Radiation-Modified Copolymer for the Extraction of Metal Ions from Water

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ABSTRACT: The modification of heavy-duty polyethylene films was carried out through the graft copolymerization of acrylamide and vinyl acetate mixtures of different compositions with the simultaneous radiation method. The influence of the synthesis conditions (the irradiation dose, comonomer composition, and dilution) on the degree of grafting was investigated. The grafted samples were characterized with Fourier transform infrared spectroscopy, scanning electron microscopy, and differential scanning calorimetry. The effect of the grafting degree on the thermal stability of the modified polymer was examined. The extraction of heavy and toxic metals such as cadmium, cobalt, copper, nickel, and lead by the modified heavy-duty polyethylene was evaluated, and the metal-ion uptake by the grafted and chemically treated samples seemed better than that of the grafted and untreated ones. Both the rate and amount of the metal-ion uptake were affected by the temperature of the feed solution and the grafting degree. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3366–3374, 2007

Key words: modification; polyethylene (PE); radiation

INTRODUCTION

Heavy metals such as lead, mercury, arsenic, copper, and cadmium are highly toxic metals when absorbed into the body.[1] They can cause accumulative poisoning, cancer, brain damage, and so forth.[2] These heavy metals are released into the environment in a number of different ways. Coal combustion, sewage wastewater, automobile emissions, the battery industry, mining activities, and the utilization of fossil fuels are just a few examples.[3] Adsorption now plays a key role in modern industries, especially in large-scale chemical, biochemical, and environmental recovery and purification and environmental protection engineering.[4] Adsorption processes are being employed widely for the removal of heavy-metal ions because of its high efficiency, easy handling, and cost effectiveness and the availability of different adsorbents.[5] The need to reduce the amount of heavy-metal ions in wastewater streams and subsequent possible reuse of these metal ions have led to increasing interest in selective sorbents.[6] Among the various methods described, radiation-induced graft copolymerization has received considerable attention for producing synthetic polymeric materials that play important roles today in practical applications of various separation processes.[7] It has attracted considerable interest because it imparts desirable properties such as blood compatibility,[8] membrane quality, ion exchange,[9–11] dyeability,[12] protein adsorption,[13] and immobilization of bioactive materials.[14,15] In this study, we focused our attention on the development of chelating sorbents for the removal of heavy-metal ions. The metals selected for this study were cobalt, cadmium, nickel, copper, and lead because of their environmental significance. The graft copolymerization of acrylamide (AAm) and vinyl acetate (VAc) in mixtures of different compositions onto heavy-duty polyethylene (HDuPE) by the simultaneous radiation of γ rays was examined. The ester groups in poly(vinyl acetate) (PVAc) and the amide groups in polyacrylamide (PAAm) graft chains were converted into hydroxyl and carboxylic groups by a reaction with KOH. This study also included the characterization and application of the modified graft copolymer to the adsorption and extraction of heavy-metal ions.

EXPERIMENTAL

Materials

HDuPE, 120 μm thick, was produced by El-Nasr Co. for Medical Supplies (Egypt). VAc (purity > 99%; Merck-Schurdardt) and reagent-grade AAm (purity > 99%) were used as received. Other chemicals, such as solvents and inorganic salts, were reagent-grade and were used without further purification.

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Graft copolymerization

The graft copolymers were prepared by the radiation grafting of AAm/VAc binary monomer systems onto HDuPE films with Co-60 γ rays at a dose rate of 0.27–1.16 Gy/S. Strips of HDuPE were washed with MeOH, dried at 50°C in a vacuum oven, weighed, and then immersed in an AAm/VAc comonomer solution. The direct radiation grafting method was used in an N_2 atmosphere. Glass ampules containing HDuPE films and comonomer solutions were then subjected to Co-60 γ rays. The grafted films were removed and washed thoroughly with hot distilled water and then with acetone to extract the residual monomers and the homopolymer, which may have accumulated in the films. The films were then dried in a vacuum oven at 50°C for 24 h and weighed. The degree of grafting was calculated from the percentage increase in the weight of the HDuPE films after the grafting process as follows:

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

where W_0 and W_g are the weights of the ungrafted and grafted films, respectively.

Alkaline treatment

The grafted films were alkali-treated with 3% KOH solutions at the ambient temperature for 24 h. The membranes thus obtained were washed with distilled water several times.

Water uptake

The dried membranes were immersed into distilled water at ~ 25°C until equilibrium was reached (almost 24 h). The surface of the membranes was blotted with adsorbent paper to remove any attached water and weighed quickly. The water uptake of the membranes was determined as follows:

$$\text{Water uptake (\%)} = [(W_s - W_g)/W_g] \times 100$$

where W_g and W_s are the weights of the dry and swollen membranes, respectively.

Fourier transform infrared (FTIR) spectrophotometry analysis

IR spectra of the ungrafted, grafted, and grafted/treated films were recorded on a Mattson FTIR-1000 spectrophotometer (Unicam Ltd., England) in the range of 500–4000 cm^{-1}.

Scanning electron microscopy (SEM)

The surface and cross-sectional topography of the ungrafted and grafted samples was examined with a JEOL SEM-25 (Japan) scanning electron microscope. Before the examination, the membranes were dried under coated gold.

Thermogravimetric analysis (TGA)

TGA for the investigated samples was performed under a nitrogen atmosphere with a Schimadzu-50 (Japan) thermal analysis system. The rate of pure nitrogen gas was 50 mL/min, and the heating rate was 20°C/min from the ambient temperature up to 600°C.

