Study of Modified Polypropylene Nonwoven Cloth. I. Graft Copolymerization of 4-Vinylpyridine onto Polypropylene Nonwoven Cloth by Preirradiation Method

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ABSTRACT: Polypropylene (PP) nonwoven cloth was grafted with 4-vinylpyridine (4-VP) by a preirradiation method. The effects of preirradiation conditions on the mechanical properties of preirradiated PP nonwoven cloth and the percentage of grafting (Pg) of 4-VP onto the preirradiated PP nonwoven cloth were systematically investigated. The results indicated that the mechanical properties of preirradiated PP nonwoven cloth decreased with increasing irradiation dose and that the Pg was greatly affected by the concentration of monomer, irradiation dose, grafting reaction temperature, and the addition of inhibitor and inorganic acid in the grafting reaction system. The grafted nonwoven cloth samples were characterized using IR spectroscopy and SEM. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1861–1868, 2000

Key words: graft copolymerization; polypropylene nonwoven cloth; 4-vinyl pyridine; preirradiation method; percentage of grafting

INTRODUCTION

Polypropylene (PP) has been used extensively because of its cheapness, low density, good thermal stability, and excellent mechanical properties. However, PP fiber possesses some drawbacks such as a hydrophobic nature with poor water absorption, dyeability, antistatic properties, and adhesion. PP fiber must be suitably modified to attain some special performances without affecting most of the original properties.

Grafting copolymerization has been adopted for this purpose using both chemical and radiation methods. Deut and Berlin[1] grafted vinylpyridine, acrylamide, and vinyl caprolactam onto PP fiber in toluene; the increase of grafting efficiency was attributed to swelling of the fiber in toluene. By treating or coating PP fiber with a solution of a sensitizer, PP fiber was grafted with acrylamine or glycidyl methacrylate after irradiation with UV light.[2] Gawish et al.[3] carried out grafting of 2-*N*-morpholino ethyl methacrylate onto preirradiated PP fabric by an electron beam. The fabric was dyed with a series of acid and dispersed dyes. Hegazy[4] made a study on the postradiation grafting of aqueous acrylamide (AAm) onto PP films, and the prepared graft copolymer possesses good hydrophilic properties, suitable specific electrical

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resistance, and acceptable mechanical properties for practical use. Gupta et al.[5] studied the grafting of 2-hydroxyethyl methacrylate onto a PP monofilament by a simultaneous γ-ray radiation technique, and the grafting copolymer could be used as a biocompatible suture material. Kaur and Barsola[6] reported on the grafting of 4-vinylpyridine (4-VP) and its mixture with acrylonitrile onto preirradiated PP fiber. The percentage of grafting has been studied as a function of different reaction parameters, and the optimum conditions for affording the maximum percentage of grafting have been evaluated.

Pyridinium-type resin is a quaternary ammonium salt that possesses strong antibacterial activity,[7] but it has some shortcomings of low surface area, high cost, poor workability, and bad mechanical properties. To overcome the problems mentioned above, 4-VP was grafted onto PP nonwoven cloth to attain an antibacterial material that was suitable for applied requirements. In the present study, the grafting of 4-VP onto preirradiated PP nonwoven cloth and some factors affecting the grafting copolymerization are reported and discussed.

EXPERIMENTAL

Materials and Chemicals

PP nonwoven cloth was received from the Chinese Foreign Joint Venture Zhongshan Letson Non-Woven Factory LTDC (Zhongshan, China), and the selected specification of the nonwoven cloth is 33 g/m^2. 4-VP (Sigma Co., St. Louis, MO, U.S.A) was freshly distilled before use. Methanol, ethanol, acetone, Mohr's salt [$FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$], and H_2SO_4 were supplied by the Guangzhou Chemical Reagent Factory (Guangzhou, China).

Preirradiation Procedure

Before irradiation, PP nonwoven cloth was washed with acetone for 1 week, then extracted with ethanol to remove any extraneous material and dried. The irradiation of samples was carried out in a ^{60}Co gamma chamber at the Irradiation Center of South China University of Agriculture, Guangzhou, China. The dry PP nonwoven cloth was exposed to irradiation of 3–20 kGy at normal temperature in the presence of air (dose rate: 3.29 kGy/h).

