

Separation and Extraction of Some Heavy and Toxic Metal Ions from Their Wastes by Grafted Membranes

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Received 17 April 2000; accepted 21 August 2000

ABSTRACT: Preparation and characterization of a series of ion-exchange membranes for the purpose of separation and extraction of some heavy and toxic metal ions from their wastes were studied. Such ion-exchange membranes were prepared by γ -radiation grafting of acrylonitrile (AN) and vinyl acetate (VAc) in a binary monomer mixture onto low-density polyethylene (LDPE) using the direct technique of grafting. The reaction conditions at which the grafting process proceeds successfully were determined. Many modification treatments were attempted for the prepared membranes to improve their ion-exchange properties. The possibility of their practical use in waste-water treatment to remove some heavy and toxic metal ions such as Pb^{2+} , Cd^{2+} , Cu^{2+} , Fe^{3+} , Sr^{2+} , and Li^+ were investigated. These grafted membranes showed great promise for possible use in the field of extraction and removal of some heavy and toxic metals from their wastes.

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Key words: γ -irradiation; grafting; membranes; metal separation

INTRODUCTION

Ion-exchange membranes play an important role in modern technology, especially in the separation and purification of materials. The search for improved membrane composition, using almost all available polymeric materials, has been the subject of extensive research because of the great practical importance of such compositions.¹ Grafting of polymers with a mixture of monomers is important since different types of chains containing various functional groups can be introduced into the polymer structure.² The properties of such ion-exchange membranes are determined by two parameters: the base polymer and the chemical structure and concentration of the fixed

ionic moieties.³ Recently, there has been a substantial growth of interest in the use of chelating sorbents in the field of water treatment and pollution control.⁴ Various forms of synthetic polymers containing complexing molecules which are available at low cost have emerged as among the most important materials for the synthesis of new sorbents.^{5,6}

In previous studies,^{7–10} copolymers of acrylic and vinyl monomers grafted onto low-density polyethylene (LDPE) were used for the extraction of several heavy metal ions. These grafted membranes can be applied for the treatment of contaminated water resources containing Pb, Cd, Fe, and Cu. They possess high thermal stability and good mechanical and hydrophilic properties. The synergistic effects of the two functional groups to selectively remove, separate, and recover metals were also studied.¹¹ The behavior of mixed weak electrolyte anion (amino) and cation (carboxylate)

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Journal of Applied Polymer Science, Vol. 81, 849–860 (2001)
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conventional ion-exchangers as an alternative to chelating polymers was investigated.¹² Graft copolymers involving acrylonitrile (AN) and vinyl acetate (VAc) have been the subject of considerable interest because these groups, acetate and nitrile, can be hydrolyzed by using different chemical reagents to give a variety of functional groups.^{13,14}

In this respect, therefore, the preparation of graft copolymers by direct radiation grafting of AN and VAc in a binary monomer mixture onto LDPE was studied. The effect of the grafting conditions, such as type of solvent and total radiation dose on the grafting process, was determined. Some chemical treatments were attempted on these graft copolymers to improve their ion-exchange property. The physical and chemical properties of the resultant grafted membranes and the possibility of their applications in various fields, such as in waste-water treatment, were investigated. Some properties of these membranes were also studied as a function of the grafting degree, such as water uptake and mechanical characteristics. Some factors that influence the ion-exchange property of the prepared ion-exchange membranes toward some selected ions were also investigated.

EXPERIMENTAL

Materials

LDPE films of 80- μm thickness were provided by the El-Nasr Co. for Medical Supplies (Cairo, Egypt). Reagent-grade AN of 99.3 % purity (Merck, Germany) and reagent-grade VAc of 99 % purity (Merck) were used as received. Other chemicals, such as solvents, inorganic salts, acids, and other reagents, were reagent grades of BDH (United Kingdom).

Graft Copolymerization

The direct radiation grafting method was used. The irradiation was carried out using Co-60 gamma rays at a dose rate ranging from 0.27–1.1 Gy/s in a nitrogen atmosphere. After irradiation, the grafted films were removed and washed, by extraction, in acetone as a solvent, at 50–60°C, to extract the embedded homopolymer. These films were then dried in an oven at 40–50°C for 24 h to a constant weight. The degree of grafting was

calculated by the percentage increase in the weight 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 blank and grafted films, respectively.

Chemical Treatment of the Graft Copolymers

Improvement of the hydrophilic and ion-exchange properties of the graft copolymers was carried out by treating them with aqueous KOH (5%) or with a 1:1 alcoholic solution containing 5% hydroxylamine-HCl at pH 7 and 90°C for 16 h. The treated films were then immersed in bidistilled water for 24 h to remove excess reagents and then dried in an oven at 40–50°C for 24 h.

Infrared Spectrophotometry

Analysis by IR spectrophotometry was carried out using a PYE Unicam SP1100 infrared spectrophotometer in the range of 4000–400 cm^{-1} .

Swelling Measurement

The clean dried grafted films of known weights were immersed in distilled water at 25°C until equilibrium was reached (almost 24 h). The films were removed, blotted quickly with absorbent paper, and then weighed. The percent of water uptake was calculated as follows:

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

where W_g and W_s represent the weights of the dry and wet grafted films, respectively.

