

Ammonia Adsorption Behavior of Polypropylene Nonwoven Fabric Grafted with Acrylic Acid

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ABSTRACT: An attempt was made to synthesize an adsorbent by the photoinduced grafting of acrylic acid (AA) onto polypropylene nonwoven fabrics using benzophenone (BP) as a photosensitizer in a CH₃OH/H₂O medium. As the BP concentration was increased, the graft yield was increased up to a specific value and then decreased, and the effect of AA concentration showed the same tendency. It was also found that the graft yield increased with the reaction time and temperature. The amounts of ammonia adsorbed onto polypropylene nonwoven fabrics grafted with AA (PP-*g*-AA) were dependent on the graft yield, adsorption time, and ammonia gas pressure. The adsorption capacity of PP-*g*-AA was 5.86 mmol/g at the graft yield of 116.6%, which was much higher than that of active carbon or silica gel. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 295–301, 2002; DOI 10.1002/app.10328

Key words: adsorption; graft copolymers; poly(propylene)

INTRODUCTION

Recently, demands for greater comfort in living spaces have grown much, and concerns for health and hygiene are constantly increasing. People are extremely sensitive to smells, and the effective and economic removal of foul-smelling molecules from living spaces is the need of the day. Inorganic materials such as active carbon and zeolite have been used for general deodorants. But their adsorption capacities of ammonia, hydrogen sulfide, and trimethylamine are quite low, and they have problems of aging and the re-release of foul-smelling molecules.

Graft polymerization is a well-known method for the modification of the chemical and physical properties of polymeric materials and is of particular interest for achieving specifically desired properties.¹ Polymeric material with high functional deodorant characteristics can be achieved by the introduction of ions or components that adsorb foul-smelling molecules without affecting the bulk properties of the substrates by graft polymerization. Graft polymerization can be achieved by ionizing radiation, UV, plasma treatment, or chemical initiators.^{2–4} Of these, photografting has been known to be a useful means for the introduction of various functional groups into polymeric substrates. The UV technique has been applied in wide fields such as for the surface modification of polymers,⁵ increase of the hydrophilicity of polymers,⁶ and synthesis of insoluble polymeric ligands for the adsorption of metallic ions.^{7,8}

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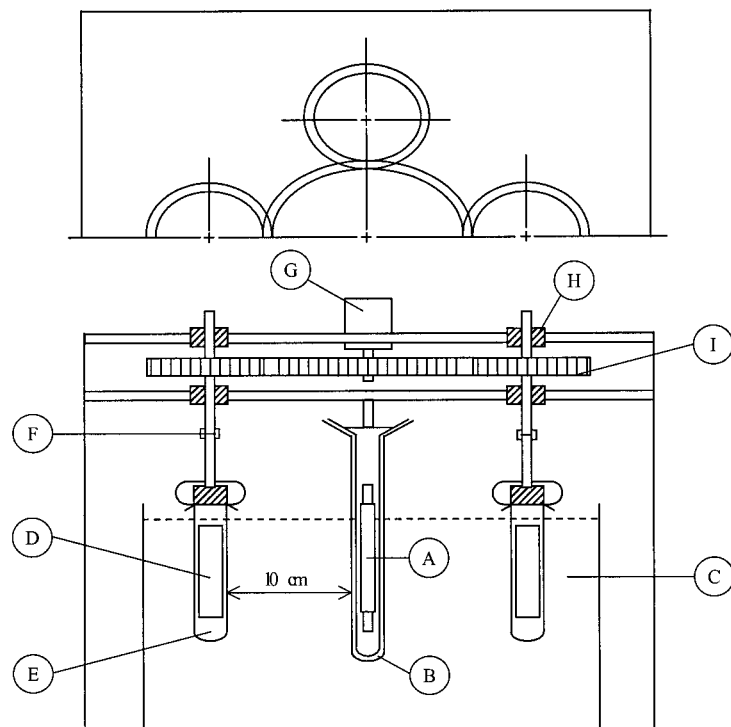


Figure 1 Schematic diagram of photoinduced graft polymerization apparatus: (A) UV lamp; (B) quartz immersion well; (C) water bath; (D) PP nonwoven; (E) Pyrex tube containing the reaction mixture; (F) connecting device; (G) motor; (H) bearing house; (I) conveyer belt.