Differential scanning calorimetry (DSC)

The thermal parameters were determined for the grafted samples with a PerkinElmer DSC 7 in an inert atmosphere of nitrogen gas at a heating rate of 20°C/min.

Metal-uptake measurements

Atomic absorption

The prepared graft copolymer was immersed in a metal-salt solution with an initial concentration of 500 ppm for a time and then removed. The concentration of the remaining metal salt was determined with an atomic absorption technique with a Unicam-939 atomic absorption spectrophotometer (England).

X-ray fluorescence (XRF)

The prepared graft copolymer was immersed in a solution mixture of cobalt, cadmium, nickel, copper, and lead ions with an overall initial concentration of 500 ppm for 4 h, removed, and dried at 50°C. XRF measurements were carried out at room temperature with a DX-95 EDAX (energy dispersive analyzer x-ray) from Philips (United States).

RESULTS AND DISCUSSION

Effect of the comonomer composition

The grafting of AAm and VAc in binary monomer mixtures of different compositions onto HDuPE was investigated at an overall comonomer concentration of 30 (wt %) in the presence of a 50/50 (w/w) MeOH/H_2O mixture as a diluent, and the results are shown in Figure 1. The presence of a low concentration of AAm in the reaction mixture enhances the grafting yield of VAc. On the other hand, the grafting of AAm is enhanced in the presence of VAc, and there is a synergistic effect, as found for other binary graft copolymerization systems with different monomers.[16] To explain these results, the partitioning of the monomers between the solvent and the polymeric substrate has to be taken into account. The increased partitioning of the

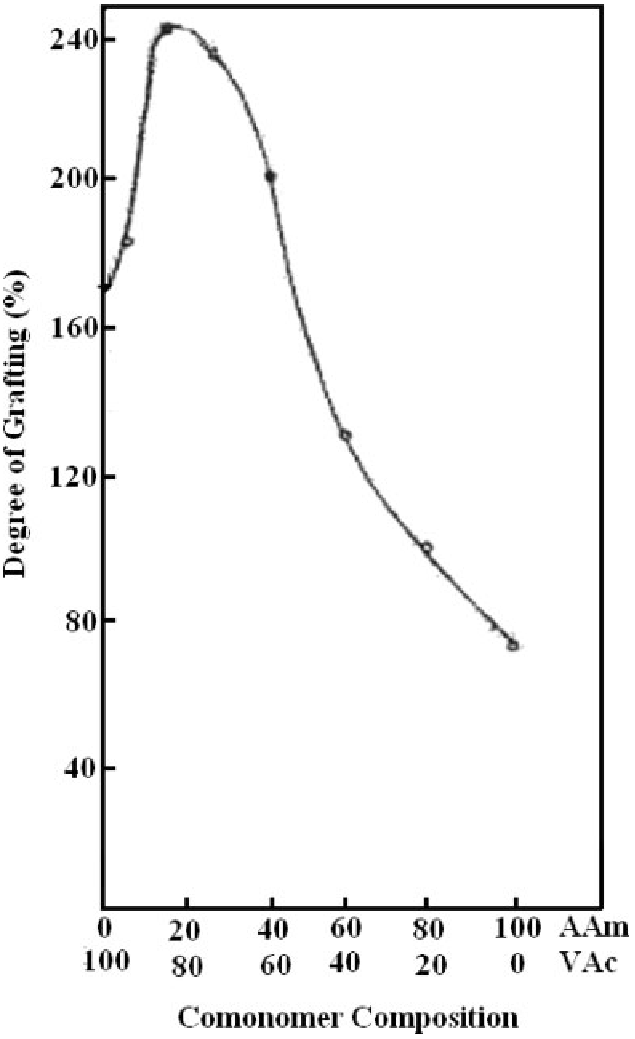

Figure 1 Effect of the AAm/VAc composition on the grafting yield (comonomer concentration = 30 wt %; $MeOH/H_2O$ = 50/50 w/w, $CuSO_4$ concentration = 0.5 wt %; irradiation dose = 20 kGy).

monomers in the graft region may occur when AAm is added at a small concentration to the grafting solution. This permits a higher concentration of the monomers to be available for grafting at a particular backbone site, leading to a high propagation rate of growing chains, and consequently, the grafting process is enhanced. Also, the solvent type and its composition have a strong influence on the total grafting yield and composition of AAm and VAc in the graft copolymer.

Effect of dilution for different comonomer compositions

The concentration and composition of the AAm and VAc comonomers play important roles in the grafting process. Figure 2 shows the effect of dilution of the AAm and VAc comonomers with weight ratios of 20/80 and 60/40 on the grafting process in the presence of a 50/50 (w/w) $MeOH/H_2O$ mixture as a diluent. The degree of grafting increases linearly with increasing comonomer concentration for an AAm/VAc ratio of 60/40 (w/w), although it tends to level off at a comonomer concentration of 50 wt % for an AAm/VAc ratio of 20/80 (w/w). Such behavior suggests that the diluent and its composition have a great effect on the graft polymerization, and there is an optimum composition of the diluent and comonomer at which the effect of chain transfer is more pronounced.