Mechanical Properties Measurement

The measurement of tensile strength and elongation at break were employed by a Zwick tester Model 1425. Dumbbell-shaped specimens of 50 mm length and a neck of 2.8 mm wide were used in these tests and the crosshead speed was 50 mm/min.

Metal-uptake Measurement

Metal uptake was measured by immersing the membrane in the metal feed solution of a concentration of 1000 ppm for different time intervals and then removing it. The remaining metal salt in its feed solution was determined by an atomic

Table I Effect of Different Solvents on the Grafting of AN/VAC Binary Monomers onto LDPE at Comonomer Concentration of 30 wt % and Composition 50/50 wt %

Solvent	DMF	Acetone/DMF (1 : 1 wt %)	Acetone	DMF/MeOH (1 : 1 wt %)	MeOH	Dioxane
Degree of grafting (%)	19.2	18.8	12.8	19.5	14.3	13.2

absorption instrument (Perkin-Elmer Model 2380) using lamps for Cu, Co, Li, Fe, Pb, Sr, and Cd. Merck atomic absorption standard solutions of these metals were used for the calibration process.

RESULTS AND DISCUSSION

Effect of Solvent

In this study, different solvents were investigated for the grafting of a binary mixture of AN and VAc

onto LDPE to find a suitable solvent which enhances both the diffusion of the reaction mixture into the interior region of the film and the grafting process. The effect of different solvents on the grafting process is shown in Table I.

It was observed that no homopolymer was formed and homogeneous grafting was obtained in the presence of either DMF or acetone and both together in a mixture. However, a high homopolymer was formed in other solvents used here. The presence of DMF, acetone, and a mixture of them as solvents may reduce the *G* value of the mono-

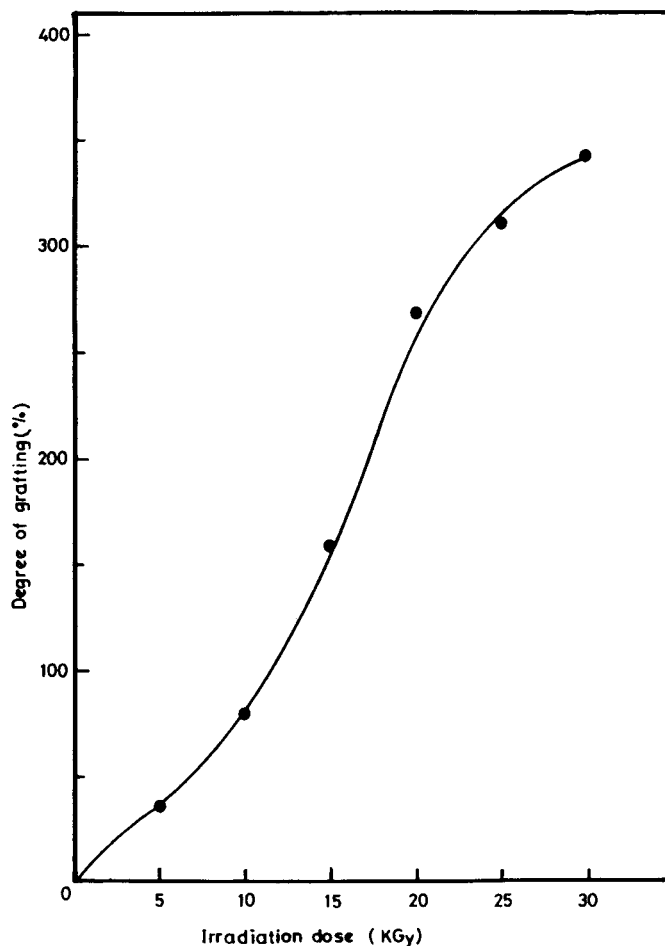


Figure 1 Effect of irradiation dose on the grafting yield of AN/VAc (70/30 wt %) onto LDPE in DMF at comonomer concentration of 60 wt %.

mers by chain transfer. This resulted in the graft polymerization's proceeding and retarding of the homopolymerization process. It was also observed that these solvents, DMF, acetone, and a mixture of them, vary in their ability to influence graft copolymerization and the following reactivity order was observed: DMF > acetone/DMF > acetone. The aforementioned results showed that the grafting of AN/VAc onto LDPE films was enhanced in the presence of DMF. This may be due to the greater diffusivity of AN/VAc into the polymer matrix in the presence of DMF. As a result, DMF was chosen to be the suitable solvent for this grafting system.

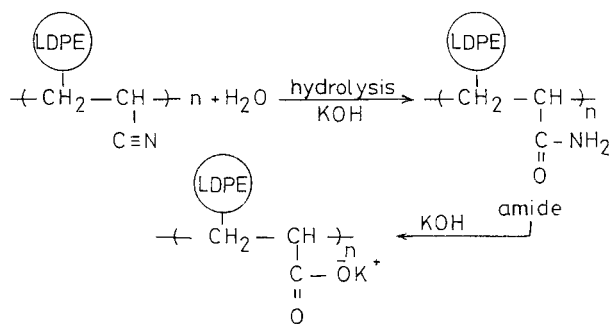
Effect of Irradiation Dose

The effect of irradiation dose on the degree of grafting of AN/VAc at a comonomer composition of 70/30 and a comonomer concentration of 60 wt % onto LDPE films is shown in Figure 1. It is found that the degree of grafting increases with the irradiation dose and it tends to level off at higher doses.

