

Preparation of Chelating Fabrics by Radiation-Induced Grafting of Itaconic Acid and Acrylonitrile onto Polypropylene Nonwoven Fabrics and Subsequent Amination of Graft Copolymer

Jianhua Zu,¹ Young Chang Nho,² Joon Pyo Jeun,² Ruiqin Liu,³ Li Liu,¹ Feng Yan,¹ Min Xia¹

¹Shanghai Applied Radiation Institute, Shanghai University, Shanghai 201800, China

²Advanced Radiation Technology Institute, Korea Atomic Energy Research Institute, Jeongseup, Jeonbuk 580-185, South Korea

³Radioprotection Department, School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai, China

Received 16 December 2009; accepted 23 June 2010

DOI 10.1002/app.33012

Published online 29 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A mixture of acrylonitrile (AN) and itaconic acid (IA) was cografted onto polypropylene (PP) nonwoven fabrics by preirradiation method. The effects of graft polymerization conditions such as temperature, reaction time, Mohr's salt concentration, solvent mixture ratio, and comonomer composition on the total grafting yield were investigated. The addition of AN as a comonomer increased the amount of IA that reacted with PP fabrics. An increase in the temperature from 40 to 60°C increased the grafting rate, but the final grafting yield decreased at high temperature. The addition of 0.01 wt % Mohr's salt to the reaction medium led to a sharp increase of grafting yield. The accelerative effect of solvent medium on the grafting yield was higher in dimethylformamide (DMF) and

methanol mixtures, when compared with DMF or methanol. Chelating fabrics was synthesized by subsequent amination of grafted fabric with ethylene diamine (EDA) and phenylhydrazine (PH). The conversion yield reached maximum value at about 90% for 80% PP-g-AN-IA fabrics at 90°C. At same amination conditions, the conversion yield is higher when PP-g-AN-IA fabrics react with EDA compared with PH. FT-IR data indicate that amine groups were introduced onto PP-g-AN-IA fabric through amide linkage between grafted AN or IA and EDA or PH. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 3483–3489, 2011

Key words: graft polymerization; acrylonitrile; itaconic acid; amination chelating fabrics

INTRODUCTION

Polypropylene (PP) nonwoven fabrics are important synthetic fabrics that are commercially produced today and have an advantage over other materials because it is economical with respect to production costs and operating pressures. Therefore, PP nonwoven fabrics can be a good polymer substrate for introduction of various functional groups such as ion-exchange groups and affinity ligands.

Radiation-induced grafting is one of the most effective techniques because of its uniform creation of radical sites on the polymer matrix, penetration effectively into the polymer, and its moderate reaction conditions.

The most recent research in radiation-induced graft copolymerization involves two main methods: simultaneous irradiation and preirradiation. In practice, the preirradiation method has been given much attention because the homopolymer formation is little, and the grafting can be carried out at anytime, away from radiation sources. In our research, preirradiation method was used to prepare the graft copolymer.

Many studies have been reported in the preparation of chelating fabrics using radiation-induced grafting technique with the aim focus on improving the adsorption affinity to heavy metals by optimization of the grafting conditions and selection of an appropriate monomer.^{1–3} There are mainly two ways to prepare chelating fabrics using radiation-induced grafting technique. The first way is various vinyl monomers such as acrylic acid, acrylamide, *N*-vinyl-2-pyrrolidone with suitable functional groups grafting onto the polymer fabrics. The second way is some monomers which have easily modified groups grafting onto polymer fabrics, and then compounds with various ligands are introduced onto fabrics by further reaction.

Acrylonitrile (AN) was grafted onto polyethylene films and hollow fabrics, and subsequently the nitrile

Correspondence to: J. Zu (zujianhua1999@163.com).

Contract grant sponsor: Shanghai Science and Technology Foundation; contract grant number: 10JC1404900.

Contract grant sponsor: Shanghai Leading Academic Disciplines; contract grant number: S30109.

Contract grant sponsor: National Natural Science Foundation, China; contract grant number: 50973059.

groups in graft chains were converted into $-C(=NOH)NH_2$ groups to synthesize amidoxime adsorbent. Such excellent adsorbent synthesized by radiation-induced grafting method was applied to the recovery of useful metal such as uranium from seawater.⁴ High hydrophilicity of metal ion adsorbent is very important in improving the aqueous metal ions adsorption rate and adsorption capacity. Some research about kinetics of metal ions adsorption on chelating fabrics indicated that the diffusion of metal ions from water to the chelating fabrics surface governs the overall adsorption rate.⁵ We had published articles about radiation synthesis of amine-functionalized adsorbent and their application to palladium ions' recovery.^{6,7} In these articles, only AN was grafted onto PP fabrics. In this research, with aim of preparing a new functionalized fabrics with good affinities to metal ions, comonomer AN and itaconic acid (IA) were grafted onto PP fabrics by electronic beam initiated preirradiation method. The introduction of hydrophilic $-COOH$ group in graft chains can increase the accessibility of functional groups toward aqueous metal ions.

