

# Preparation of Acrylic Acid Grafted Polypropylene Nonwoven Fabric by Photoinduced Graft Polymerization with Preabsorption of Monomer Solution

Choon-Ki Na, Hyun-Ju Park

Department of Environmental Engineering, Mokpo National University, Jeonnam 534-729, South Korea

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**ABSTRACT:** We improved photoinduced graft polymerization by absorbing the monomer solution onto the substrate (Ab-type) instead of immersing the substrate in the monomer solution (Im-type) before photoirradiation to yield a more practical and effective grafting system. With this system, acrylic acid (AA) was effectively grafted onto polypropylene (PP) nonwoven fabric. The maximum degree of grafting obtainable was restricted by the amount of monomer preabsorbed onto the PP fabric. However, we effectively enhanced the degree of grafting by increasing the monomer concentration, adding trimethylolpropane triacrylate (TMPTA) to the monomer solution, and repeating the photoirradiation with supplementation of the monomer solution. The net availability of the monomer for graft polymerization was 50% or greater; this increased to 90% or greater with the addition

of TMPTA and was much higher than for conventional Im-type photografting ( $\leq 13\%$ ). Fourier transform infrared spectra, scanning electron microscopy morphology observations, and the adsorption–regeneration properties confirmed that the PP-g-AA fabric prepared by the improved Ab-type photografting method had comparable qualities to those of fabric prepared by conventional Im-type photografting. Thus, the improved Ab-type photografting system provides potential for the preparation of graft adsorbents on a large scale at a competitive cost with a continuous reactor, such as a conveyor belt system, instead of a batch reactor. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 114: 387–397, 2009

**Key words:** adsorption; graft copolymers; ion exchangers; modification; photopolymerization

## INTRODUCTION

In recent years, graft polymerization has been widely used to develop adsorbents with various functional groups, high efficiency, and ion-selective properties. Many methods, such as photoirradiation,  $\gamma$ -ray irradiation, electron beam irradiation, and plasma discharge grafting, are available.<sup>1–6</sup> Among these methods, photoirradiation-induced graft polymerization is expected to be the most convenient because grafting can be restricted to the surface of the substrate polymer without effects on the bulk properties because of the lower energy source, and thus, various shapes and qualities can be adopted for the substrate polymer. Previously, we reported the photoirradiation-induced graft polymerization of acrylic acid (AA) onto polypropylene (PP) nonwoven fabric and the excellent adsorption–regeneration properties of the resulting products.<sup>7–10</sup> Photoirradia-

tion-induced graft polymerization is an excellent and well-established technology for introducing ion-exchange and chelation functions into a variety of shapes of conventional polymers, such as films, membranes, and fibers.<sup>11–13</sup> However, there are several problems that must be solved to make photoirradiation-induced graft polymerization more effective and economically advantageous for the surface modification of polymer substrates and to allow wider application of the method. One of the major problems limiting its wider application is the generation of large volumes of waste liquid containing homopolymer and unreacted monomer that must be treated before discharge; this increases the production costs. This problem is mainly due to the lower energy source, which leads to restricted conditions for graft polymerization. A photoinitiator must be used to initiate graft polymerization by photoirradiation, and UV light irradiation must be on the surface of the substrate polymer in contact with the monomer dissolved in a solvent containing a photoinitiator. Therefore, the conventional one-step photoinduced graft polymerization method, in which the substrate is immersed in a monomer solution containing a photoinitiator and irradiated with UV light, inevitably results in the generation of a large volume

Correspondence to: H.-J. Park (hyunju@mokpo.ac.kr).

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of waste liquid because of the simultaneous monomer polymerization both on the substrate surface and in the residual monomer solution. Many studies have been carried out to improve the one-step photoinduced graft polymerization system. Ogiwara et al.<sup>14</sup> improved the system by precoating the photoinitiator onto the substrate. More recently, Ma et al.<sup>15</sup> proposed a method to improve photoinduced graft polymerization with a sequential grafting technique. The photoinitiator was grafted onto the substrate in the first step, and then, the monomer was grafted onto the active substrate with a photoinitiator by repeated exposure to UV irradiation. In their improved system, monomers could be effectively grafted onto substrate polymers, and the amount of photoinitiator coated or grafted onto the substrate surface and the monomer concentration principally contributed to the graft polymerization efficiency. However, they also used a conventional simultaneous irradiation method for grafting, and it might be difficult to recover or reuse unreacted monomer in the monomer solution, but this was not taken into account.

In this study, we aimed to improve the conventional one-step photoinduced graft polymerization system by absorbing the monomer solution onto the substrate (Ab-type) instead of immersing the substrate in the monomer solution (Im-type) before photoirradiation to yield a more practical and effective grafting system. The fundamental concept was inspired by the high absorbability of the nonwoven fabric used as the substrate polymer in this study, which featured porosity and a large surface area. Thus, the fabric could absorb sufficient monomer solution to allow graft polymerization, although its individual fibers were hydrophobic. To identify the optimal conditions for improved photoinduced graft polymerization by the preabsorption of the monomer solution onto the substrate, the effects of several principal factors were investigated. Experiments were also conducted to confirm the effects of different grafting conditions on the adsorption properties, such as the adsorption capacity, adsorption kinetics, and regeneration efficiency of products, and the availability of PP-g-AA fabrics as a polymeric adsorbent in comparison with commercially available adsorbents.

## EXPERIMENTAL

### Materials

PP nonwoven fabric (180 g/m<sup>2</sup>) was used as the substrate polymer for grafting after it was cut into pieces 1 cm × 10 cm and washed with a neutral detergent solution. AA (Daejung Chemical Co., Seoul,

