

Development of Membranes by Radiation Grafting of Acrylamide into Polyethylene Films: Properties and Metal Ion Separation

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ABSTRACT: Polyethylene-*g*-polyacrylamide membranes were prepared by graft polymerization of acrylamide into polyethylene films using a preirradiation technique. The membranes showed good swelling in water and a maximum of 232% swelling was achieved for a graft level of 590%. The electrical resistance of the membranes decreased with increase in the degree of grafting to 200% and then stabilized with a further increase in grafting to 590%. The membranes had an excellent binding capacity for mercury ions. Almost 99% mercury separation was achieved from a metal solution of 200 ppm. The metal binding capacity increased with increase in the degree of grafting in the membranes. A binding capacity as high as 6.2 mmol/g in a membrane with 590% grafting was achieved. The pH of the metal solution did not have any significant influence on the binding ability of the membranes. The mercury-loaded membranes showed better thermal stability as compared to those without metal binding. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 282–291, 2002

Key words: polyethylene; acrylamide; membrane; radiation grafting; mercury separation

INTRODUCTION

Water contamination is a universal problem where toxic materials from different sources, such as the leaching of minerals from rocks and industrial effluent, contribute to ecodegradation.¹ Following strict legislative regulations, it becomes a prerequisite to remove toxic metals from effluents before discharging them into drains. Consequently, great effort has been made to separate and recover these metal ions from heavy metal contaminated waste water using the concept of the chelating ability of polymeric materials.² This

is being done by the proper tailoring of polymeric structures by chemical means in such a way that it may perform a chelating function for a specific metal ion.^{3–8}

Radiation-induced graft polymerization of vinyl and acrylic monomers into polymer films has generated considerable interest toward the development of membranes for various technologically important fields.^{9–16} It offers a versatile way to impart desirable properties into a polymer without much affecting its original characteristics. Moreover, graft distribution may be achieved throughout the matrix because of the radiation activation of the film across its thickness.¹¹ The modification may be achieved for a polymer already existing in the film form, which overcomes the rheological problems asso-

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ciated with the transformation of a grafted matrix into a thin foil.

The grafting of acrylic monomers into polyethylene films to produce membranes has been reported by several workers.¹⁷⁻²¹ These membranes have been found to be very effective in separating different metal ions from waste water. Recently, we carried out the grafting of acrylamide into polyethylene films to develop membranes for the separation of toxic metals from textile waste water.²²⁻²⁵ These membranes undergo considerable changes in the surface morphology as well as in the bulk structure as a function of the grafted polyacrylamide component.^{24,25} Membranes undergo considerable deterioration in the crystalline structure and have very little crystallinity at higher graft levels. In the present study, the physical properties, such as swelling characteristics and electric resistance as well as mercury binding, of these radiation-grafted polyethylene-*g*-polyacrylamide membranes with different degrees of grafting were investigated.

EXPERIMENTAL

Materials

Polyethylene (PE) films of 40 microns were received from Reliance Industries (India). A gamma radiation chamber (900 curies) supplied by the Bhabha Atomic Research Center, India was used for the irradiation of films.

Acrylamide (SISCO, India) was used as received without any further purification. Mercuric acetate was received from Loba Chemie (India). Glaxo supplied potassium chloride and sodium hydroxide. Hydrochloric acid was received from Merck (India). Double-distilled water was used for all experiments.

Graft Copolymerization

Polyethylene-*g*-polyacrylamide (PE-*g*-PAAm) membranes with different degrees of grafting were prepared by graft polymerization of acrylamide onto PE films by preirradiation method.^{22,23} γ -Irradiation was carried out under air at a radiation dose rate of 0.36 kGy/h.

Graft polymerization was carried out on γ -irradiated PE films under nitrogen atmosphere in a glass tube containing a monomer solution of a desired concentration. Acetone-water was used as a medium for the grafting reaction. After the

reaction, grafted films were extracted with hot water to remove traces of any homopolymer adhering to the film surface. The grafted films were dried under vacuum and weighed. The degree of grafting in PE films was calculated from the following equation:

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

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

Swelling Measurements

The equilibrium swelling of membranes was measured in distilled water as reported earlier.¹⁹ Dried membranes were immersed in the water for 24 h under ambient conditions ($\sim 30^\circ\text{C}$). After removing the membranes from the water, the excess water adhering to the surface was removed by blotting them with an adsorbent paper and then they were quickly weighed. The percent swelling was measured from the increase in the weight of the membranes as follows:

$$\text{Percent swelling} = \frac{W_s - W_d}{W_d} \times 100 \quad (2)$$

where W_d and W_s are the weights of the dry and wet membranes, respectively.