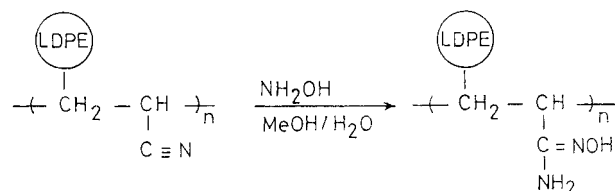
Increasing the grafting yield with the irradiation dose can be attributed to the increase of active sites. The acceleration occurs at doses ranging from 10 to 20 kGy and may be attributed to a "gel effect." At higher irradiation doses (>20 kGy), the grafting yield tends to level off due to the recombination of free radicals formed without initiating new sites for grafting. Meanwhile, a high homopolymer is formed at such high doses and the diffusion of the comonomer is restricted.¹⁵

Chemical Treatment of the Graft Copolymer

Further chemical treatment was made of the graft copolymers to improve their hydrophilic properties by treating them with KOH or an alcoholic hydroxylamine-HCl solution. The nitrile



Scheme 1



Scheme 2

groups can be hydrolyzed to give either amides or carboxylic acids (Scheme 1). The amide is initially formed, but since amides are also hydrolyzed with

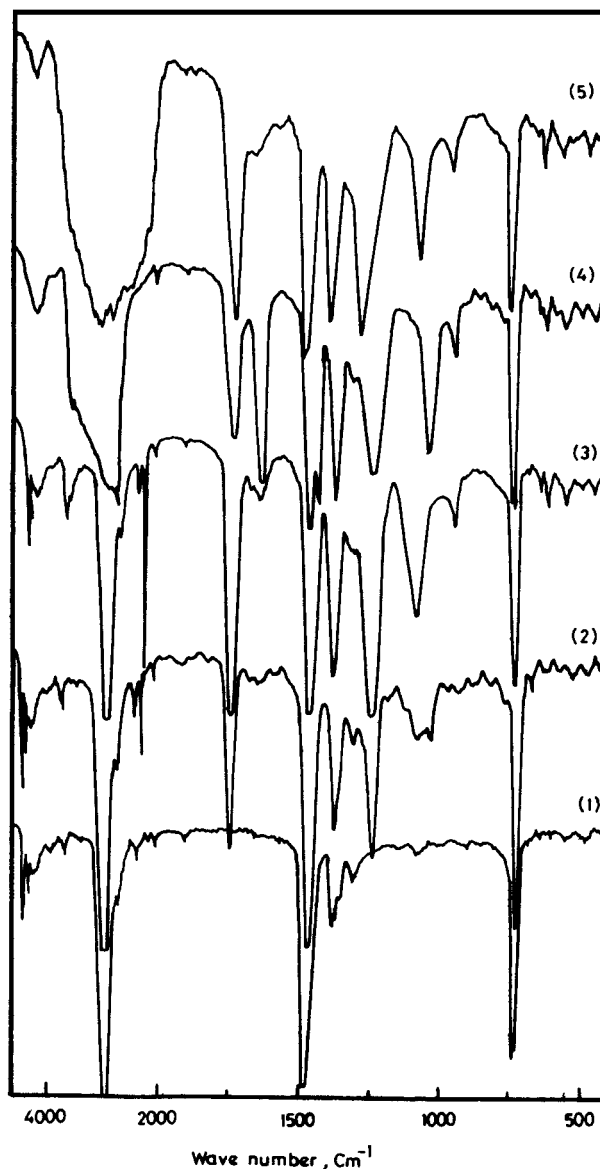


Figure 2 IR spectra of (1) LDPE-blank; (2) LDPE-g-P(AN/VAc), 9.2%, (3) LDPE-g-P(AN/VAc), 21.4%, (4) 21.4% treated with NH_2OH , and (5) 21.4% treated with KOH.

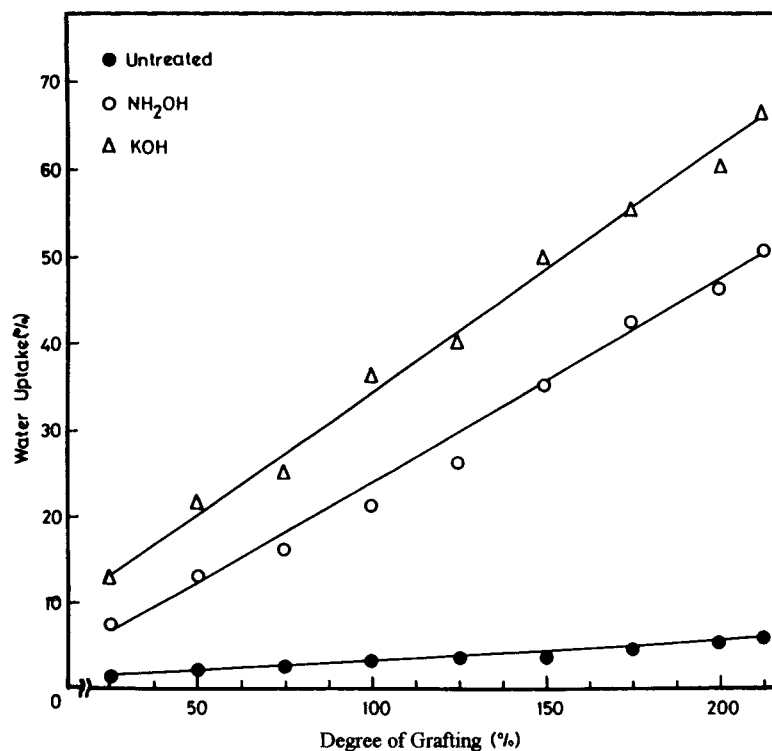


Figure 3 Water uptake as a function of grafting yield of AN/VAc (70/30 wt%) onto LDPE films.

