

# Radiation-Induced Graft Polymerization of Glycidyl Methacrylate Onto PE/PP Nonwoven Fabric and Its Modification Toward Enhanced Amidoximation

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**ABSTRACT:** A nonwoven fabric made of polypropylene coated by polyethylene was used as the trunk polymer in the preparation of a highly efficient new adsorbent. Metal ion uptake capacity has been aimed to be increased by introducing double amidoxime groups per repeating unit of the chains grafted to trunk polymer. The base polymer was irradiated by electron beams with a dose of 200 kGy under N<sub>2</sub> atmosphere and glycidyl methacrylate (GMA) was grafted onto irradiated nonwoven fabric. Grafting conditions were optimized, and GMA-grafted polymer was modified with 3,3'-iminodipropionitrile in ethanol at 80°C. GMA grafting (150%) was determined to be the optimum degree given that higher extent of

grafting rendered the materials brittle. Pendant nitrile groups were then amidoximated by using 6% hydroxylamine in methanol–water mixture (1 : 1). The all-polymeric structures were characterized by using FTIR, SEM, and thermal analysis methods, confirming the grafting, modification, and amidoximation stages gravimetrically, spectroscopically, and visually. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 1551–1558, 2007

**Key words:** fibers; electron beam irradiation; graft copolymers; adsorption; functionalization of polymers

## INTRODUCTION

The design and synthesis of polymer supported reagents that can selectively complex metal ions from multi-component solutions have been an important area of research during the last decades. Chelating resins and fibers are effective adsorbents used to enrich and separate various metal ions. Uranyl ions have been one of the target ions to be removed from aqueous systems. The concentration of uranium in seawater is about 3 mg/m<sup>3</sup>. To recover an economically significant quantity of uranium from seawater, an adsorption method using a suitable solid adsorbent seems to be feasible with regard to economical and environmental impacts. Extensive investigations of adsorbents capable of recovering uranium from seawater and aqueous systems have been carried out during the last two decades especially in Takasaki Radiation Chemistry Research Establishment, and the results compiled recently in a nomogram by Saito and Sugo.<sup>1</sup> Among various organic resins, chelating resins containing amidoxime groups have been selected for their selectivity toward uranyl ions in the works of Egawa and Harada<sup>2–4</sup> and Asthemier and Schenk.<sup>5</sup>

Amidoxime chelate fibers typically contain functional amidoxime (—C=NOH(NH<sub>2</sub>)) groups that can chelate some metal ions and create stable chelating systems, so that very pure metal ions can be obtained by elution. Conventionally, amidoxime group-containing adsorbents are synthesized through the reaction of acrylic resins and hydroxylamine. The acrylic resin used is generally made from a copolymer of acrylonitrile and crosslinked monomer such as divinyl benzene, which has been extensively studied by Okamoto et al.<sup>6</sup> and Omichi et al.<sup>7</sup> Amidoxime chelate fibers have been presented by Sugo et al.<sup>8–10</sup> and Lin et al.<sup>11</sup> and found it to be very useful for recovering uranium from seawater and enriching or separating noble metal ions from aqueous systems. Various attempts have also been made to introduce hydrophilic monomers, and enhancement of uranyl selectivity into copolymeric adsorbents by Güven et al.<sup>12–15</sup> Work on fibrous systems has generated wide interest in the last decade because of improvements with respect to flow rate through such porous adsorbents and the mechanical stability of the fibers.

Radiation-induced grafting is a powerful tool capable of controlling the introduction of various functional groups to the polymeric materials, keeping the original properties and especially the mechanical strength of the base material, and thus, allowing the synthesis of more stable polymeric adsorbents.<sup>8</sup>

Nonwoven fabrics can be easily functionalized by radiation-induced graft polymerization (RIGP). In this

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work, nonwoven PP fabric coated by PE was used as the trunk polymer, and by RIGP of precursor monomer, glycidyl methacrylate (GMA,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{COOCH}_2\text{CHOCH}_2$ ), and subsequent chemical modification with 3,3'-iminodipropionitrile ( $\text{NH}(\text{—CH}_2\text{—CH}_2\text{—CN})_2$ ), a copolymer with enriched acrylonitrile groups was synthesized and this polymer was reacted with hydroxylamine to obtain graft chains containing two amidoxime groups per repeating unit.

## EXPERIMENTAL

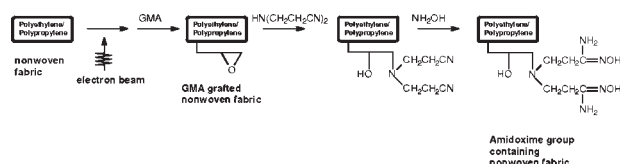
### Materials and methods

Nonwoven fabric polypropylene coated by polyethylene fiber was supplied by Kurashiki Sen-I Kako (Okayama, Japan). Methacrylic acid glycidyl ester was purchased from Tokyo Kasei (Japan). Iminodipropionitrile was purchased from Kanto Chemical Co., Tokyo, Japan and used without purification. Other reagents were of analytical or higher grade. A 6 (w/v) % solution of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) was prepared using 50/50 (v/v) % water/methanol as the solvent, and its pH was adjusted to 7 with solid KOH.