Effect of the irradiation dose

The influence of the total exposure dose on the grafting yield has been investigated and is shown in Figure 3. The degree of grafting increases with the irradiation dose up to 20 kGy; thereafter, it tends to level off. The results indicate that the concentration of free radicals that form in the polymer and the comonomers increases with the irradiation dose. This results in an increase in the number of grafted chains and their length; consequently, the grafting yield increases. The plateau trend observed at doses greater than 20 kGy is due to the fact that the diffusion of the comonomers into the films competes with their polymerization, and as the rate of polymerization increases, a steady state is reached at which the reaction medium becomes dependent on the monomer diffusion.

IR spectroscopy investigation of the graft copolymer

FTIR spectra of the grafted films show absorption bands corresponding to carbonyl groups of AAm and VAc at 1720 and 1744 cm^{-1}, respectively (Fig. 4). A new broad band around 3200–3363 cm^{-1} appears, indicating the presence of NH_2 stretching vibrations, which are characteristic for the structure of AAm. The alkali-treated graft copolymer shows a broad band around 3200–3600 cm^{-1} and another peak at 1030–1100 cm^{-1}, which have been assigned to OH and C—O of alcoholic groups, respectively. Absorption at 1560 cm^{-1} can also be observed and is usually ascribed to carboxylate groups. The characteristic peak corresponding to the carbonyl of the amide group at 1744 cm^{-1} of the alkali-treated sample is somewhat smaller than that of the untreated ones, indicating possible hydrolysis of the remaining amide groups.

SEM

To analyze the morphology of the graft copolymer, micrographs of the surfaces and sections of the un-

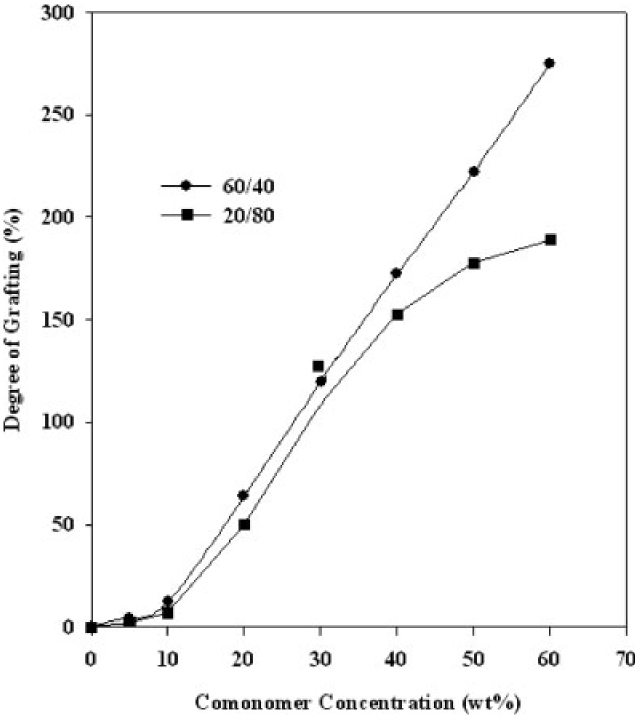

Figure 2 Effect of dilution on the grafting process for different AAm/VAc compositions in a 50/50 (w/w) MeOH/H_2O mixture as a diluent ($CuSO_4$ concentration = 0.5 wt %; irradiation dose = 20 kGy).

grafted and grafted films were taken with SEM and are shown in Figure 5. When ungrafted HDuPE is viewed through SEM, the surface is smooth. This smoothness is, however, altered when poly(acrylamide/vinyl acetate) [P(AAm/VAc)] is grafted onto HDuPE. It is obvious that the top surface of the grafted film is characterized by numerous spots. As the percentage of grafting increases, the portions of the surface covered with these spots increase and appear to be homogeneous. Cross-sectional observations of the graft copolymer show that grafted chains not only exist near the surface regions but also are distributed in the bulk of the polymer substrate.

Thermal properties

Knowledge about changes in the thermal properties of the grafted membranes is important for their applications and for the characterization and determination of the chemical and physical changes. The thermal behavior of HDuPE grafted with P(AAm/VAc) with the simultaneous irradiation technique was evaluated with TGA and DSC.

TGA

TGA monitors the weight changes in a sample as a function of the temperature. The decomposition temperatures at different weight losses are presented in Table I. For the grafted samples, the loss in weight upon heating in the earlier stage is due to the desorption of water; this takes into account that the amount of desorbed water increases as the percentage of grafting increases. Table I shows that the weight loss increases as the temperature is elevated. Also, ungrafted HDuPE has lower thermal stability than the graft copolymer (79%) because of the formation of a crosslinked network structure as a result of grafting and irradiation. When the percentage of grafting increases, the decomposition temperature of the graft copolymer decreases because of the tacticity and sequence distribution of the AAm and VAc comonomers in the graft copolymer, which affect the thermal behavior, in addition to the nature of the comonomers. However, only about 70% weight loss occurs up to 488°C for 129% grafted HDuPE, although in the ungrafted polymer, 70% weight loss occurs at 474°C; in the 79% grafted samples, it occurs between 470 and 500°C. For the same sample treated with an alkali, the major weight loss (70%) occurs between 453 and 487°C. Thus, the grafting of P(AAm/VAc) onto HDuPE imparts better thermal stability to the polymer substrate.

