

Studies on Grafting of Acrylic Acid onto Polypropylene Melt-Blown Nonwovens Induced by Electron-Beam Preirradiation

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ABSTRACT: We report the graft copolymerization of acrylic acid onto the polypropylene (PP) melt-blown nonwovens induced by electron beam (EB) preirradiation in this article. The occurrence of the graft copolymerization was confirmed by means of XPS, FTIR, and SEM. The effects of preirradiation dose, monomer concentration, bath ratio, reaction time, and temperature on the graft ratio were investigated. The water conservation, water absorption rate, and K⁺ exchange capacity were also determined

on the grafted PP melt-blown nonwovens, which showed that EB preirradiation-induced grafting was an effective way to improve the hydrophilicity of PP melt-blown nonwovens. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 4971–4977, 2006

Key words: polypropylene melt-blown nonwovens; electron beam preirradiation; graft copolymerization; acrylic acid; hydrophilicity

INTRODUCTION

Polypropylene (PP) melt-blown nonwovens possess a 3-dimensional network structure fabricated by ultra-fine fibers, which gives them small pore size, high porosity, and in addition, good filtration and absorption properties. On the other hand, PP has many advantages such as chemical and physical stability, a good resistance to biodegradation, and low cost. Because of these advantages, PP melt-blown nonwovens have found wide application as surgical clothes, bandages, diapers, and filters. However, polypropylene is a typical nonpolar and hydrophobic polymer and, therefore, its melt-blown nonwovens have poor hydrophilicity, which limits their use in some areas. To improve their wettability, many researchers have adopted chemical methods to modify and finish PP nonwovens, in which graft copolymerization is one of the effective methods. Graft copolymerization can be achieved by chemical initiators,^{1–3} ultraviolet light,^{4–6} plasma,^{7–9} or ionizing radiation.^{10–13} Radiation grafting is one of the most promising modification methods because of its unmatched advantages, for example, large penetration in polymer substrate, rapid and uniform formation of active sites for initiating grafting throughout the substrate, being free of chemical initiator, and so forth.¹⁴

When polymers are subjected to electron beam (EB) irradiation, the trapped radical or macromolecular peroxides and hydroperoxides that are capable of initiating graft copolymerization reaction are formed. EB irradiation-induced graft can be realized simultaneously, which is called coirradiation, or after the irradiation, which is called preirradiation.¹⁵

Modification of textiles including fabrics and fibers using irradiation-induced graft copolymerization was reported in literature. For example, in He and Gu's study,¹⁴ acrylic acid (AA) was grafted onto polyester fabrics by the EB preirradiation method. The AA-grafted polyester fabrics were found to have good water vapor permeability and excellent water-impermeable ability. Shao and coworkers¹⁶ used both the coirradiation and preirradiation process to graft hydroxyethyl methacrylate on silk fabrics to improve the crease resistance of silk. Ion exchange fibers, reactive filters,¹⁵ and hydrogels¹⁷ were also prepared by means of preirradiation-induced graft copolymerization of monomers such as AA and methylmethacrylate onto polypropylene fabrics, using EB. But most of the aforementioned studies were carried on traditional textile materials, e.g., fibers and fabrics, and few were done on nonwovens, although nonwovens made of polypropylene are finding applications in more and more fields. In the present work, AA was first grafted onto melt-blown polypropylene nonwovens through the EB irradiation method to improve their wettability, and the performances of the grafted nonwovens were

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then evaluated by measuring their water conservation, water absorption rate, and K^+ exchange capacity.

EXPERIMENTAL

Materials

Polypropylene melt-blown nonwovens with a surface weight of 88.5 g/m^2 was provided by TEDA. Analytical reagent grade AA, toluene, and Tween 80 (polyoxyethylene sorbitan monooleate) were all purchased from Tianjin Chemical Reagents and used without further purification except AA was distilled under vacuum before use.