In this study, an attempt was made to fabricate, as a deodorant, fabric by photoinduced grafting with acrylic acid (AA) onto polypropylene (PP) nonwoven fabric using benzophenone (BP) as a photosensitizer in a $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ medium. The effects of BP concentration, AA concentration, reaction temperature, and reaction time were checked. The deodorizing performance of PP grafted with AA was evaluated for the adsorption capacity of ammonia as an index material for a foul-smelling compound.

EXPERIMENTAL

Materials

PP nonwoven fabrics (12 den and 180 g/m^2 , Chonbang Industry Co., Eumsung, South Korea) were washed with a detergent solution at 60°C and then rewashed with distilled water several times. After that, the PP nonwoven fabrics were vacuum-dried at 50°C . AA (Junsei Chemical Co., Japan) was purified by distillation, and BP (Junsei Chemical Co.), by recrystallization from EtOH

(Junsei Chemical Co.). Other chemicals were reagent grade and used without further purification.

Grafting Procedure

Photoinduced grafting in the liquid phase was carried out using an apparatus shown in Figure 1. PP nonwoven fabrics were cut into strips of $3 \times 10 \text{ cm}$ and immersed in a Pyrex glass tube containing the reaction medium ($\text{CH}_3\text{OH}/\text{H}_2\text{O}$) with a given concentration of AA and BP. After introducing nitrogen gas into the system for 5 min, the system was closed and liquid-phase grafting was carried out. A 450-W medium-pressure mercury vapor lamp (Ace Glass) was evenly irradiated at $30-60^\circ\text{C}$ for 30–180 min to Pyrex glass tubes which rotated around the lamp. After the reaction, the grafted PP (PP-g-AA) nonwoven fabrics were taken out, dried to a constant weight, and then Soxhlet-extracted with methanol for 48 h to remove the poly(AA) homopolymer from the nonwoven fabrics. The graft yield, graft efficiency, and homopolymer yield were obtained by the

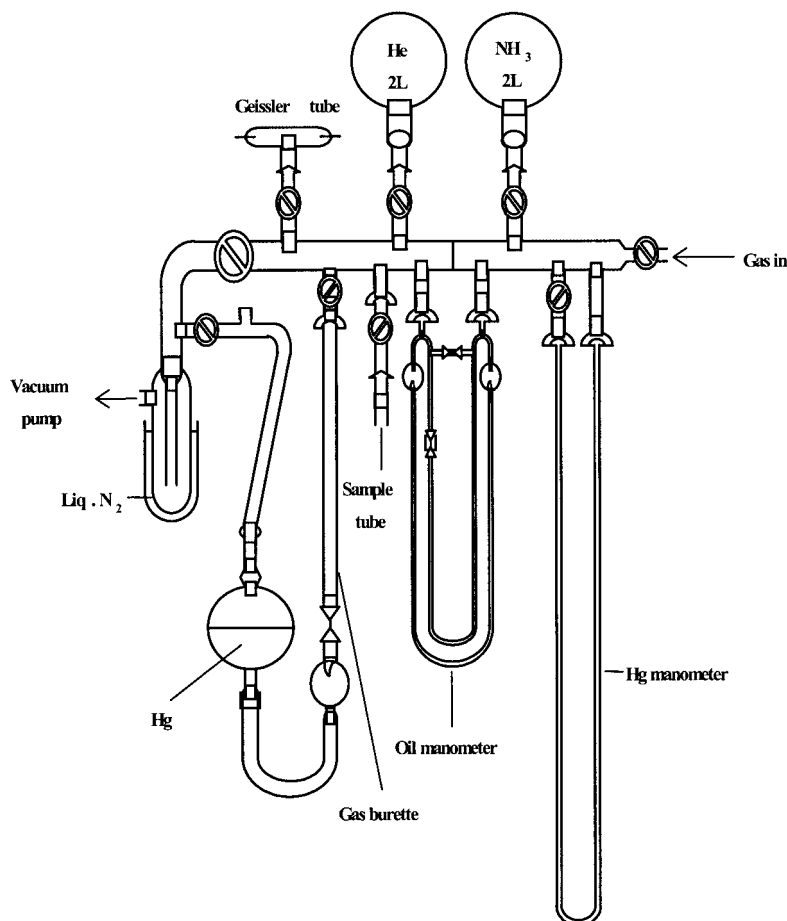


Figure 2 Apparatus for gas adsorption.

gravimetric method according to the following definitions:

Graft yield (%) = (weight of grafted polymer/weight of original PP) \times 100.