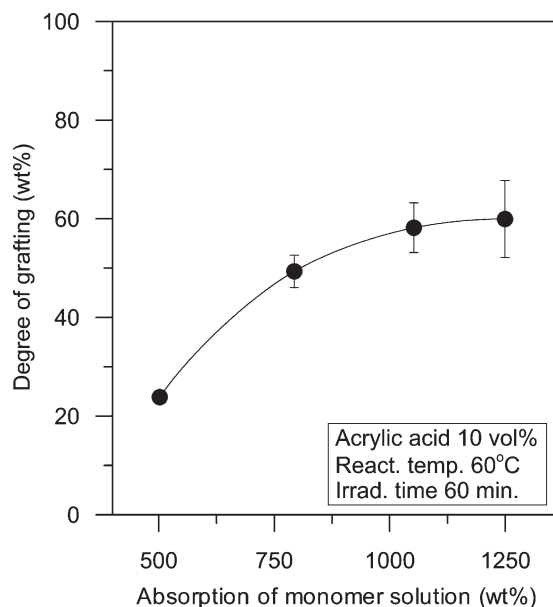
Korea) and benzophenone (BP; Yakuri Pure Chemical Co., Osaka, Japan) were used as the monomer and photoinitiator, respectively. H<sub>2</sub>SO<sub>4</sub> and FeSO<sub>4</sub>·7H<sub>2</sub>O were used as the graft accelerator and homopolymer inhibitor,<sup>16</sup> respectively, and methanol and deionized water were used as solvents. The monomer solution was prepared with 70/30 (v/v)% water/methanol as the solvent and contained 10–40 vol % AA, 0.2 wt % BP, 0.2M H<sub>2</sub>SO<sub>4</sub>, and 5 × 10<sup>-3</sup> M FeSO<sub>4</sub>·7H<sub>2</sub>O. Trimethylolpropane triacrylate (TMPTA; Daejung Chemical Co.) was used as the crosslinking reagent to enhance the grafting of AA onto the PP fabric. To prepare artificial wastewater for the adsorption experiments, NH<sub>4</sub>OH was used as the NH<sub>4</sub>-N source. All reagents were of extrapure or higher grade and were used without further purification.

### Photografting procedures

PP-g-AA fabrics were prepared by the improved photoirradiation method, in which the monomer for graft polymerization is first absorbed onto the substrate polymer and subsequent UV irradiation leads to graft polymerization. The preparation scheme consisted of the following three steps: (1) absorption of the monomer solution onto the PP fabric, (2) grafting of AA onto PP by UV irradiation, and (3) removal of the unreacted monomer solution and homopolymer with suitable solvents. First, we saturated the PP fabric with monomer solution by immersing it in monomer solution containing AA and BP for 10 min. The fabric was then removed from the monomer solution and passed through a roller press to control the amount of monomer solution absorbed. The fabric was then placed in a Pyrex glass tube, purged with nitrogen gas to eliminate oxygen, and then sealed. The tube was exposed to UV light under predetermined experimental conditions. The light source used was a 400-W high-pressure mercury lamp (Miya Electric Co., Gwangju, Korea), and the glass tubes were rotated and simultaneously revolved around the light source at a distance of 10 cm. After the grafting reaction, the samples were removed from the glass tubes, washed three times with hot water, extracted with methanol for 10 h in a Soxhlet apparatus to remove unreacted monomer and homopolymer, and dried at 60°C until a constant weight was reached. The degree of grafting was calculated from the weight gain:

$$\text{Degree of grafting (wt \%)} = 100(W_1 - W_0)/W_0$$

where  $W_0$  and  $W_1$  are the weights of the substrate and grafted fabric, respectively. At least three parallel experiments were carried out for each condition, and good reproducibility was obtained.



**Figure 1** Increases in AA grafted onto PP nonwoven fabric with the absorption amount of monomer solution in the PP nonwoven fabric. The error bars represent  $\pm 1 \sigma$  for three repetitions.

### Surface characterization

The structure of the PP-*g*-AA fabric was analyzed with a Fourier transform infrared (FTIR) spectrophotometer (Magna IR-550, Madison, WI). The surface morphology of the PP-*g*-AA fabric was observed with a scanning electron microscope (Shimadzu S-3000N, Kyoto, Japan).

To evaluate the adsorption capacity and kinetics of the PP-*g*-AA fabric, batch adsorption tests were carried out, in which 0.3 g of each adsorbent was added to a 250-mL flask containing 100 mL of ammonium solution of known concentration. The flask was then placed in an incubator shaker and shaken at 120 rpm for 24 h at 20°C to ensure adsorption equilibrium. The initial concentration ( $C_0$ ) and equilibrium concentration ( $C_e$ ) were determined by UV-visible spectrometry (Shimadzu UV-2401PC) at a defined wavelength. The adsorbent-phase ammonium concentration ( $Q_e$ ; mg/g) was calculated from the ammonium mass balance with the following formula:

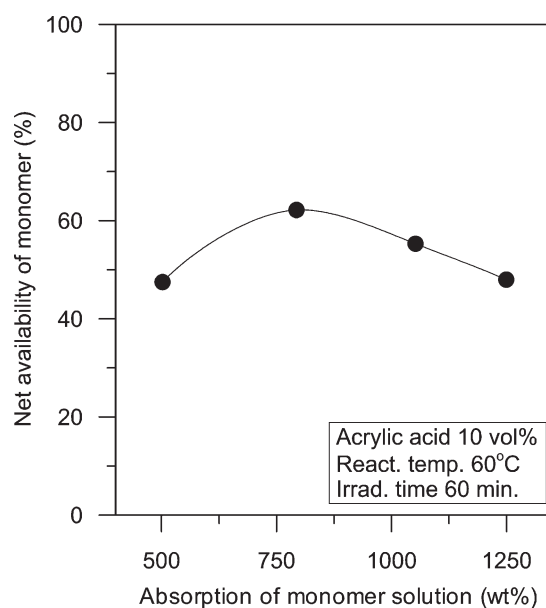
$$Q_e = V(C_0 - C_e)/W$$

where  $V$  is the volume of the solution and  $W$  is the mass of dry adsorbent. For regeneration experiments, ammonium-adsorbed PP-*g*-AA fabric was regenerated with 0.1M HCl and then reused for adsorption. The adsorption and regeneration cycles were repeated 10 times. After each regeneration cycle, the PP-*g*-AA fabric was washed with deionized water and dried at 60°C until a constant weight was reached.