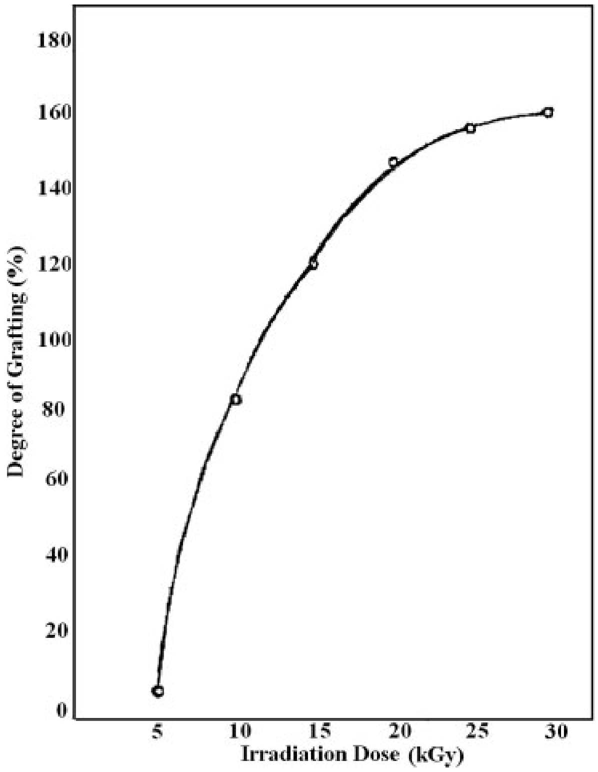

Figure 3 Effect of the irradiation dose on the grafting of 60/40 (w/w) AAm/VAc in a 50/50 (w/w) MeOH/H_2O mixture as a diluent ($CuSO_4$ concentration = 0.5 wt %; comonomer concentration = 30 wt %).

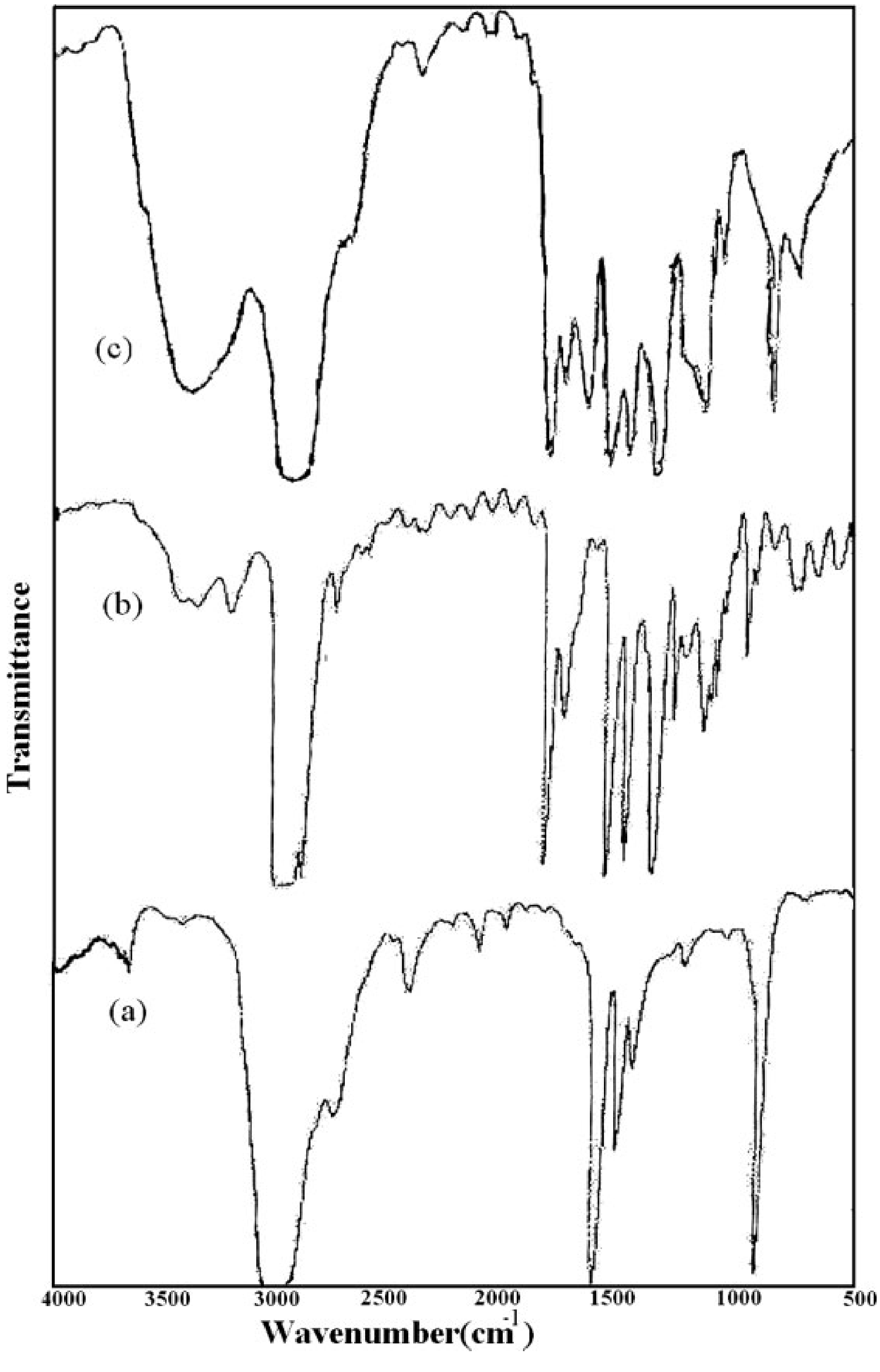

Figure 4 IR spectra of (a) an HDuPE-blank, (b) HDuPE-*g*-P(AAm/VAc) (19%), and (c) HDuPE-grafted/KOH-treated (19%).