Grafting Procedure

After irradiation, the samples were immediately weighed and immersed in monomer solutions of different concentrations containing Mohr's salt and H_2SO_4 in flasks. The solutions were purged with nitrogen gas for 20 min to ensure an oxygen-free solution and then sealed. The flasks were thermostated at different temperatures for specific periods. The grafted samples were thoroughly washed with water and finally extracted with ethanol to remove any residual homopolymer. The samples were dried and the percentage of grafting (Pg) was calculated as follows:

$$\mathrm{Pg}\ (\%) = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

where W_0 and W_g are the weights of the initial and grafted samples, respectively.

Characterization

Mechanical properties of irradiated PP nonwoven cloth were determined at once after the irradiation according to F2/T60005-91 using an Instron Model 1121 lab tester. At ambient temperature and 100 mm/min rate of extension, more than five sheets of samples with a 50-mm width and a gauge length of 200 mm were estimated in both vertical and horizontal directions.

Infrared spectra of the grafted samples were recorded in the forms of KBr pellets using a Perkin–Elmer 1700 instrument. Scanning electron microscopy was used to view the morphology of the samples with a Japanese JEOL JSM-T300 instrument using secondary electron imaging.

RESULTS AND DISCUSSION

Effect of Irradiation Dose on the Mechanical Properties of Preirradiated PP Nonwoven Cloth

In general, the peroxide preirradiation method adopted to induce graft copolymerization of PP nonwoven cloth is more convenient and more likely to be used in industry, but there is an oxidative degradation when PP nonwoven cloth is irradiated in air. The preirradiation conditions must be controlled to ensure suitable mechanical properties of the graft polymers.

The strength and elongation at break were determined as a function of irradiation dose, and the

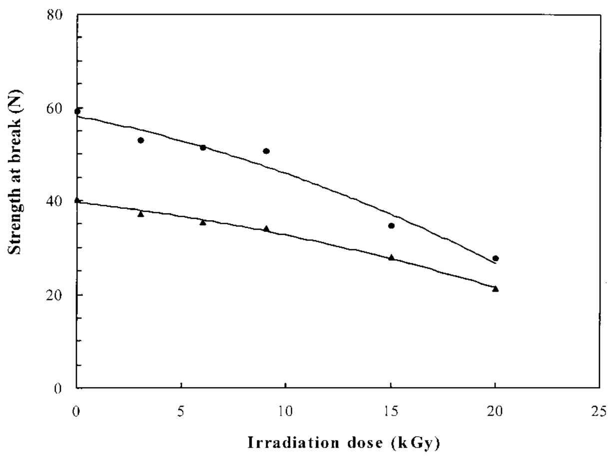

Figure 1 Strength at break versus irradiation dose of PP nonwoven cloth irradiated in the presence of air: (●) vertical; (▲) horizontal.

results are presented in Figures 1 and 2. It was observed from the figures that the strength and elongation at break decreased with increasing irradiation dose. The reason for it was that degradation occurred when PP nonwoven cloth was irradiated in air, and degradation became more serious at higher irradiation doses. The strength and elongation at break of the original PP nonwoven cloth were 59.0 N (vertical) and 40.3 N (horizontal) and 46.5% (vertical), and 39.5% (horizontal), respectively. The strength at break decreased from 59.0 N (vertical), 40.3 N (horizontal) to 50.5 N (vertical) and 34.1 N (horizontal), and the elongation at break, from 46.5% (vertical), 39.5% (horizontal) down to 40.5% (vertical) and 35.5% (horizontal) when the irradiation dose was 9 kGy. Beyond 9 kGy, a further increase in the irradiation dose led to a sharp decline in strength and elongation at break. According to the abovementioned facts, a relatively low irradiation dose can ensure that the irradiated PP nonwoven cloth will have suitable mechanical properties.

Effect of Monomer Concentration on Pg

The Pg as a function of the monomer concentration is presented in Figure 3. Grafting was carried out for a monomer concentration of 0.190 to 3.810 mol/L. It was observed from Figure 3 that the percentage of grafting increased sharply at a lower monomer concentration, then started leveling off beyond 1.905 mol/L. This fact can be explained by that more monomer is available to the grafting sites with an increase in monomer concentration. The graft copolymerization appears to be diffusion-controlled in the present system, and the grafted layer is initially formed on the cloth surface and then gradually moves inward into the cloth. This means that the monomer diffuses into the cloth bulk, followed by grafting to the active site. It seems that the grafted 4-VP chains restrict the monomer to diffusion to the initiating site on the polymeric backbone only after a percentage of grafting of 39% is attained, that is, at a monomer concentration of 1.905 mol/L, resulting in the Pg leveling off.