Graft copolymerization

In the present study, the EB is provided by a high-frequency and high-voltage Great Power Electron Accelerator (GJ-1.5 type; Accelerator Institute, Xianfeng Electrical Machinery Plant, Shanghai). The irradiation was carried out at 1.5 MV, and the average beam current is 5 mA. The dose rate is 220 Gy s^{-1} . The dose was measured with a FWT-60-00 radiachromic Dosimeters (Far West Technology), and dose can be controlled by irradiation time. Both the directly coirradiation and preirradiation method were used. In coirradiation, the nonwovens samples were soaked in AA solution for a certain time and then irradiated under EB. After irradiation for a desired time, the samples were taken out and washed five times with copious hot distilled water to remove homopolymerized poly(AA), and then dried in air.

In preirradiation, after the sample was irradiation for a desired time, it was transferred to a refrigerator and kept at -18°C for use. A definite amount of AA was introduced into a 100-mL stoppered conical flask in a temperature-controlled water bath, and then toluene and Tween 80 were also added into the flask to a concentration of 15 and 2 mL/L, respectively. The flask was immediately stoppered, then the irradiated sample was introduced and the graft copolymerization was initiated, the reaction system was refluxed. After the desired reaction period, the sample was taken out from the flask and rinsed repeatedly with water to remove homopolymer adhering to the sample, followed by extraction with boiled methanol three times, and then dried to a constant weight in a vacuum oven. The graft ratio (G) was calculated using the following equation:

$$G = (w_1 - w_0)/w_0 \times 100\%$$

Characterization

XPS, SEM, and FTIR techniques were used to characterize the grafted products. XPS spectra were recorded with a PHI 5000C XPS spectrometer (Perkin-Elmer

Instruments) using a monochromatic Al $K\alpha$ X-ray source at a 45° take-off angle. Infrared spectra were obtained from a Bruker VECTOR 22 FTIR, using the KBr pellet technique. Sample surface were observed with a KYKY-2800 SEM operated at 15 kV; before SEM analysis a 10-nm-gold layer was spray-coated onto the sample surface.

Water conservation, water absorption rate, and K^+ exchange capacity were measured following the Japan VC58160 standards.

RESULTS AND DISCUSSION

XPS analysis of the preirradiated nonwovens

The XPS spectra of the blank and the 7.8 Mrad-preirradiated polypropylene nonwovens sample were shown in Figure 1. We can see from Figure 1(a) that the amount of oxygen in the two samples was different. The O_{1s} peak of the irradiated was increased to 6.06% from the original 2.22% of the blank sample, indicating that oxygen atoms in the atmosphere were introduced into the polymer structure after irradiation, and peroxides, including hydrogen peroxide, were formed. It was these peroxides that decompose and generate macromolecular radicals when heated in vacuum or in an inert atmosphere. And higher irradiation dose produced more hydrogen peroxide, and therefore results in more radicals. Note that the O_{1s} peak in the blank sample was due to the exposure of the treated nonwovens to the atmosphere.⁷ The high-resolution spectra of C_{1s} were shown in Figure 1(b). The half-height width of the blank and preirradiated samples were 1.28 and 1.52 eV, respectively. The increasing half-height width indicates that the C atom in the sample has a chemical shift and maybe existing in different states.

Figure 1(c) shows the resolved spectrum of carbon in the preirradiated sample, from which we can see that they are two types of carbon atoms, whose bonding energy are 284.83 and 286.74 eV, respectively, corresponding to C—O and/or C—H and C—O, respectively. This indicates that C—O bonds originated in the polypropylene macromolecule chains after preirradiation, in other words, peroxides formed during preirradiation.

The high-resolution spectra of O_{1s} in the blank and preirradiated samples were shown in Figure 1(d). The bonding energy of O_{1s} in the blank sample is 531.7 eV, and after irradiation, the bonding energy chemically shifted to 532.4 eV, which is very close to the bonding energy of C—O. This is also a proof that oxygen exists as C—O in the preirradiated samples.