DSC

The DSC scans of various copolymers were carried out in the temperature range of 50–200°C, and the results are given in Table II. The ungrafted HDuPE shows the double-melting behavior found in many polymers: the magnitude of the lower melting peak (T_{m1}) and the magnitude of the higher melting peak (T_{m2}). These two thermal transitions are at 108.2 and 119.9°C, corresponding to the melting temperature (T_m) of HDuPE. The reported value of melting for PAAm is 84.8°C. The 79% grafted copolymer is observed to give a single T_m at 112.67°C, and this indicates the compatibility of the graft chains with the main-chain polymer. The sudden increase in the heat of fusion (ΔH) is a further indication of such compatibility. Therefore, ΔH is the heat of fusion obtained from the area under the

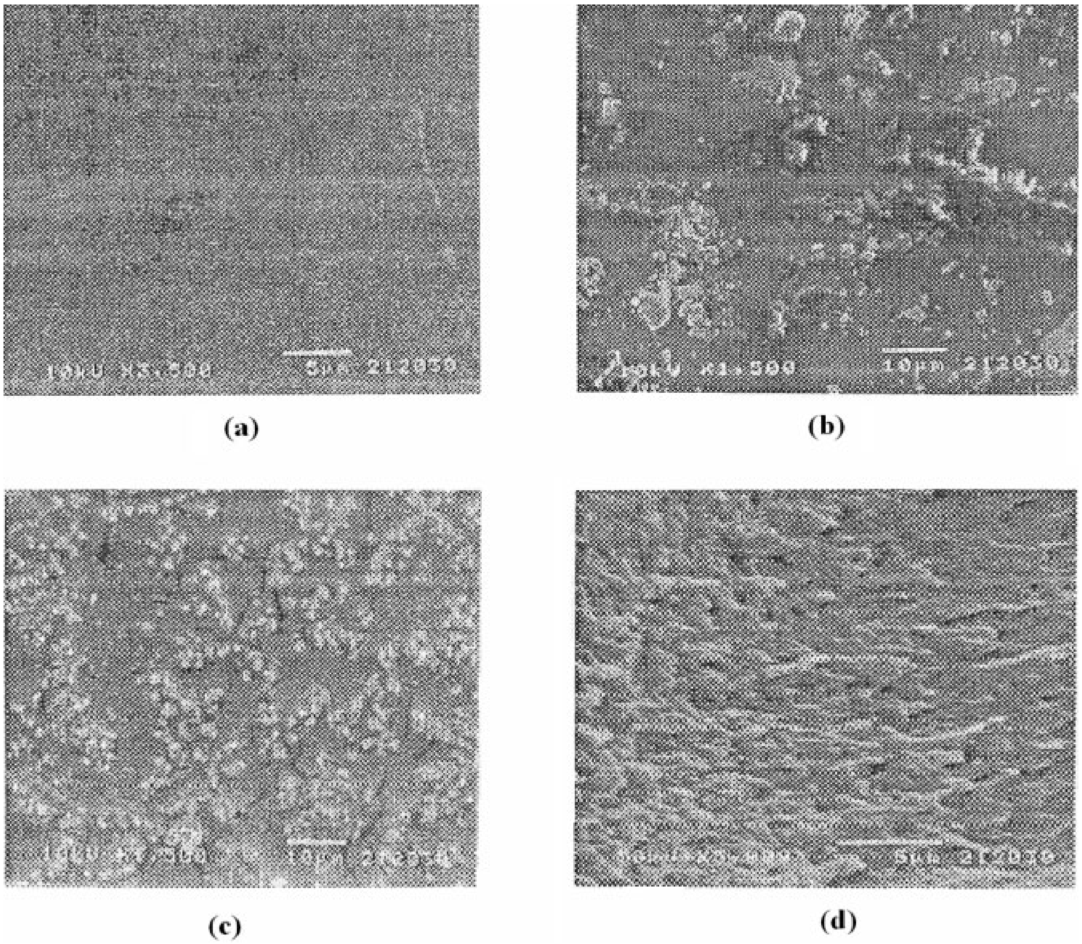

Figure 5 (a–c) Surface micrographs of an HDuPE blank, HDuPE-*g*-P(AAm/VAc) (37%), and HDuPE-*g*-P(AAm/VAc) (136%), respectively, and (d) section micrograph of HDuPE-*g*-P(AAm/VAc) (136%).

thermograms due to the cumulative fusion of the backbone and the graft side chains. However, T_{m2} and ΔH decrease with an increase in the percentage of grafting versus those of ungrafted ones because of the decreased crystalline character of the graft copolymer. The grafting takes place through the incorporation of amorphous PVAc and PAAm chains into the noncrystalline regions, so the crystallinity decreases because of crystallinity dilution and distortion. On the other hand, the T_m values for the alkali-treated copolymers are higher than those obtained for untreated ones. The increase in their T_m values upon treatment may be attributed to polar–polar interactions between the ionic groups that arise during this process. Such interactions restrict the segmental motion of the polymer chains.