The best amination conditions were optimized for introduction of amine groups onto graft copolymer by reacting with ethylene diamine (EDA) and phenyl hydrazine.

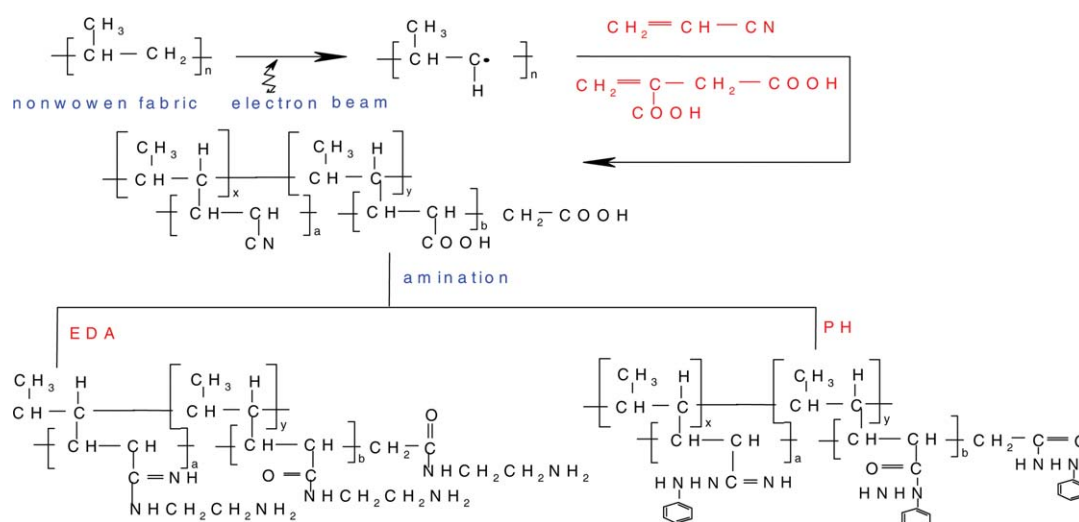
EXPERIMENTAL

Materials and reagents

PP fabrics were supplied by Korea Nonwoven Tech Co. (Seoul). AN and IA monomers were obtained from Japan Shaowha Chemical Reagent Co. (Tokyo). Methanol and ethanol were obtained from Kanto Chemical Company (Tokyo). EDA (99%) and phenylhydrazine (PH; 97%) were obtained from Merck (Germany). All materials were used as supplied.

Preparation of chelating fabrics

The preparation of chelating fabrics by radiation-induced cograft polymerization and subsequent chemical modifications is illustrated as follow:



Preparation scheme of chelating adsorbent

Preparation of PP-g-AN-IA graft copolymer

First, a mixture of AN and IA was cografted onto the PP fabrics using a preirradiation technique. Irradiation of PP by an electron beam was performed at a dose of 100–300 kGy in a nitrogen atmosphere at ambient temperature. The irradiated PP fabrics were immersed in a monomers mixture solution previously deaerated with nitrogen. The mixture was deaerated by bubbling nitrogen again for 5 min, and the reaction tube was sealed. The grafting reaction was carried out in a water bath maintained at the constant temperature. The total concentration of the two monomers was set at 3–8 mol L⁻¹ in dimethyl-

formamide (DMF) and methanol mixture as solvent. After reaction, the grafted fabrics were removed, washed thoroughly with DMF and water mixture for several times, and immersed in the mixture for 24 h at 80°C to eliminate the unreacted monomers, homopolymer and copolymer which accumulated on the surface of fabrics. The total grafting yield was defined below:

$$\text{The total grafting yield (\%)} = \frac{W_g - W_o}{W_o} \times 100\%$$

where W_o and W_g are the weights of ungrafted PP and PP-g-AN-IA grafted fabrics.

