5 h.

change adsorption was determined by means of complexometric titration⁴ and a spectrophotometric method⁵ for transition and rare-earth metal ions, respectively. The exchange adsorption amount (E) was calculated as follows:

$$E \text{ (mg/g)} = \frac{(M_0 - M) \times V}{W} \times W_m$$

where M_0 , M are the concentration of metal ion solution before and after exchange adsorption (mol/L), V is the volume of solution used for exchange adsorption (mL), W is the weight of exchange fiber, and W_m is the atomic weight of metal.

RESULTS AND DISCUSSION

Graft Copolymerization of MAA onto PP Nonwoven Fabric

Effects such as monomer concentration, reaction time and temperature, and amount of Mor's salt used, which influence the graft copolymerization, have been investigated. Figure 1 is the grafting rate vs. time curve. It demonstrates that the preirradiation-induced graft copolymerization of MAA onto PP fabric proceeds very fast. The reaction finishes in a half hour at 70°C , and the extent of grafting is 500%. It is noted that Mor's salt is used usually during radiation-induced graft copolymerization of vinyl monomers. Fe^{2+} as a promoter can accelerate the dissociation of hydrogen peroxide groups at low temperature, which exists in the preirradiated polymeric chain. On the other hand it can also destroy the $\cdot\text{OH}$ radical and the homopolymerization of monomer can be inhibited. However, Fe^{2+} also can play a role of termination of propagating chain rad-

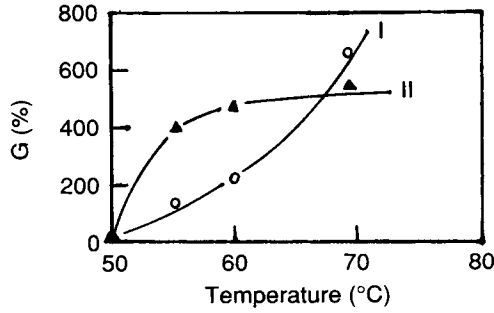


Figure 3 Grafting percentage vs. temperature curves, amount of Fe^{2+} is 0 wt % (I) and 0.2 wt % (II).

icals and reduce the grafting yields. Therefore, the optimum quantity must be found. From Figure 2 it can be seen that the maximum extent of grafting appears at 0.1 wt %. Over this amount the graft percentage reduces quickly and is lower than that given in the absence of Fe^{2+} . The relationships between graft percentage and reaction temperature, as well as the role of Mor's salt at various temperatures, are demonstrated in Figure 3. Curves I and II show variation of degree of grafting with reaction temperature in the absence and presence (0.2 wt %) of Fe^{2+} , respectively. It is clear that at 50°C the grafting proceeds slowly and the weight gains are less in both systems, but grafting in the presence of Fe^{2+} is still somewhat faster than when Fe^{2+} is absent. However, when the temperature rises from 55 to 60°C, curve II increases faster than curve I. It is obvious that the Mor's salt accelerated the dissociation of hydrogen peroxide groups existing in preirradiated PP, causing an increased concentration of active centers.

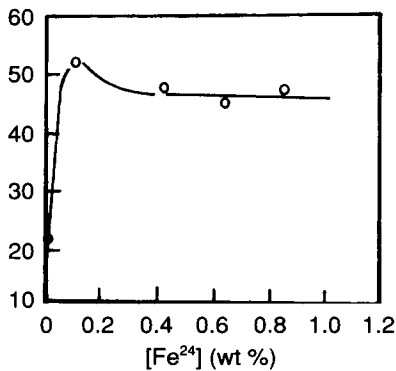


Figure 4 Relationship between grafting percentage and amount of the Mor's salt used. [AA] is 30 vol %; temperature is 40°C.

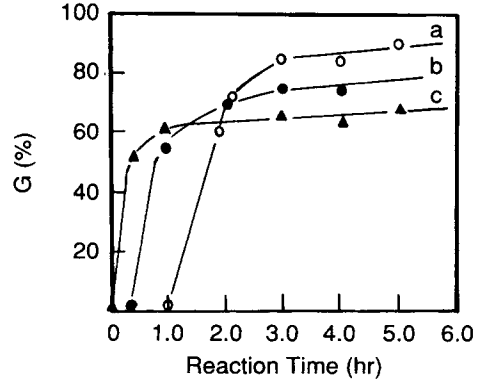


Figure 5 Grafting percentage vs. time. [AA] is 50 vol %; $[\text{Fe}^{2+}]$ is 0.1 wt %; temperature is (a) 30°C, (b) 40°C, and (c) 50°C.