Graft efficiency (%) = (weight of grafted polymer/weight of polymer formed) \times 100.

Homopolymer efficiency (%) = (weight of homopolymer/weight of polymer formed) \times 100.

Analyses and Measurements

The chemical structure of the surface of PP grafted with AA was analyzed with an FTIR spectrophotometer. The adsorption capacity for ammonia gas was checked by the BET adsorption apparatus shown in Figure 2, changing the gas pressure with 50–200 mmHg at 293 K. The deodorizing performance of the PP fabric was evaluated based on the amount of ammonia adsorbed.

To measure the physical-adsorption capacity, adsorption and desorption were repeated.

RESULTS AND DISCUSSION

Characterization of PP Grafted with AA

Figure 3 shows FTIR spectra of the original PP nonwoven and PP-*g*-AA nonwoven fabrics. In the spectra of the grafted samples, the new absorption band was observed at the region of 1715 cm^{-1} . It may be ascribed to the stretching vibration of the carbonyl groups from the grafted poly(AA). The intensity of this band was increased with increasing of the graft yield. From these results, we confirmed that poly(AA) was successfully grafted onto the PP nonwoven fabrics.

Grafting Behavior

The effect of the BP concentrations on the graft yield is shown in Figure 4. The reaction temper-

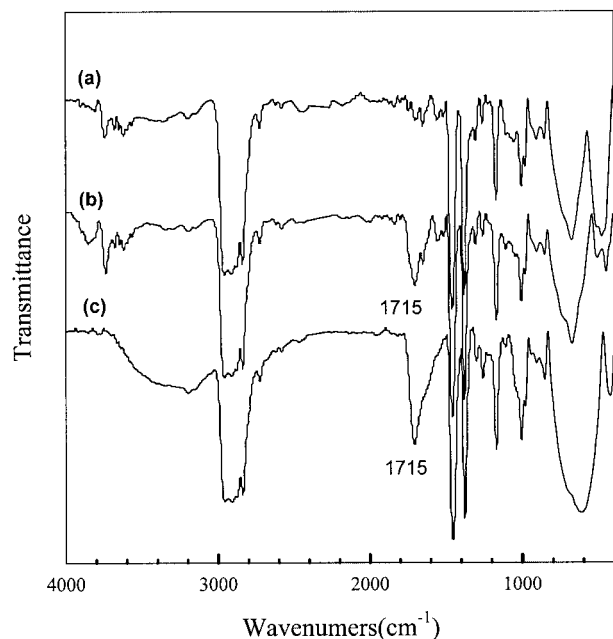


Figure 3 FTIR spectra of (a) original PP nonwoven and PP-g-AA nonwoven fabrics. Graft yield (%): (b) 15.0; (c) 32.1.

ature was 50°C, the reaction time was 60 min, and the reaction medium was CH₃OH/H₂O(3/7). The choice of the reaction medium is very important. In preliminary experiments, we tried various reaction media. Acetone was not effective in photografting on account of its poor solubilizing ability to poly(AA)⁹ and methanol was also ineffective.¹⁰ But methanol aqueous solutions were effective, and CH₃OH/H₂O(3/7) was the most effective among these. Regardless of the concentration of AA, the graft yield increased with increasing amounts of BP, but decreased gradually after passing a maximum value. A maximum graft yield was recorded at 0.01 mol/L of BP. Generally,