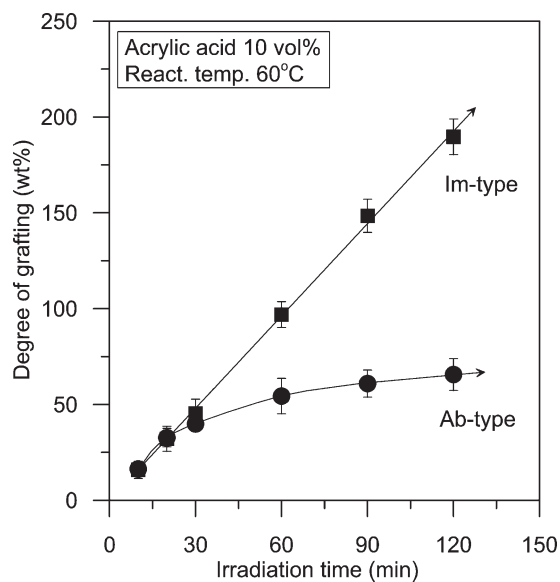
## RESULTS AND DISCUSSION

### Grafting efficiency

In contrast to the conventional one-step photoinduced graft polymerization, in which the substrate immersed in monomer solution (Im-type) is subjected to UV irradiation, the improved photografting method in this study was characterized by the pre-absorption of the monomer solution onto the substrate followed by its exposure to UV irradiation (Ab-type). Therefore, the amount of monomer solution preabsorbed onto the substrate was a principle factor determining the degree of grafting in the Ab-type photoinduced graft polymerization. Thus, the effects of the amount of monomer solution preabsorbed onto the substrate on the degree of grafting were first investigated with a monomer solution containing 10 vol % AA with photoirradiation for 60 min at 60°C. The maximum monomer absorbability of the PP fabric used in the experiments was approximately 1300 wt %. The amount of monomer in the PP fabric was controlled in the range 500–1250 wt % with a roller press at various pressures. The degree of grafting for different monomer amounts in the PP fabrics is shown in Figure 1. The degree of grafting increased with the amount of monomer. However, the relative rate of increase in the degree of grafting decreased, whereas the standard deviation ( $\sigma$ ;  $n = 3$ ) increased, with increasing monomer absorption. This was mainly due to the increase in the gravitational flow of the absorbed monomer in the substrate during photoirradiation, which led to the heterogeneous distribution of the



**Figure 2** Net availability of the monomer for the graft polymerization at different absorption amounts of monomer solution in the PP nonwoven fabric. The data were taken from Figure 1.



**Figure 3** Increases in AA grafted onto the PP nonwoven fabric with the photoirradiation time for different photografting methods. The error bars represent  $\pm\sigma$  for three repetitions.

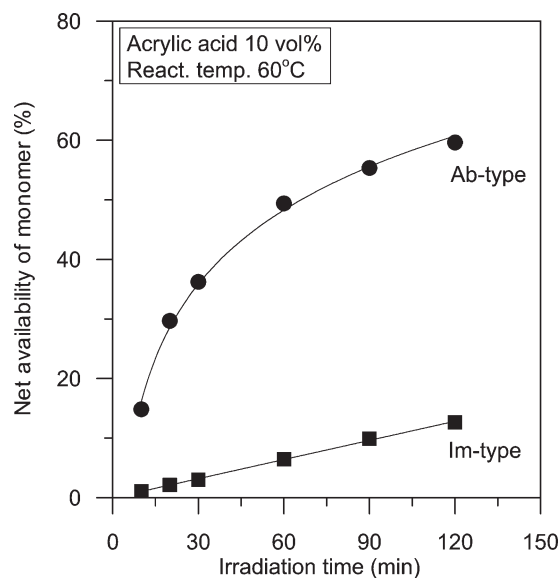
monomer. Figure 2 shows the net availability of the monomer for the grafted polymer on the PP fabric for different monomer absorption amounts; we calculated this by dividing the amount of monomer grafted onto the substrate by the amount of monomer absorbed onto the substrate. The maximum net availability of the monomer was observed at approximately 800 wt % monomer absorption, with 60% of the monomer absorbed converted to polymer grafted onto PP. With the degree of grafting and the net availability of monomer under consideration, approximately 1000 wt % monomer absorption seemed to be optimal and was, therefore, used for the evaluation of the graft reactions.

To determine the best conditions for the Ab-type photografting, the effects of photoirradiation time and reaction temperature on the graft polymerization were investigated. Figure 3 shows the degree of grafting obtained with 10 vol % AA solution at 60°C for photoirradiation times in the range 10–120 min. Figure 3 also shows the degree of grafting obtained for the conventional Im-type photografting. PP fabric was immersed in 30 mL of monomer solution in a Pyrex tube, instead of the preabsorption procedure, before UV exposure under the same conditions used in the Ab-type photografting. Regardless of the grafting method, the degree of grafting increased with the photoirradiation time; this confirmed the reinitiation ability of the polymer chain ends, as reported by other researchers.<sup>17</sup> However, the degree of grafting showed a different pattern of increase with the photoirradiation time for the different grafting methods. For the conventional Im-type photo-

grafting, the degree of grafting increased linearly with the photoirradiation time; this was because the monomer concentration was nearly constant because of low conversion (Fig. 4). On the other hand, the degree of grafting for the Ab-type photografting increased logarithmically with the photoirradiation time. This was because the monomer available for graft polymerization was limited by the amount pre-absorbed by the PP fabric, and thus, the monomer concentration rapidly decreased as the degree of grafting increased. Figure 4 shows that the net availability of monomer for graft polymerization during the Ab-type photografting increased to about 60% with increasing photoirradiation time and was much higher than that during the Im-type photografting, for which the maximum monomer availability was 12.6% under our experimental conditions.

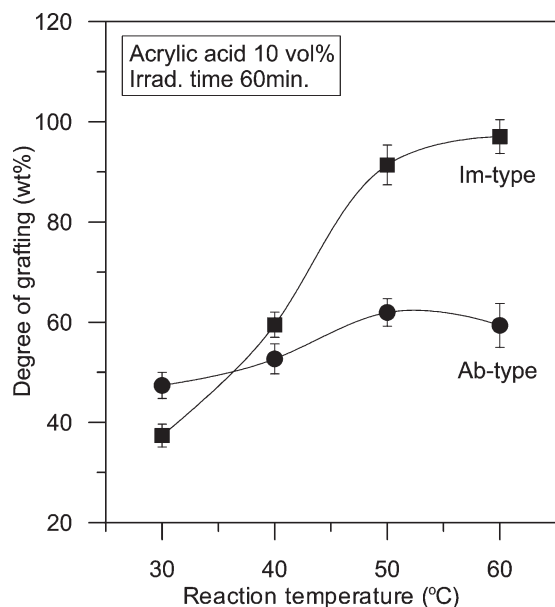
Figure 5 shows the degree of AA grafting onto PP at different reaction temperatures. The degree of grafting increased with the reaction temperature up to 50°C and then tended to decrease with further increases, probably because of an increase in the solvent evaporation and subsequent lower monomer mobility, which would have prevented the grafting of AA onto PP. The net availability of the monomer for the graft polymer at different reaction temperatures is shown in Figure 6. The maximum net availability was observed at 50°C for the Ab-type photografting.

From these observations, a photoirradiation time of 60 min and a reaction temperature of 50°C seemed to be optimal and were, therefore, used for further experiments.



**Figure 4** Increases in the net availability of the monomer for graft polymerization with the photoirradiation time for different photografting methods. The data were taken from Figure 3.