acid or basic treatment, the carboxylic acid is the more common product.¹³ Therefore, both acetate and nitrile groups in the prepared graft copolymer are converted into hydroxyl and carboxylate ions, respectively, by treatment with the KOH solution. However, the treatment with alcoholic hydroxylamine-HCl results in amidoximation of nitrile groups¹⁴ (Scheme 2) and the acetate groups are also hydrolyzed.

IR Spectroscopy

Infrared analysis was made for the grafted LDPE films to confirm the formation of the graft copolymer (Fig. 2). The spectrum of the LDPE-g-poly(AN/VAc) [P(AN/VAc)] films shows a characteristic band of the C=N group of polyacrylonitrile (PAN) at 2250 cm⁻¹. New absorption bands appeared around 1740, 1240, and 1099 cm⁻¹ which correspond to the C=O groups of VAc and C—O and O—C=O stretching of acetate, respectively. It is also noted that the intensity of these absorption bands increases with increasing of the graft percent (spectra 2 and 3). The IR spectra for NH₂OH- and KOH-treated membranes (spectra 4 and 5) show that the absorbance at 2250 cm⁻¹

disappeared and a broad absorption band appeared around 3200–3600 cm⁻¹ and another peak around 1050 cm⁻¹ which are assigned to OH and C—O alcoholic groups, respectively. For KOH-treated films, new bands appeared around 1711 and 1290 cm⁻¹, which are the characteristic bands of the C=O and C—O stretching of carboxylic groups. For NH₂OH-treated films, new absorption bands appeared around 1425 and 1650 cm⁻¹ which are characteristic for C—N and amidoxime groups. The appearance of a broad band around 3170–3350 cm⁻¹ is assigned to the N—H group of amidoxime that resulted from the treatment of the nitrile group with NH₂OH—HCl.¹⁶

Swelling Behavior

Water content is very important for practical application, especially in the ion-exchangers, that is, the membrane should exhibit suitable hydrophilicity. Swelling of the membranes in water was measured as a function of the degree of grafting for the alkali-untreated and alkali-treated LDPE films grafted with PAN and polyVAc (PVAc) (Fig. 3). It can be seen that water-uptake percent in-

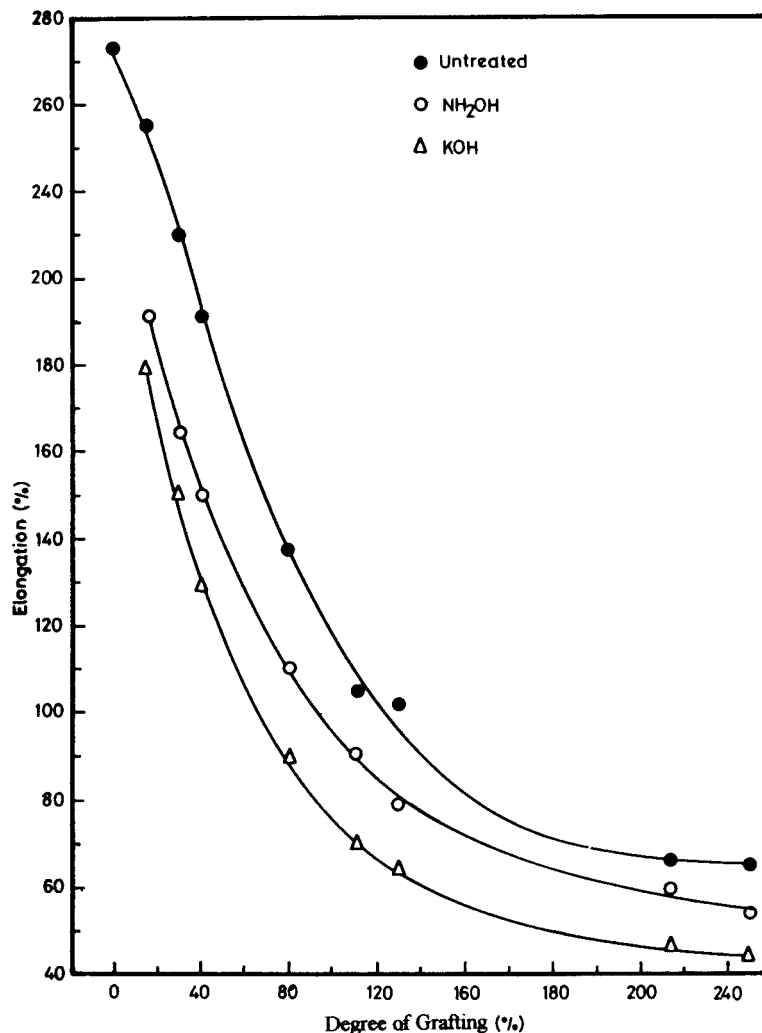


Figure 4 Change in elongation percent for untreated and treated grafted LDPE with degree of grafting.

creases linearly with the degree of grafting for both the alkali-untreated and alkali-treated grafted films. However, the alkali-treated graft copolymers possess much higher water uptake.