Electric Resistance Measurements

The electric resistance of the membranes was measured after conditioning them in 0.5M KCl solution for 24 h as reported earlier.¹⁹

Mercury Uptake Measurements

The mercury uptake of membranes was studied on a mercury analyzer-MA 5800E, supplied by the Electronics Corp. of India Ltd. A calibration plot of optical density versus the mercuric acetate concentration was made and the Hg^{2+} concentration of the unknown solution was obtained from this calibration plot.

For metal ion separation, the mercuric acetate solution was prepared by dissolving it in distilled water and the desired pH was adjusted using acetic acid or sodium hydroxide solutions. The mercuric acetate concentration was used in the range of 200–20,000 ppm and the liquor ratio was maintained at 1:500. To study the metal separa-

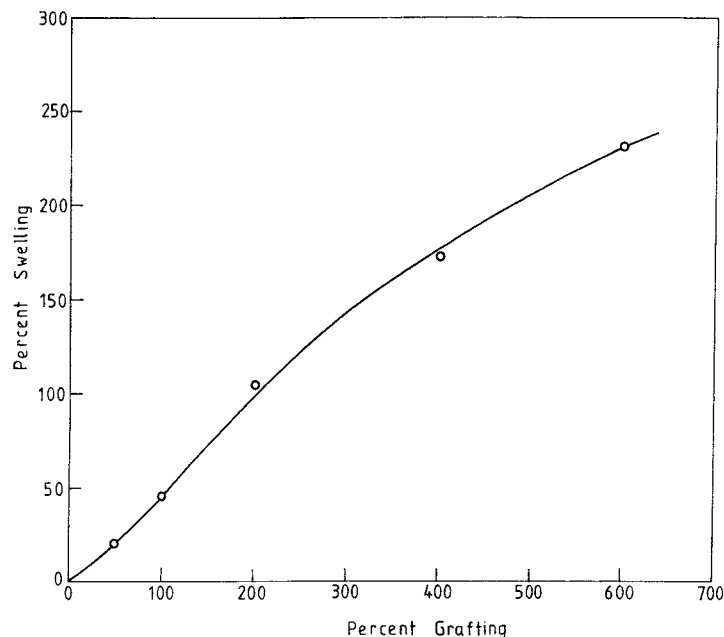


Figure 1 Variation of percent swelling with percent grafting in PE-g-PAAm membranes.

tion at a low metal ion concentration of 200 ppm, a liquor ratio of 1:100 was maintained. Membranes were immersed in the metal ion solution for a desired period at room temperature under stirring. The membranes were subsequently removed from the solution and the remaining solution was analyzed for the metal ion concentration.

The regeneration of metal ion-loaded membranes was studied by eluting them in 1M hydrochloric acid. The supernatant liquid was then analyzed for the mercury ions. The regenerated membrane was reused for mercury chelation in four repeated cycles at a Hg^{2+} concentration of 10,000 ppm and at a pH of 4.6. The liquor ratio was maintained at 1:500.

Thermogravimetric Analysis (TGA)

TGA studies on the samples were carried out on a Perkin-Elmer TGA-7 system. The thermograms were obtained under a nitrogen atmosphere at a uniform heating rate of $10^\circ\text{C}/\text{min}$ in the temperature range of $50\text{--}550^\circ\text{C}$. The relative thermal stability of the samples was evaluated in terms of the initial decomposition temperature (IDT).