### Preparation of nonwoven fabric containing graft chains with two amidoxime groups per repeating unit

The preparation of nonwoven fabric grafted with side chains containing two amidoxime groups per monomeric unit requires the three steps as illustrated in Figure 1 (1) grafting of an epoxy-group containing monomer, GMA by preirradiation grafting technique; (2) modification of epoxy group with 3,3'-iminodipropionitrile; and (3) amidoximation reaction of CN groups on the grafted chains.

Firstly, GMA was grafted onto PE coated PP nonwoven fibers by preirradiation technique: irradiation by electron beam was performed in nitrogen atmosphere at ambient temperature using a cascade electron accelerator (Dynamitron, IEA-3000-25-2, Radiation Dynamics) which was operated at a voltage of 2 MeV and current of 1 mA at Takasaki Radiation Chemistry Research Establishment, Japan Atomic Energy Research Institute (JAERI). The concentration of GMA



**Figure 1** Schematic preparation of polymeric fiber adsorbent containing two amidoxime groups per repeating unit of grafted chains.

solution was set at 10 (w/w) % in methanol as the solvent. The degree of grafting, defined below, was calculated from the weight gain.

$$\text{Degree of grafting (\%)} = 100[(W_1 - W_0)/W_0] \quad (1)$$

where  $W_0$  and  $W_1$  are the weights of the trunk and GMA grafted nonwoven fibers in dry state, respectively.

Secondly, the GMA-grafted nonwoven fabric was immersed in 0.425M 3,3'-iminodipropionitrile in ethanol solution. The reaction was performed at 80°C for different time periods to construct the conversion curve. After binding of iminodipropionitrile groups onto the epoxy group of grafted polymer branches, the remaining unreacted epoxide groups were hydrolyzed with acid solution for 2 h at 80°C. Subsequently nonwoven fabric was washed with methanol and then was dried at room temperature and in a vacuum oven at 40°C. The percent replacement of the epoxide groups with the iminodipropionitrile group was calculated as follows:

$$\text{Conversion(\%)} = \text{mmol iminodipropionitrile/mmol GMA} \quad (2)$$

Finally, 6 (w/v) % solution of hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) was prepared using 50/50 (v/v) % water/methanol as the solvent, and its pH was adjusted to 7 with KOH. The iminodipropionitrile (IDPN) grafted nonwoven fabrics were immersed in the hydroxylamine solution at 80°C to convert the cyano groups into amidoxime (AO) groups for reaction times ranging from 0.5 to 2 h. AO group density was evaluated as follows:

$$\text{AO density (mmol/g)} = 1000(W_3 - W_2)/33/W_2 \quad (3)$$

where  $W_3$  and  $W_2$  are the weights of the amidoximated nonwoven fiber and IDPN nonwoven fabric, respectively. The molecular weight of the hydroxylamine is 33. After the completion of amidoximation reaction, amidoximated graft polymer was treated with 2.5% KOH solution at 80°C for 2 h, and followed by washing with pure water until the washing was alkali-free.

### Characterization of trunk and grafted nonwoven fabrics

#### FTIR analysis

To characterize the structure of trunk PP/PE nonwoven fiber and fiber grafted with GMA modified with iminodipropionitrile and amidoximated, small pieces were cut and mixed with KBr and then pressed into thin pellet forms. The spectra of all samples were taken by Nicolet 520 FTIR spectrophotometer.

### Thermogravimetric analysis (TGA)

The thermogravimetric analyses were performed by utilizing Du Pont Instruments-Thermal Analyser, Model 951. Thermogravimetric studies were carried out under dry nitrogen atmosphere and 10°C/min heating rate.

### Differential scanning calorimeter (DSC)

Du Pont Instruments-Thermal Analyser, equipped with DSC module 910 was used to investigate DSC behavior of samples under the conditions mentioned earlier.

### Scanning electron microscopy (SEM)

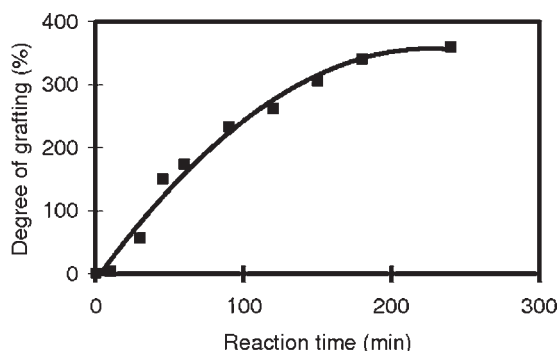
Scanning electron microscope (SEM) pictures were taken for pristine and grafted and modified samples coated with gold layer by using Hitachi scanning electron microscope.