Effects of process parameters on graft ratio

Coirradiation

We first tried the coirradiation method, in which graft and irradiation occurred simultaneously. Table I gives

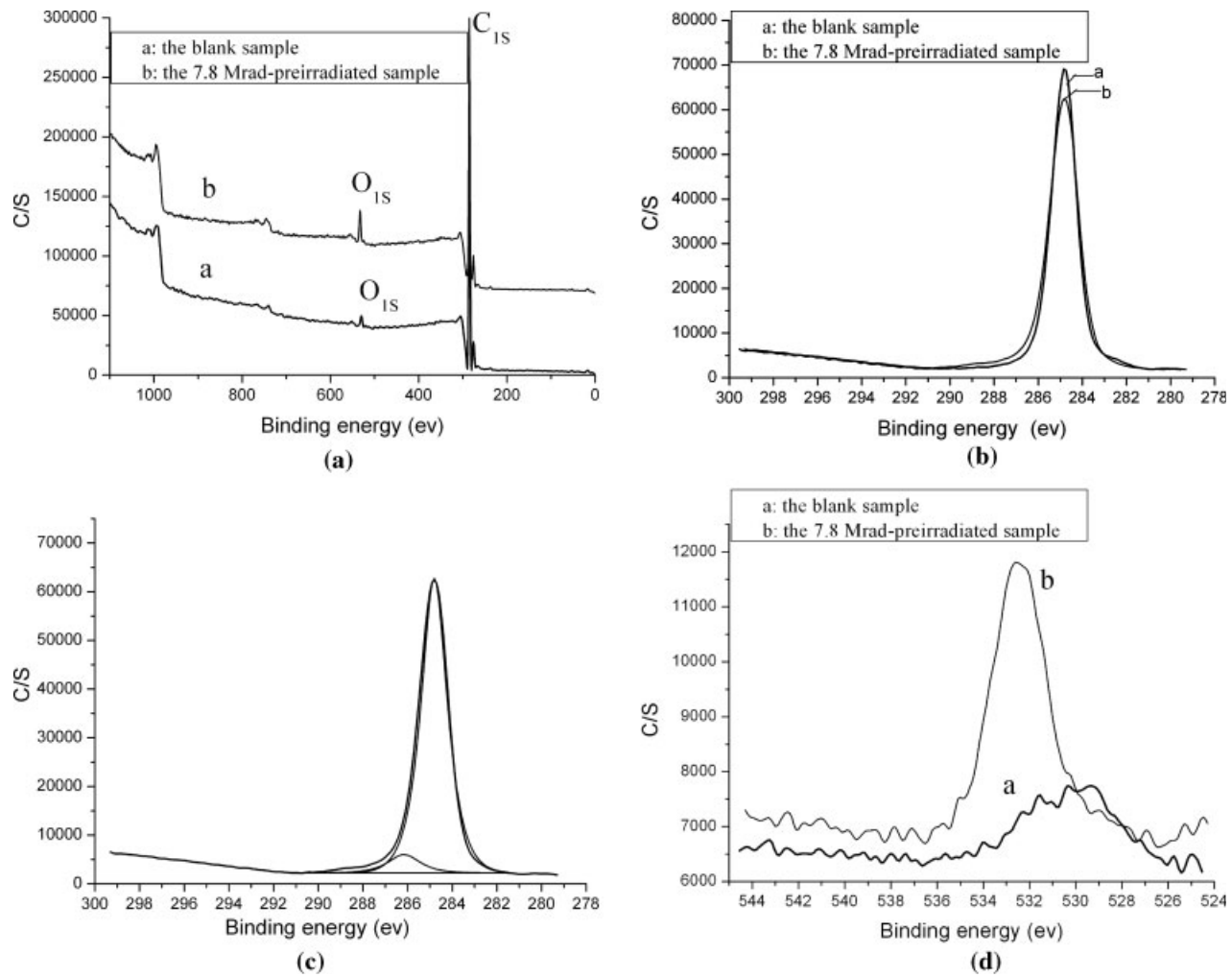


Figure 1 (a) XPS spectra of the blank and the preirradiated sample. (b) High-resolution spectra of C_{1s}. (c) Resolved spectra of C_{1s}. (d) High-resolution XPS spectra of O_{1s}.

the graft ratio of samples coirradiated with different dose. It was found that higher dose gives higher graft ratio because higher dose generates more active macromolecular radicals, and therefore, more active sites for graft reaction. However, the graft ratio of all the coirradiated samples is relative low, which maybe due to the short irradiation time and the homopolymerization, which suppresses over graft copolymerization. As a result, to effectively improve the performances of polypropylene nonwovens, we chose the preirradiation method to induce the graft copolymerization of AA onto polypropylene nonwovens.