This results in a large increase in the rate of initiation of growing chains and the graft percentage is enhanced significantly. However, the grafting proceeds quickly with higher yields of grafting at 70°C even in the absence of Fe^{2+} . This can be interpreted that, in the presence of Fe^{2+} , the rate of termination of growing chain radicals increases significantly and that the graft percentage reduces significantly at higher temperature.

Graft Copolymerization of AA onto PP Nonwoven Fabric

The results (Fig. 4) once again show the obvious role of Mor's salt in increasing the graft percentage at low reaction temperature (40°C). The maximum extent of grafting appears at 0.1 wt % Fe^{2+} . Though

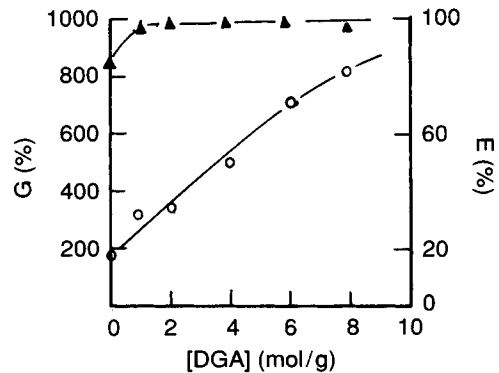


Figure 6 Effect of DGA on the grafting percentage and grafting efficiency. [AA + DGA] is 50 vol %; $[\text{Fe}^{2+}]$ is 0.1 wt %; temperature is 40°C; time is 3 h.

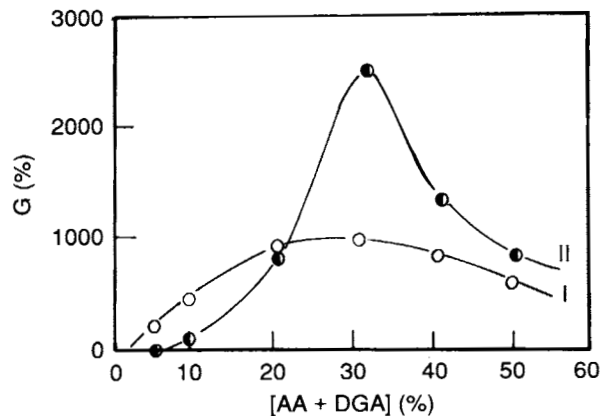


Figure 7 Grafting percentage vs. monomer concentration. $[\text{Fe}^{2+}]$ is 0.1 wt %; temperature is 40°C ; time is 3 h; $[\text{DGA}]$ is (I) 4 mol % and (II) 8 mol %.

the graft yields slowly reduce with increasing Fe^{2+} amount, the graft percentage is still double that of the case in which Fe^{2+} was absent. This shows that the role of Mor's salt in increasing the rate of grafting is more than just termination of chain radicals at low temperature.

Kinetic curves of graft copolymerization at various temperature (Fig. 5) show that at higher reaction temperature a higher degree of grafting was evident at the beginning of the 2 h of reaction. Con-