## RESULTS AND DISCUSSION

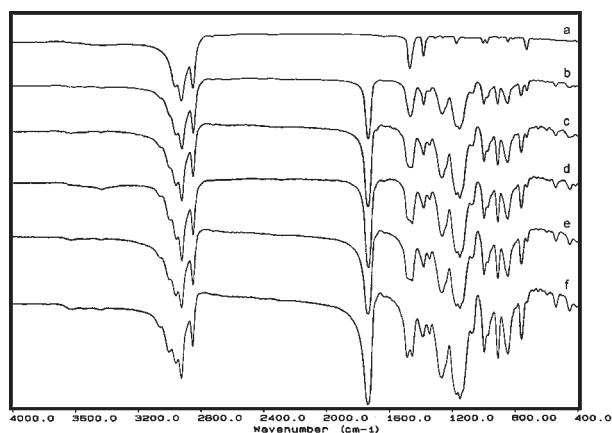
### Characterization by FTIR

#### Grafting of GMA onto trunk nonwoven fabric

The degree of GMA grafting (dg) on nonwoven fabric (polypropylene fiber coated by polyethylene) previously irradiated to a total dose of 200 kGy by an electron accelerator is shown in Figure 2 as a function of reaction time. The optimum GMA grafting conditions were previously determined to be 10 w/w % GMA/methanol at 40°C.<sup>16</sup> As can be seen from Figure 2, degree of grafting increases almost linearly with increasing reaction time up to 100 min. The degree of grafting reached about 350% (w/w) upon contacting the e-beam activated trunk polymer with the GMA solution for 3 h. After 3 h reaction time, no appreciable increase in grafting of GMA was observed and equilibrium degree of grafting value was reached.



**Figure 2** Grafting of GMA onto trunk PP/PE fiber, preirradiated to 200 kGy by accelerated electrons.



**Figure 3** The FTIR spectra of (a) trunk polymer, (b) 58%, (c) 150%, (d) 175%, (e) 200%, and (f) 300% GMA grafted polymer.

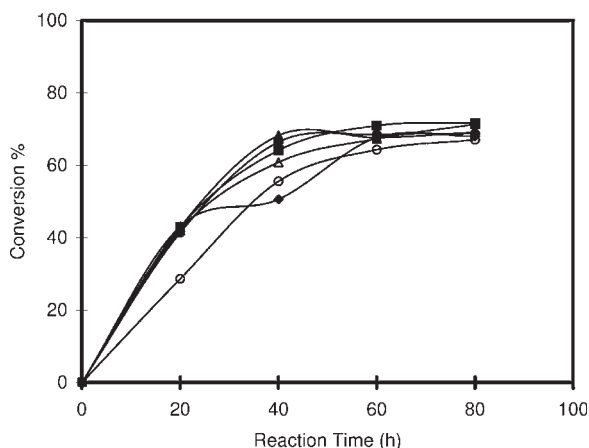
The FTIR spectra of trunk polymer and 58, 150, 175, 200, and 300% GMA-grafted polymers are presented in Figure 3. The characteristic absorption bands of  $-\text{CH}_3$  antisymmetric stretching (at  $2966\text{ cm}^{-1}$ ),  $-\text{CH}_2$  antisymmetric stretching (at  $2917\text{ cm}^{-1}$ ), and  $-\text{CH}_2$  symmetric stretching (at  $2847\text{ cm}^{-1}$ ) groups were observed in the FTIR spectrum of trunk polymer. Upon grafting of GMA onto the trunk polymer, the additional bands, which are characteristic of GMA structure, appeared. The  $-\text{CH}$  stretching vibrations of epoxy rings occur in  $3065\text{--}3008\text{ cm}^{-1}$ . The  $-\text{C}=\text{O}$  stretching vibration band belonging to GMA at  $1736\text{ cm}^{-1}$  and symmetrical stretching frequency of the epoxy ring, all ring band stretching and contracting in phase occurring at  $1265\text{ cm}^{-1}$  are clearly seen.<sup>17</sup>

#### Functionalization of GMA-grafted polymer with IDPN

As has been explained in detail in the experimental part, the epoxy rings of GMA grafts were tried to be opened by attaching iminodipropionitrile groups. Figure 4 shows the percent replacement of the epoxide groups by IDPN groups for fibers with different degree of GMA grafts as a function of reaction time. The extent of conversion value was calculated by using eq. (2) given in the experimental part.

Figure 4 shows that the conversion of epoxy groups has not been fully completed and a maximum of 70% conversion has been achieved for all systems. This may be due to inactivation of some epoxy groups during the grafting process and difficulty in access to sterically hindered epoxy groups, especially at high degree of grafts.

