Use of Radiation Grafting of Polyethylene-Coated Polypropylene Nonwoven Fabric by Acrylamide for the Removal of Heavy Metal Ions from Wastewaters

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ABSTRACT: The graft copolymerization of acrylamide (AAm) monomer onto polyethylene-coated polypropylene (PE-*co*-PP) nonwoven fabric was carried out by the mutual irradiation method. The general peculiarities of the grafting have been studied by gravimetric, scanning electron microscope (SEM), mechanical properties, and Fourier transform infrared (FTIR) methods. The influence of absorbed dose, dose rate, as well as the monomer concentration on the degree of grafting has been determined. Metal ions uptake of Cu^{2+}, Co^{2+}, Ni^{2+} by the grafted fabrics was evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3240–3245, 2006

Key words: PE-*co*-PP; radiation grafting; hydrophilicity; sorption

INTRODUCTION

In recent years, there has been an increasing interest of investigation affiliated with the radiation grafting of functional monomers onto different substrates. This technique can be successfully used for the preparation of selective sorbents, hydrophilization of surfaces, modification of membrane properties of different materials, and enhancing the biocompatibility of medical devices.[1–3]

Electron beam (E.B) radiation grafting of hydrophilic monomer, namely (AAm), onto solid polyethylene was studied. Kinetics and morphology of the grafted substrate were also investigated.[4]

Moreover, the electron beam (E.B) radiation grafting of glycidyl methacrylate on polyethylene-coated polypropylene was studied. It was found that the grafted substrate process rapid elimination properties of heavy metal ions, such as Cu, Pb, Ca, from waste water.[5]

Studies were made on the preparation of the cation exchange membranes by preirradiation grafting of acrylic acid (AA) and sodium styrene sulfonate onto high-density polyethylene.[6]

Also, radiation stability of low-density polyethylene (LDPE) has been studied through radiation-induced graft polymerization of styrene onto LDPE. It has been reported that relatively high degree of grafting (DG) could be obtained by mutual and pre-irradiation technique.[7]

Also, it was found that the degree of grafting of water soluble monomers, such as acrylic acid, methacrylic acid, acrylamide, *N*,*N*-dimethylacrylamide, and 1-vinyl-2-pyrrolidone, on ultrahigh molecular weight polyethylene (UHMWPE) increases linearly with irradiation dose till a gelation state is reached, and varies between 12% and 40% depending on the monomer.[8]

In an earlier investigation by the authors,[9] the suitability of the irradiation technique on using nylon-6 as a hydrophilic substrate has been confirmed in the graft copolymerization of AAm onto nylon-6 fabric.

In very recent study,[10] chemical and γ-irradiation grafting of itaconic acid onto chitin was studied. Grafting was confirmed by FTIR. The effect of different factors such as radiation dose and monomer concentration was also studied. The metal uptake of different metal ions, namely Cu, Co, Ni, Zn, and Pb, was evaluated by using UV-Spectroscopy.

In the present work, the preparation of PE-*co*-PP nonwoven fabric grafted with acrylamide monomer through γ-irradiation technique has been undertaken. Since the physical feature of this substrate is different than PE or PP separately, then it would be expected to have characteristics neither belongs to PE nor PP separately. Factors affecting the preparation as well as some properties of prepared material were followed up. The efficiency of the prepared substrate for metal uptake of some cations, namely copper, cobalt, and nickel, were evaluated.

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EXPERIMENTAL

Materials

Polyethylene-coated polypropylene nonwoven fabric (diameter 13 μm) was provided by Kurashiki Textile MFG Co., Osaka, Japan. A laboratory grade acrylamide was supplied from Merck, Germany, and it was used without further treatment. The other chemicals were of pure grade and were used without further purification.

