

Electron-Beam-Radiation-Induced Grafting of Acrylonitrile onto Polypropylene Fibers: Influence of the Synthesis Conditions

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ABSTRACT: Electron-beam-radiation-induced grafting of acrylonitrile onto polypropylene fibers was investigated with a pre-irradiation method. Grafting conditions such as the solvents, additives, monomer concentration, radiation dose, and temperature were varied, and the effects on the degree of grafting were studied. The nature of the reaction medium and additives had a considerable influence on the degree of grafting. The dilution of acrylonitrile with *N,N*-dimethylformamide significantly enhanced the degree of grafting in comparison with other solvents. The addition

of sulfuric acid to the reaction mixture led to an increase in the degree of grafting and an acceleration of the rate of grafting. The order of dependence of the rate of grafting on the pre-irradiation dose and monomer concentration was found to be 1.31 and 1.21, respectively, in the presence of sulfuric acid. The activation energy for grafting was calculated to be 21.9 kJ/mol. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 222–228, 2010

Key words: poly(propylene) (PP); radiation

INTRODUCTION

Radiation-induced grafting of vinyl monomers onto hydrophobic polymers has frequently been used to synthesize adsorbents or to produce membranes with particular desired properties.^{1–4} Among all hydrophobic polymers, polypropylene (PP) is one of the most available polymers and has attracted attention as a chelating polymer substrate for various reasons: it is a highly useful thermoplastic, it is broadly used as molding in many extruded forms, and it can be grafted with most kinds of monomers. From the point of view of adsorbent synthesis, the radiation-induced graft polymerization technique is an excellent method for introducing the chelating function into conventional polymers in various forms, such as films, membranes, and fibers.^{5–8} Fibers containing amidoxime groups prepared by the grafting technique have excellent affinity for almost all toxic metals.⁹ Acrylonitrile (AN) is first grafted onto the polymer substrate to synthesize fibers containing amidoxime. Second, the grafted polymer is immersed into a hydroxylamine solution to convert

the cyano groups into amidoxime groups. In some studies, fibers containing amidoxime groups have also been prepared with a binary grafting system.¹⁰

Choi and Gupta^{10–13} reported ⁶⁰Co γ -radiation-induced grafting of AN onto PP or polyethylene with a pre-irradiation method. In their research, the degree of grafting was less than 30%. We adopted an electron-beam radiation source because of its higher dose rate in comparison with γ -ray radiation. It was found that the rate of grafting significantly increased when the radiation source was changed. The degree of grafting yield could reach more than 70% in several minutes.

In this study, the grafting of AN onto PP fibers was carried out to produce fibers with different degrees of grafting. Control of the degree of grafting was easily achieved by the proper selection of the reaction conditions. Our long-term aim is to develop fibers with different degrees of grafting and transform them into fibers containing amide and carboxylic groups so that the material can act as a chelating fiber for the separation and recovery of specific metal ions from industrial waste.

EXPERIMENTAL

Materials

Isotactic PP nonwoven fibers (weight = 40 g/m², thickness = 0.35 mm) were supplied by Korea Nonwoven Tech Co., Ltd., (Korea), and AN (including 0.004% hydroquinone) and *N,N*-dimethylformamide

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(DMF) were obtained from Shaowha Chemical Reagent Co., Ltd. (Japan). Methanol and ethanol were obtained from Kanto Chemical Co. (Japan). All materials were used as supplied.

Grafting procedure

PP fibers were cut into strips (7×3.5 cm) and then dried in a vacuum oven at 60°C to a constant weight. The PP fibers were sealed in polyethylene bags after the atmosphere in the bags was replaced by purified nitrogen. The sealed PP fibers were irradiated by electron beams from an accelerator with a beam energy of 10 MeV and a current of 1 mA. The irradiated fibers were kept in liquid nitrogen before the grafting reaction.