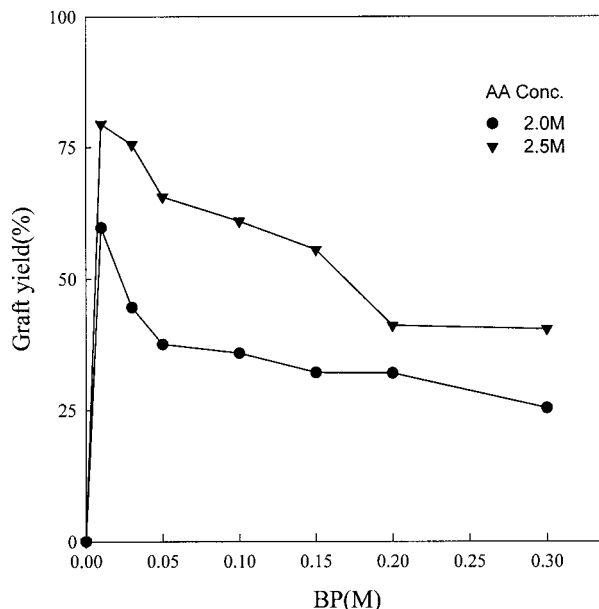


Figure 4 Effect of BP concentrations on the graft yield. Temperature, 50°C; irradiation time, 60 min; CH₃OH/H₂O(3/7), 30 mL.

photografting with BP is initiated mainly by hydrogen abstraction by an excited triplet $n-\pi^*$ benzophenone (3BP*¹¹). The mechanism of grafting is considered as follows:

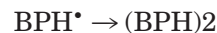
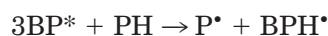


Table I Effect of BP Concentration on Grafting to PP Nonwoven Fabric

BP Concentration (M)	AA Conversion (%)	Homopolymer Yield (%)	Graft Efficiency (%)	Grafting (%)
0.01	5.1	31.5	68.5	79.5
0.03	5.3	35.9	64.1	75.0
0.05	4.9	46.5	53.5	65.5
0.10	4.9	52.2	47.8	61.0
0.15	5.2	55.4	44.6	55.3
0.20	5.3	67.9	32.1	40.5
0.30	6.8	71.9	28.1	40.0

AA, 2.5M; liquor ratio, 1 : 150; temperature, 50°C; irradiation time, 60 min; CH₃OH/H₂O(3/7) = 30 mL.

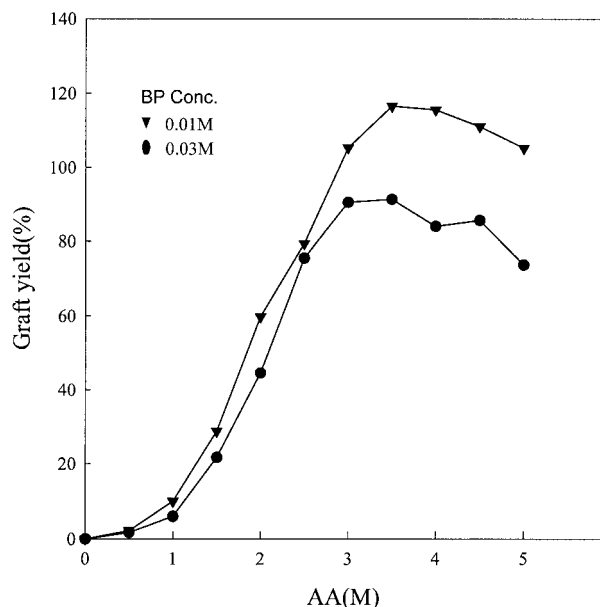


Figure 5 Effect of AA concentrations on the graft yield. Temperature, 50°C; irradiation time, 60 min; CH₃OH/H₂O(3/7), 30 mL.

PH = polymer, M = monomer,

P[•] = polymer radical

As long as the concentration of BP is below 0.01 mol/L, the activated reaction sites of PP by hydrogen abstraction increase with increasing BP concentration. However, any addition of BP above the 0.01 mol/L level makes the radicals generated from the reaction of activated BP with methanol in the reaction medium, which initiate monomers and cause enhanced homopolymerization of AA. Table I shows the effect of the BP concentration

on the formation of the homopolymer. It was found that the homopolymer yield increased continuously with the BP concentration. The graft efficiency was maximum at 0.01 mol/L of BP.