Improvement of the water-uptake property

The water content is very important for the practical applications of membranes, especially in ion-exchange and reverse-osmosis processes. Figure 6 shows the water-uptake percentage as a function of the degree of grafting for both the untreated and alkali-treated grafted films. The water-uptake percentage increases with an increasing degree of grafting for both alkali-treated and untreated grafted films. However, at a given degree of grafting, the alkali-treated graft copolymers have better hydrophilicity than the untreated ones because of hydrolysis of the ester groups to hydroxyl groups and of the amide groups to highly solvated ionic units of the type —COOK. It is reasonable to conclude that the water uptake of the grafted films is dependent mainly on the number and form of the hydrophilic groups introduced into the graft copolymers. On the other hand, the crystalline–amorphous changes in membranes are another important factor influencing the water uptake. With a decrease in the crystallinity of a membrane, water molecules can easily penetrate the noncrystalline region. As a result, the water uptake increases with an increasing grafting level, that is, with decreasing crystallinity.[17]

TABLE I
Weight Losses of Ungrafted, Grafted, and KOH-Treated/Grafted HDuPEs as a Function of the Temperature

Sample	Grafting (%)	Decomposition temperature (°C)								
		10% weight loss	20% weight loss	30% weight loss	40% weight loss	50% weight loss	60% weight loss	70% weight loss	80% weight loss	90% weight loss
Ungrafted	—	417	431	444	452	463	470	474	480	488
Grafted	79	362	415	470	480	490	497	500	504	510
Grafted	129	242	343	362	410	439	477	488	495	502
Grafted/treated	79	260	333	453	467	474	480	487	498	504
Grafted/treated	129	249	308	460	475	477	484	491	500	505

Testing of the membranes in wastewater treatments

The prepared membranes, which contained functional groups acting as ligands, were tested for use in wastewater treatment from heavy metals such as copper, cobalt, nickel, cadmium, and lead. The factors affecting the treatment process were investigated on the basis of the metal uptake by adsorption and/or chelation with the prepared functionalized membrane.

Effects of the treatment time and temperature

Economically, the time of treatment is a very important factor, as is the temperature, which affects the amount of metal-ion uptake by the unit mass of the functional groups of the grafted membrane. Figures 7–9 show the metal uptake by the grafted/treated HDuPE films and untreated HDuPE films as a function of the operation time, at 70 and 100°C, for different metal ions under the same experimental conditions. The metal uptake increases with time within the first 4 h, but thereafter, there is no significant increase in the metal uptake. This behavior has been observed for each metal under investigation. The lead-ion uptake and rate of exchange are much higher than those of the other metals, and this indicates that the rate and amount of the metal-ion uptake are dependent on the type of chelated metal ions, that is, on the stability of the chelate with the functional groups added to the polymer. When the amide and acetate groups are converted to carboxylate and hydroxyl groups by alkaline hydrolysis, the rate and amount of the metal-ion uptake are enhanced by the higher hydrophilic character of the treated membranes versus that of the untreated ones. As the temperature increases, the kinetic energy of the metal ions and mobility of the polymer graft chains increase as well, leading to a high diffusion of the metal-ion solution into the membrane functional groups and a high metal uptake.

Effect of the degree of grafting

The degree of grafting (the number of functional groups in the membrane) plays an important role in determining the amount of metal uptake by the membrane. Figures 10 and 11 show that the metal uptake increases with the degree of grafting and gives a nonlinear relationship. When the graft yield is below 125%, the rate of metal uptake is high, and then it decreases. The results suggest that the content of hydrophilic units increases as the degree of grafting increases; consequently, the diffusion of the metal-ion solution through the membrane increases. At a high grafting yield of approximately 150%, the content of the crosslinked network structure is high and restricts the diffusion of the metal-ion solution through the membrane.

Selectivity toward metal ions in a mixture

Figure 12 shows the selectivity of the grafted and KOH-treated membranes toward nickel, cobalt, cadmium, copper, and lead in the same feed solution with the XRF technique. These membranes show the ability to chelate these metal ions from their mixture in the sequence of copper > lead > cobalt > nickel, and no peak appears for cadmium. Moreover, such membranes are highly selective toward copper when

TABLE II
DSC Data for KOH-Treated and Untreated HDuPE-*g*-P(AAm/VAc)

Grafting (%)	Untreated HDuPE				Treated HDuPE		
	T_m (°C)	T_{m1} (°C)	T_{m2} (°C)	ΔH (J/g)	T_{m1} (°C)	T_{m2} (°C)	ΔH (J/g)
Blank	—	108	119.94	110.08	—	—	—
79	80	—	112.67	148.72	114.54	121	39.56
122.7	93	107	119.44	77.45	112.1	121.02	54.02
177	—	106	119	36.93	111.7	120.76	36.65