Grafting was carried out in a Pyrex tube. The solvent and AN were added first. After 15 min of bubbling with nitrogen, a preweighed amount of pre-irradiated fibers was immersed in a Pyrex tube containing the mixture of AN and the solvent. The mixture was deaerated by 5 min of bubbling with nitrogen, and the Pyrex tube was sealed. The grafting reaction was carried out in a water bath maintained at a constant temperature. After the reaction, the grafted membrane was removed, washed thoroughly with DMF several times, and immersed in DMF for 8 h at 70°C to eliminate the unreacted monomer and the homopolymer that had accumulated on the surface of the fibers. The fibers were dried in a vacuum oven at 60°C to a constant weight. The degree of grafting was calculated with the following equation:

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

where W_0 and W_g are the weights of the ungrafted and AN-grafted fibers, respectively.

Characterization

Fourier transform infrared/attenuated total reflectance spectra of the ungrafted and AN-grafted PP films were analyzed with a Bruker (Germany) Tensor 37 spectrometer. The surface morphology of the PP fibers was investigated with scanning electron microscopy (SEM). Detailed images of PP fibers were obtained with SEM (JSM-5200, JEOL, Japan). The SEM samples were gold-sputtered before observation. Thermogravimetric analysis (TGA) was conducted with a TA Instrument (USA) SDT Q600 at a heating rate of $10^\circ\text{C}/\text{min}$ from 50 to 600°C ; the TGA samples were cut into small pieces and were machined with a mechanical grinder to maintain sample weights between 9 and 11 mg. All TGA tests were run in nitrogen gas.

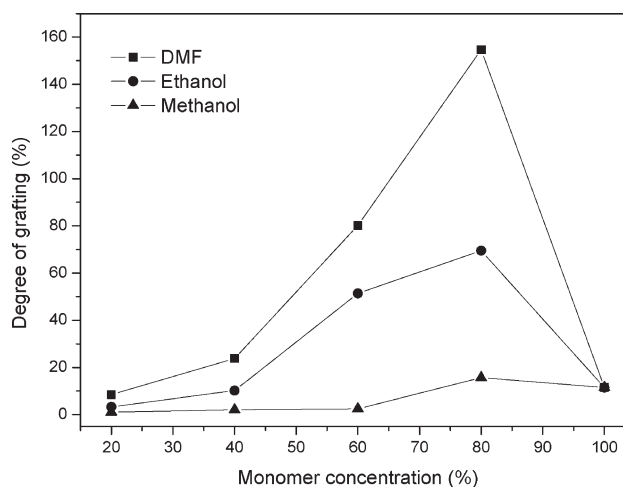


Figure 1 Variation of the degree of grafting with the monomer concentration in various solvents (pre-irradiation dose = 200 kGy, temperature = 60°C , time = 3 h).

RESULTS AND DISCUSSION

Effect of the solvents on the degree of grafting

The effect of the type of solvent on the grafting yield is shown in Figure 1. The employed solvents include methanol, ethanol, and DMF. The grafting yield increases with an increase in the monomer concentration up to 80% and then decreases abruptly. This is related to the swelling behavior of PP in the grafting reaction and subsequent availability of the monomer to grafting sites. It can be explained as follows: AN is a nonsolvent for polyacrylonitrile (PAN) chains and diminishes the swelling of the grafted PP; hence, the diffusion of the monomer through the grafted zone is reduced, and this leads to a low graft yield. Diluting AN with DMF was found to cause a large increase in the degree of grafting versus that obtained by dilution with methanol and ethanol. The results can be explained if we take into account the solubility parameter and the nature of the three solvents. DMF strongly affects the degree of fiber swelling, whereas methanol and ethanol have an impact on the termination step of the graft growing chains. The solubility parameter of PP is 9.4, which is close to that of DMF (12.1) versus those of methanol (14.5) and ethanol (13.0). This would lead to greater swelling of PP in DMF than in methanol and ethanol. Furthermore, PAN dissolves in DMF, and this also contributes to the increase in the degree of grafting. On the contrary, when the graft reaction is carried out in solutions of ethanol and methanol, the low swelling rate of the grafted layers leads to a slower diffusion rate of the monomers in comparison with that obtained with DMF as the solvent. However, the high chain transfer constant of methanol or ethanol causes fast termination of growing PAN chains. This is accompanied by insolubility of

the PAN homopolymer formed in methanol or ethanol, which leads to an increase in the viscosity of the grafting medium, and therefore AN diffusion is hindered; this leads to surface grafting. For different radiation-induced grafting systems, different solvents bring about the best swelling of the base polymer and hence enhance monomer accessibility to the grafting sites.¹⁴ Accordingly, the correct choice of solvents is one of the essential elements in obtaining higher degrees of grafting.¹⁵ It has been established already that the nature of the solvent determines not only the degree of grafting but also the location of grafting. If a good-swelling solvent is used, bulk grafting is highly favored, and homogeneous grafting is most likely obtained. This is very important for achieving chelating fibers with good performance for the treatment of metal ions.