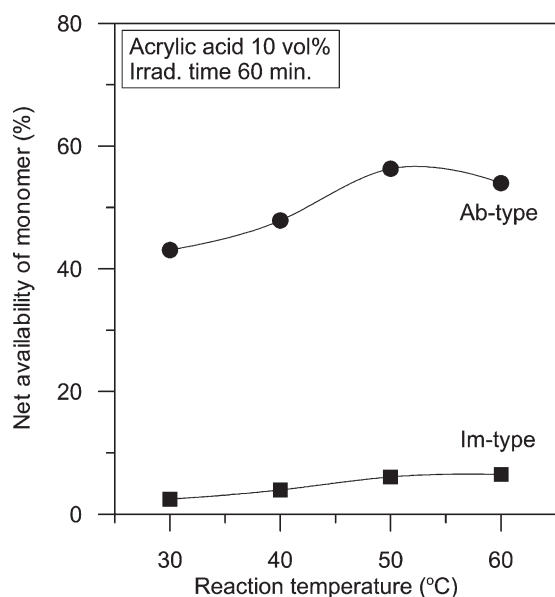




**Figure 5** Increases in AA grafted onto the PP nonwoven fabric with the reaction temperature for different photografting methods. The error bars represent  $\pm\sigma$  for three repetitions.

### Enhancing the degree of grafting

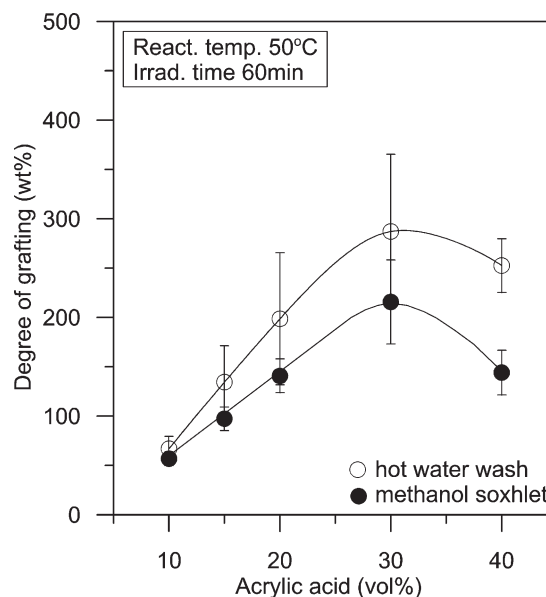
As described previously, the maximum degree of AA grafting onto PP for the Ab-type photografting was restricted by the amount of monomer preabsorbed onto the PP fabric and was thus much lower than that obtainable by the conventional Im-type photografting. Therefore, it was necessary to enhance the degree of grafting for wider application of the Ab-type photografting. Three alternatives, an



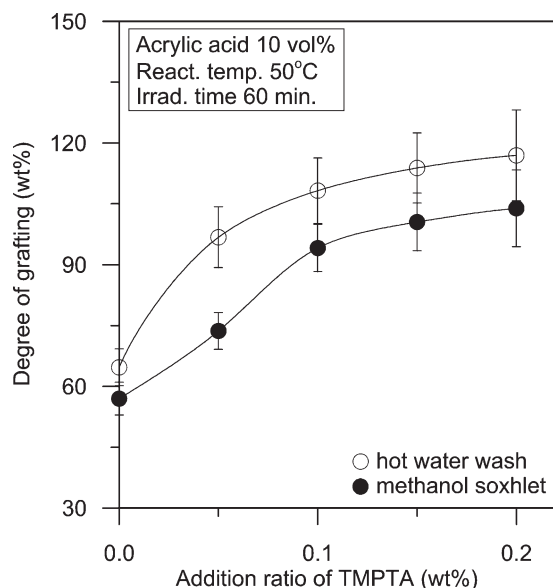
**Figure 6** Net availability of the monomer for graft polymerization versus the reaction temperature for different photografting methods. The data were taken from Figure 5.

increase in AA concentration, the addition of TMPTA, and the repetition of photografting with supplementation of monomer solution, were investigated in terms of enhancement of the degree of grafting for the Ab-type photografting.

As the simplest method to enhance the degree of grafting, the AA concentration in the monomer solution was gradually increased to 40 vol %, and the effect on the degree of grafting was determined. In all experiments, PP fabric preabsorbed with 1000 wt % monomer solution, a photoirradiation time of 60 min, and a reaction temperature of 50°C were used. As shown in Figure 7, the degree of grafting increased with the AA concentration up to 30 vol % and then decreased with further increases. Similar observations were noted by Kim and Na<sup>7,18</sup> in their study on the photografting of AA and styrene onto PP. A decrease in the degree of grafting at high monomer concentration is a general phenomenon observed in graft reactions with a solvent and is known as the *Trommsdorff effect*.<sup>19</sup> The difference in weight gain between washing with hot water and subsequent methanol Soxhlet extraction increased with the AA concentration. This indicated an increase in homopolymer formation with increasing AA concentration because the homopolymer could not be completely removed by simple washing, even with hot water. Thus, the weight gain of the PP fabric after simple washing with hot water included almost all of the homopolymer formed in the reaction. The high degree of homopolymer formation may have resulted from chain transfer to poly(acrylic acid)



**Figure 7** Degree of AA grafting onto the PP nonwoven fabric versus the AA concentration in the monomer solution. The preabsorbed amount of monomer solution in the PP nonwoven fabric was controlled to 1000  $\pm$  50 wt %. The error bars represent  $\pm\sigma$  for three repetitions.



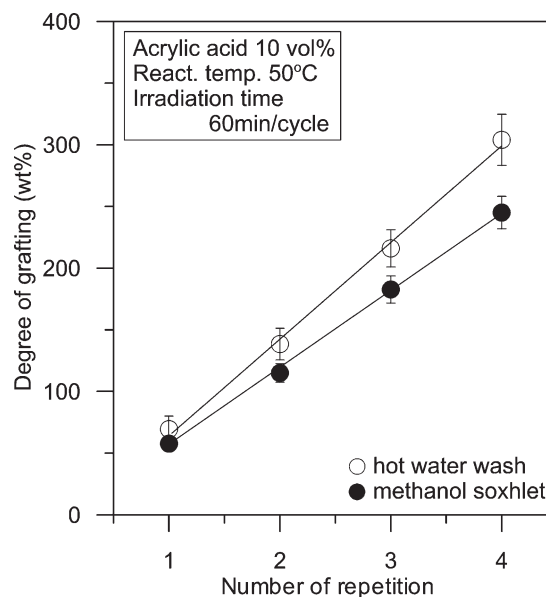
**Figure 8** Increases in AA grafted onto the PP nonwoven fabric with TMPTA concentration added to the monomer solution. The error bars represent  $\pm\sigma$  for three repetitions.

grafts being formed, as reported by Ma et al.<sup>15</sup> Furthermore, the increase in  $\sigma$  ( $n = 3$ ) for the degree of grafting with increasing AA concentration indicated that the reproducibility of the graft polymerization decreased with increasing monomer concentration. Thus, although increasing the AA concentration was a facile method for enhancing the degree of grafting in the Ab-type photograft polymerization, it was difficult to enhance the degree of grafting to greater than 200 wt % and to control the reproducibility for high degrees of grafting.