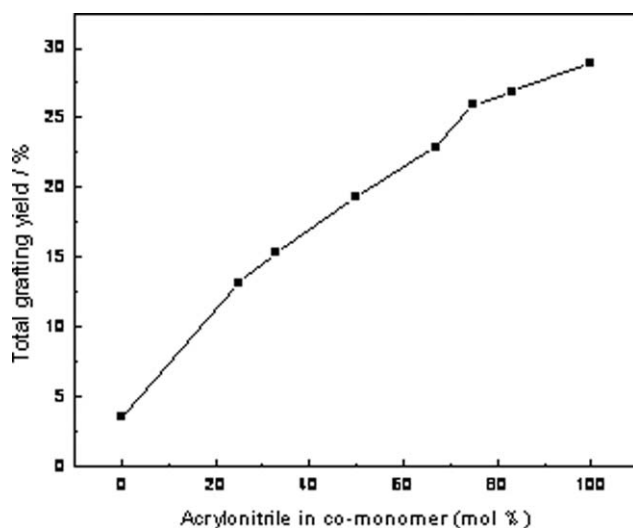


Figure 1 The effect of acrylonitrile content in comonomer on total grafting yield. Temperature: 60°C; radiation dose: 200 kGy; monomer concentration: 4 mol L⁻¹; reaction time: 5 h.

Amination of graft copolymer

The PP-*g*-AN-IA grafted fabrics and 100% EDA or PH were mixed into a three-neck flask and refluxed for 10 h at 100°C in the condition of stirring. After the amination reaction, the fabrics was washed with distilled water until neutral and subsequently rinsed with distilled water for 12 h, and then dried in a vacuum oven at 60°C to constant weight.

When the grafted fabrics were aminated with EDA or PH, both nitrile and carboxyl acid groups on the graft chains can react with amine groups of EDA or PH. So, it is difficult to calculate conversion yield. In this article, we use weight increase of fabrics before and after amination reaction to show the amination degree of grafted fabrics. The weight increase was defined below:

$$\text{Weight increase (\%)} = \frac{W_a - W_g}{W_g} \times 100\%$$

where W_a is the weight of aminated fabrics.

RESULTS AND DISCUSSIONS

Effect of the monomer mixture ratios on the graft yield

Figure 1 shows the grafting yields obtained by the grafting of PP fabrics with IA, AN, and their mixtures. The AN/IA mixture concentration was kept constant at 4 mol L⁻¹. The single monomer concentration employed in grafting was also 4 mol L⁻¹. As shown in Figure 1 for grafting with IA alone, the grafting yield remained as low as 3.5%. Similar results were observed in the grafting of IA upon PP

fabrics.⁸ Subsequently the grafting yield increased with increasing AN concentration and reached 26.9% when molar ratio of AN to IA is 5 : 1. The use of AN and IA monomers together in grafting caused a significant increase in the grafting yield. The graft yield was highly dependent on the monomer ratio. This synergistic effect was observed in every mixture ratio. The reactivity ratios for the copolymerization of AN and IA is $r_1 = 0.59$ and $r_2 = 0.86$, respectively,⁹ both of which are < 1. These values signify that AN or IA monomer radicals on the grafting chains prefer to react with each other rather than reacting with those of their own kind. A monomer, which cannot be satisfactorily grafted to polymer when used alone, may be grafted to polymer to a significant extent with the help of the synergistic effect of a comonomer.

Effect of time on the grafting yield at different temperature

The effects of the reaction time on grafting yield at different temperature are shown in Figure 2. Increasing the temperature from 40 to 60°C increased the rate of grafting, but the highest grafting yield, 85.9%, was obtained at 40°C, and it decreased to 59.3% at 60°C. In the initial reaction stage, the grafting rate and total grafting yield increase with increasing reaction temperature. The increase of reaction temperature can increase the diffusion rate of monomer, but at the same time also accelerate the decay rate of the substrate radicals. In our grafting system, a high final total grafting yield is obtained at 40°C.

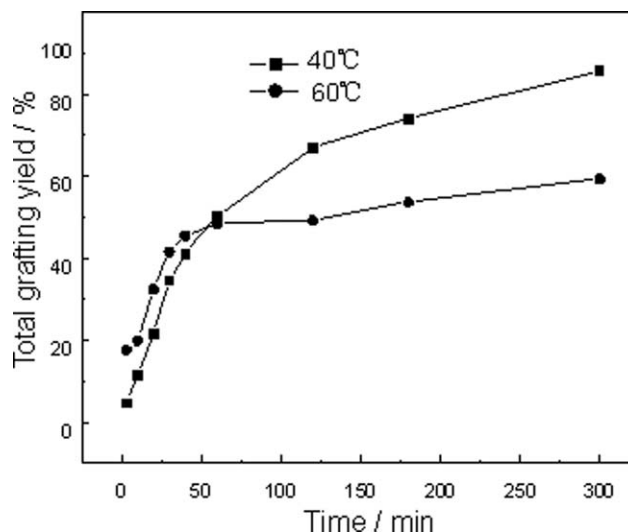


Figure 2 The effect of reaction time on total grafting yield at different temperature. Radiation dose: 200 kGy; monomers concentration: 8 mol L⁻¹; molar ratio of AN to IA: 3 : 1; solvent: methanol-DMF mixture (vol. 75 : 25).