Effect of the additive on the degree of grafting

Adding sulfuric acid to the reaction medium leads to an acceleration in the degree of grafting. A sharp increase in the degree of grafting was observed when only 0.01 mol of sulfuric acid was added (Fig. 2). This behavior was also reported by Gupta et al.¹⁶ for the grafting of AN onto PP monofilaments by the pre-irradiation method in the presence of air. In their studies, they reported that the higher the sulfuric acid concentration was, the greater the homopolymerization was. Gupta et al. concluded that the presence of an acid favors the decomposition of hydroperoxide, which forms a large amount of OH·, which can then initiate homopolymerization. In our research, PP fibers were irradiated in a nitrogen atmosphere, so there could be no formation of hydroperoxides. We also found that homopolymerization was generated very quickly by the addition of 0.01 mol of sulfuric acid to the reaction medium. The formation of extensive homopolymerization enhanced the viscosity of the medium. The movement of high-molecular-weight grafting chains was inhibited, and this hindered termination by combination with other growing chains; however, the movement of low-molecular-weight monomers was not affected by the high viscosity of the medium. The rate of chain propagation was faster than chain termination. The addition of sulfuric acid caused the Trommsdorff phenomenon in our grafting medium, so the degree of grafting increased remarkably.¹⁷

The mechanism of acid enhancement in the process of grafting onto polyolefins and cellulose was initially understood to be a purely radiolytic phenomenon in which the irradiation of the solvent increases the hydrogen atom yield.¹⁷⁻¹⁹ The hydrogen radicals can abstract hydrogen atoms from the polymer substrate and create additional sites for grafting initiation.^{17,18} As was later revealed, there

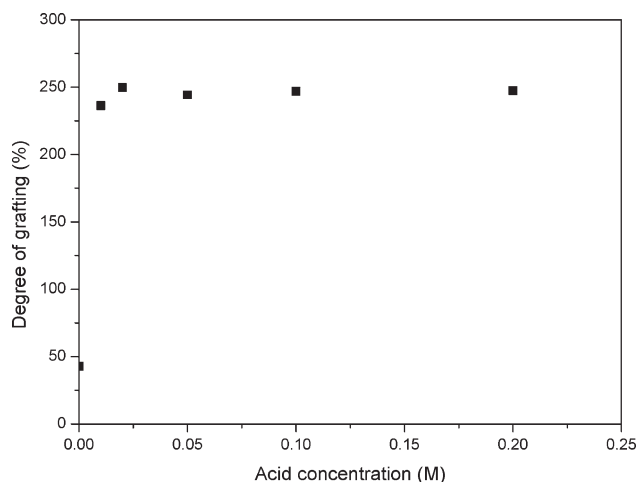


Figure 2 Effect of the sulfuric acid concentration on the degree of grafting [pre-irradiation dose = 200 kGy, monomer concentration = 60%, temperature = 60°C, time = 3 h, reaction medium = DMF, additive (sulfuric acid) = 0.1 mol/L].

were some discrepancies with this theory. An enhancement in the degree of grafting was also seen when the pre-irradiation method was adopted. Later, it was found that an acid changes the partition coefficient of the monomer between the polymer substrate and the external liquid phase, leading to an increase in the monomer concentration around the growing chains. More research is needed to give a proper explanation of the effects of acids on the grafting process. However, adding sulfuric acid to the grafting mixture is an effective method for enhancing the degree of grafting of AN onto PP. The role of acids is important in radiation grafting processes because the required radiation dose or monomer concentration can be lowered in the presence of an acid. We predict that this approach will become an effective and economical method for the preparation of chelating fibers with good adsorption abilities.