TABLE I
Effects of Coirradiation Dose on Graft Ratio

Coirradiation dose (Mrad)	Graft ratio (%)
1.5	1.8
4	2.34
7.8	5.49

The graft ratio of samples preirradiated under different dose is shown in Table II, while other factors are given. It was found that the graft ratio increases with the preirradiation dose because higher preirradiation dose generates more peroxides, which heat-decompose to give more free radicals, and therefore, provide more active sites for graft polymerization. However, the samples will be harmed by side-reactions of irradiation such as degrade under very high preirradiation

TABLE II
Effects of Preirradiation Dose on Graft Ratio

Preirradiation dose (Mrad)	Graft ratio (%)
11.3	17.3
14.7	18.16
26	19.1
52	—*

* The sample was destroyed under the high-dose irradiation and the graft ratio was not available.

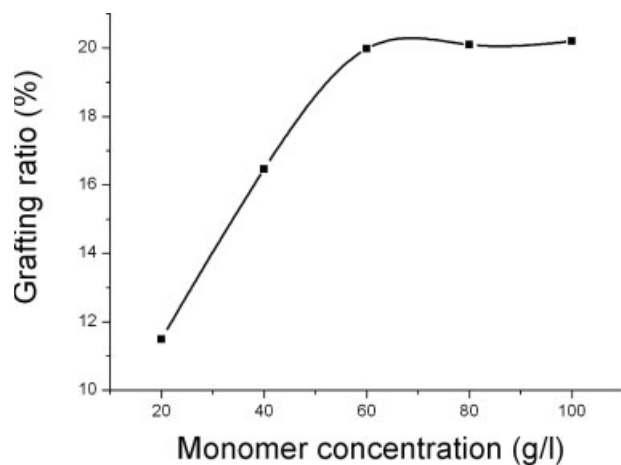


Figure 2 Dependence of monomer concentration on graft ratio (temperature 80°C, bath ratio 1 : 50, and reaction time 1.5 h).

dose. Therefore, it is necessary to select a moderate dose to get a relatively high graft ratio and protect the samples from EB irradiation. In the present work, all the experiments were conducted under 11.3 Mrad dose and divided into four groups. In every group, only one of the four factors (monomer concentration, bath ratio, reaction time, and temperature) was modified.

Monomer concentration

As shown in Figure 2, the graft ratio first increases as monomer concentration and then levels off when monomer concentration reaches 60 g/L. In the copolymerization system, there are two competing reactions, one is the desired graft copolymerization and the other is the undesired homopolymerization. At lower

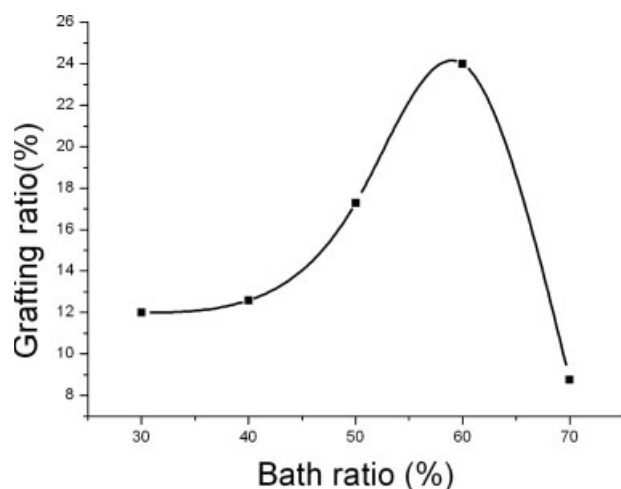


Figure 3 Dependence of bath ratio on graft ratio (monomer concentration 60 g/L, temperature 80°C, and reaction time 1.5 h).