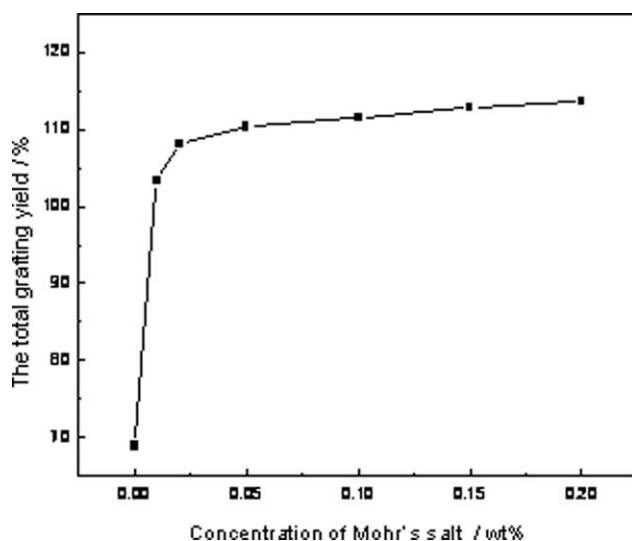


Figure 3 The effect of Mohr's salt concentration on the total grafting yield. Temperature: 40°C; radiation dose: 200 kGy; monomers concentration: 8 mol L⁻¹; molar ratio of AN to IA: 3 : 1; solvent: methanol-DMF mixture (vol. 75 : 25); reaction time: 5 h.

Effect of the inhibitor concentration on the grafting yield

The effect of the Mohr's salt concentration on the grafting yield of an AN/IA (3 : 1) mixture onto PP fabrics is shown in Figure 3. The grafting yield increased with increasing concentration of Mohr's salt, and then level off. In the preirradiation method, monomers can homopolymerize by the active sites formed by chain transfer reaction of growing polymer radicals or by dissociation of hydroperoxide which can initiate homopolymerization. In our radiation atmosphere (PP fabrics were irradiated at nitrogen atmosphere), the formation of hydroperoxide is relatively low, but we found a very viscous reaction medium was formed without any radical inhibitors and that addition of Mohr's salt to the grafting system is effective for depressing the homopolymerization. In our system, AN or IA may be homopolymerized by active sites which are formed by reactions between HO and monomers. In the presence of Fe²⁺, homopolymerization and copolymerization of monomers will be suppressed; at same time, the viscosity of grafting system decrease, so diffusion rate of monomers to PP fabrics increase. If we continue increasing Mohr's salt concentration, the grafting yield almost level off. This result suggests that a part of growing chain radicals is deactivated as follows:

$\text{Fe}^{2+} + -\text{R}^{\cdot} \rightarrow -\text{R}^{-} + \text{Fe}^{3+}$ (-R is growing chain radicals).

The effect of methanol content in DMF-methanol mixture on grafting yield

The relationship between the grafting yield and methanol content in DMF-methanol mixture is

shown in Figure 4. It is well known that a polymer swollen in a solvent represents a medium of high viscosity and that it is the viscosity of the grafted layers controls the diffusion of the monomer to the grafting sites.¹⁰⁻¹² The swelling of PP fabrics in methanol and DMF was found to be 0.25 and 0.15 wt %, respectively. This can be explained by the higher proximity of the solubility parameter of the methanol (14.5) to the value of PP (15.4) than DMF (9.5). Therefore, a higher diffusibility of methanol into PP substrates is obtained when the monomers are in solution with methanol than with DMF. So the grafting yield increase dramatically with increasing methanol content in mixture of solvents until it reached a maximum value at a methanol/DMF mixture composition 75 : 25 (v : v). As the content of methanol further increased, the grafting yield fell. The solubility parameter of various solvents has influence on grafting yield; in addition, the nature of solvents also contributes to the variation in the grafting yield. The higher chain transfer constant of methanol compared with DMF caused a fast termination in growing chains, so grafting yield fell when 100% methanol was used as solvent compared with methanol/DMF mixture (75 : 25). Accordingly, the correct choice of the solvents is one of the essential elements toward obtaining higher grafting yield.¹³ It has been established that the nature of the solvent not only determines the grafting yield but also the location of grafting. If good-swelling solvent is used, bulk grafting is highly favored and homogenous grafting is most likely obtained. This is very important for getting chelating fabric with good performance for treatment of metal ions.