Effect of Irradiation Dose on Pg

Figure 4 shows Pg versus reaction time curves at various irradiation doses. It can be seen that the Pg linearly increased with the reaction time when the irradiation doses were lower than 6 kGy, but the Pg quickly increased with the reaction time at first and then tended to level off above 2 h with irradiation doses higher than 9 kGy. This behavior was observed for the Pg at the irradiation doses ranging from 3 to 20 kGy. The grafting process levels off with a certain Pg, which is termed the final Pg. The higher the irradiation dose, the higher the initial grafting rate and the final Pg. Generally, the process of radiation grafting depends largely on the concentration of active trapped radicals in the irradiated polymer. The concentration of such trapped radicals increases

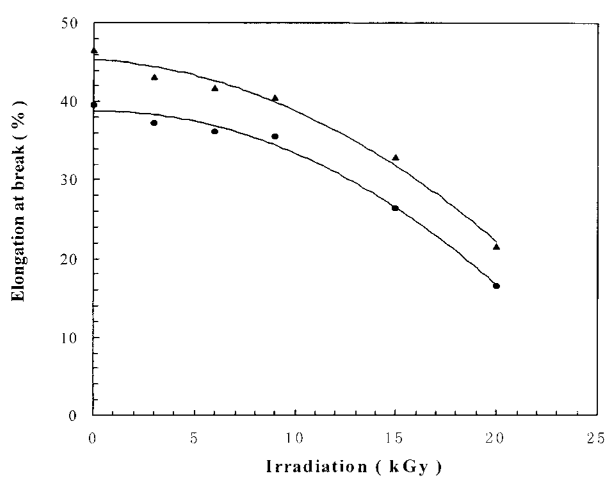

Figure 2 Elongation at break versus irradiation dose of PP nonwoven cloth irradiated in the presence of air: (●) vertical; (▲) horizontal.

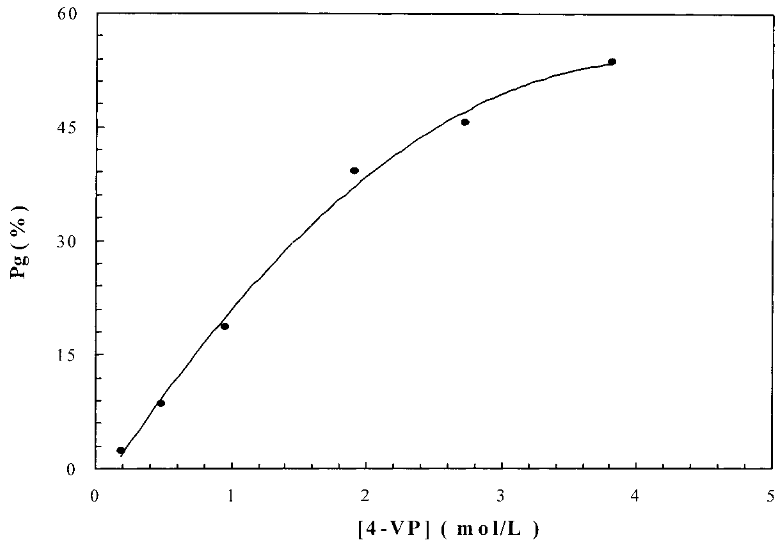

Figure 3 Effect of 4-VP concentration on Pg. Irradiation dose, 9 kGy; Mohr's salt concentration, 2.5×10^{-3} mol/L; [H_2SO_4], 0.2 mol/L; reaction temperature, 90°C; reaction time, 4 h.

with an increase in irradiation dose, so the initial grafting rate and final Pg increase.[4]

Effect of Reaction Temperature on Pg

Figure 5 shows the Pg versus time curves at different reaction temperatures. It was found that at relatively low reaction temperatures (60–70°C) the Pg was low and increased linearly with the lapse of reaction time up to 4 h. At relatively high temperatures (80–90°C), the Pg values were much higher than the corresponding Pg values obtained at relatively low reaction temperatures (60–70°C). At 90°C, a quick increase in the Pg