The effect of the AA concentration on the graft field at 50°C for 60 min is shown in Figure 5. Regardless of the BP concentration, the maximum graft yield was recorded around the concentration of 3.5 mol/L. Above this concentration of AA, the graft yield decreased with increase of the AA. At a low concentration, the monomer would be able to diffuse very easily to the grafting sites of the substrate and a smooth graft polymerization would proceed. Further, it was known that the homopolymerization was not much affected by the concentration of the monomer. Both these competing polymerizations proceed smoothly until a certain concentration of the monomer has been reached. Beyond this concentration, a slow decrease in the graft yield appeared and we considered that there was an increase in the rate of homopolymerization compared with the rate of graft polymerization. Table II shows the effect of AA concentration on the formation of the homopolymer. Below 3.5 mol/L of AA concentration, the homopolymer yield decreased gradually with the AA concentration, but it increased with the AA concentration beyond this concentration. In our system, it was considered that the grafting was not affected up to an AA concentration of 3.5 mol/L, due to the regular accessibility of AA to the grafting sites of PP.

The effect of the reaction temperature on the graft yield at various monomer concentrations is shown in Figure 6. The concentration of BP was 0.01 mol/L, and the reaction time was 60 min. By

Table II Effect of AA Concentration on Grafting to PP Nonwoven Fabric

AA Concentration (M)	AA Conversion (%)	Homopolymer Yield (%)	Graft Efficiency (%)	Grafting (%)
0.5	4.2	83.1	16.9	3.5
1.0	4.8	77.6	22.4	10.2
1.5	5.6	58.3	41.7	28.3
2.0	5.6	42.1	57.9	60.2
2.5	5.1	31.5	68.5	79.5
3.0	5.3	25.2	74.8	104.5
3.5	4.7	21.7	78.3	116.7
4.0	4.5	37.7	62.3	115.0
4.5	4.8	49.8	50.2	110.2
5.0	4.2	50.4	49.6	105.1

BP, 0.01M; liquor ratio, 1 : 150; temperature, 50°C; irradiation time, 60 min; CH₃OH/H₂O(3/7) = 30 mL.

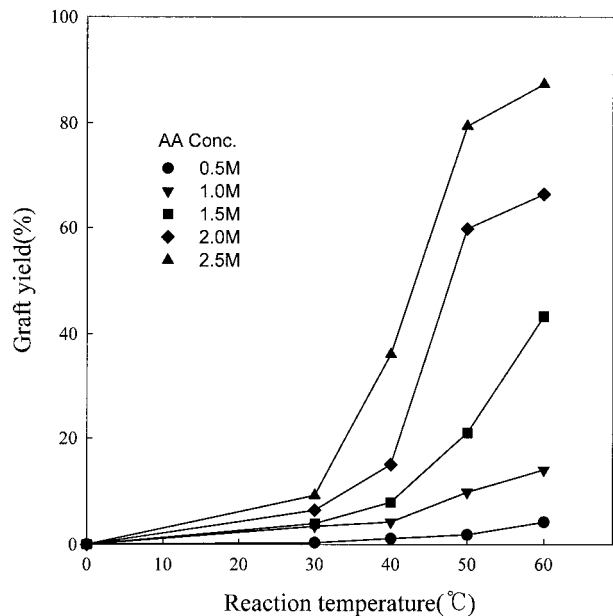


Figure 6 Effect of reaction temperature on the graft yield. Irradiation time, 60 min; BP concentration, 0.01 mol/L.

increasing the temperature, the graft yield rapidly increased. By introducing thermal energy into the system, the mobility of PP macromolecules increased and the monomer would diffuse easily. The more monomer that diffused into the

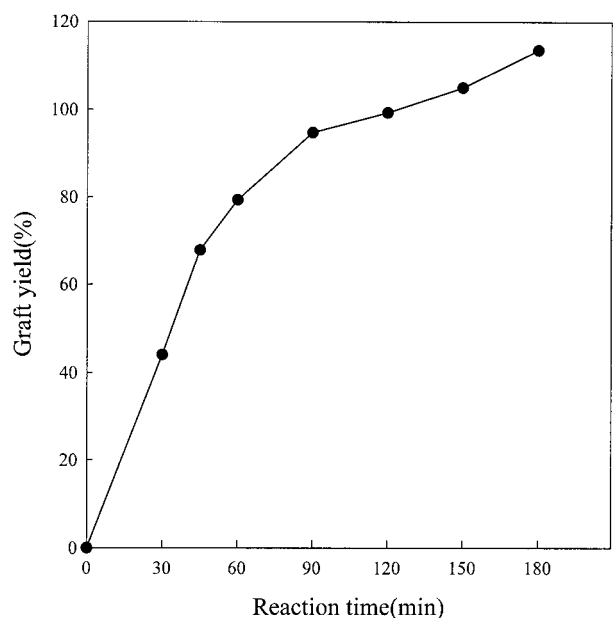


Figure 7 Effect of reaction time on the graft yield. AA concentration, 2.5 mol/L; BP concentration, 0.01 mol/L; temperature, 50°C.