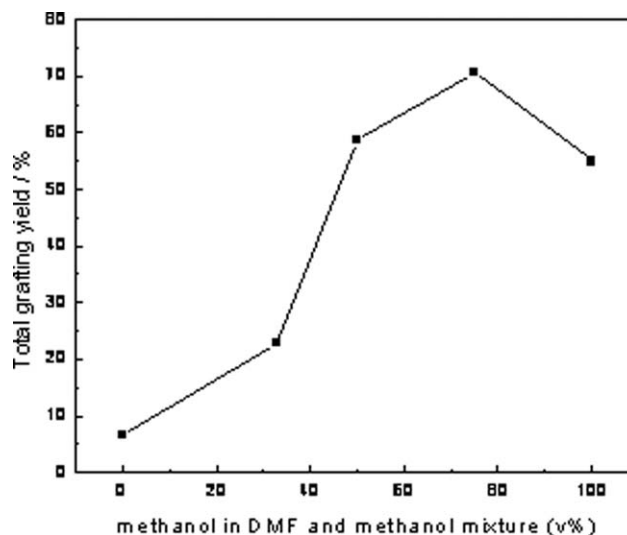


Figure 4 The effect of methanol content in DMF-methanol mixture on total grafting yield. Temperature: 60°C; radiation dose: 200 kGy; monomers concentration: 6 mol L⁻¹; molar ratio of AN to IA: 3 : 1; reaction time: 5 h.

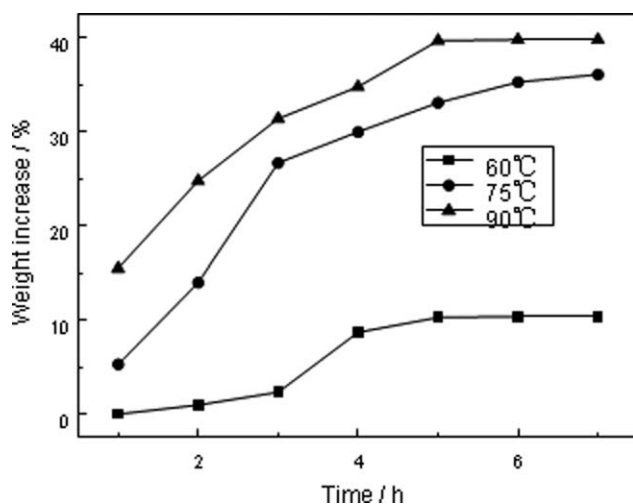


Figure 5 The relationship of weight increase with reaction time when PP-g-AN-IA fabrics were reacted with EDA at different temperature. Total grafting yield: 80%; concentration of EDA: 100%.

The relationship of grafting yield with weight increase of aminated fabrics

We obtained chelating fabrics with different amine groups by varying amination conditions, such as temperature and time. Figure 5 shows the effect of reaction time on the weight increase when 80% PP-g-AN-IA fabrics were used for amination with 100% EDA. In all cases at 60, 75, and 90°C, the weight of aminated fabrics increased with increasing reaction time. At high amination temperature, weight increase is high. Figure 6 shows the effects of grafting yield on the weight increase using 100% EDA at 60°C. For PP-g-AN-IA fabrics with high grafting yield, the percentage of weight increase is less than fabrics with low grafting yield. The conversion yield

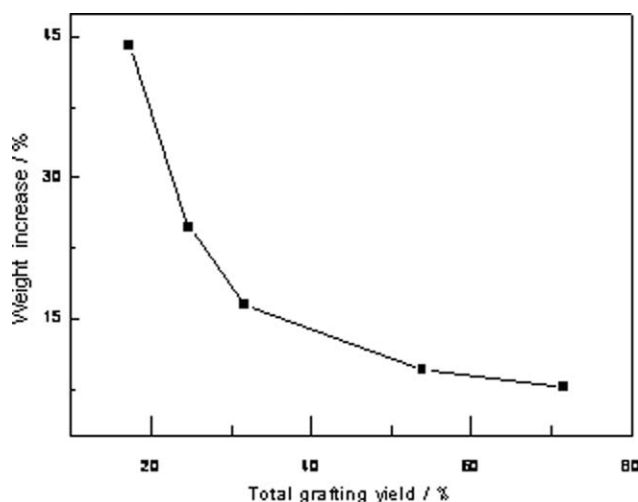


Figure 6 The relationship of total grafting yield with weight increase when PP-g-AN-IA fabrics were reacted with EDA. Temperature: 60°C; reaction time 12 h; concentration of EDA: 100%.