Upon grafting of AN and VAc onto LDPE, no significant increase in their water uptake with an increasing grafting yield was observed. These results are attributed to the introduction of hydrophobic groups: nitrile from AN and acetate from VAc. In Figure 3, the chemically treated membranes had a higher water uptake than that for the untreated ones, at a given degree of grafting, due to the increase in hydrophilicity. Moreover, the water uptake increases with an increasing grafting yield because of the increase in hydrophilic groups introduced into the graft copolymer by hydrolysis or amidoximation processes.¹⁷ The

results showed also that for the untreated LDPE membrane having 150% grafting the swelling percent is only 3.5%, which became 10 times higher for the NH₂OH-treated membrane while it reached 46% for the KOH-treated membrane having the same degree of grafting. The alkaline treatment resulted in hydrolyzing the acetate groups to hydroxyl ones which are hydrophilic in nature. Therefore, the swelling character for KOH-treated graft copolymers is higher than that for ones treated with NH₂OH, due to the influence of the carboxylate structure, which is highly solvated in water and affects the properties of the graft copolymer. These results indicated that the swelling behavior depends mainly on the amount and form of functional reactive groups introduced into the polymer substrate by grafting. The KOH

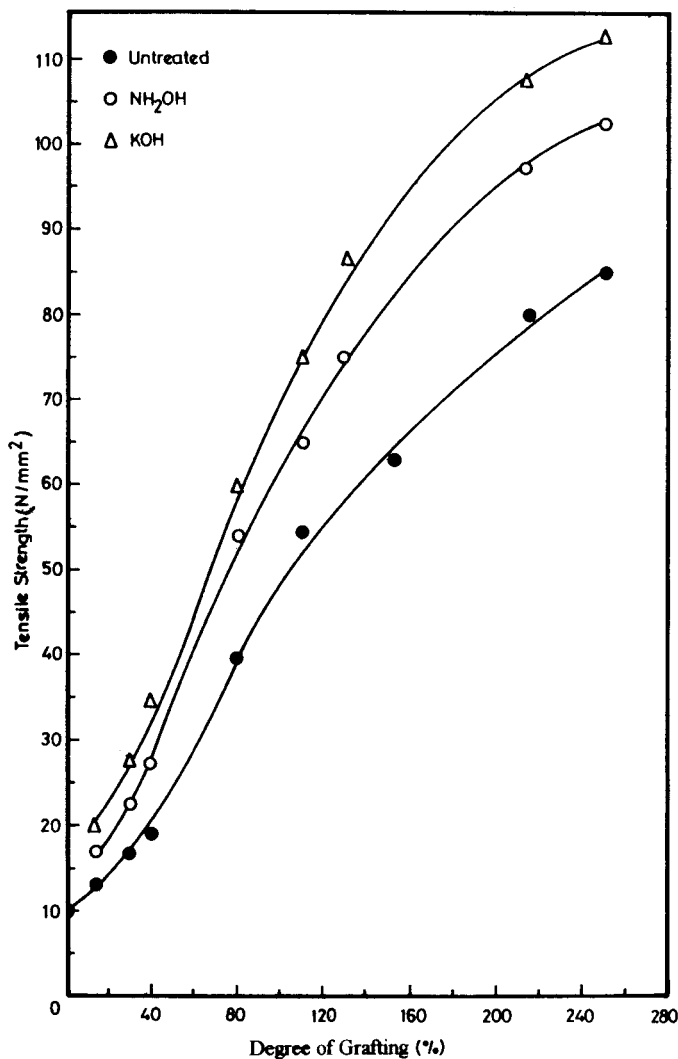


Figure 5 Change in tensile strength for untreated and treated grafted LDPE with degree of grafting.

hydrolyzed membranes have a stronger affinity to water than have the NH_2OH -treated ones.

Mechanical Properties

One of the necessities for the membrane properties is to exhibit mechanical properties acceptable for practical use. Figures 4 and 5 show the changes of the elongation percent (E_b) and tensile strength (T_b) at break for the original, grafted, and alkali-treated grafted LDPE membranes. It can be seen that T_b increases with the degree of grafting but E_b decreases. The T_b of the graft copolymer increases with the degree of grafting due to incorporation of the polar nitrile groups of PAN and their interactions and also to the crosslinking formation due to grafting and irradi-

ation, leading to a restriction in the chain mobility and, consequently, a decrease in E_b occurred. But at a lower degree of grafting, the crosslinking network structure is located close to the film surface.