Effect of the reaction time on the degree of grafting at different doses

The degree of grafting at 60°C versus pre-irradiation doses is shown in Figure 3. The degree of grafting increases sharply in the beginning for all doses and then levels off. This is a general observation made by many researchers. Irradiation of PP chains is always more or less accompanied by the fragmentation of PP and so reduces the molecular weight. It is generally accepted that the degradation of PP proceeds only through β scission, and the degree of degradation depends on the radiation dose. However, the higher the radiation dose is, the higher the achieved rate of grafting is. This behavior may be attributed to the fact that at higher doses, the number of radicals generated in the PP fibers also

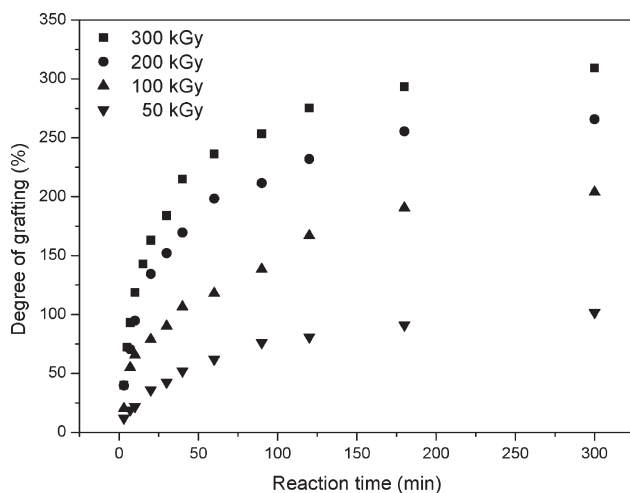


Figure 3 Variation of the degree of grafting with the reaction time at various irradiation doses [monomer concentration = 60%, temperature = 60°C, reaction medium = DMF, additive (sulfuric acid) = 0.1 mol/L].

increases, and more radicals lead to increased grafting. Figure 4 shows the relationship between the initial rate of grafting and the pre-irradiation doses. The initial rates of grafting at different pre-irradiation doses were calculated from the slopes of the corresponding curves in Figure 3 during the initial stage of the grafting reaction. From the slope of the plot, the dependence of the grafting rate on the dose was found to be 1.31. This value is higher than the value for classical free-radical polymerization (0.5). The higher dependence of the grafting rate on the irradiation dose indicates that the radicals produced during irradiation are highly efficient in initiating grafting. The possibility of deactivation of the trapped radicals by mutual recombination can be neglected. A higher dependence of the grafting rate on the pre-

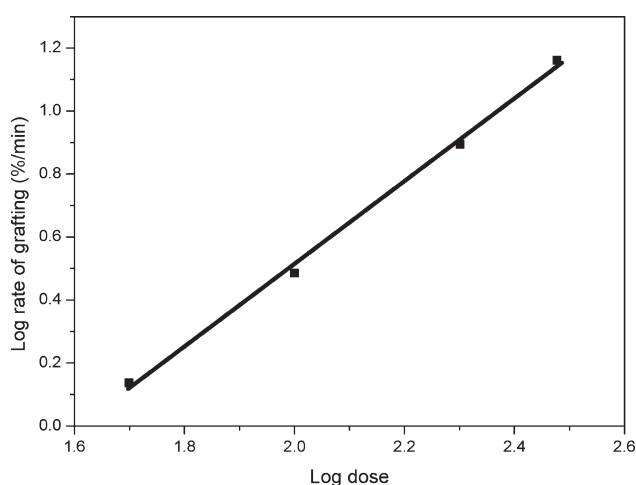


Figure 4 Log-log plot of the initial rate of grafting versus the pre-irradiation dose.

irradiation dose of 1.30 was also reported for the grafting of acrylamide onto PP films by Hegazy.²⁰

Effect of the reaction time on the degree of grafting at different monomer concentrations