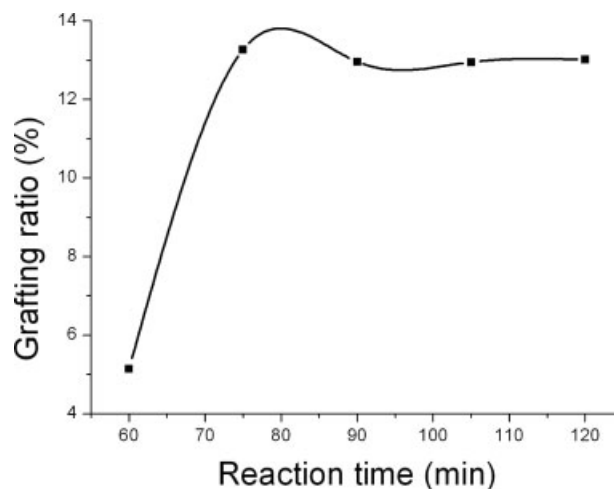


Figure 4 Dependence of reaction time on graft ratio (monomer concentration 60g/L, temperature 80°C, and bath ratio 1 : 50).

monomer concentration, the graft copolymerization is predominant, that is, most monomers were consumed by the graft reaction and fixed as the graft chains on the PP backbones, and contributed to the increase of the graft ratio. While the monomer concentration continuously increases, the monomer then has much difficulty to diffuse into the interior of the substrate to react with free radicals in the sublayer and the short propagating chains sheltered by other grafting chains formed earlier.¹⁴ Therefore, the monomer has more chance to homopolymerize. As a result, most monomer was consumed by the undesired homopolymerization and gave little contribution to the increase of the graft ratio. Therefore, when the monomer concentration exceeds a certain value, the graft ratio does not increase significantly.

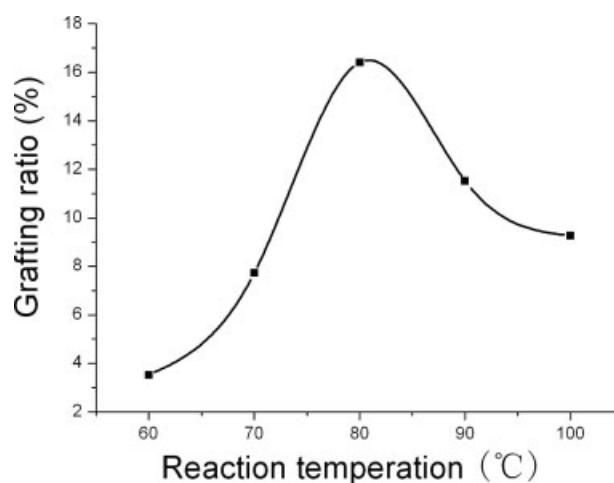


Figure 5 Dependence of reaction temperature on graft ratio (monomer concentration 60 g/L, bath ratio 1 : 50, and reaction time 1.5 h).

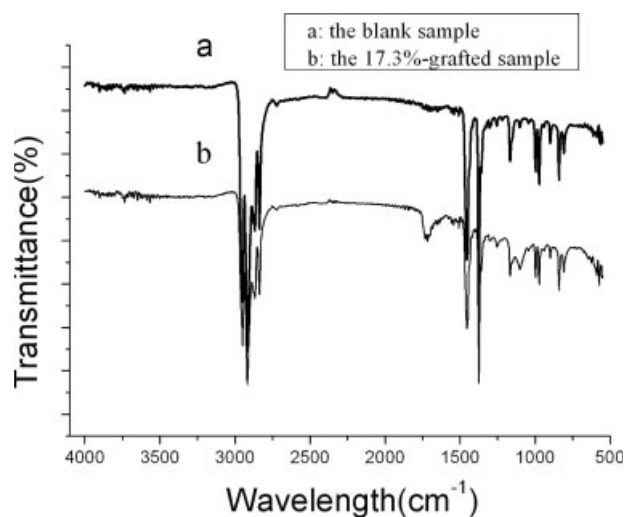


Figure 6 FTIR spectra of blank (a) and 17.3%-grafted (b) PP melt-blown nonwovens.