The results showed that the alkaline treatment of such grafted films either with KOH or $\text{NH}_2\text{OH}\text{--HCl}$ resulted in increasing the T_b and decreasing the E_b compared with the untreated graft copolymer. These results indicated that the conversion of nonpolar acetate groups to the polar hydroxyl groups and their interactions and the formation of amidoxime and carboxylate groups by the alkaline treatment of nitrile groups with $\text{NH}_2\text{OH}\text{--HCl}$ or KOH has an effect. It was also observed that, at a given graft percent, the T_b of

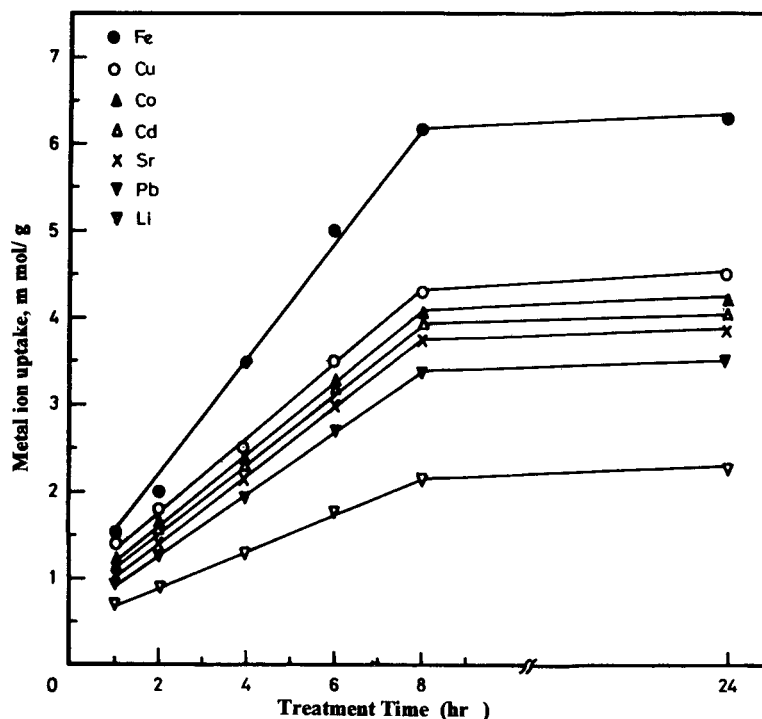


Figure 6 Effect of treatment time on metal uptake for 200% grafted LDP treated with KOH. Initial feed concentration: 1000 ppm; pH for Fe, 3; for Cu, Pb, and Sr, 5; and for Li, Cd, and Co, 6 at 100°C.

the KOH-treated membranes was higher than that of NH_2OH -treated ones due to the carboxylate groups formed by the KOH treatment. The formation of such $-\text{COO}^-$ groups leads to a polar-polar interaction and, consequently, the T_b increased and the E_b decreased.

Application of Grafted Membranes in Metal Uptake

Separation of some selected metal ions, which commonly exist in waste water, was investigated. Among the factors affecting the treatment process of such metal ions from their wastes using the prepared membranes are the following:

1. Treatment time.
2. pH of metal-ion feed solution.
3. Temperature.

Effect of Treatment Time

From an economical point of view, the time of treatment is an important factor. Also, the efficiency of the membrane in waste treatment can be determined from the time required to adsorb

the maximum capacity of metal ions by chelation or adsorption with its functional groups.

Figures 6 and 7 show metal uptake as a function of time for different metals using grafted LDPE films treated either with KOH or NH_2OH . It can be seen that metal uptake increases with time to reach its maximum value (which is termed here as the maximum membrane capacity) at almost 8 h of treatment for the different metal ions investigated. Increasing the treatment time higher than 8 h causes no significant increase in metal uptake even after 24 h. It can be seen that the maximum metal uptake is of the sequence $\text{Fe}^{3+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cd}^{2+} > \text{Sr}^{2+} > \text{Pb}^{2+} > \text{Li}^+$. It is also observed that, under the same reaction conditions, KOH-treated membranes show a higher tendency to metal chelation or adsorption than that of the NH_2OH -treated ones, but the sequence order of the metal uptake remains the same.

These results are reasonably explained by considering the diffusion coefficients of these metal ions through the ionic membrane, which are dependent mainly on their polarity, electronic configuration, ionic radii, etc., and also, importantly,

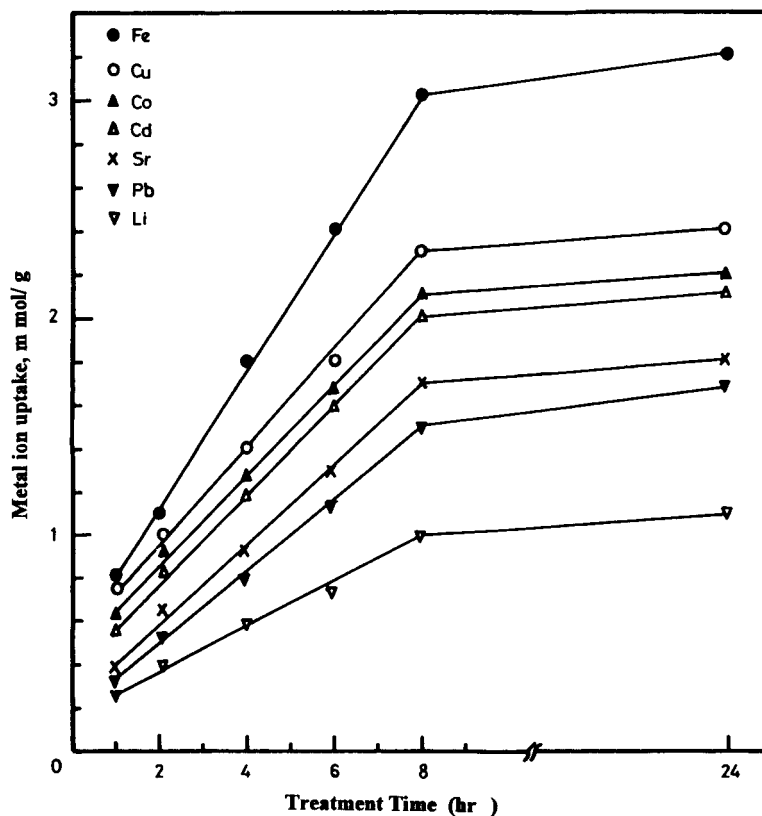


Figure 7 Effect of treatment time on metal uptake for 200% grafted LDPE treated with NH_2OH . Initial feed concentration, 1000 ppm; pH for Fe, 3; for Cu, Pb, and Sr, 5; and for Li, Cd, and Co, 6 at 100°C .