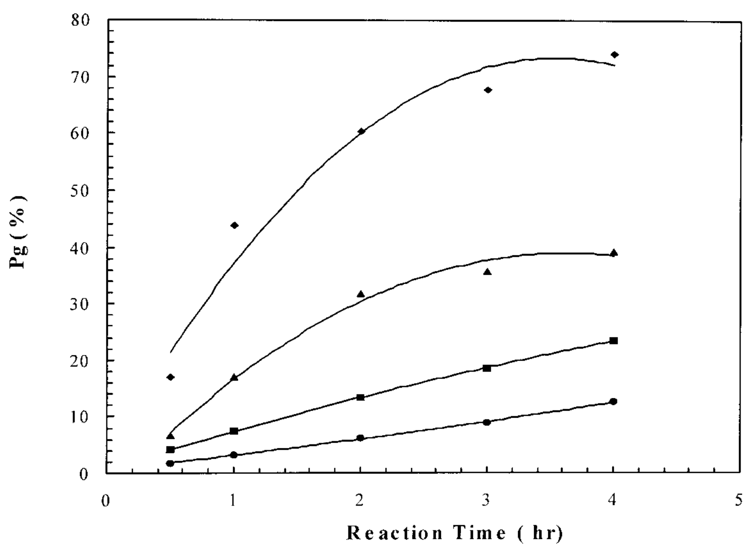

Figure 4 Effect of reaction time on percentage of grafting at various irradiation doses. Irradiation doses: (●) 3 kGy; (■) 6 kGy; (▲) 9 kGy; (◆) 20 kGy; [4-VP], 1.905 mol/L; Mohr's salt concentration, 2.5×10^{-3} mol/L; [H_2SO_4], 0.2 mol/L; reaction temperature, 90°C.

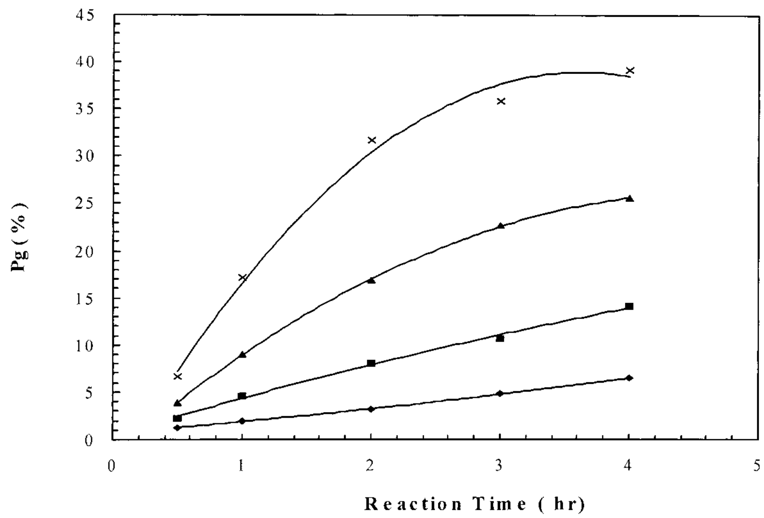

Figure 5 Influence of reaction time on percentage of grafting at various reaction temperatures. Reaction temperatures: (◆) 60°C; (■) 70°C; (▲) 80°C; (×) 90°C; irradiation dose, 9 kGy; [4-VP], 1.905 mol/L; Mohr's salt concentration, 2.5 × 10^{-3} mol/L; [H_2SO_4], 0.2 mol/L.

with time occurred initially and then leveled off above 2 h. The increasing reaction temperature brought about a higher initial grafting rate and final Pg as well.