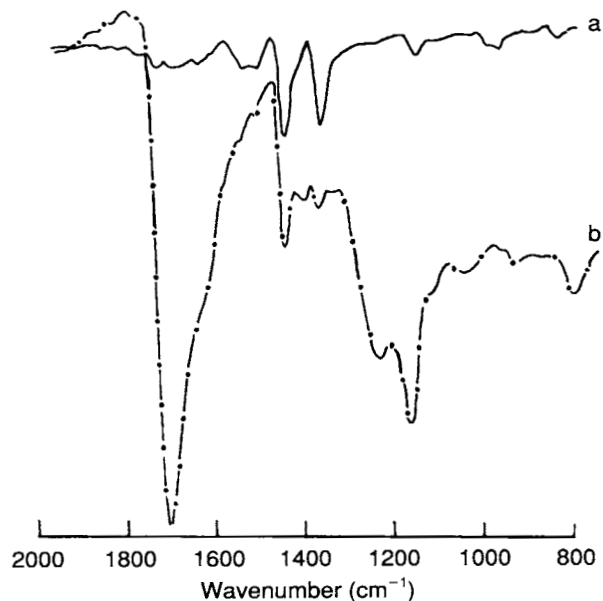


Figure 8 IR spectra of the fibers before and after graft copolymerization. (a) PP fiber; (b) PP-g-AA-GDA grafted fiber with grafting percentage of 611%.

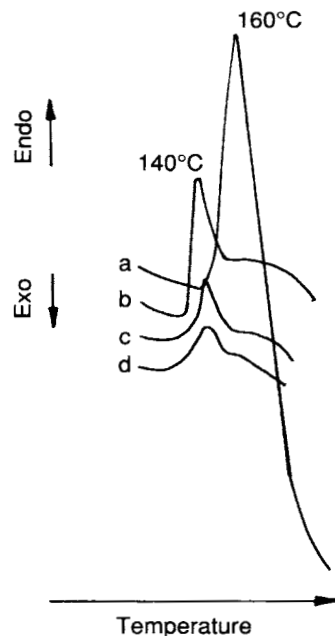


Figure 9 DSC curves of the PP nonwoven fabric and its grafting products with various grafting percentage. (a) PP, (b) PP-g-AA-DGA 191%, (c) PP-g-AA-DGA 446%, and (d) PP-g-AA-DGA 611%.

versely after 3 h of reaction, much more rapid formation of graft copolymer occurred at low temperature. After 6 h reaction the order of final degree of grafting was $30^{\circ}\text{C} > 40^{\circ}\text{C} > 50^{\circ}\text{C}$. This has been confirmed by the fact that the $[\eta]$ of polyacrylic acid in homopolymerization is greatly reduced with increasing polymerization temperature.⁶

The above experimental results indicate that the weight gain of AA on PP fabric is not very high; it is disadvantageous for preparation of material with

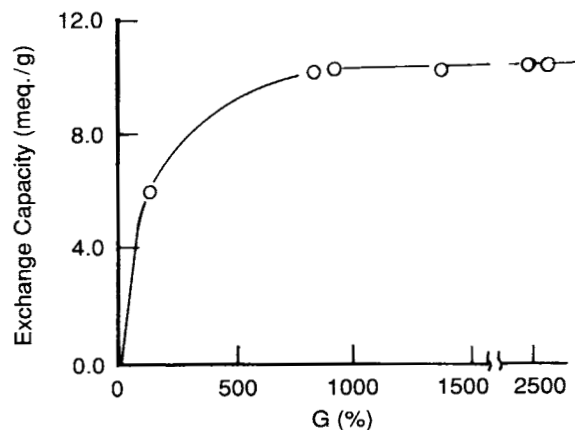


Figure 10 Relationship between grafting percentage and exchange capacity. $[\text{DGA}]$ is 8 mol %.

Table I Exchange Adsorption Property of PP-g-PAA-DGA Fiber Toward Transition Metal Ions (30°C)^a

Metal Ion	Fe ³⁺	Zn ²⁺	Mn ²⁺	Ni ²⁺	Cu ²⁺	Cd ²⁺	Hg ²⁺	Pb ³⁺	Co ²⁺
H-type fiber adsorption amount (mmol/g)	0.52	0.28	0.28	0.37	0.79	0.47	0.21	—	—
NH ₄ ⁺ -type fiber adsorption amount (mmol/g)	2.69	4.76	4.46	4.86	4.50	4.46	4.78	4.62	4.21

^a Graft percentage 611%, pH 4–5, 8 h.