Experimental techniques

Direct radiation grafting of acrylamide onto PE-*co*-PP nonwoven fabric

Polethylene-coated polypropylene nonwoven fabric was placed in contact with the grafting solution containing different concentrations of aqueous solution of acrylamide monomer (5, 7, 10, 15%) (vol %) in a glass tube. Ferric chloride aqueous solution of 0.7 wt % as inhibitor was added to the grafting solution.[11] The glass tubes were then exposed to γ-irradiation at the required doses and at different dose rates, namely 1 kGy/h and 4 kGy/h, in the Co-60 γ-source under atmospheric air. The grafted samples were then washed thoroughly with hot distilled water to remove unreacted monomer and surface homopolymer. The grafted samples were extracted in boiling water to constant weight. The degree of grafting was determined by the percentage increase in weight as follows:

$$\text{Degree of grafting (\%)} = (W_g - W_0)/W_0 \times 100 \quad (1)$$

where W_0 and W_g represent the weights of the initial and grafted sample, respectively.

Testing

Determination of swelling percentage

A known weight of the grafted samples with different degree of grafting was soaked in water and left for different time intervals at room temperature. The swelling percentage is determined by:

$$\text{SW (\%)} = (W_2 - W_1)/W_1 \times 100 \quad (2)$$

where W_1 and W_2 represent the weights of the dry and wet samples, respectively.

Scanning electron microscope

The surface morphology of grafted samples of different degree of grafting was investigated by SEM technique. The micrographs were taken with a JSM-5400 instrument of Jeol (Japan).

Mechanical properties

The ungrafted and grafted samples were tested for tensile strength and elongation at break properties, according to ASTM 638 specifications. An Instron Universal Tester (England) model 1195 was used throughout this work by applying a crosshead speed of 10 mm/min at room temperature.

IR spectroscopic analysis

FTIR spectrophotometer model Mattson 100, made by Unicam, (UK) was used for FTIR measurements over the range 500–4000 cm^{-1}.

Sorption of heavy metal ions

An attempt was undertaken to use grafted sample for the removal of the heavy metals ions, Cu(II), Co(II), and Ni(II), which may possibly exist in waste water. For accomplishing this purpose, separate solutions of these metal ions were prepared by dissolving 1 g of suitable metal salt in 100 mL water. A UV–vis Pye Unicam (Cambridge, UK) spectrophotometer type SP 8-200 was used to determine the initial (C_0) and final (C_1) concentration of metal ions in used solutions. The metal ions uptake was determined by using the following equation:

$$\text{Metal uptake (\%)} = [(C_0 - C_1)/C_0] \times 100 \quad (3)$$

All spectrophotometric measurements were carried out at 25°C and the characteristic wave length of each metal is equal to: 650, 515, and 400 nm for Cu, Co, and Ni, respectively.

RESULTS AND DISCUSSION

Radiation grafting measurements

Although the direct method of grafting in which the polymer and monomer solvent mixture was exposed to γ irradiation is simple and involves a single step, it is associated with homopolymer formation. Therefore, a suitable inhibitor, such as $FeCl_3$, was added to the grafting solution to minimize such homopolymer formation and force the reaction to the grafting site.

To increase the efficiency of grafting, the different factors, which affect the grafting yield, such as dose, dose rate, and monomer concentration, were followed up.

Figure 1 illustrates the effect of irradiation dose on the DG of 10% (vol %) acrylamide onto PE-*co*-PP substrate at two dose rates, namely 1 and 4 kGy/h. It may be observed that on applying the lowest dose of irradiation, namely 5 kGy, an abrupt increase in DG has been attained for both dose rates. The value

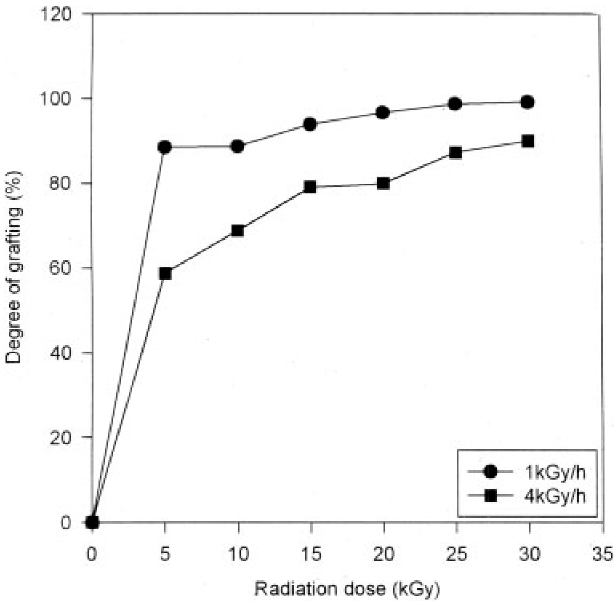

Figure 1 Effect of radiation dose on the degree of grafting of acrylamide monomer concentration at 10% onto PR-*co*-PP nonwoven fabric at different dose rate.