Effect of Mohr's Salt and H_2SO_4 on Pg

Polymeric material was irradiated in air so that macroradicals formed were converted to peroxides and hydroperoxides. This polymer can be stored at room temperature until ready for reaction with the monomer. The advantage of this process is that the intermediate oxidized polymer can be kept for long periods of time before performing the final grafting reaction. When the irradiated PP nonwoven cloth was heated in the presence of a monomer, the peroxides decomposed to give $PO^\bullet$ radicals that served as active sites for

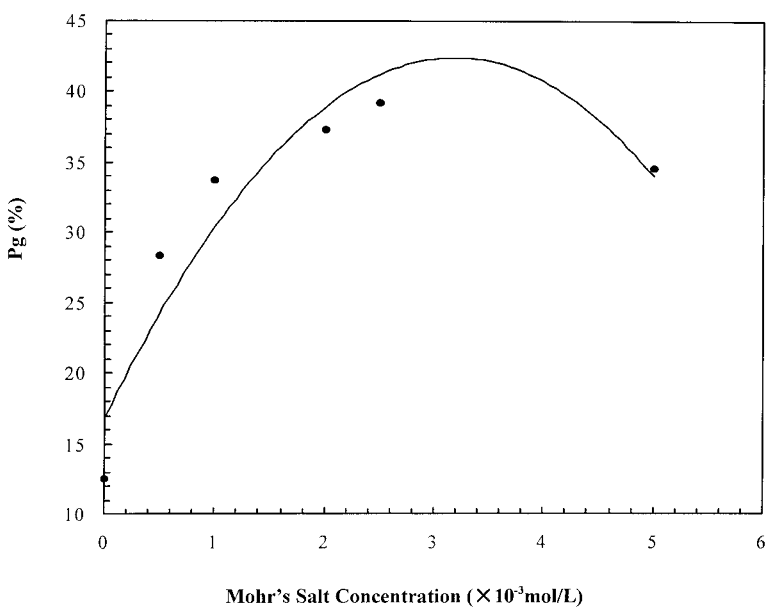

Figure 6 Effect of Mohr's salt concentration on Pg in the presence of 0.2 mol/L H_2SO_4. Irradiation dose, 9 kGy; [4VP], 1.905 mol/L; reaction temperature, 90°C; reaction time, 4 h.

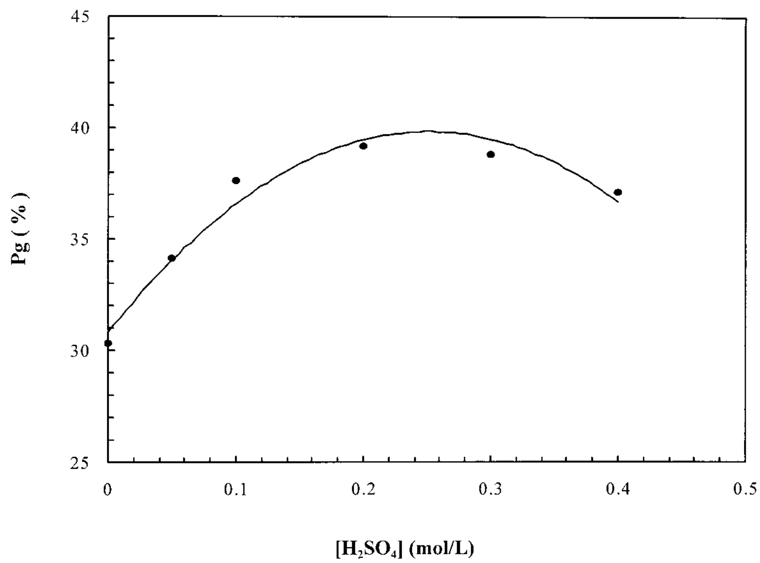

Figure 7 Effect of H_2SO_4 concentration on Pg. Irradiation dose, 9 kGy; [4-VP], 1.905 mol/L; Mohr's salt concentration, 2.5×10^{-3} mol/L; reaction temperature, 90°C; reaction time, 4 h.