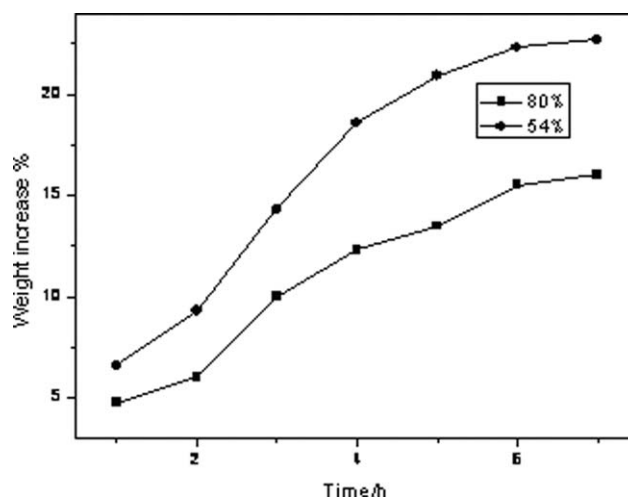


Figure 7 The relationship of weight increase with reaction time when PP-g-AN-IA fabrics with different grafting yield were reacted with PH. Reaction temperature: 90°C; concentration of PH: 100%.

decrease with increase of grafting yield. This may attribute to structure of grafted fabrics. At high grafting yield, surface of grafted copolymer become more compact, so diffusion rate of EDA to position of functional groups in fabrics decrease; at the same time, part of functional groups cannot react with EDA. Compare Figure 5 with Figure 7, at the same amination condition the weight increase percentage is higher when grafted fabrics reacted with EDA than with PH.

Characterization of samples

FTIR

The FTIR spectra of ungrafted PP, grafted PP with different grafting yield and aminated PP are given in Figure 8. The peaks of ungrafted PP fabrics [Fig. 8(a)] can be assigned as follows: 2945 cm^{-1} $\nu(\text{CH}_2, \text{CH})$, 1440 cm^{-1} $\delta_s(\text{CH}_2)$. After grafting with AN/IA [Fig. 8(b,c)], the adsorption peaks of 1680 cm^{-1} assign to $\nu(\text{C}=\text{O})$ of IA, and 3500–3250 cm^{-1} is $\nu(\text{OH})$ of IA. 2245 cm^{-1} corresponds to $\nu(\text{C}\equiv\text{N})$ of AN. Furthermore, the intensity of these characteristic peaks increases with increasing grafting yield. After amination with EDA and PH, The IR spectra of Figure 8(d,e) change greatly. The peaks can be assigned as follows: 3365 cm^{-1} $\nu(=\text{N}-\text{H})$, 1686 cm^{-1} $\delta(\text{C}=\text{N}-\text{H})$, 1601 and 1497 cm^{-1} $\nu(\text{C}=\text{C}$ of benzene), 760 and 697 cm^{-1} $\nu(\text{C}-\text{H}$ of benzene), where ν is a stretching vibration, δ a bending vibration.

Thermal properties of the fabrics before and after grafting

The thermal properties of ungrafted PP and grafted PP with different grafting yield have been investigated

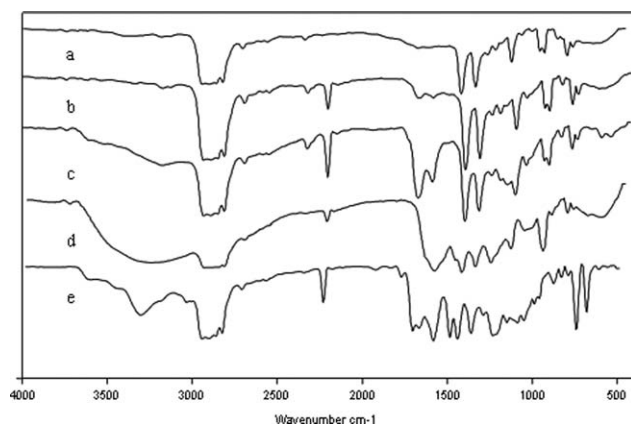


Figure 8 FTIR spectra of ungrafted PP (a), PP-g-AN-IA with different grafting yield (b) 31.7%, (c) 71.5% and PP-g-AN-IA with grafting yield 71.5% aminated with EDA (d), and PH (e).