As another alternative for enhancing the degree of grafting, the effects of TMPTA addition to the monomer solution were investigated. TMPTA, a multifunctional acrylate, is a reactive additive that forms crosslink bridges via an irradiation-induced free-radical mechanism. The interaction of TMPTA with growing grafted chain radicals has been described in detail elsewhere.<sup>20–22</sup> Figure 8 shows the degree of AA grafting onto PP fabric for different TMPTA concentrations. All experiments were performed with a monomer solution containing 10 vol % AA and 0–0.2 wt % TMPTA for a photoirradiation time of 60 min at 50°C. The increase in the degree of AA grafting with TMPTA concentration confirmed that TMPTA reacted with the growing grafted chain radicals, probably to form crosslinks. Furthermore, the net availability of AA monomer for the graft polymerization, although the crosslink polymers may not have been grafted onto the PP substrate with covalent bonds, increased to  $\geq 90\%$  with increasing TMPTA concentration up to 0.1 wt %. These results indicate that TMPTA addition was efficient in enhancing the photopolymerization of AA onto PP,

although the hardness of the resulting products increased with TMPTA addition, probably because of the increased crosslink density, which may have led to undesirable product properties.

Together with the results shown in Figure 3, the relatively smaller rate of increase in the degree of grafting for TMPTA concentrations greater than 0.1 wt % shown in Figure 8 confirmed that the degree of AA grafting onto the PP fabric for the Ab-type photografting was ultimately restricted by the amount of monomer preabsorbed onto the PP fabric. However, from the results shown in Figures 1 and 7, where the degree of grafting increased with the amount of AA preabsorbed and AA concentration in the monomer solution, we expected that the more AA we supplied to the substrate, the more AA would be grafted onto the substrate. On the basis of this expectation, the effects of multiple supplementation of PP-g-AA fabric with monomer solution on the degree of grafting were investigated. The monomer absorption and photoirradiation procedures for the Ab-type photografting were repeated a certain number of times before we finally subjected the samples to the extraction procedure for the removal of unreacted monomer solution and homopolymer. The results are presented in Figure 9. As expected, the degree of AA grafting onto PP increased linearly with the number of photografting cycles, which confirmed the reinitiation ability of the polymer chain ends. It has been reported that the reactivity of radicals decreases with increasing graft chain length.<sup>15</sup> During repeated Ab-type photografting, however,



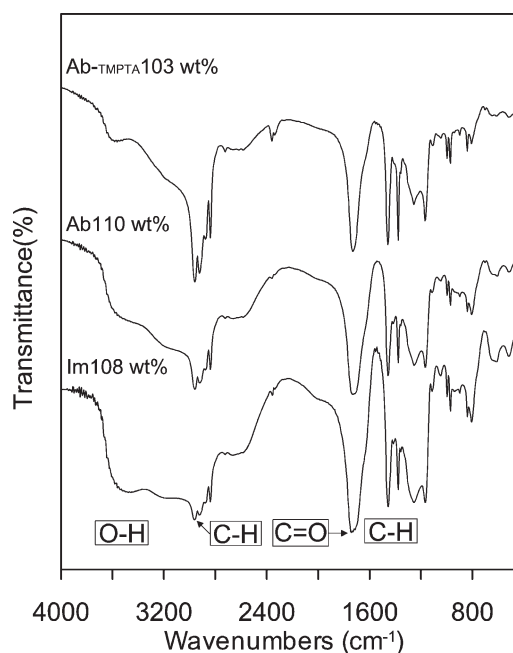
**Figure 9** Increases in AA grafted onto the PP nonwoven fabric with repeating number of photografting cycles. The AA concentration was 10 vol % in the monomer solution, and the photoirradiation time was 60 min for a cycle. The error bars represent  $\pm\sigma$  for three repetitions.

the grafting rate was nearly constant for each photografting cycle and followed a first-order regression line passing through the origin (intercept = 0) with slope of 60.5 and a goodness of fit of  $R^2 > 0.997$  (Fig. 9). This indicated that the radical reactivity did not decrease with increasing graft chain length, probably because both the AA monomer and BP photoinitiator were added to the substrate in each cycle. This resulted in a sufficient increase in radical formation at the polymer chain ends to compensate for the decrease in radical reactivity with increasing graft chain length. It is known that BP is excited to the triplet state by photoirradiation, which could extract a hydrogen atom from the polyolefin substrate to yield polymer radicals capable of initiating graft polymerization of the monomers.<sup>23</sup> The products obtained from repeated Ab-type photografting exhibited a small amount of homopolymer formation but also a low  $\sigma$  ( $n = 3$ ) for the degree of grafting compared to the other enhancement methods. Thus, we concluded that repeated Ab-type photografting enhanced the degree of AA grafting onto PP with good reproducibility without excessive homopolymer formation.

### Structural characterization

The structural changes in the PP-g-AA fabrics prepared by the conventional Im-type and the improved Ab-type photografting methods were analyzed with FTIR spectroscopy. As shown in Figure 10, the PP-g-AA fabrics were characterized by a peak at  $1740\text{ cm}^{-1}$ , attributed to the C=O double bond, and a peak at  $3600\text{ cm}^{-1}$ , attributed to the -OH of carboxyl groups in the grafted AA. No different peaks were observed for the different conditions, which indicated that AA was grafted onto the PP substrate regardless of the photografting conditions.