Bath ratio

As shown in Figure 3, the graft ratio increases as the bath ratio increases. Higher ratio could swell the fibers in the nonwovens to a greater degree, increase the reaction area, and decrease the system viscosity, and therefore, facilitate the graft polymerization. The graft ratio reaches the maximum when the bath ratio is 1 : 60. If the bath ratio increases further, due to the increase of the chance for homopolymerization, the graft ratio decreases instead.

Reaction time

The effect of reaction time on graft ratio was shown in Figure 4. Graft ratio initially increases with time rapidly and then levels off. In the initial stage, the

macromolecular free radicals rapidly react with the added monomer and form graft chains, and the propagating reaction is predominant, and thus graft ratio has an increasing trend in this stage. However, as the graft reaction proceeds, the chance for chain terminating and homopolymerization rises, and as a result the graft ratio gradually equilibrated at a certain value.

Temperature

It is well known that the initiating centers are mainly peroxide and hydroperoxide groups when polymer substrates are preirradiated in air. Temperature is the primary dynamic parameter of the decomposition of peroxide and hydroperoxide groups into free radicals. Higher temperatures can accelerate the formation of free radicals through the decomposition of these groups, which will increase the grafting rate and the graft ratio. On the other hand, higher temperature benefits the terminating rate of the free radicals and propagating chains. Moreover, higher temperature favors homopolymerization, which is a competitive reaction to graft copolymerization. Therefore, due to the two competing factors, the graft ratio first increases as the graft temperature increases and reaches a maximum around 80°C, and then drops when the temperature continues to rise, as shown in Figure 5.

Characterization of the grafted melt-blown polypropylene nonwovens

FTIR analysis

Figure 6 shows the FTIR spectra of the blank sample and the grafted sample with a 17.3% graft ratio. There appears a new peak around 1715.67 cm⁻¹ in the grafted sample, which can be attributed to the —COO⁻. This confirms that the AA containing the carboxyl groups

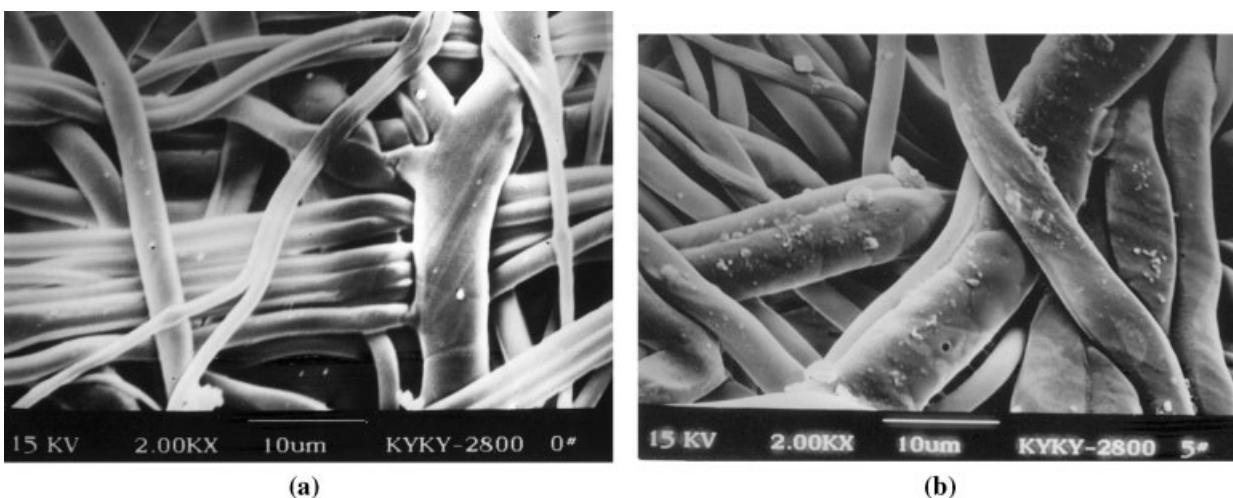


Figure 7 SEM images of the blank (A) and 17.3%-grafted PP melt-blown nonwovens (B).