Depending upon the degree of grafting and replacement by IDPN, the nonwoven cloth became increasingly less flexible and it was observed that at higher degrees of grafting ( $>150\%$ ), the cloth became even brittle. Considering these limitations 150% of GMA



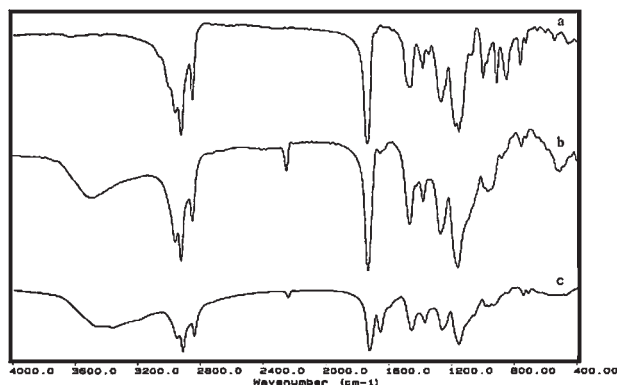
**Figure 4** Conversion of epoxide groups of GMA graft chains with various degree of grafting into iminopropionitrile, (◆)58%, (■)151%, (▲)175%, (●) 266%, (△) 307%, and (○) 340%.

grafting and 80 h of IDPN reaction time were selected as optimum conditions for the preparation of GMA-grafted fibers containing iminodipropionitrile pendant groups. The graft fibers synthesized under these conditions were later used in all experimental studies for characterization and further metal ion uptake studies.

The FTIR spectra of 150% GMA-grafted polymer and its 3,3'-iminodipropionitrile modified form prepared at different reaction times is given in Figure 5. A sharp band at  $2249\text{ cm}^{-1}$  very characteristic of  $\text{C}\equiv\text{N}$  band and new absorption bands between  $1000$  and  $1100\text{ cm}^{-1}$  region for  $\text{C}\equiv\text{N}$  stretching vibration which come from 3,3'-iminodipropionitrile structure are clearly seen in Figure 5(b). The broad hydroxyl band, which originates from ring opening of epoxy group, was observed in the  $3400\text{--}3800\text{ cm}^{-1}$  region.

#### Amidoximation of functionalized GMA grafts

The final aim of this study was to prepare a new fibrous adsorbent containing surface grafted chains car-



**Figure 5** FTIR spectra of (a) 150% grafted polymer (b) 150% grafted polymer modified with 3,3'-iminodipropionitrile at 80 h, and (c) amidoximation of modified graft polymer at 1.5 h.

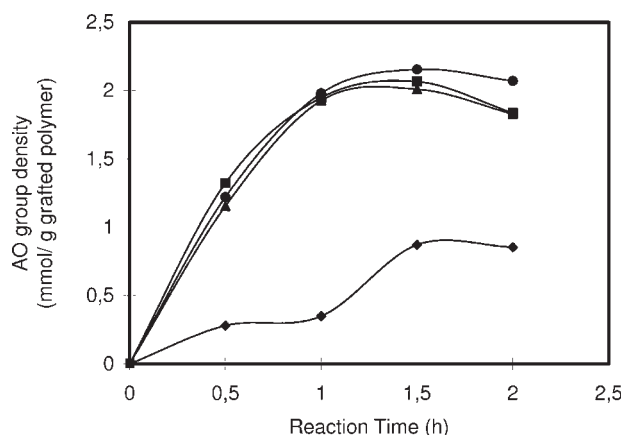
rying excess amidoxime groups. This has been tried to be reached by converting the double nitrile groups attached to epoxy units of GMA chains into amidoxime (AO) groups. The nitrile groups were converted into AO groups by reacting them with  $\text{NH}_2\text{OH}$ . The AO group density was calculated by using eq. (3). The density of AO groups reached a maximum at 1.5 h of contact time as given in Figure 6. The density of AO groups slightly decreases at longer reaction times. This is assumed to be due to degradation of the GMA groups after 1.5 h of reaction time. For 58% GMA-grafted fiber, the density of amidoxime groups showed lower values,  $0.85\text{ mmol/g}$  product. The other grafts, however, showed similar behavior yielding an AO density of  $2\text{ mmol/g}$  fiber at around 1.5 h of reaction time.

After 1.5 h of amidoximation time,  $\text{C}\equiv\text{N}$  band at  $2249\text{ cm}^{-1}$  was observed to decrease because of the depletion of CN groups of original samples from the FTIR study in Figure 5(c) with the appearance of  $\text{C}=\text{N}$  stretching vibration at  $1650\text{ cm}^{-1}$  indicating the formation of amidoxime groups.