by differential scanning calorimetry (DSC). DSC thermograms were obtained by a Netzsch DSC-200PC over a temperature range of -80 to 250°C at a heating rate of $10^{\circ}\text{C min}^{-1}$ under nitrogen atmosphere. The heat of fusion of fabrics (ΔH_F) was calculated from the DSC thermograms. The variations of ΔH_F with the grafting yield are presented in Figure 9. The result shows that ΔH_F does not follow a linear decrease. Instead, the decrease is faster for lower grafting yield, when compared with the higher grafting yield. In our grafting system, the grafted monomer IA is hydrophilic. The decrease of ΔH_F is caused by two reasons. On one hand, the addition of amorphous grafting chains in the amorphous region of the PP fabrics exerting a dilution effect on inherent crystallinity of PP. On the other hand, when $-\text{COOH}$ groups of IA are firstly grafted onto PP fabrics, it may be assumed that some of the chains grow from the crystallite surface as well. The grafted fabric absorbs water, and strain is created between hydro-

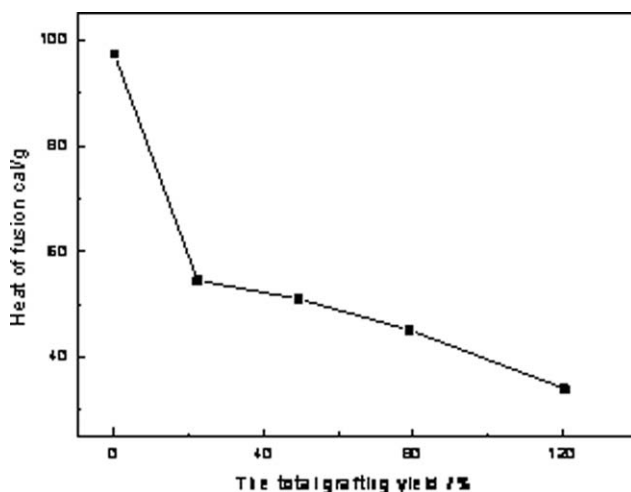


Figure 9 Variation of ΔH_F with the total grafting yield.

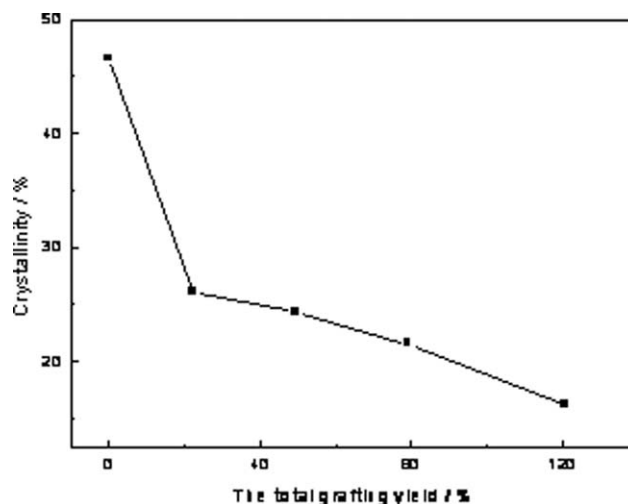


Figure 10 Variation of crystallinity with the total grafting yield.

philic grafting chains and the hydrophobic PP matrix. As a result, some of these chains are cleaved off, leading to the crystal disruption.¹⁴ At a higher grafting yield, the distribution of grafted chains is more homogenous. This leads to a more uniform swelling of the matrix. As a result, the influence of the “crystal disruption” in reducing the crystallinity slows down. The disruption of the crystalline region during sulfochlorination of polyethylene fabric has also been reported by Zevin and Messalem.¹⁵

The relationship between the degree of crystallinity and grafting yield is shown in Figure 10. The degree of crystallinity decreases with increase of grafting yield. The cumulative influence of diluting effect and crystal disruption is so high that the crystallinity in a fabric with 49.3% grafting yield decrease to almost one-half of its original value. In

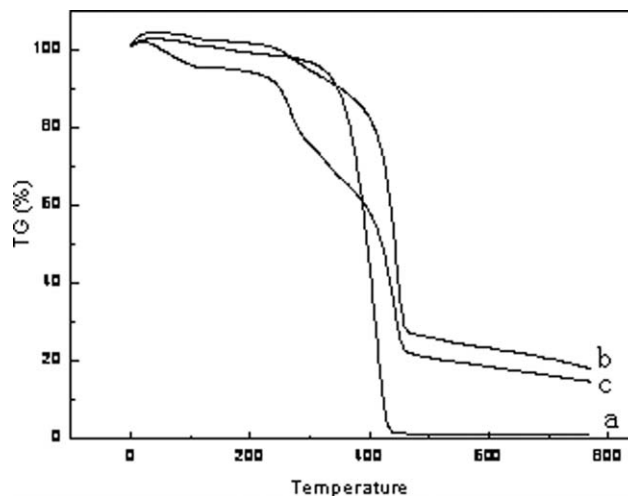


Figure 11 TGA thermograms of ungrafted PP (a), PP-g-AN-IA (b), and aminated PP-g-AN-IA (c).