high ion-exchange capacity. In our early work³ it was confirmed that, in the presence of a second monomer with two functional groups (DGA) as a crosslinking agent, higher yields of grafting were found. At the same time, owing to partial crosslinking of grafting chains, material swelling can be reduced and the mechanical stability improved. In this case DGA was used to increase the exchange capacity of this grafted product. The maximum extent of grafting appears to be at 8 mol % DGA and weight increases up to 800% were obtained, but the efficiency of grafting reached 100%, when DGA was used at only 1 mol % (Fig. 6). This experimental result once again helps to explain the role of gel effect. Figure 7 shows the effects of overall concentration of monomers upon the graft percentage. The maximum extent of grafting was obtained when the total monomer concentration was 30 vol % in cases where the content of DGA was 4 and 8 mol %. The reduced extent of grafting in the cases of excess monomer concentration, particularly when the content of DGA was 8 mol %, can be explained by the fact that the increase of overall monomeric concentration means greater take-up of DGA, which has a lower solubility in water. The result is that a heterogeneous system, which is unfavorable for grafting, is formed. Therefore the extent of grafting reduces quickly with increase of total monomeric concentration.

Characterization of Graft Copolymers

In IR spectra of grafted products the absorption band corresponding to a carbonyl peak (1744 cm⁻¹)

is present (Fig. 8). This confirms that the grafting of MAA, AA onto PP fabric, respectively, has taken place. DSC spectra of products (Fig. 9) indicate that with rising graft percentage, the melting temperatures of grafts decrease. This means that grafting was carried out not only in the amorphous range but also in the crystal.

Exchange Adsorptive Properties of Graft Copolymers

Figure 10 shows the exchange capacities vs. graft percentage. The exchange capacity increases rapidly with the increased extent of grafting, when the graft percentage is below 500%, and then increases slowly. When the extent of grafting is over 800%, the exchange capacity does not increase with increased extent of grafting.

Tables I and II illustrate the exchange adsorptive properties of the fibers obtained toward transition and rare-earth metal ions, respectively. It can be seen from Table I that the H-type fiber has little exchange capacity with transition metal ions. This is because PAA is a weak polyelectrolyte. The exchange equilibrium requires a long time (days even weeks). However, when the carboxylic group changes to a carboxylate, the rate of exchange becomes very fast.⁷ NH₄⁺-type and Na⁺-type fiber have suitably large exchange adsorption toward transition and rare-earth metal ions. At the same time the rate of exchange is very fast. The half times to reach the saturated exchange amount toward rare earth metal ions are in the range of 1.4–4.0 min. This means that the graft fiber PP-g-PAA-DGA is an excellent

Table II Saturated Adsorption Amount and Rate of Adsorption of Na⁺-type of PP-g-AA-DGA Fiber Toward Rare-Earth Metal Ions (30°C)^a

Metal Ion	La ³⁺	Pr ³⁺	Nd ³⁺	Eu ³⁺	Ho ³⁺	Tm ³⁺	Er ³⁺	Y ³⁺
Saturated adsorption amount (mmol/g)	3.46	3.30	3.74	3.36	3.03	3.55	3.26	3.77
t _{1/2} (min) ^b	2.10	3.56	1.39	2.10	1.87	2.96	2.10	4.00

^a Graft percentage of fiber 611%, pH 5–6.

^b Calculated according to data of exchange adsorption kinetics.

exchanger for both transition and rare-earth metal ions.

REFERENCES

1. M. P. Zverev, *Zhim. Volokna*, (5) 3 (1975).
2. Lu Yun, Tang Liyuang, Wu Dongyang, and Zeng Hanmin, *Synthetic Fiber Industry*, **12** (1), 6 (1989).
3. Lu Yun, Tang Liyuang, Ye Tinen, and Zeng Hanmin, *Synthetic Fiber Industry*, **11** (6), 1 (1988).
4. Chen Yongzao, *Complexometric Titration*, Science Press, Beijing, 1986, p. 208.
5. Teaching & Research Section of Analytical Chemistry, Department of Chemistry, Hangzhou University, *Handbook of Analytical Chemistry, Part III*, Chemical Industry Press, Beijing, 1983, p. 410.
6. Lin Shangan, Lun Yun, and Liang Zaoyi, *Polymeric Chemistry*, Science Press, Beijing, 1987, p. 483.
7. Robert Kunin, *Ion Exchange Resins* (trans. Zhu Xiuchang), Science Press, Beijing, 1962, p. 51.

Received May 18, 1993

Accepted December 12, 1993