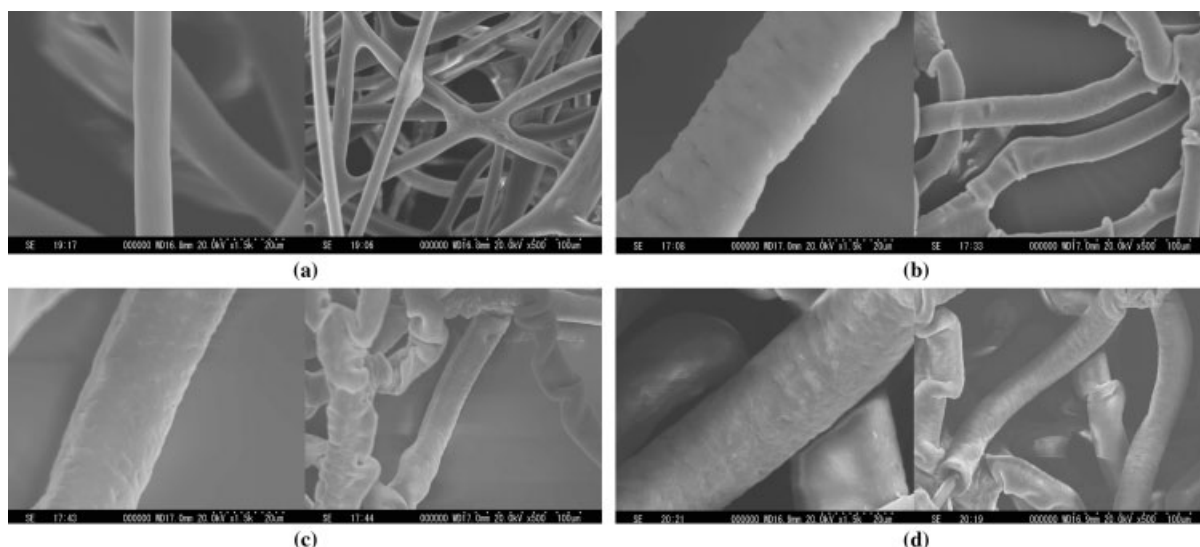
#### Characterization by SEM

Characterization of the nonwoven fibers by SEM was made to compare the difference in the physical appearance of grafted and original samples, functionalized and amidoximated samples, and to see if there were any observable physical changes on the fibers which might have occurred during the conversion process and subsequent treatment with iminodipropionitrile or after amidoximation reaction.

SEM photographs of trunk polymer, 150% GMA-grafted nonwoven fiber, iminodipropionitrile modified, and amidoximated fibers are given in Figure 7 (a-d). The average diameters of the fibers of trunk polymer and 150% GMA-grafted fibers are deter-



**Figure 6** Amidoxime group density versus amidoximation time for various degrees of grafts, (◆)58%, (■)151%, (▲)175%, and (●) 266%.



**Figure 7** SEM photographs of (a) trunk nonwoven fiber, (b) 150% GMA-grafted nonwoven fiber, (c) IDPN modified nonwoven fiber, and (d) amidoximated nonwoven fiber, at two different magnifications (500 $\times$  and 1500 $\times$ ).

mined to be 11.6 and 27.4  $\mu\text{m}$ , respectively. The iminodipropionitrile modified and amidoximated fibers have average diameters of 27.6 and 27.6  $\mu\text{m}$ , respectively. The increase in the diameter of fibers after grafting with GMA and change in their physical appearance are the additional physical evidences for the grafting process. No physical changes have been observed upon amidoximation reaction which has been expected.