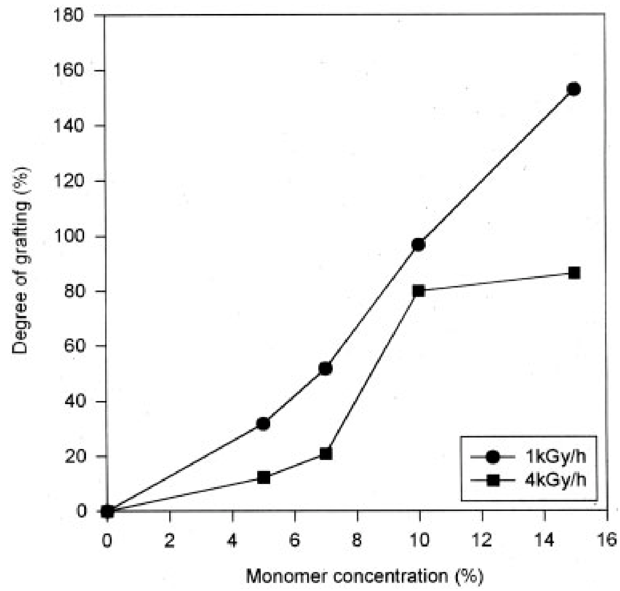

Figure 2 Effect of monomer concentration on the degree of grafting of acrylamide monomer onto PE-*co*-PP nonwoven fabric irradiated at 20 kGy at different dose rates.

of the DG attained at 5 kGy is ~ 60 and 90% for higher and lower dose rate, respectively. Moreover, it can be seen that at low dose rate, the DG has changed from ~ 90 to 100 on increasing the irradiation dose from 5 to 30 kGy, respectively, whereas for the higher dose rate, the DG increase from ~ 60 to 93 on increasing the irradiation dose from 5 to 30 kGy.

The results obtained are explained as follows:

In the direct method of grafting, the number of free radicals formed and their lengths are influenced by radiation dose and dose rate, respectively. The dose rate, which determines the rate of initiation of polymerization, will therefore affect the kinetics of the grafting reaction and consequently the length of the grafted chains.[12] Therefore, generally the increase of DG may be attributed to the increased number of free radicals formed on both the polymer backbone and the monomers.

At low dose rate and low irradiation dose, the rate of propagation of the grafting reaction is higher than the rate of formation of homopolymer, while at the same dose rate and higher irradiation dose, the monomer radicals tend to recombine to form homopolymer to a very limit extent due to the presence of inhibitor. On the other hand, it would be expected that at high dose rate, for low dose as well as high irradiation dose, the termination reaction of the grafting process takes place much faster than propagation ones,[13] which would lead to lower degree of grafting.

Figure 2 shows the dependence of DG on monomer concentration at the two dose rates. The DG increases with increasing monomer concentration at the two dose rates under investigation.

The previous mentioned weight measurement is considered as a direct proof of the grafting process. On other hand, IR measurements on grafted material are considered as an indirect evidence for the occurrence of grafting process due to the appearance of absorption bands affiliated with the characteristic groups of acrylamide.