researches of methacrylic acid and 2-hydroxyethyl-methacrylate grafting onto PP, the similar behavior was also observed.^{16,17}

Thermogravimetry analysis of the grafted fabrics

The effect of grafting yield on the thermal stability of grafted fabrics was studied using the thermogravimetric technique. Figure 11(a) represents the TG curves of ungrafted fabric. There is only one sharp weight loss that was ascribed to the decomposition of polymer main chains. For grafted and aminated fabrics as shown in Figure 11(b,c), the TG curves exhibit three different steps of thermal degradation: (1) around 100°C is the desorption of water bonded to the carboxyl or amine groups; (2) the second occurs between 200 and 300°C is related with the carboxyl acid or amine groups decomposition. The same results were reported when dimethyl itaconate was grafted onto microcrystalline cellulose¹⁹; (3) the third step between 350 and 420°C is assigned to degradation of the polymer main chains.

CONCLUSIONS

A mixture of AN and IA was cogenerated onto PP fabrics by preirradiation method. The maximum grafting yield was 3% when only IA was grafted onto PP fabrics, whereas the use of AN as a comonomer increased the amount of IA that reacted with PP fabrics. An increase in the temperature from 40 to 70°C increased the grafting rate. The highest final grafting yield was obtained at 40°C. The addition of 0.01 wt % Mohr's salt to the reaction medium led to a sharp increase of grafting yield. The highest grafting yield was obtained when volume ratio of methanol to DMF is 75 : 25.

A new chelating adsorbent was prepared by subsequent amination of graft copolymer with EDA and PH. The weight increase percentage reached maximum value at about 90% for 80% PP-g-AN-IA fabrics at 90°C. At same amination conditions, the

weight increase percentage is higher when PP-g-AN-IA fabrics react with EDA compared with PH. FTIR data indicate that carboxyl acid, nitrile and amine groups were introduced onto grafted and aminated fabrics, respectively.

DSC test indicated the ΔH_F of grafted fabrics decreased obviously with increasing grafting yield, which due to dilution effect of amorphous grafting chains and disruption of inherent crystal of PP fabrics.

The adsorbent prepared by our method has a very high content of amine groups, which can absorb heavy metallic ions by chelating effect. Now adopting this kind of adsorbent the removal of vanadium ions is carrying on in our research groups by designing a series of adsorption conditions.

References

1. Kavaklı, P. A.; Kavaklı, C.; Seko, N.; Tamada, M.; Güven, O. *Nucl Instrum Methods Phys Res B* 2007, 265, 204.
2. Coşkun, R.; Soykan, C.; Saçak, M. *Sep Purif Technol* 2006, 49, 107.
3. Kabay, N.; Katakai, A.; Sugo, T. *Radiat Phys Chem* 1995, 46, 833.
4. Choia, S. H.; Nho, Y. C. *Radiat Phys Chem* 2000, 57, 187.
5. Lin, W. P.; Hsieh, Y. L. *Ind Eng Chem Res* 1996, 35, 3817.
6. Zu, J. H.; He, S. Q.; Yan, F. *Radiat Phys Chem* 2009, 78, 328.
7. Jeun, J. P.; Zu, J. H.; Kang, P. H.; Nho, Y. C. *J Appl Polym Sci* 2010, 115, 222.
8. Novak, I.; Chodak, I. *J Mater Sci Lett* 1995, 14, 1298.
9. Brandrup, J.; Immergut, E. H.; Grulke, E. A. *Polymer Handbook*. Wiley: New York, 1999, II/196.
10. Nasef, M. M. *Polym Int* 2001, 50, 338.
11. Nasef, M. M.; Saidi, H.; Hashi, K. *J Appl Polym Sci* 1999, 73, 2095.
12. Gupta, B.; Scherer, G. G. *Chimia* 1994, 48, 127.
13. Kabanov, V.; Aliev, R.; Sidorova, L. *Polym Sci Polym Chem Ed* 1980, 18, 871.
14. Gupta, B.; Anjum, N. *J Appl Polym Sci* 2001, 82, 2629.
15. Zevin, L.; Messalem, R. *Polymer* 1982, 23, 601.
16. Mukherjee, A. K.; Gupta, B. *J Appl Polym Sci* 1985, 30, 2253.
17. Gupta, B.; Highfield, J.; Scherer, G. G. *J Appl Polym Sci* 1994, 51, 1659.
18. Isihara, A.; Guth, E. *Adv Polym Sci* 1967, 5, 233.
19. Reluert, J.; Yazdani, P. M. *J Macromol Sci Chem* 1992, 1, 31.