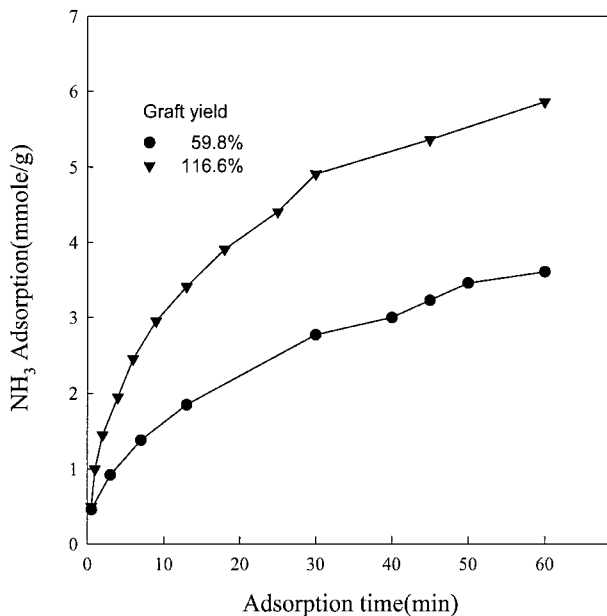


Figure 8 Effect of graft yield on the ammonia-adsorption capacity.

PP substrate, the greater probability that grafting would occur. So, by increasing the temperature, the graft yield increased. Also, at the same temperature, the graft yield increased with the concentration of AA, as shown in Figure 5.

Figure 7 presents the effect of the reaction time

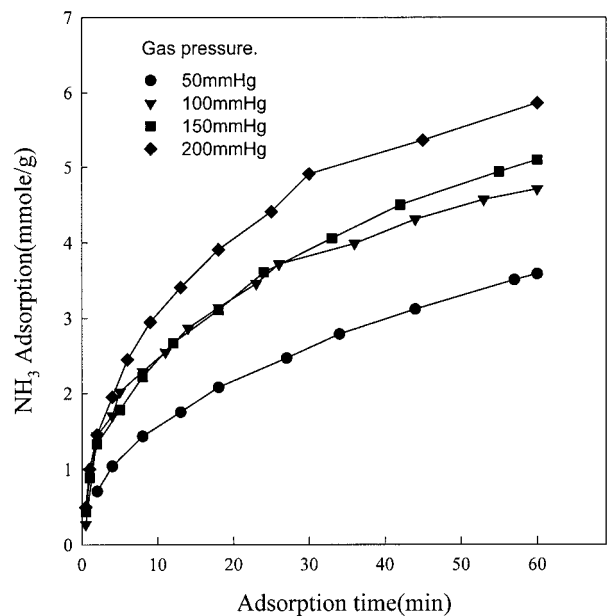


Figure 9 Effect of gas pressure on the ammonia-adsorption capacity; Graft yield, 116.6%.