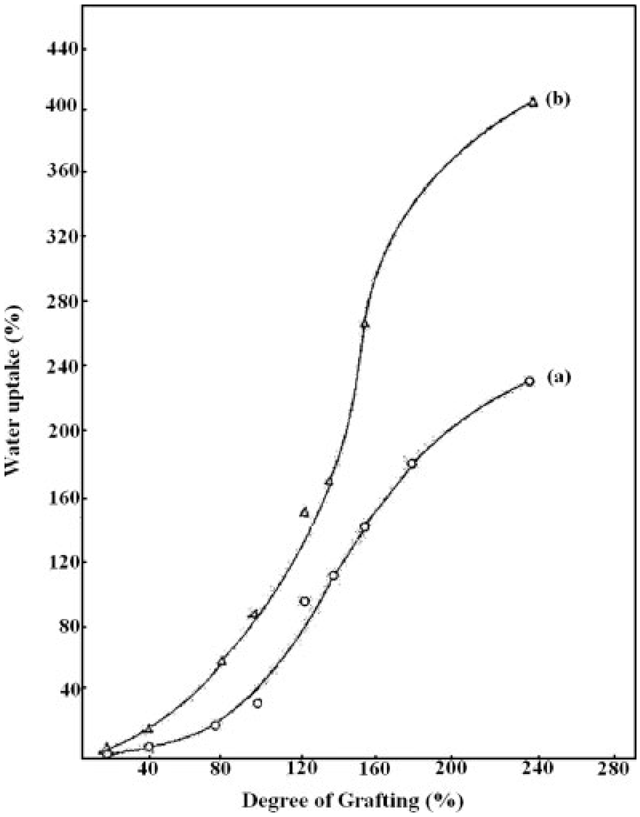

Figure 6 Water uptake as a function of the degree of grafting for (a) HDuPE-*g*-P(AAm/VAc) and (b) grafted/KOH-treated HDuPE.

it exists in a mixture with other metals. This means that divalent copper may form a more stable chelate with the functional groups added to the polymer by grafting and chemical treatment rather than the other metal ions investigated. The competition between these metal ions when they exist in a mixture and their size play important roles in their separation.

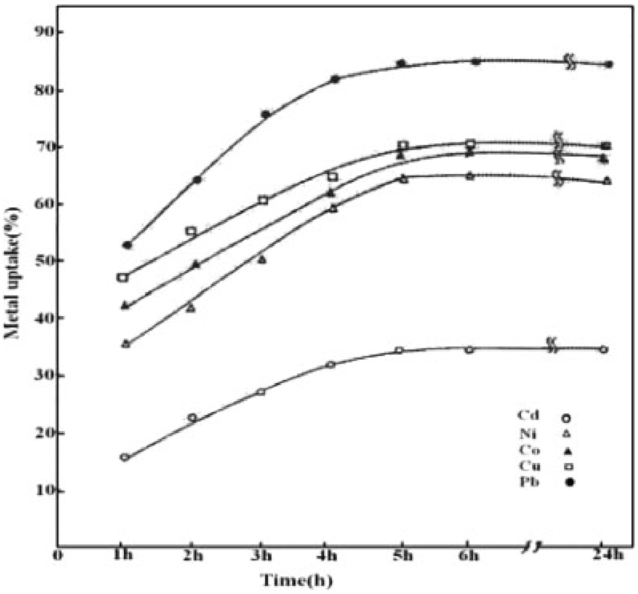

Figure 7 Effect of time on the metal uptake for grafted/KOH-treated HDuPE (degree of grafting = 123%; initial feed concentration = 500 ppm; temperature = 70°C).

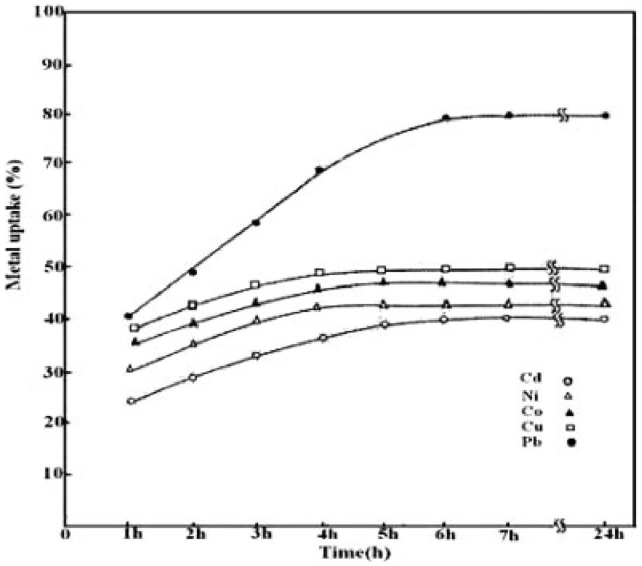

Figure 8 Effect of time on the metal uptake for grafted and untreated HDuPEs (degree of grafting = 123%; initial feed concentration = 500 ppm; temperature = 100°C).

CONCLUSIONS

For the graft copolymerization of a binary mixture of AAm and VAc in a MeOH/H_2O mixture as a diluent onto HDuPE films by the simultaneous method in an N_2 atmosphere, the degree of grafting depends on the comonomer composition and concentration as well as the irradiation dose. Graft copolymers that

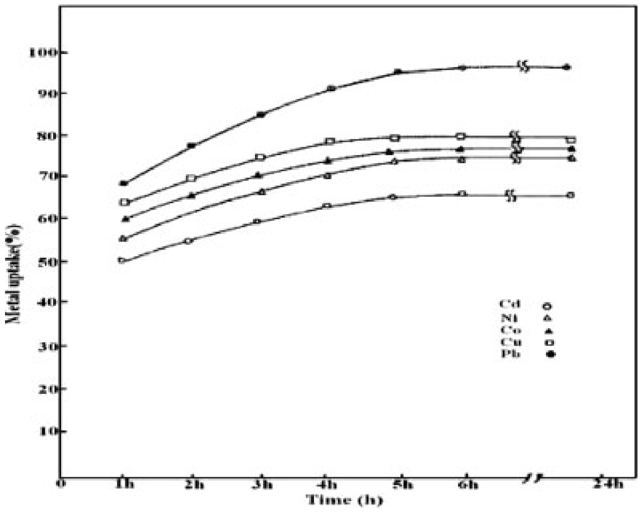

Figure 9 Effect of time on the metal uptake for grafted/KOH-treated HDuPE (degree of grafting = 123%; initial feed concentration = 500 ppm; temperature = 100°C).