To examine the effects of different grafting conditions on the surface structure of the PP-g-AA fabric, scanning electron microscopy (SEM) observations were also conducted. The SEM images shown in Figure 11 indicate that the surface structure of the PP-g-AA fabrics depended on the preparation conditions. In general, fabrics prepared by Ab-type photografting showed a clear tendency for a more heterogeneous surface than fabrics prepared by conventional Im-type photografting. It is interesting that the PP-g-AA fabric prepared by repeated Ab-type photografting with monomer supplementation showed a highly crumpled surface structure [Fig. 11(c)]. In fact, the crumpled surface structure increased with the number of Ab-type photografting cycles. In contrast, the PP-g-AA fabric prepared in the presence of TMPTA showed not only a smoother and denser surface than the other samples but also an interconnected structure among its fibers [Fig. 11(d)]; this

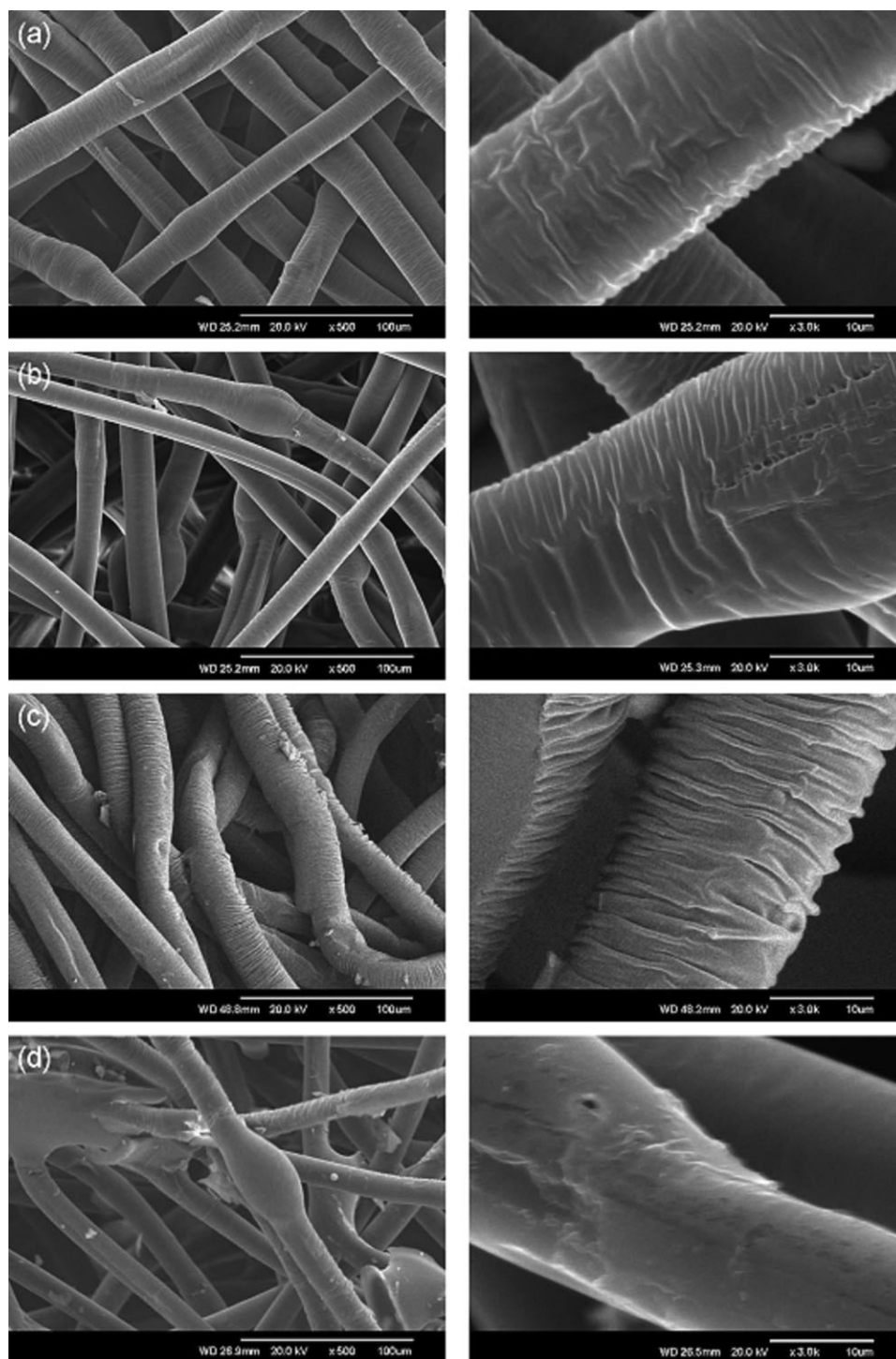


**Figure 10** FTIR spectra of the PP-g-AA nonwoven fabrics prepared by conventional Im-type photografting and improved Ab-type photografting with or without the addition of TMPTA. The numbers in legend are degree of grafting.

provided evidence of a significant increase in the crosslink density. Although the reasons for the different structures are not yet completely clear, it is likely that they played a key role in the adsorption properties of the PP-g-AA fabrics prepared under different photografting conditions.

### Adsorption and regeneration characteristics

To evaluate the adsorption capacities of the PP-g-AA fabrics prepared under different photografting conditions, batch  $\text{NH}_4\text{-N}$  adsorption tests were conducted on fabrics with degrees of grafting in the range 40–200 wt %. The initial  $\text{NH}_4\text{-N}$  concentration was 300 mg/L at pH 10.5 in deionized water. Figure 12 shows the  $\text{NH}_4\text{-N}$  adsorption capacity of the PP-g-AA fabrics prepared under different photografting conditions as a function of the degree of grafting. For comparison, the adsorption capacities of commercially available activated carbons and zeolites were evaluated under the same experimental conditions. As shown in Figure 12, PP-g-AA prepared by Ab-type photografting without TMPTA showed a slightly higher  $\text{NH}_4\text{-N}$  adsorption capacity than the fabric prepared by conventional Im-type photografting, whereas the opposite was observed when TMPTA was used during Ab-type photografting. Given that no FTIR spectral differences were observed among the PP-g-AA fabrics (Fig. 10), the differences in adsorption capacity were likely due to the different surface structures, as

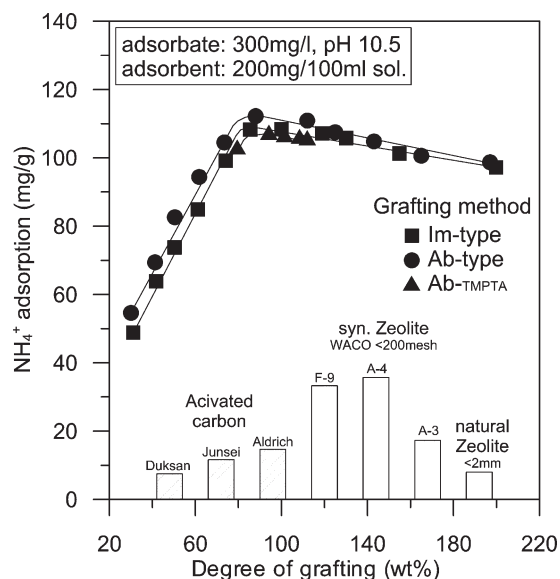


**Figure 11** SEM micrographs of the PP-g-AA nonwoven fabrics prepared under different photografting conditions. (a) conventional Im-type, (b) improved Ab-type, (c) twice-repeated Ab-type, and (d) Ab-type with TMPTA addition.