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR measurements on the samples were recorded on a Jasco Micro FTIR. The membranes

were vacuum-dried at 50°C before carrying out the measurements and the FTIR measurements were recorded in the absorbance mode.²⁶

RESULTS AND DISCUSSION

Swelling Behavior

The variation of the equilibrium swelling with the degree of grafting is presented in Figure 1. Swelling increases with increase in the degree of grafting in membranes and a maximum of 232% swelling for a graft level of 590% is achieved. This may be understood from the fact that the membranes acquire hydrophilicity due to the presence of PAAm-grafted domains. The hydrophilicity of the membranes increases with increase in the PAAm content within the matrix, which is reflected in an increase in the swelling of the membranes. Similar observations were made by Dessouki et al. for acrylamide-grafted PE membranes.²⁷ However, in our studies, the degree of swelling is much higher than that observed by these authors. Probably, the structure of the membranes developed in our system is more amenable to water uptake due to the sharp decrease in the crystallinity by grafting.²⁵ As a result, large amorphous volumes may be available for water penetration within the membrane.

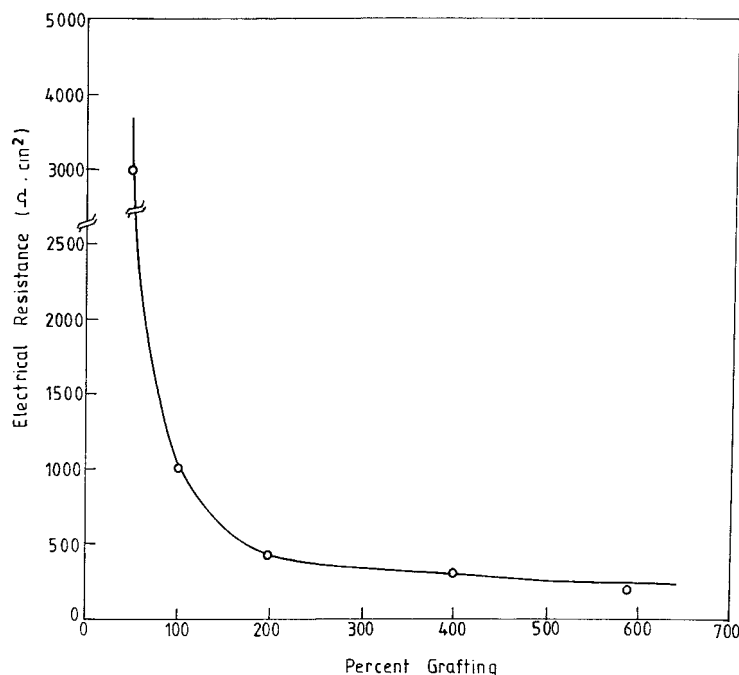


Figure 2 Variation of electrical resistance with percent grafting in PE-g-PAAm membranes.

Electric Resistance Measurements

The electric resistance of membranes as a function of the degree of grafting is presented in Figure 2. The resistance decreases with increase in the degree of grafting and a minimum of 176 $\Omega \text{ cm}^2$ is achieved for a graft level of 590%. A similar trend in the resistance of polyacrylic acid-grafted PE membranes was also observed in our earlier studies.¹⁹ However, the absolute values of the membrane resistance in the present work are much higher than those in our previous work on PE membranes. It may be stated that initial grafting takes place at the film surface only and proceeds further by progressive diffusion of the monomer within the film through the water-swollen-grafted domains.^{14,19} The high resistance at low graft levels is due to the nonhomogeneity in the graft distribution, where very few grafted chains are present, and this middle portion offers high resistance in the membrane. At higher graft levels of 200% and more, the film appears thoroughly grafted as well as homogeneous and shows the least resistance.¹⁴ A slow decrease in the electrical resistance even after 200% grafting is due to efficient water management within the membranes at a higher graft level.²⁸

Mercury Separation

The binding of mercury ions to the membranes with degrees of grafting in the range of 54–590% was evaluated to optimize their metal sorption behavior. The variation of the mercury sorption with the contact time for a graft level of 398% is presented in Figure 3. The initial concentration of mercury was 200 ppm at a pH of 4.6. The results show that mercury binding by the membrane is quick, and almost complete mercury separation was achieved within 2 h under our experimental conditions. Following this observation, a contact time of 2 h was maintained for subsequent sorption studies. It is interesting to see that the membrane is effective even for the low level of 200 ppm mercury concentration. It may, therefore, be mentioned that the amide groups within the membrane are unique sites for mercury binding. Bicak and Sherrington²⁹ reported a very high mercury uptake of 3 g/g of the crosslinked PAAm polymer, which corresponds to nearly 9 mmol/g of the polymer.