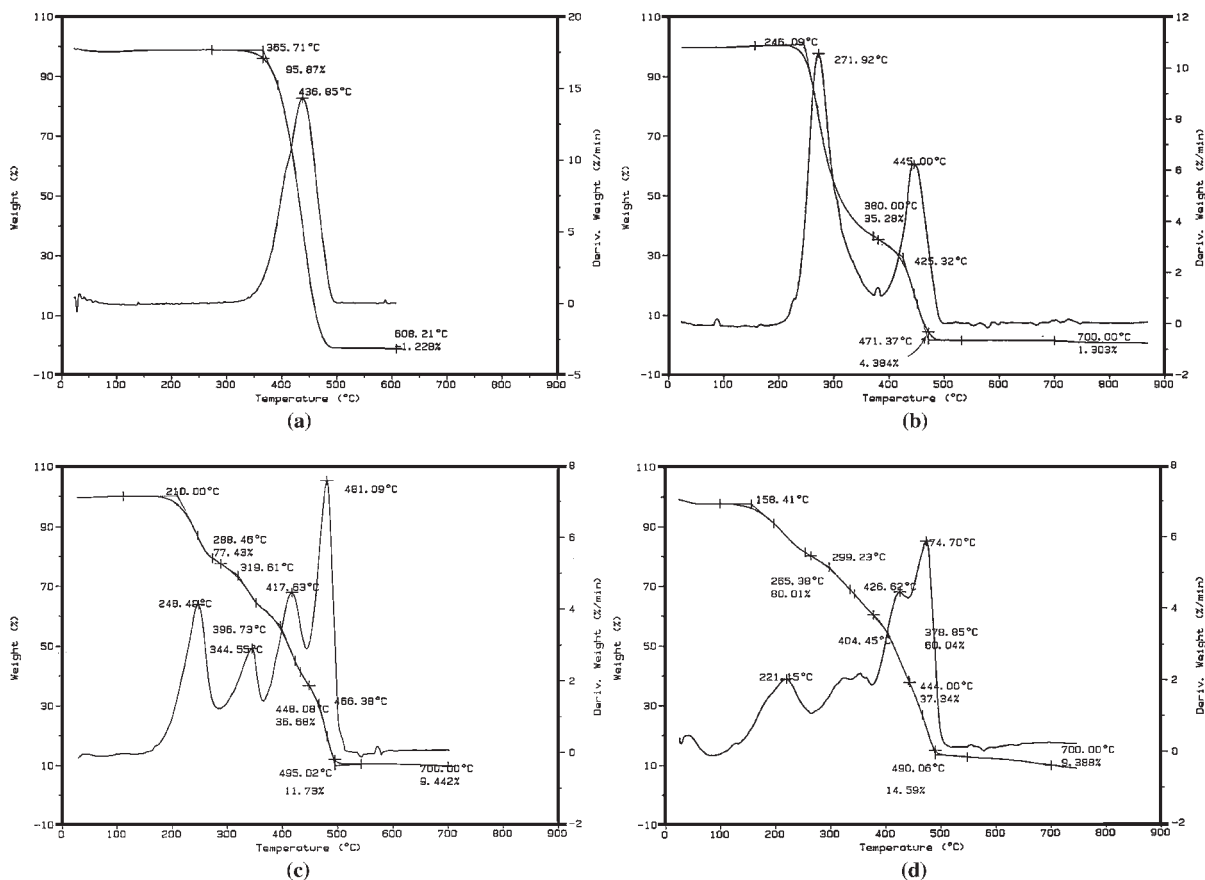
### Thermal characterization

Thermal characterization of trunk NWF and 150% GMA-grafted NWF

The dynamic and derivative thermograms of the trunk polymer under  $\text{N}_2$  atmosphere are shown in Figure 8(a). The thermal degradation of trunk polymer proceeds by a one-step process with a maximum decomposition temperature at 437 $^\circ\text{C}$ . Degradation started at  $\sim 300^\circ\text{C}$  and ended at 500 $^\circ\text{C}$ , giving a 1.23% residue at 600 $^\circ\text{C}$ . Figure 8(b) shows TGA and DTGA curves of 150% GMA-grafted polymer. Two-stage degradation is observed for the decomposition of grafted polymer. Major weight loss of the first step started at  $\sim 240^\circ\text{C}$  and ended around 380 $^\circ\text{C}$  with an accompanying 65% weight loss. As the graft contains 150% by weight of GMA chains, this loss of  $\sim 65\%$  corresponds very well to the loss of GMA units. The second step of degradation started little below 380 $^\circ\text{C}$  and ended at 480 $^\circ\text{C}$  and with a measured weight loss of 34%. The derivative of the second stage weight loss is very similar to the curve obtained for pure trunk polymer. Maximum degradation temperature for first step and second step are 272 and 445 $^\circ\text{C}$ , respectively. It gives 1.3% residue at 700 $^\circ\text{C}$ .

The course of thermal degradation of GMA-grafted trunk polymer was studied by FTIR as well. For this purpose, the samples were heated to different degradation extents in the furnace of TG apparatus and their FTIR spectra were taken. The FTIR spectra of 150% GMA-grafted polymer and those degraded to 30, 50, and 70% weight losses are shown in Figure 9. The progress of degradation is most remarkably represented by the changes in the FTIR spectra in the form of a decrease in the intensity of the 1736  $\text{cm}^{-1}$  band because of C=O stretching vibration coming from GMA groups. After 60% degradation, Figure 9(e), the spectrum looked very similar with trunk polymer spectrum with the small exception of presence of a band remaining of around 1700  $\text{cm}^{-1}$ . This has further been substantiated by the close overlap of maximum degradation temperature of second step (446 $^\circ\text{C}$ ) of graft polymer with the maximum degradation temperature of trunk polymer (437 $^\circ\text{C}$ ). The characteristic absorption bands of  $-\text{CH}_3$  antisymmetric stretching (2966  $\text{cm}^{-1}$ ),  $-\text{CH}_2$  antisymmetric stretching (2917  $\text{cm}^{-1}$ ), and  $-\text{CH}_2$  symmetric stretching (2847  $\text{cm}^{-1}$ ) groups can be observed in the FTIR spectrum of trunk polymer and these bands are also observed in the spectrum of GMA-grafted polymer after 60% degradation. These results show that, during the first stage of thermal degradation, the grafted GMA chains are stripped off leaving behind the trunk polymer.