on the nature of interaction with the functional groups of the membranes. Li^+ , which is tested as a toxic metal ion, is not capable of chelation or adsorption with the functional groups of the membranes. It is well known that lithium, because of its high charge density, has a large hydrated radius and, therefore, low mobility; consequently, its adsorption capacity is low. In general, the grafted and treated membranes showed good affinity toward the chelation and/or adsorption of different heavy or toxic metal ions investigated here and the efficiency of such membranes was high and the maximum metal uptake was reached after 8 h.

Effect of pH of Feed Solution:

The availability of the membranes under investigation for metal-ion chelation or adsorption is pH-dependent. The sorption characteristics of such membranes treated either with KOH or NH_2OH toward Fe^{3+} , Cd^{2+} , Co^{2+} , Cu^{2+} , Pb^{2+} , and Li^+ were investigated over a pH that ranged

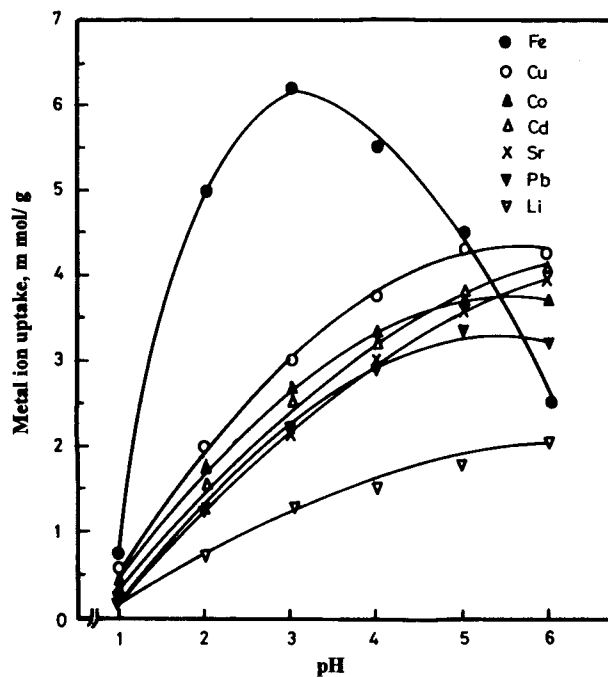


Figure 8 Effect of pH on metal uptake for 200% grafted LDPE treated with KOH. Initial feed concentration, 1000 ppm; immersion time, 8 h at 100°C .

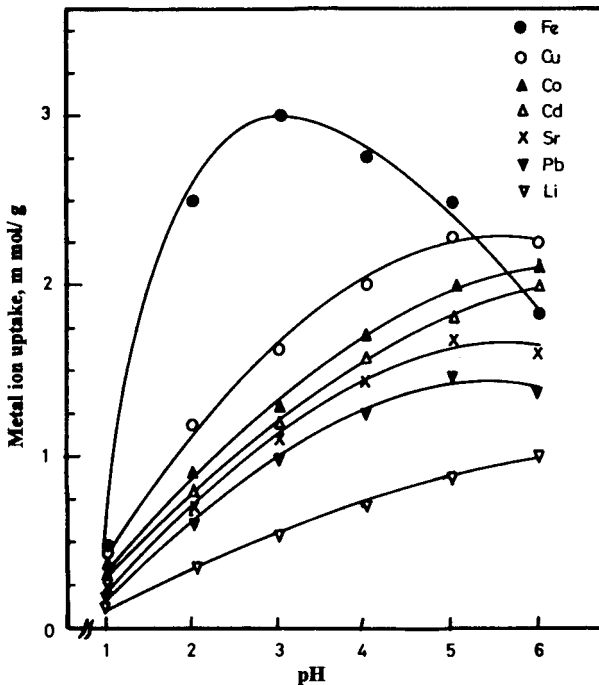


Figure 9 Effect of pH on metal uptake for 200% grafted LDPE treated with NH_2OH . Initial feed concentration, 1000 ppm; immersion time, 8 h at 100°C .

from 1 to 6 (Figs. 8 and 9). It can be seen that the amount of metal-ion uptake by these membranes increases significantly as the pH increases and the maximum uptake was reached at pH 5. The uptake of Fe^{3+} ions reaches its maximum at pH 3; then it decreases due to the formation of its hydroxide. On the other hand, the metal-ion uptake under highly acidic conditions is sharply decreased for almost every chelating exchanger due to the competition of hydrogen ions. The above results indicated that each metal ion has its optimum pH at which it can be easily extracted by these membranes, that is, the metal uptake is very dependent on the pH of its feed solution.