The mercury uptake increases with increase in the mercury concentration and tends to stabilize at 10,000 ppm (Fig. 4). A mercury binding capacity of 6.2 mmol/g was achieved for a membrane with 590% grafting under specified sorption con-

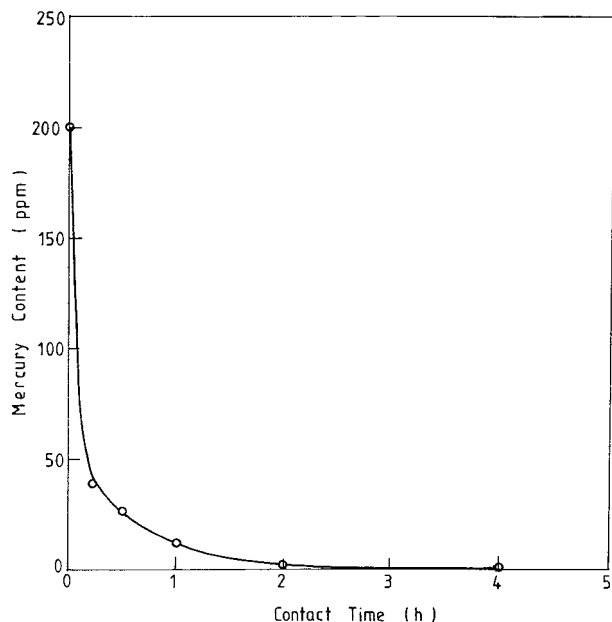


Figure 3 Variation of mercury content with contact time in PE-g-PAAm membranes. Percent grafting, 398%; pH, 4.6; Hg^{2+} , 200 ppm; liquor ratio, 1:100.

ditions. The variation of the mercury binding capacity of the membranes with the degree of grafting is presented in Figure 5. The binding capacity increases with increase in the PAAm graft level in the membranes. The results indicate excellent in-

teraction between the mercury ions and the amide groups within the membrane, which leads to their high binding capacity. The crystalline structure of the membranes is disrupted significantly and a highly amorphous structure develops at the high graft levels of 590%.²⁵ The loss of crystallinity makes the matrix highly permeable, which may be a favorable factor in the accessibility of mercury ions to the amide groups within the membrane. Bicak et al. also reported that acrylamide-grafted cellulose acts as a very effective sorbent for the removal of mercury ions and a mercury loading capacity of 3.55 mmol/g was achieved.³⁰

Variation of the binding capacity with the pH of the metal solution is presented in Figure 6. It is interesting to note that the pH does not have any significant impact on the metal binding capacity of the membranes. Mercury binding has been shown to be considerably affected by the pH in the membranes containing carboxyl groups, where protonation of the carboxylate ions is favored over mercury binding at a lower pH.³¹ Probably, such a scenario is not operating with the mercury sorption in the membranes with amide groups, which leads to a very little change in the mercury binding. Similar behavior of the pH medium in mercury binding by hydrazide chelating fibers was reported by Liu et al.³²

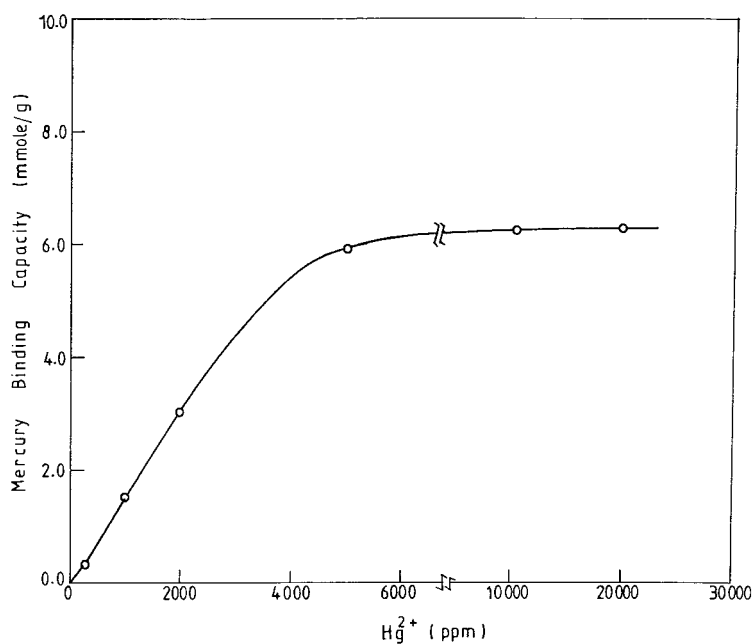


Figure 4 Variation of mercury binding capacity with Hg^{2+} concentration. Percent grafting, 398%; pH, 4.6; time, 2 h; liquor ratio, 1:500.