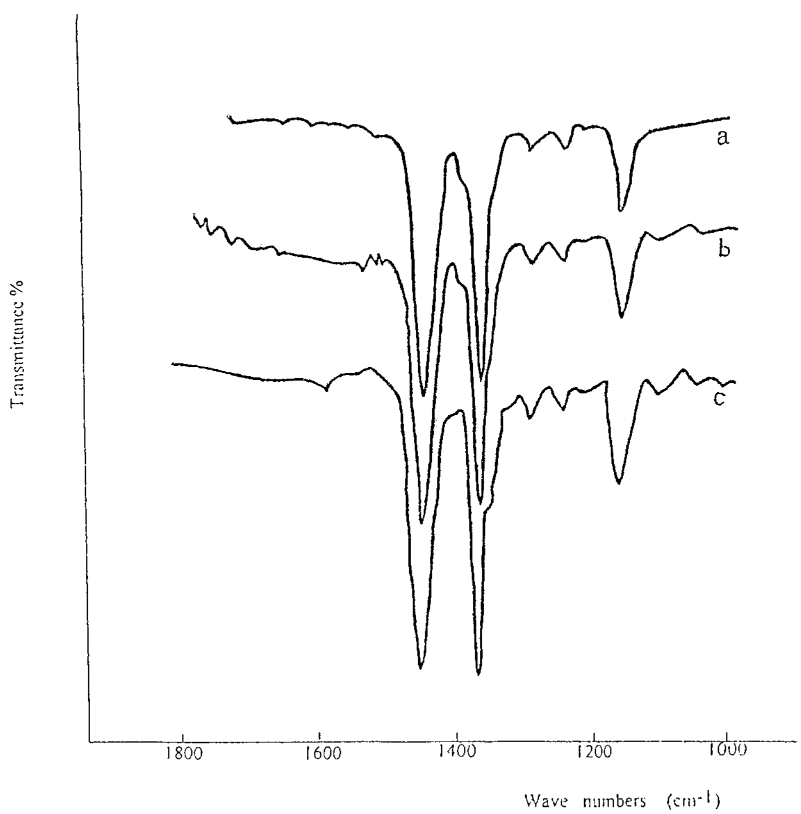

Figure 8 FTIR spectra of grafted PP nonwoven cloth; (a) PP nonwoven cloth; (b) irradiated PP nonwoven cloth (irradiation dose, 9 kGy); (c) grafted PP nonwoven cloth (Pg, 2.3%).

the grafting reaction. Meanwhile, when the hydroperoxide was heated, the dissociation of the hydroperoxide led to an equal number of $PO^{\bullet}$ and $HO^{\bullet}$ radicals. The $HO^{\bullet}$ radical was the direct cause of homopolymerization. The homopolymer can be reduced by using an inhibitor (Mohr's salt) as follows[8]:

$$POOH + Fe^{2+} \rightarrow PO^{\bullet} + Fe^{3+} + OH^{-} \quad (2)$$

Figure 6 shows the effect of Mohr's salt on the Pg in the presence of 0.2 mol/L H_2SO_4. The addition of Mohr's salt to the grafting system led to a great increase in the Pg, except for the concentration of Mohr's salt of more than 2.5×10^{-3} mol/L.

Fe^{2+} played an important role in decomposing the hydroperoxides by the redox system. On the other hand, Fe^{2+} deactivated a part of the growing grafting chain radicals as follows:

$$PO^{\bullet} + Fe^{2+} \rightarrow PO^{-} + Fe^{3+} \quad (3)$$

This reaction led to the reduction of the Pg.

Figure 7 shows the effect of H_2SO_4 on the Pg. The Pg increased with increasing H_2SO_4 concentration in the range of lower concentration and then decreased when the H_2SO_4 concentration was more than 0.2 mol/L. By the addition of H_2SO_4 to the grafting system, the OH^{-} accumulated in eq. (2) could be consumed with the reaction with H^{+}, which was dissociated from H_2SO_4. Therefore, eq. (2) could be favorable in the presence of H_2SO_4 by the Le Chartelier's principle.[8]

FTIR Analysis

The FTIR spectra of PP nonwoven cloth, irradiated PP nonwoven cloth (irradiation dose was 9 kGy), and grafted PP nonwoven cloth (Pg 2.3%) are given in Figure 8(a)–(c). The FTIR spectrum of irradiated PP nonwoven cloth [Fig. 8(b)] showed a peak at 1105.0 cm^{-1} assigned to C—O stretching, as a result of the combination of active free radicals formed in the course of irradiation with air oxygen at ambient temperature. But this peak was absent in the FTIR spectrum of PP nonwoven cloth [Fig. 8(a)]. Compared with the FTIR spectrum of irradiated PP nonwoven cloth, the FTIR spectrum of grafted PP nonwoven cloth [Fig. 8(c)] showed a new peak at 1598.7 cm^{-1} due to C—N stretching peak of vinylpyridine.