TABLE III
Effect of Graft Degree on Water Conservation

Graft ratio (%)	Water conservation (%)
0	0
12.59	231
15.48	246
17.6	253
19.2	260
24.02	287

was fixed on the polypropylene mainchains as grafting chains.

SEM observation

The SEM images of the blank samples (A), and the grafted sample with a graft ratio of 17.3% (B) were shown in Figure 7. Evidently, the surface of the fibers in the grafted samples was rough and covered with many concaves and bulges, while the fibers in the blank sample are smooth, which is also a proof of the success of the graft copolymerization.

Performances of the grafted polypropylene melt-blown nonwovens

Water conservation

Water conservation, which characterizes the capacity of samples to contain and keep water, is related to factors such as hydrophilicity, structure, etc. of the sample. During the measurement of water conservation, the sample was first immersed in water and then taken out and hung in the air for a certain time. The water contained in the sample, after the water adherent to the sample surface was wiped off, can be divided into two parts, one is called "chemical water" which is hydrogen-bonded to the polar groups in the sample, and the other is "physical water" which is filled in the capillaries among the fibers in the sample. As can be seen from Table III, water conservation monotonously increases with the rise of the graft ratio. The reason is that the higher the graft ratio, the more the water can be bonded to the $-\text{COOH}$ in the AA-grafted samples

TABLE IV
Effect of Graft Ratio on Water Adsorption Rate

Graft ratio (%)	Water adsorption rate (mm/30 min)
0	0
12.59	42
15.32	51
17.6	60
19.2	72
24.02	88

TABLE V
Effect of Graft ratio on K^+ Exchange Capacity

Graft ratio (%)	K^+ exchange capacity (meq/g)
0	0
12.59	0.38
15.32	0.5
17.6	0.75
19.2	0.8
24.02	1.1

through hydrogen bonds, and therefore, the higher the water conservation.

Water adsorption rate

Water adsorption rate reflects the adsorption speed of samples for liquid water. Apparently, the PP nonwovens possess an ability to adsorb water after being grafted, and the sample with a higher graft ratio has a faster water adsorption rate than the less grafted samples, as shown in Table IV. It is also due to that higher graft ratio means higher amount of $-\text{COOH}$ groups, which can adsorb more water in the unit time.

K^+ exchange capacity

The AA-grafted polypropylene melt-blown nonwovens has the ability of ion exchange due to the presence of weak acidic $-\text{COOH}$ groups.¹⁸ And apparently higher graft ratio means more acidic $-\text{COOH}$ groups, which can exchange with more K^+ , as shown in Table V.

CONCLUSIONS

1. XPS analysis shows that there were hydrogen peroxide and/or peroxides generated in the polypropylene melt-blown nonwovens after pre-irradiation, which can be decomposed to macromolecular active centers when heated and initiate the graft copolymerization of monomer.
2. Both the coirradiation and preirradiation method can be used to initiate the graft of AA onto polypropylene nonwovens. Although coirradiation induced graft can be performed at one step at the ambient temperature, the graft ratio is relatively low. The preirradiation method is more effective than the coirradiation method, and therefore was employed in the present work.
3. Graft copolymerization can be proved by the change of the surface morphology: there are many bulges in the surface of the grafted samples while the blank one is smooth; and the presence of the characteristic peak of the $-\text{COOH}$ in the grafted samples is also a proof of the graft copolymerization.

4. The three index characterizing the hydrophilicity of the sample, water conservation, water adsorption rate, and K^+ exchange capacity, increase with the rise of the graft ratio, indicating that the wettability of the polypropylene nonwovens was improved.

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