Infrared measurements

IR measurements were carried out as a further conformation for occurrence of grafting, and the results observed are given in Figure 3. In the spectrum of

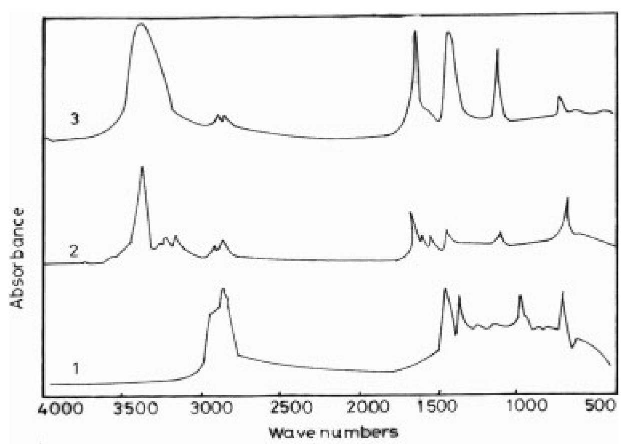

Figure 3 IR spectra of PE-*co*-PP fabrics of (1) ungrafted fabric, (2) grafted to 80%, (3) grafted to 152%.

the starting polyethylene-coated polypropylene, there are bands at 2915, 2848, 1463, and 719 cm^{-1} responsible for the deformation vibrations of CH— groups. IR spectrum of the grafted fabrics shows new bands around 1700 cm^{-1} due to C=O absorption characteristic of the group CO—NH—. The NH stretching vibration gives rise to absorption at 3250–3300 cm^{-1} to the left of the aliphatic —CH band (2800–3000 cm^{-1}). The presence of these new bands in the spectra confirms the grafting process. Moreover, an increase of the grafting yield leads to an increase in the intensity of these bands.

Hydrophilic properties of grafted samples

In general, the grafting of hydrophilic monomer on hydrophobic PE-*co*-PP results in the enhancing ability of the substrate to absorb water. For this reason, hydrophilic properties of the grafted samples were investigated.

Swelling measurements

Figure 4 illustrates the variation of the swelling percentage as a function of immersion time for samples having different degrees of grafting. It may be observed that considerable increase in the value of the swelling percentage has been attained for times up to 6 h reaching practically its maximum value for degrees of grafting up to 93.9%. For times higher than that, the value of swelling percentage increases slightly but with a rate that is proportional to the degree of grafting. This behavior is affiliated with the extent of polar groups introduced to the structure of the PE-*co*-PP substrate due to the grafting process. Such polar groups would result in opening of the substrate structure and hence leading to its swelling with water.

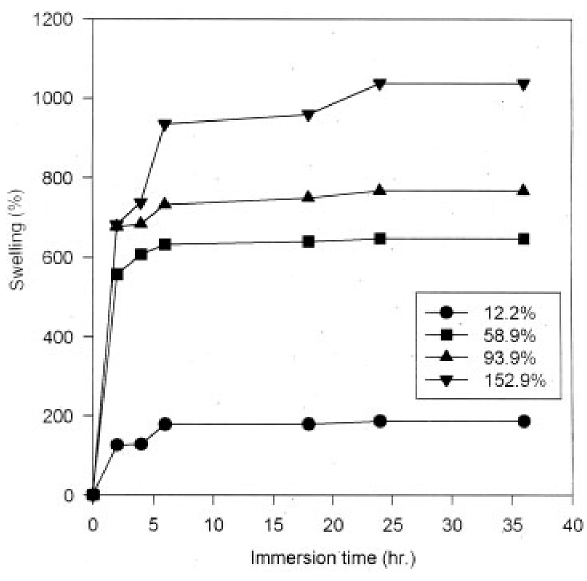

Figure 4 Effect of different time intervals on swelling (%) of grafting samples at different degree of grafting.