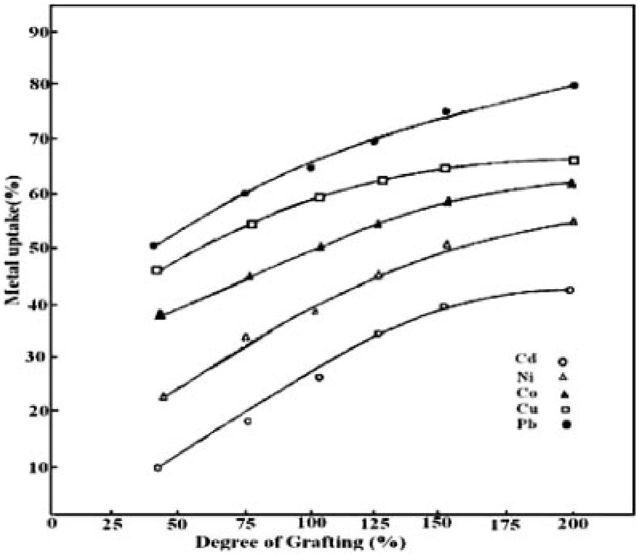

Figure 10 Effect of the degree of grafting on the metal uptake for grafted/untreated HDuPE (initial feed concentration = 500 ppm; temperature = 100°C; operation time = 4 h).

contain both carboxyl and hydroxyl groups have been successfully prepared and examined by alkali hydrolysis. The graft copolymerization results in increasing thermal stability of the base polymer. The metal-ion uptake of these prepared membranes is influenced by the operating conditions, such as the time and temperature. The rate and amount of metal-ion uptake increase with increasing temperature and degree of grafting. The alkali hydrolysis of HDuPE grafted with AAm and VAc improves the performance for wastewater treatment. On the basis of these experimental studies, it can be concluded that through the radiation grafting of PAAm and PVAc chains onto HDuPE, an effective membrane can be developed for the treatment of wastewater.

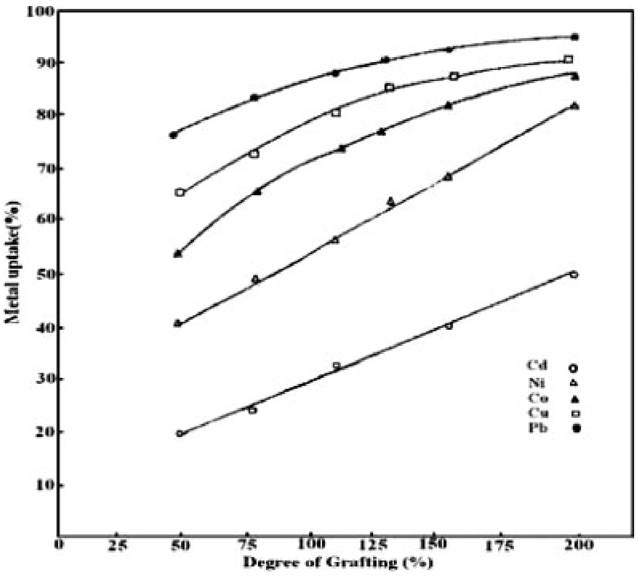

Figure 11 Effect of the degree of grafting on the metal uptake for grafted/KOH-treated HDuPE (initial feed concentration = 500 ppm; temperature = 100°C; operation time = 4 h).

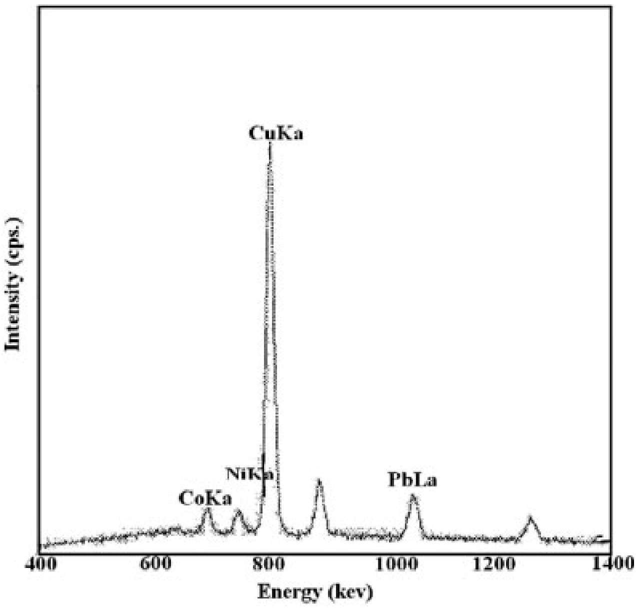

Figure 12 XRF scan for a mixture of lead, copper, cobalt, nickel, and cadmium ions chelated by grafted/KOH-treated HDuPE (initial feed concentration = 500 ppm; temperature = 100°C; operation time = 4 h).

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