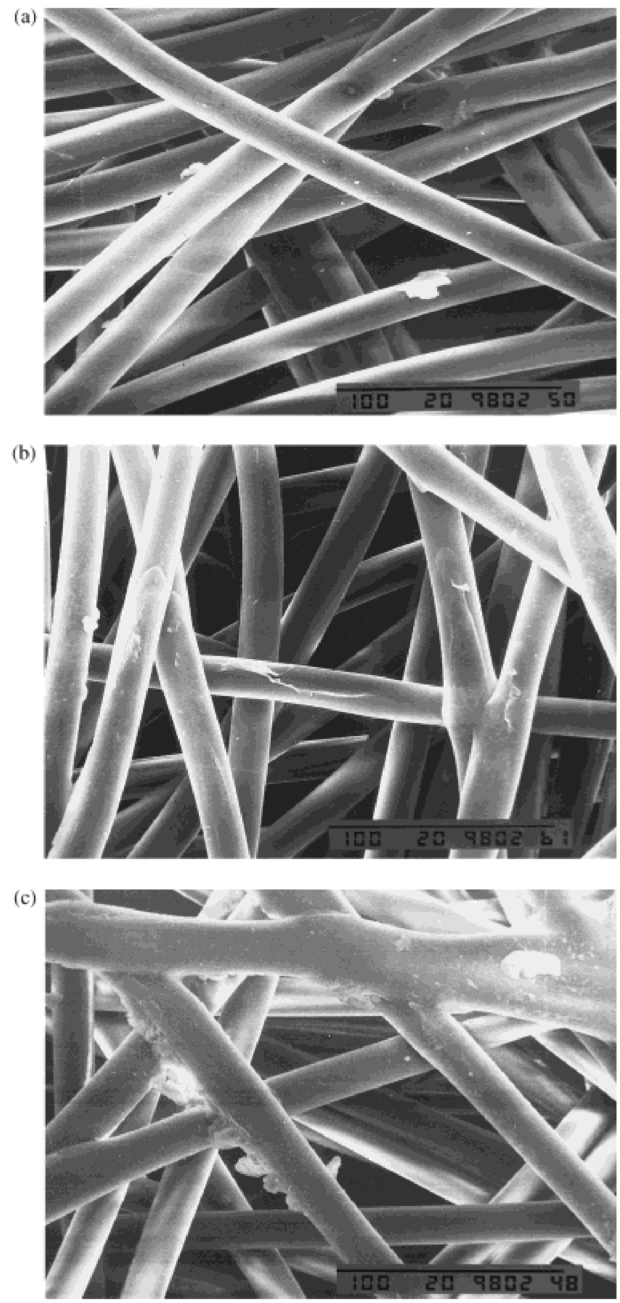

Figure 9 SEM images of grafted PP nonwoven cloth samples: (a) irradiated PP nonwoven cloth (irradiation dose, 9 kGy); (b) grafted PP nonwoven cloth (Pg, 2.3%); (c) grafted PP nonwoven cloth (Pg, 53.7%).

Scanning Electron Microscopy Images

Figure 9(a–c) shows SEM images of irradiated PP nonwoven cloth (irradiation dose, 9 kGy), the grafted PP nonwoven cloth with a low percentage of grafting (Pg 2.3%), and the grafted PP nonwoven cloth with a high percentage of grafting (Pg 53.7%), respectively. From the images, it can be seen that the morphologies of the PP fibers did not show a marked change at a low Pg, but the morphologies of the PP fibers became rough with some fragments at a high Pg.

CONCLUSIONS

In this article, 4-VP was grafted onto PP nonwoven cloth by a preirradiation method using ^{60}Co as the irradiation source. The results obtained are the following:

1. PP nonwoven cloth must be irradiated at a relatively low irradiation dose to ensure its suitable mechanical properties.
2. The Pg increased with increasing irradiation dose, monomer concentration, and reaction temperature and the addition of Mohr's salt and H_2SO_4 to the grafting system could promote graft copolymerization.
3. The spectra of FTIR showed the presence of 4-VP in grafted PP nonwoven cloth, and from the SEM images, it could be seen that the morphologies of PP fibers did not show a marked change except for a relatively high Pg.

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