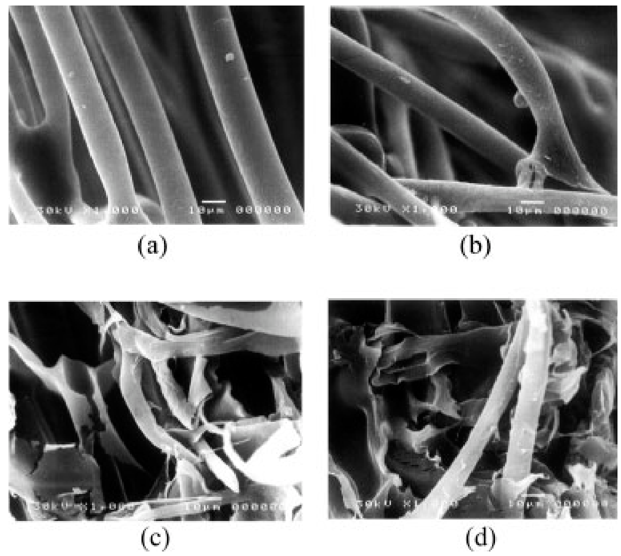

Figure 5 SEM micrographs of PE-*co*-PP fabrics (a) Ungrafted fabrics, (b) grafted to 31%, (c) grafted to 80%, and (d) grafted to 152%.

Morphological structure of graft copolymer of PE-*co*-PP with acrylamide

The structural morphology of the grafted PE-*co*-PP nonwoven fabric with different degree of grafting is shown in Figure 5. The presence of higher grafting changes the structural characteristics of the resulting substrate. SEM also confirms the presence of grafted polyacrylamide on PE-*co*-PP, which exists in the form of anchors, i.e., attachments on the surface of fibers of the fabric. These findings are in a good accord with the SEM investigation by studying the morphology of radiation-grafted copolymers of PE and polyacrylic acid.[14]

Mechanical properties

The tensile strength and elongation at break of grafted PE-*co*-PP nonwoven fabric with different degree of grafting are measured. The results are shown in Figures 6 and 7. From these figures, it was found that tensile strength increases with increasing degree of grafting. On the other hand, elongation at break decreases with increasing degree of grafting. These characterizations can be attributable to an increase in crosslinking density, as the degree of grafting in grafted samples increase.

Application of grafted fabrics in metal uptake

Many authors studied the separation of some selected metal ions, such as Cu, Co, and Ni, which commonly

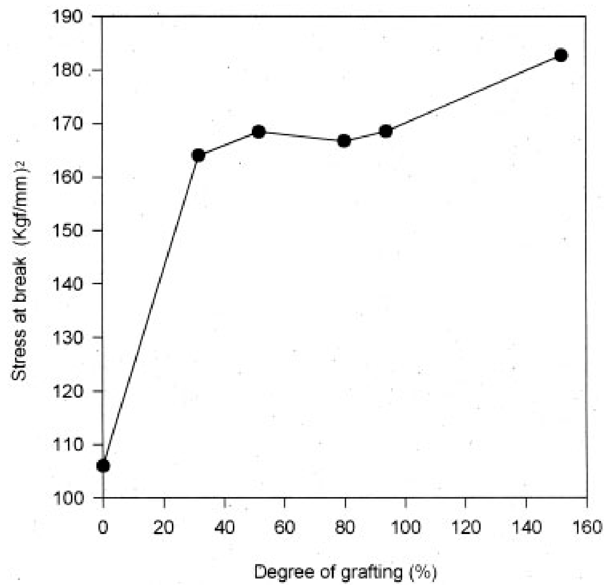

Figure 6 Effect of different degree of grafting on the stress at break of the grafted sample.

exist in waste water, by different prepared substrate. Also, the efficiency of these substrates for uptaking metal ions can be determined from the time required to adsorb the maximum capacity of metal ions by chelation or adsorption with its functional groups.

Nurkeeva et al.[15] studied the efficiency of prepared polyethylene films grafted with vinyl monomers by radiation for Cu^{2+} ions uptake. It was found that increasing of grafting degree of the substrate increase the amount of metal ions uptake.

TABLE I
Sorption of Different Heavy Metals by PE-*co*-PP Grafted with Acrylamide

	Metal sorption (%)	
Metals	2 h	24 h
Cu(II)	2.4	2.8
Ni(II)	16.75	19.85
Co(II)	20.35	27.41

Moreover, Don et al.[16] studied the Cu^{2+} ions uptake of chitosan-*graft*-polyvinylacetate copolymers. They found that the specific adsorption is proportional to the degree of grafting.