A simple calculation can be used to support the above reached conclusions; 150% GMA-grafted NW fiber is composed of 60% GMA and 40% trunk polymer. Stage-wise thermal degradation of grafted polymer takes place around 60% weight loss. The spectrum of almost pure trunk polymer appears after 60%



**Figure 8** The dynamic and derivative thermograms of (a) trunk nonwoven fiber, (b) 150% GMA-grafted nonwoven fiber, (c) IDPN modified nonwoven fiber, and (d) amidoximated nonwoven fiber.

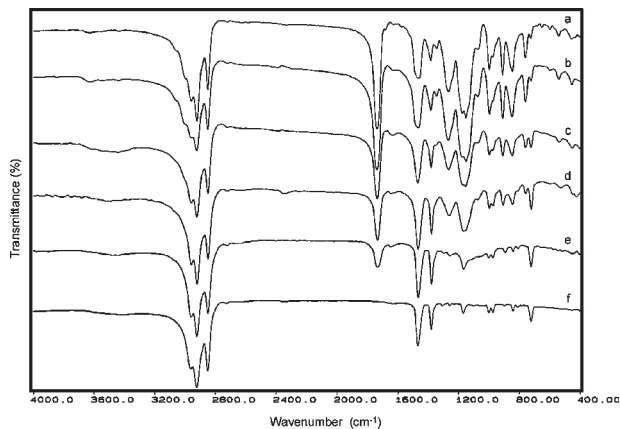
weight loss of grafted polymer. Figure 10(a) shows DSC thermograms of trunk polymer and 150% GMA-grafted trunk. The trunk polymer is composed of polypropylene coated with polyethylene. The melting temperature of PE is  $\sim 129^{\circ}\text{C}$  and melting temperature of PP is approximately  $166^{\circ}\text{C}$ , which are very close to the melting temperatures of pure polymers.<sup>18</sup> In the DSC thermogram of 150% GMA-grafted NWF, the melting endotherms due to PE and PP are retained and two broad endothermic peaks with rate maxima at 231 and  $331^{\circ}\text{C}$  appeared. The major difference observed between the two thermograms is the additional endothermic peaks because of decomposition of GMA moieties, which was also observed as the weight loss in the first stage in the dynamic TGA curves, Figure 8(a).

#### Characterization of IDPN functionalized and amidoximated graft nonwoven fiber

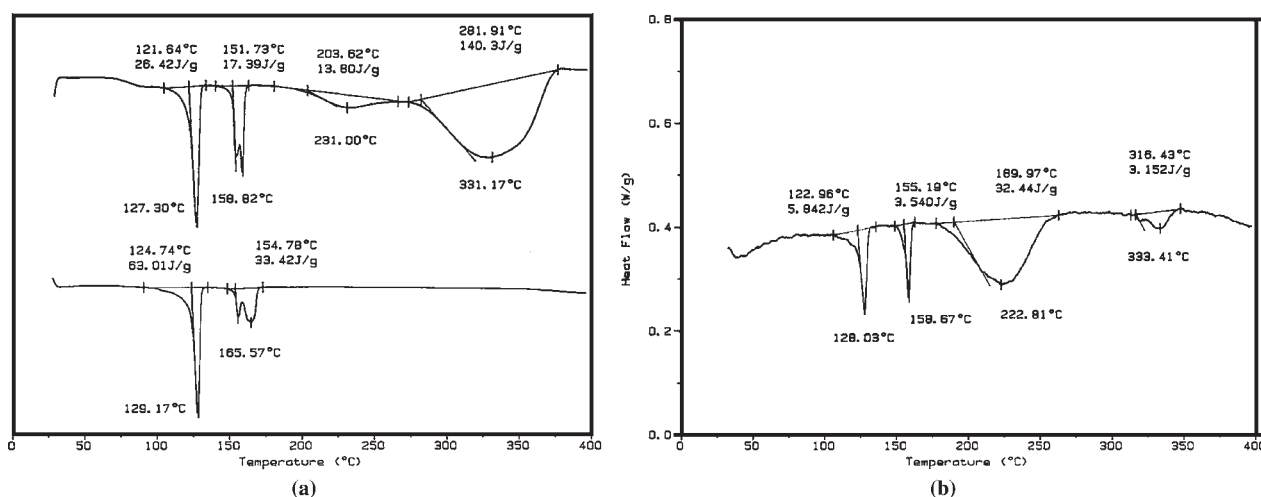
The dynamic thermograms of 150% GMA-grafted polymer modified with iminodipropionitrile are shown in Figure 8(c). Four stages of degradation are evident in these curves. The first stage of weight loss starts at  $\sim 200^{\circ}\text{C}$  and ends around  $290^{\circ}\text{C}$ . Second stage of degradation starts from about  $290^{\circ}\text{C}$  and ends

around  $400^{\circ}\text{C}$ . The third and fourth stages of degradation take place between 350 and  $495^{\circ}\text{C}$  overlapping around  $450^{\circ}\text{C}$ . Complete degradation of sample gives 9.4% residue at  $700^{\circ}\text{C}$ .