Figure 5 shows that the degree of grafting increases with the reaction time and reaches equilibrium at 1 h. The higher the monomer concentration is, the higher the achieved degree of grafting is. The grafting depends largely on the monomers available to the radical sites within the fibers. At a higher monomer concentration, the availability of AN in the fibers increases. One important requirement for monomers to diffuse into the bulk of the fiber is high swelling in the grafting medium. If the dilution of the monomer has an impact on the swelling of the grafted matrix, then the diffusion rate of the monomer will be influenced accordingly. Fortunately, grafted copolymer chains swell in DMF, which is used to dilute the monomer. As a result, this also enhances the degree of grafting. A log-log plot of the initial rate of grafting versus the monomer concentration is presented in Figure 6. The order of dependence of the rate of grafting on the monomer concentration was found to be 1.21 from the slope of the plot. This value is larger than the formula for classical radical polymerization:

$$R_g \propto [M]$$

where R_g is the rate of grafting and $[M]$ is the monomer concentration. Gupta et al.¹⁶ reported the grafting of acrylamide onto PP monofilaments with the pre-irradiation method in the presence of air. The dependence of the rate of grafting on the monomer concentration was also very high (1.86) in that

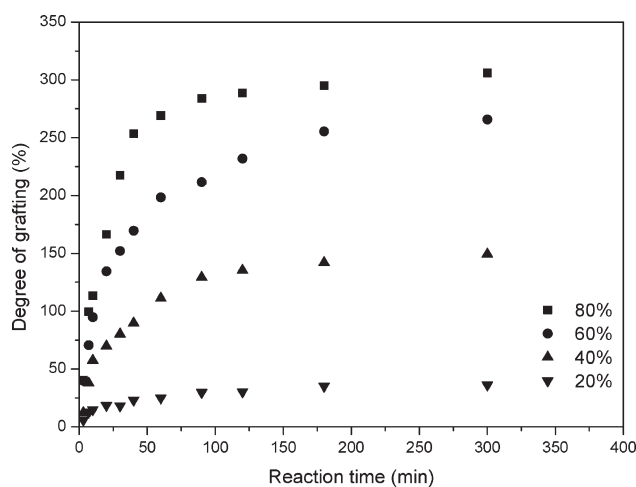


Figure 5 Variation of the degree of grafting with the reaction time at various monomer concentrations [pre-irradiation dose = 200 kGy, temperature = 60°C, reaction medium = DMF, additive (sulfuric acid) = 0.1 mol/L].

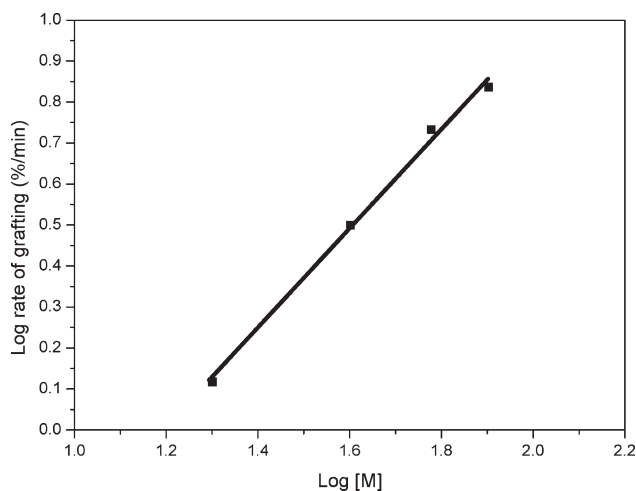


Figure 6 Log-log plot of the initial rate of grafting versus the monomer concentration ($[M]$).

grafting system. The grafting reaction takes place by a diffusion-controlled mechanism. The initial grafting takes place at the fiber surface. These grafted surface layers swell in the grafting medium, and further grafting proceeds deep into the middle of the fiber by progressive diffusion of the monomer through the swollen grafted layers. The grafted copolymer, swollen in DMF, leads to a high viscosity of the grafted layers. The viscosity is so high that monomer diffusion through grafted layers to the grafting site is hindered. The propagation rate may be considerably lowered, and the rate of termination due to the interaction of two growing polymer chains is also hindered in the high-viscosity medium. As a result, many of the growing chains are terminated by chain transfer because of impurities present in the grafting medium, and this leads to the higher dependence of the rate of grafting on the monomer.²¹

From these results, the kinetic equation for the grafting of AN onto PP fibers can be presented in the form of the following expression:

$$R_g \propto [M]^{1.21} [D]^{1.31}$$

where D is the pre-irradiation dose.