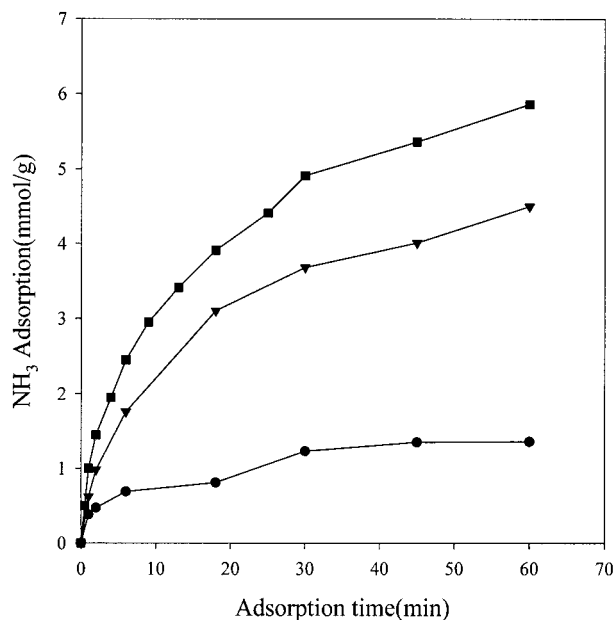


Figure 10 Comparison of the ammonia-adsorption capacity of AA-grafted PP nonwoven fabric between chemical and physical adsorption at 200 mmHg. Graft yield, 116.6%. (▼) Chemical; (●) physical; (■) total adsorption.

on the graft yield at 2.5 mol/L of AA, 0.01 mol/L of BP, and 50°C. The graft yield increased with an increase of the reaction time. The longer the irradiation time, the more radicals would be generated on the PP surface. The mobility of the grafted chain is slow, so chain-end radicals have a low probability of being in the position to affect the termination reaction. Eventually, the number of reaction sites on the surface increased with increase of the irradiation time. Because the small monomer molecules still diffuse to the active chain ends even when the termination rate is low, there is a marked increase in the graft yield.^{12,13}

Ammonia Adsorption Behavior

Figure 8 shows the ammonia-adsorption capacity of PP nonwoven fabrics grafted with AA at a 200-mmHg gas pressure. It may be observed that the adsorbed amounts of ammonia gas increased with an increasing graft yield. At the adsorption time of 60 min, PP-*g*-AA nonwoven fabric with a 59.8 % graft yield adsorbs ammonia at the level of 3.61 mmol/g, and with a 116.6% graft yield, at 5.86 mmol/g. The active carbon is at the level of 3.5 mmol/g for ammonia adsorption, and silica gel

is at 2.75 mmol/g under the same condition.¹⁴ From these results, it was considered that the ammonia-adsorption capacity of PP-*g*-AA nonwoven fabrics was very excellent, compared with that of active carbon or silica gel. The ammonia-adsorption capacity increased with increasing gas pressure (Fig. 9). The ammonia gas can be adsorbed onto substrate chemically or physically. Figure 10 shows the tendency of chemical and physical adsorption at 200-mmHg gas pressure for the PP nonwoven fabrics with a 116.6% graft yield. The chemical adsorption rapidly increased at an initial period and then increased slowly. On the other hand, the physical adsorption gradually increased with time and equilibrated after 45 min. Based on the above investigation, it was found that the ammonia-adsorption ability of PP-*g*-AA nonwoven fabrics was not largely dependent on the physical adsorption. But the chemical adsorption which is due to grafted poly(AA) seems to play an important role.

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REFERENCES

1. Yao, Z. P.; Ranby, B. *J Appl Polym Sci* 1990, 41, 1459.
2. Jahagirdar, C. J.; Venkatakrishnan, S. *J Appl Polym Sci* 1990, 41, 117.
3. Kim, K. J. *J Appl Polym Sci* 1986, 32, 6017.
4. Koo, K.; Wakida, T. *Sen-i Gakkaishi* 1992, 48, 57.
5. Uyama, Y.; Ikada, Y. *J Appl Polym Sci* 1988, 36, 1087.
6. Kim, S. Y.; Song, S. K. *J Kor Soc Text Eng Chem* 1988, 25(3), 19.
7. Kubota, H.; Ujita, S. *J Appl Polym Sci* 1995, 56, 25.
8. Kubota, H.; Shigehisa, Y. *J Appl Polym Sci* 1995, 56, 147.
9. Yang, W.; Ranby, B. *J Appl Polym Sci* 1996, 62, 545.
10. Mehta, I. K.; Kumar, S.; Chauhan, G. S.; Misra, B. N. *J Appl Polym Sci* 1990, 41, 1171.
11. Tazuke, S. *J Polym Sci Polym Lett Ed* 1978, 16, 497.
12. Li, Y.; Desimone, J. M.; Poon, C.-D.; Samilski, E. T. *J Appl Polym Sci* 1997, 64, 883.
13. Zhang, X.; Baker, W. E. *J Appl Polym Sci* 1998, 67, 427.
14. Park, J. S.; Nho, Y. C. *Polymer (Korea)* 1997, 21, 325.