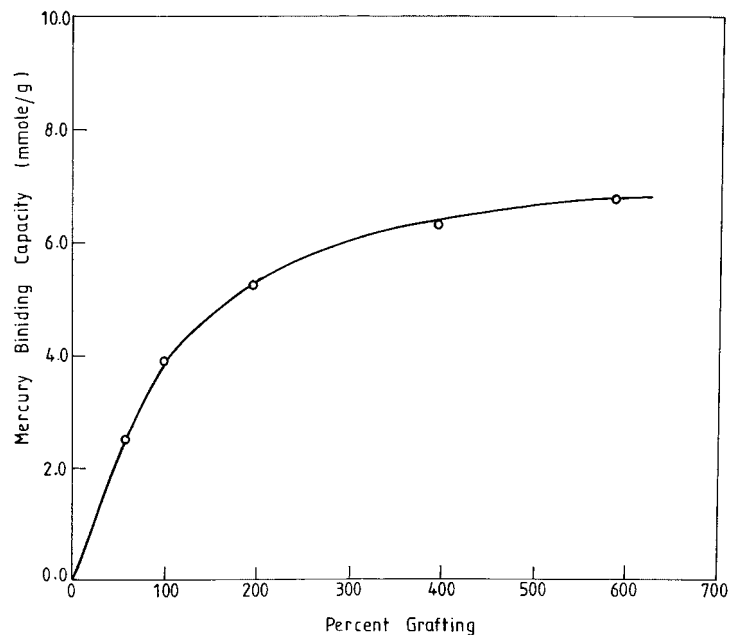


Figure 5 Variation of mercury binding with percent grafting. pH, 4.6; time, 2 h; Hg^{2+} , 10,000 ppm; liquor ratio, 1:500.

Figure 7 shows the metal binding capacity and amide content in the membranes as a function of the degree of grafting. The mercury:amide ratio stands slightly higher than 0.5 for all the membranes (Table I). This suggests that the chelation

of mercury involving two amide linkages may be the most appropriate binding mechanism; at least, some other route of metal interaction also operates in the system. Probably, a fraction of mercury is also linked in the form of monosubsti-

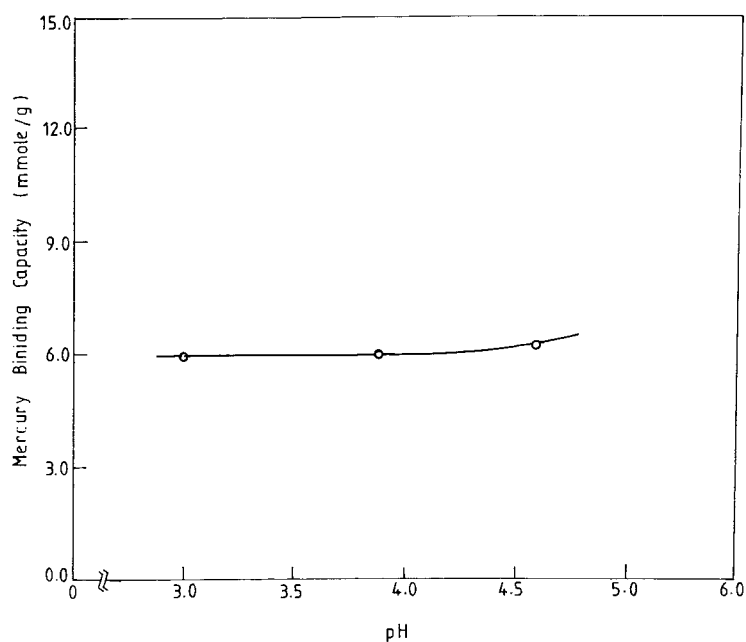


Figure 6 Variation of the mercury binding capacity with pH of the medium. Percent grafting, 398%; time, 2 h; Hg^{+2} , 10,000 ppm; liquor ratio, 1:500.