shown in the SEM images of Figure 11. Also, regardless of the photografting conditions, the  $\text{NH}_4\text{-N}$  adsorption capacities of the PP-g-AA fabrics increased with the degree of grafting up to approximately 100 wt % and then decreased with further increases. The decreasing trend for high degrees of grafting may have occurred because the fibers grad-

ually increased in thickness with the degree of grafting and, thereby, relatively decreased the effective surface area with adsorption functionality on the PP-g-AA fabrics so that a longer contact time was probably required to reach adsorption equilibrium. Furthermore, the  $\text{NH}_4\text{-N}$  adsorption capacities of the PP-g-AA fabrics were much higher than that of





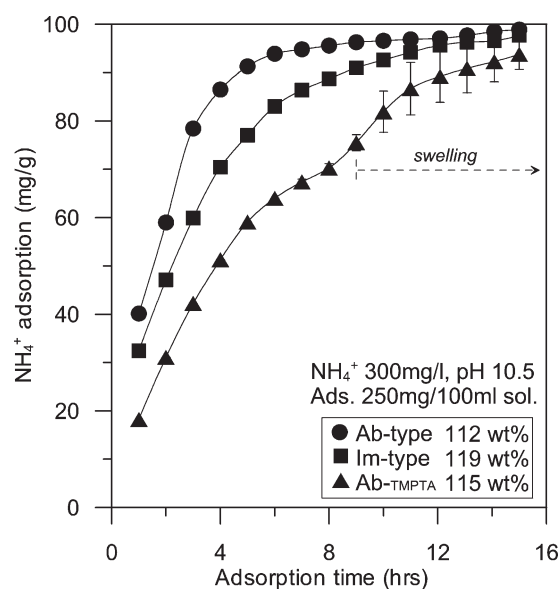
**Figure 12** Adsorption capacity of  $\text{NH}_4\text{-N}$  on the PP-g-AA nonwoven fabrics with various degrees of grafting prepared by conventional Im-type photografting and improved Ab-type photografting with or without the addition of TMPTA and comparison with that of commercial adsorbents under the same experimental conditions.

activated carbon and zeolite. From these results, the optimal degree of grafting was found to be  $100 \pm 10$  wt % in terms of  $\text{NH}_4\text{-N}$  adsorption capacity, and the efficiency of PP-g-AA as a cation adsorbent was found to be excellent, regardless of the photografting conditions.

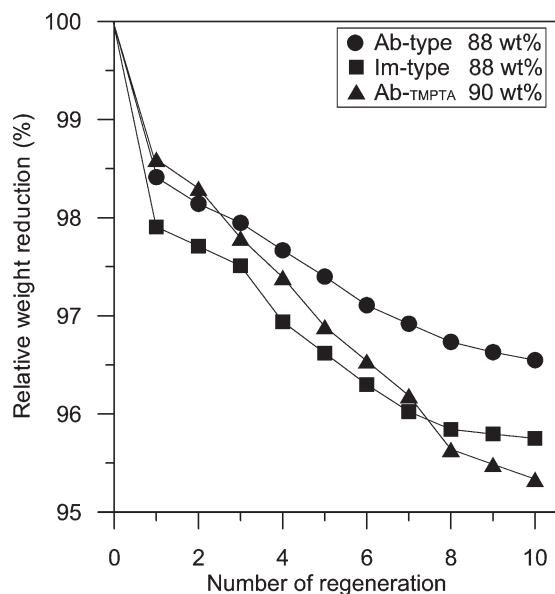
The adsorption kinetics of the PP-g-AA fabrics prepared under different photografting conditions were also investigated with  $\text{NH}_4\text{-N}$ . We determined the amount of  $\text{NH}_4\text{-N}$  adsorbed onto PP-g-AA as a function of contact time by shaking samples in solution for 15 h at  $20^\circ\text{C}$ . The results are presented in Figure 13. All of the curves exhibited similar characteristics, with a rapid initial adsorption process and a slower second adsorption process, except for the bimodal increasing curve observed for PP-g-AA prepared by Ab-type photografting with the addition of TMPTA. This bimodal increasing kinetic curve was attributed to the swelling of the graft layer, which disappeared when the PP-g-AA fabric swelled on immersion in a suitable solvent, such as water, before the adsorption experiments. The rate of  $\text{NH}_4\text{-N}$  adsorption by the PP-g-AA fabrics increased in the following order: Ab-type without TMPTA > Conventional Im-type > Ab-type with TMPTA. This order seemed to reflect the differences in the surface structures shown in Figure 11.  $\text{NH}_4\text{-N}$  adsorption by the PP-g-AA fabric prepared by Ab-type photografting without TMPTA addition was greater than 90% in 5 h, with adsorption tending to increase continuously and gradually and reaching adsorption equilibrium at about 10 h. For

the PP-g-AA fabrics prepared by conventional Im-type photografting or Ab-type photografting with TMPTA addition, adsorption equilibrium was reached at greater than 12 h.

To evaluate the regeneration efficiency of the PP-g-AA fabrics prepared under different photografting conditions, repeated adsorption–regeneration experiments were performed. Regeneration was conducted with an acid-washing process, in which  $\text{NH}_4\text{-N}$  adsorbed PP-g-AA fabric was immersed in a 0.1N HCl solution and shaken for 1 h at room temperature. After complete desorption, PP-g-AA was regenerated by repeated washing with deionized water until the pH was neutral and drying at  $60^\circ\text{C}$ . The adsorption–regeneration cycle was repeated 10 times, and the  $\text{NH}_4\text{-N}$  adsorption capacity and PP-g-AA weight loss were measured for each cycle. As shown in Figure 14, the weight of PP-g-AA continuously decreased with increasing number of regeneration cycles, but the weight loss range was less than 5%, even after 10 regeneration cycles. Moreover, no significant difference in weight loss was observed among the photografting conditions. On the other hand, the adsorption capacity remained almost constant ( $< \pm 1\%$ ) regardless of the number of regeneration cycles (Fig. 15). Furthermore, the adsorption capacity recalculated with the weight measured for each regeneration cycle instead of the initial PP-g-AA fabric weight increased with the number of regeneration cycles. Thus, we felt that it was reasonable that the weight losses for PP-g-AA after regeneration shown in Figure 14 were mainly caused by the loss of impurities rather than graft chains during