These degradation steps were also analyzed with FTIR spectrometry. Figure 11 shows the original FTIR



**Figure 9** The FTIR spectra of thermally degraded 150% GMA-grafted trunk polymer. Spectra corresponding to (a) 0%, (b) 10%, (c) 30%, (d) 40%, (e) 60% weight losses, and (f) represents trunk polymer.



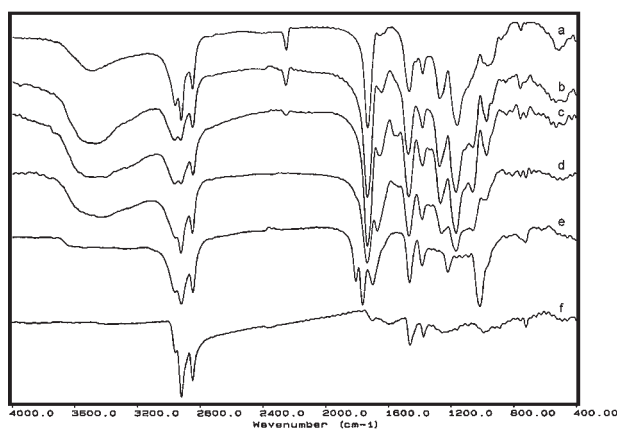
**Figure 10** DSC thermograms of (a) trunk nonwoven fiber, below and 150% GMA-grafted nonwoven fiber, above; (b) IDPN modified nonwoven fiber.

spectrum of IDPN modified NWF and spectra of 25, 40, 60, and 70% degraded samples. Gradual disappearance of CN bands at  $2249\text{ cm}^{-1}$  and appearance of shoulders around  $1750\text{ cm}^{-1}$  due to formation of anhydrides which is also depicted as C—CO—O—CO—C stretching vibrations at  $1011\text{ cm}^{-1}$  and asymmetric and symmetric C=O couple stretching vibration bands at  $1806, 1764\text{ cm}^{-1}$ , respectively, show a behavior parallel to stage-wise degradation observed in Figure 8(c). This result indicates that the first step of degradation is due to the decomposition of imino groups on the polymer. After 40% degradation, the C=O bands of GMA group were kept, but the structure of polymer launched into an anhydride structure. The spectrum of 70% degraded sample is very similar with trunk polymer spectrum, and maximum degradation temperature of fourth step ( $481^\circ\text{C}$ )

can be considered to be close to the maximum degradation temperature of trunk polymer ( $437^\circ\text{C}$ ).

Figure 10(b) shows the DSC thermogram of IDPN modified graft NW fiber. The first and second melting peaks are those due to the melting of PE and PP, respectively. The third and fourth endothermic peaks comply with corresponding TGA curve and they are related to the first and second stages of degradation of IDPN modified graft fiber, respectively.

To complete the thermal characterization of final product, i.e., amidoximated fiber, its dynamic thermogram was taken and shown in Figure 8(d). The main difference observed in this thermogram when compared with that given in Figure 8(c) is that upon amidoximation, the grafted fiber becomes thermally less stable and degradation starts at around  $150^\circ\text{C}$ . The overall trend of four stage weight loss has generally been retained.



**Figure 11** The FTIR spectra of thermally degraded IDPN modified graft nonwoven fiber taken at the following weight losses: (a) 0, (b) 25%, (c) 40%, (d) 50%, (e) 65%, and (f) 70%.

## CONCLUSIONS

Environmentally stable PE coated PP nonwoven fibers were used as base material for the synthesis of a new adsorbent for metal-ions. To introduce specific functional groups to the trunk polymer, GMA was first grafted onto preirradiated fibers. The optimum degree of grafting was found to be 150% as higher grafts rendered the grafted fabric brittle. The resultant epoxy groups were opened and replaced with iminodipropionitrile groups. The IDPN groups were found to be introduced onto PP/PE nonwoven fiber at a conversion of 70% while maintaining the necessary physical strength of the fiber. The nitrile groups were later converted to amidoxime groups which are known to exhibit good affinity toward several metal-ions, uranyl being the most selected. GMA grafted, IDPN modified, and finally amidoximated PE/PP substrates were

characterized by detailed FTIR and thermal analysis measurements. The uniformity of grafting was shown by measuring the thickness of the fibers by SEM. The advantages of this new polymeric adsorbent containing two amidoxime groups per repeating unit of GMA side chains are the presence of excess amidoxime groups and an additional diethylene spacer unit between the neighboring amidoxime groups in each monomeric unit when compared with the conventional adsorbents having only one amidoxime group per repeating unit.<sup>19,20</sup>

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