This equation demonstrates that the grafting rate depends not only on the efficiency of the reaction between trapped radicals and the monomers but also on the rate of diffusion of monomers toward the grafted layers.

Effect of the reaction temperature on the degree of grafting

Figure 7 shows the degree of grafting versus the reaction time at different temperatures with a 200-

kGy pre-irradiation dose. In the initial reaction stage, the grafting rate increases with an increase in the reaction temperature. This may be explained by the fact that during this period, the radical concentration on the substrate is very high, so the grafting reaction is controlled by the rate of monomer diffusion. The higher temperature allows more monomers to react with substrate radicals, and this results in higher grafting rates under the same reaction conditions. After the reaction has continued for 1 h, the degree of grafting remains almost constant at different temperatures. This can be attributed to the decay of the trapped radicals or the termination of growing chain radicals before monomers diffuse into grafting sites. In summary, the pre-irradiation graft reaction is controlled by two factors: (1) the rate of decay of the substrate radicals and (2) the monomer diffusion rate. An increase in the reaction temperature can speed up the diffusion rate of the monomers, but at the same time, it also accelerates the rate of decay of the substrate radicals.

Activation energy of the grafting reaction

An Arrhenius plot of the initial rate of grafting versus the inverse of temperature is presented in Figure 8, demonstrating a linear dependence over the temperature range of 30–70°C. The overall activation energy, calculated from the slope of the plot and the Arrhenius formula [$\log k = -E/(2.303RT)$, where k is the rate constant, E is the activation energy, R is the gas constant, and T is the temperature], was 21.9 kJ/mol. The grafting process includes not only the diffusion of AN into the PP matrix but also the reactivity of radicals. Because of the complexity of the system, the overall activation energy of the grafting process may be termed the apparent activation

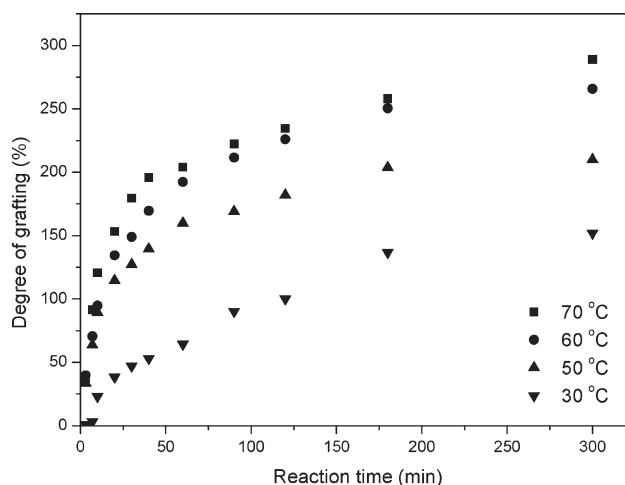


Figure 7 Variation of the degree of grafting with the reaction time at various temperatures [pre-irradiation dose = 200 kGy, monomer concentration = 60%, reaction medium = DMF, additive (sulfuric acid) = 0.1 mol/L].

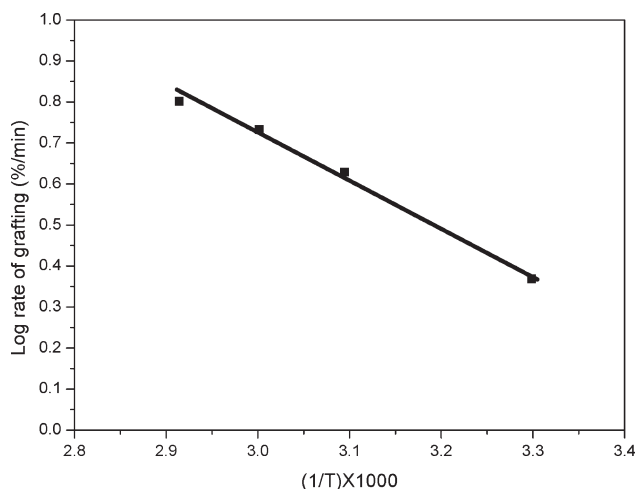


Figure 8 Arrhenius plot of the rate of grafting versus $1/T$ (where T is the temperature).