Effect of Temperature:

Temperature is another important factor which affects the chelation or adsorption of metal ions by the membrane functional groups. Figures 10 and 11 show the relation between the amount of metal-ion uptake expressed in mmol/g and the temperature for grafted LDPE membranes that were treated with either KOH or NH_2OH . It can be seen that the amount of metal-ion uptake increases with increasing temperature for all membrane forms investigated. This can be attributed

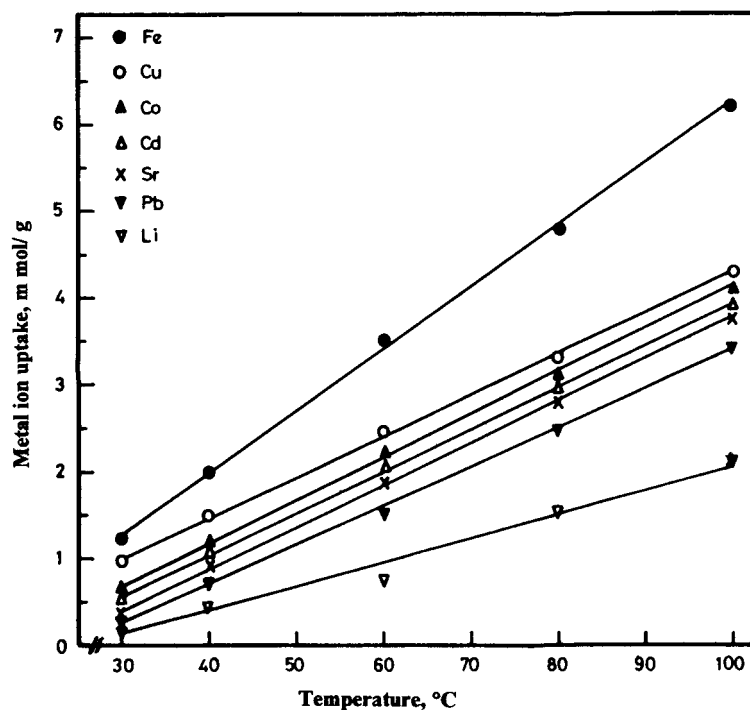


Figure 10 Effect of temperature on the metal uptake for 200% grafted LDPE treated with KOH. Initial feed concentration, 1000 ppm; pH for Fe, 3; for Cu, Pb, and Sr, 5; and for Li, Cd, and Co, 6; immersion time, 8 h.

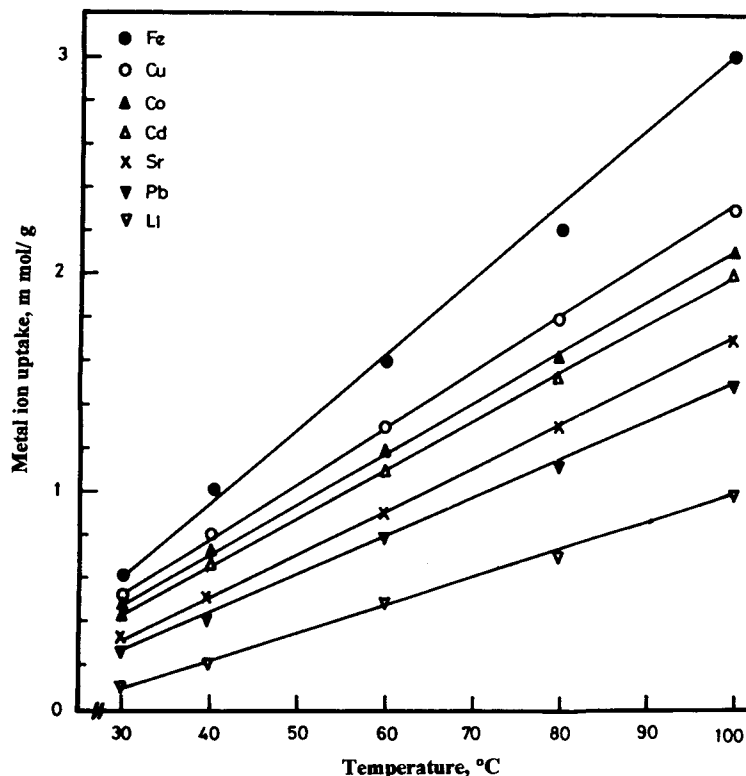


Figure 11 Effect of temperature on the metal uptake for 200% grafted LDPE treated with NH_2OH . Initial feed concentration, 1000 ppm; pH for Fe, 3; for Cu, Pb, and Sr, 5; and for Li, Cd, and Co, 6; immersion time, 8 h.

to the increase in kinetic energy of the metal ions with the temperature and the increase in the flexibility of the polymer graft chains as well. The diffusion of the metal ion solution in the membrane and the amount of metal-ion uptake also increase with the temperature. It was observed that the maximum metal-ion uptake is obtained at the boiling point at which the highest diffusion occurred.

CONCLUSIONS

It can be concluded that the prepared graft copolymer possessed good mechanical and hydrophilic properties. The grafted films thus obtained, containing both acetate and nitrile groups which were then hydrolyzed with KOH or NH_2OH to confer an ionic character of easily ionizable groups, may be of interest in some practical uses such as in the field of waste-water treatment. These synthetic grafted membranes can be used for the removal of some toxic and heavy metals

such as Fe^{3+} , Cu^{2+} , Co^{2+} , Cd^{2+} , Sr^{2+} , Pb^{2+} , and Li^+ .

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