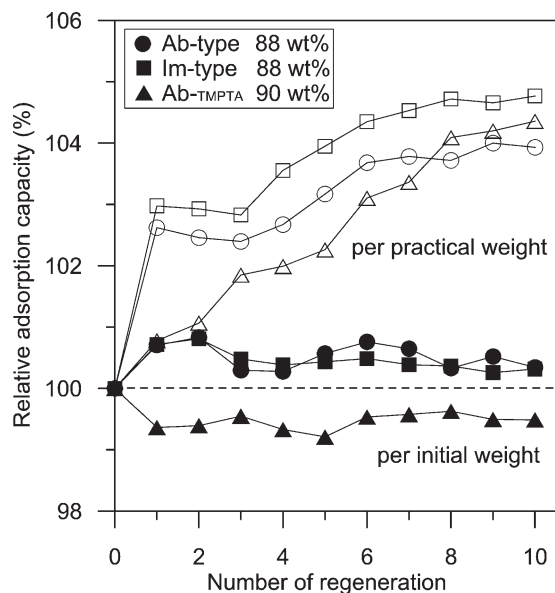


**Figure 13** Adsorption kinetics of  $\text{NH}_4\text{-N}$  on the PP-g-AA nonwoven fabrics prepared by conventional Im-type photografting and improved Ab-type photografting with or without the addition of TMPTA.

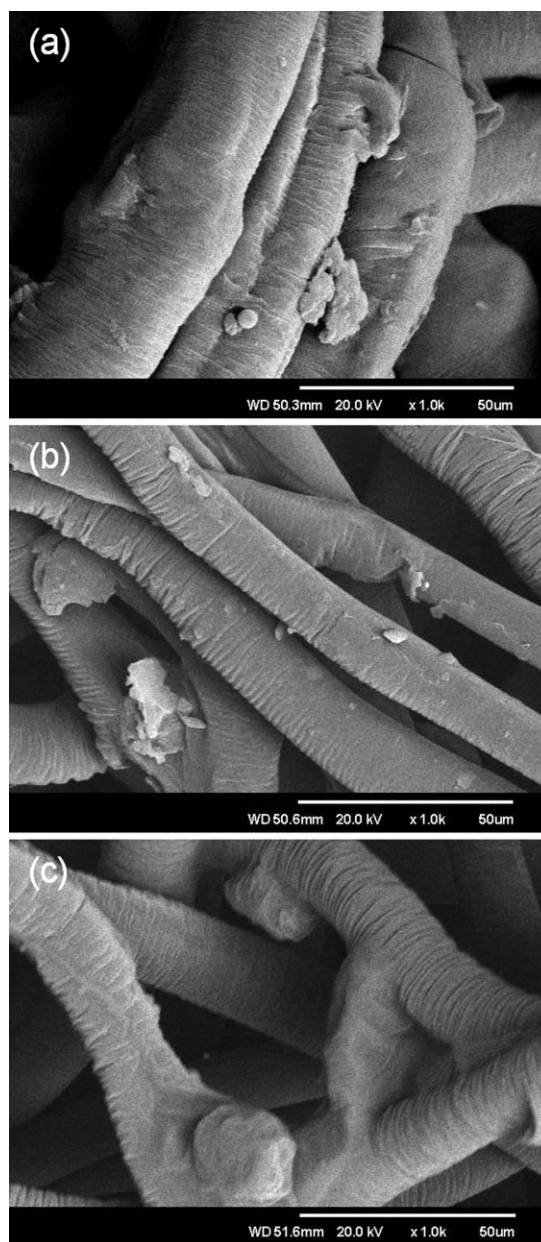


**Figure 14** Relative weight loss of the PP-g-AA nonwoven fabrics versus the number of regenerations with 0.1N HCl.

regeneration. Figure 16 shows the SEM images of the PP-g-AA fabric surface after 10 regeneration cycles. The regenerated fabric exhibited a greater roughness and a crumpled structure on the surface compared to the virgin fabric. This may have been because of the abrasive or washing loss of impurities and physical deformation on repeated swelling and shrinking of graft layers during the regeneration process. The PP-g-AA fabric could be regenerated by a simple acid-washing process without a decrease in the adsorption capacity or durability and could be used more than 10 times while retaining the same



**Figure 15** Relative adsorption capacity of the PP-g-AA nonwoven fabrics versus the number of regenerations with 0.1N HCl.



**Figure 16** SEM micrographs of the PP-g-AA nonwoven fabrics after 10 regeneration cycles: (a) Im-type, (b) Ab-type, and (c) Ab-type with TMPTA addition.

adsorption capacity. The adsorption-regeneration results also demonstrate that the Ab-type method was comparable to the conventional Im-type photo-grafting for graft polymerization.

## CONCLUSIONS

The conventional one-step photoinduced graft polymerization was improved by the preabsorption of the monomer solution onto the substrate instead of the immersion of the substrate in the monomer solution to yield a more practical and effective grafting system. The system was used for the effective graft

polymerization of AA onto PP fabric. The maximum degree of grafting obtainable was restricted by the amount of monomer solution preabsorbed onto the PP fabric, which indicated that the absorption capacity of the substrate polymer for the monomer solution was a principal parameter in the graft polymerization. The PP nonwoven fabric used here could absorb the monomer solution at approximately 1300 wt %, but the optimum monomer absorption for the graft polymerization was in the range 800–1000 wt % when we considered the degree of grafting and its reproducibility. The degree of grafting increased with increasing photoirradiation time and reaction temperature, but the latter response was not linear and reached a maximum at 50°C because of the restricted availability of monomer and increasing evaporation of the solvent at high temperatures. Therefore, the degree of grafting for the improved Ab-type photografting system was lower than that for the conventional Im-type photografting under the same experimental conditions. However, we effectively enhanced the degree of grafting by increasing the monomer concentration, adding TMPTA to the monomer solution, and repeating the photoirradiation with the supplementation of monomer solution. The net availability of the monomer for the graft polymerization during the Ab-type photografting was 50–60% and was further increased to 90% or greater with the addition of TMPTA; this was much higher than for the conventional Im-type photografting, for which the maximum availability of monomer was less than 13% under our experimental conditions. FTIR spectra, SEM morphology observations, and the adsorption–regeneration properties confirmed that the PP-g-AA fabric prepared by the improved Ab-type photografting method had qualities comparable to those of fabric prepared by conventional Im-type photografting. We concluded that the improved Ab-type photografting system provides the potential for photoinduced graft polymerization on a large scale

at a competitive cost with a continuous reactor, such as a conveyor belt system, instead of a conventional batch reactor.

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