energy (E_a). E_a can be expressed as $E_a = (1/n)E_i + E_p - (1/n)E_t$. If two radicals terminate, n is 2; if a single radical terminates, n is 1. E_i , E_p , and E_t are the activation energies of chain initiation, chain propagation, and chain termination, respectively. When graft copolymerization is initiated by an initiator, $E_i \approx 120\text{--}200$ kJ/mol. E_i is so high that graft copolymerization initiated by an initiator cannot take place at low temperatures. On the other hand, when graft copolymerization is induced by radiation, $E_i \approx 0$, and E_t can be neglected. Then, E_a can be replaced by E_p , which is 8–32 kJ/mol. Because of the lower E_a value in comparison with reactions initiated by an initiator, radiation-induced graft copolymerization can be carried out at relatively low temperatures, and this may lead to new products in the absence of competing side reactions. In addition, radiation-induced graft copolymerization may result in a purer product because when radiation replaces the initiator, contamination resulting from incomplete removal of the catalyst is not a problem.

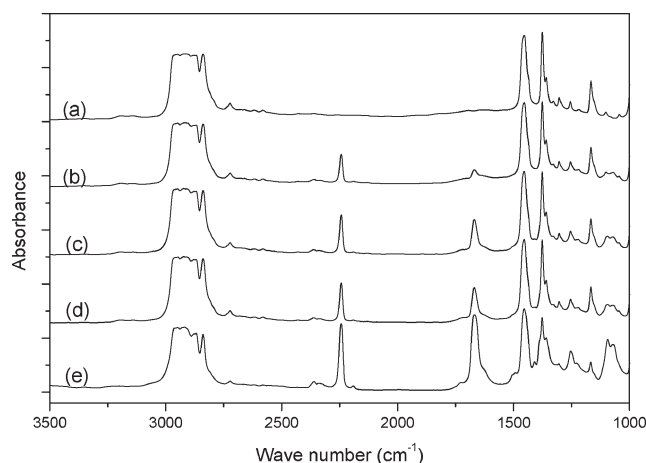


Figure 9 Fourier transform infrared spectra of (a) ungrafted PP, (b) AN-g-PP with a degree of grafting of 91%, (c) AN-g-PP with a degree of grafting of 190%, (d) AN-g-PP with a degree of grafting of 246%, and (e) AN-g-PP with a degree of grafting of 293%.

Characterization of the grafted fibers

The grafted fibers were analyzed by IR spectroscopy (Tensor 37, Bruker). Figure 9(a) presents the spectrum of the ungrafted fiber, and Figure 9(b–e) presents the IR spectra of the grafted PP fibers with different degrees of grafting. The prominent bands in the PP fiber appear at 1460 and 2800–3000 cm^{-1} , which correspond to C–H bending and stretching vibrations. A characteristic peak at 2243 cm^{-1} appears in the IR spectrum of grafted PP fibers and is due to the cyano groups of PAN. The peak intensity at 2243 cm^{-1} increases with increases in the degree of grafting.

To demonstrate the topological changes in the grafting reactions, the micrographs of the prepared samples are presented with instrument magnification. Figure 10 shows SEM images of the ungrafted and AN grafted PP fibers. The diameter of the fiber