In this work, the metal ion uptake (%) for different metal ions using grafted PE-*co*-PP nonwoven fabric after 2 and 24 h was evaluated. The results obtained are shown in Table I. It can be seen that the maximum metal uptake is of the sequence $Co^{2+} > Ni^{2+} > Cu^{2+}$. Moreover, it can be seen that the metal uptake percentage increases with increasing the immersion time.

The dependence of the metal uptake percentage as a function of different degree of grafting was evaluated. The results obtained are shown in Figure 8. It can be seen that the increase of the degree of grafting result on increasing the amount of metal ions uptake percentage due to increase of chelating sites on the surface. Moreover, the presence of electron donating primary amino group in acrylamide monomer provides the ability of its polymer to for polycomplexes with transition metals.[17]

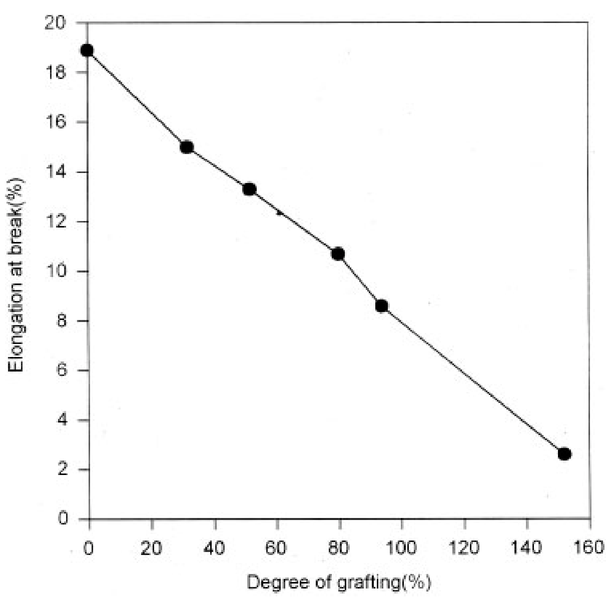

Figure 7 Effect of different degree of grafting on the elongation at break of the grafted sample.

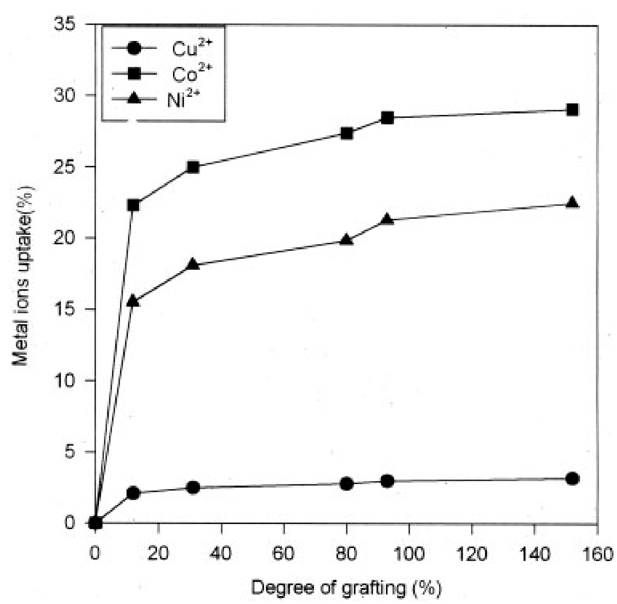

Figure 8 Dependence of metal ions uptake on grafting of the grafted nonwoven fabric.

It is interesting to mention that the grafted fabrics immersed into solution of Co^{2+}, Ni^{2+}, and Cu^{2+} have attained pink, green, and blue color, respectively. The color of these grafted fabrics was still stable even after several time of washing and also after complete drying. These data support the binding of heavy metal ions into grafted chains.

CONCLUSIONS

Novel polymeric materials were prepared by radiation grafting of acrylamide monomer onto polyethylene-coated polypropylene. It was found that the degree of grafting of the substrate is a function of the absorbed dose, dose rate, as well as monomer concentration. The different grafting degree of the substrates affects their ability for swelling. The obtained substrates possesed the ability to absorb heavy metal ions due to the presence of primary amino groups in the grafted macrochains.

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