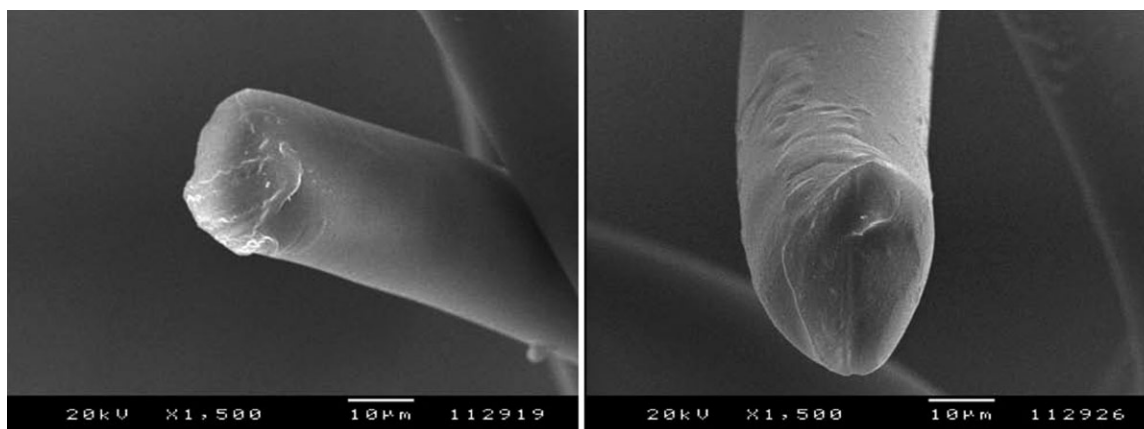


Figure 10 SEM images of (left) ungrafted and (right) AN-g-PP (degree of grafting = 91%) fiber surfaces.

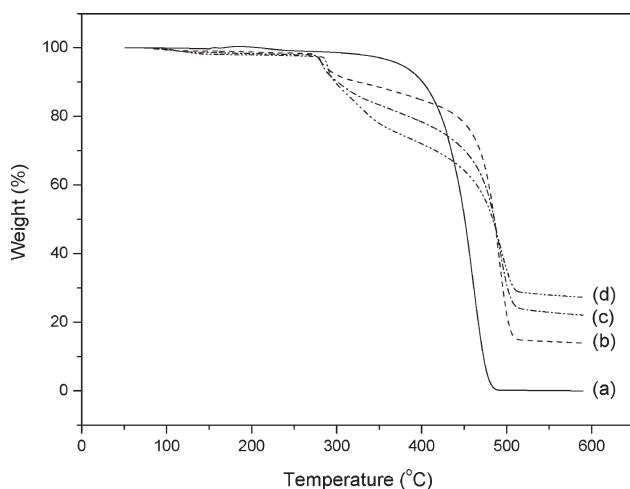


Figure 11 TGA of (a) ungrafted PP, (b) AN-g-PP with a degree of grafting of 91%, (c) AN-g-PP with a degree of grafting of 190%, and (d) AN-g-PP with a degree of grafting of 246%.

increased obviously after the grafting polymerization, and the smooth surface of the pristine PP fiber became rough. A heterogeneous grafting layer formed on the surface of the fiber, and this resulted in the fiber becoming thick and coarse.

The degradation process and thermal stability of ungrafted and grafted PP fibers were evaluated through TGA experiments, and the results are shown in Figure 11. The overall degradation of ungrafted PP [Fig. 11(a)] involved only a single step. The sample began to decompose at 420°C. However, the grafted PP [Fig. 11(b–d)] had a different course of thermal degradation in comparison with pristine PP. Two consecutive weight-loss steps were observed in grafted PP. The first stage occurred in the range of 270–280°C and corresponded to the degradation of PAN, and the second weight loss occurred in the range of 470–480°C and corresponded to the thermal decomposition of PP. However, the final residue at 600°C increased with the AN grafting yield increasing. This phenomenon can be explained as follows: the amount of residue was dependent on the molecular weight of PAN.²² The molecular weight of the grafted PAN increased with the increase in the grafting yield.

CONCLUSIONS

Electron-beam-radiation-induced grafting of AN onto PP fibers was investigated with the pre-irradiation method. The degree of grafting could be easily controlled by the proper selection of the reaction conditions. The nature of the solvent and additives played an important role in the grafting reaction. A

higher degree of grafting was obtained by the dilution of AN with DMF, but methanol and ethanol led to a lower degree of grafting. The addition of sulfuric acid to the grafting mixture further enhanced the degree of grafting and was an effective method for obtaining a graft copolymer at low expense.

The grafting kinetic equation was calculated as follows:

$$R_g \propto [M]^{1.21} [D]^{1.31}$$

The grafting reaction depended on the efficiency of the trapped radicals in initiating the grafting reaction and on the monomer diffusion rate toward the grafted layers. The activation energy of the grafting reaction was 21.9 kJ/mol.

The absorption peaks of cyano groups appeared in the IR spectrum of the grafted fibers when AN was grafted onto PP, and the thermal stability of grafted PP fibers increased with the grafting yield increasing.

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