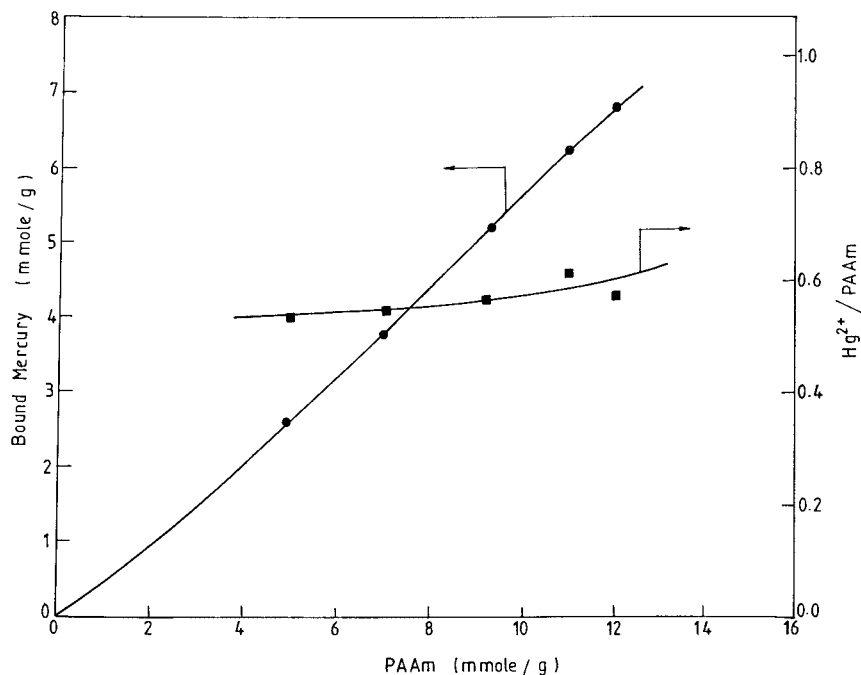


Figure 7 Variation of bound mercury and $\text{Hg}^{2+}/\text{PAAm}$ with PAAm content in the membranes.

tuted linkages such as $-\text{NH}-\text{HgOAc}$ as mentioned in mercury separation by Bicak and Sherrington and by Sreedhar and Anirudhan and account for the higher ratio of mercury binding.^{29,31}

Desorption of mercury was carried out to investigate the regeneration and rebinding ability of the membranes. The results are presented in Table II. It may be seen from the results that the metal binding capacity of the membranes decreases marginally in subsequent cycles of sorption. The metal binding declined from 6.22 to 5.92 mmol/g after four cycles. However, the membrane after each cycle is regenerated to nearly 98%. The loss in the metal binding capacity is nearly 4.8% after four successive cycles. It is also possible that

some of the PAAm (which is a water-soluble component) that might be in the occluded state is leached out during the regeneration process and is reflected in the loss of binding capacity. However, it may be stated that hydrochloric acid treatment is an efficient way to regenerate membranes for subsequent reuse in metal separation.

Thermogravimetric Analysis (TGA)

Primary thermograms of ungrafted PE, the PE-g-PAAm membrane (100% grafting), and mercury-loaded PE-g-PAAm membranes (100% grafting) are presented in Figure 8. The thermogram of PE

Table I Mercury Binding of PE-g-PAAm Membranes with Different Degrees of Grafting

Percent Grafting	PAAm (mmol/g)	Hg^{2+} (mmol/g)	$\text{Hg}^{2+}/\text{PAAm}$
54	4.94	2.61	0.53
100	7.04	3.82	0.54
198	9.29	5.21	0.56
398	11.09	6.22	0.61
590	12.11	6.80	0.56

Hg^{2+} , 10,000 ppm; pH, 4.6; liquor ratio, 1 : 500.

Table II Adsorption and Desorption of Mercury Ions by PP-g-PAAm Membranes with 398% Degree of Grafting

Repeat Cycle	Hg^{2+} Adsorption (mmol/g)	Hg^{2+} Desorption (mmol/g)	Recovery (%)
I	6.22	6.10	98.1
II	6.01	5.95	99.0
III	5.96	5.92	99.3
IV	5.92	5.84	98.6

Hg^{2+} , 10,000 ppm; pH, 4.6; liquor ratio, 1 : 500.

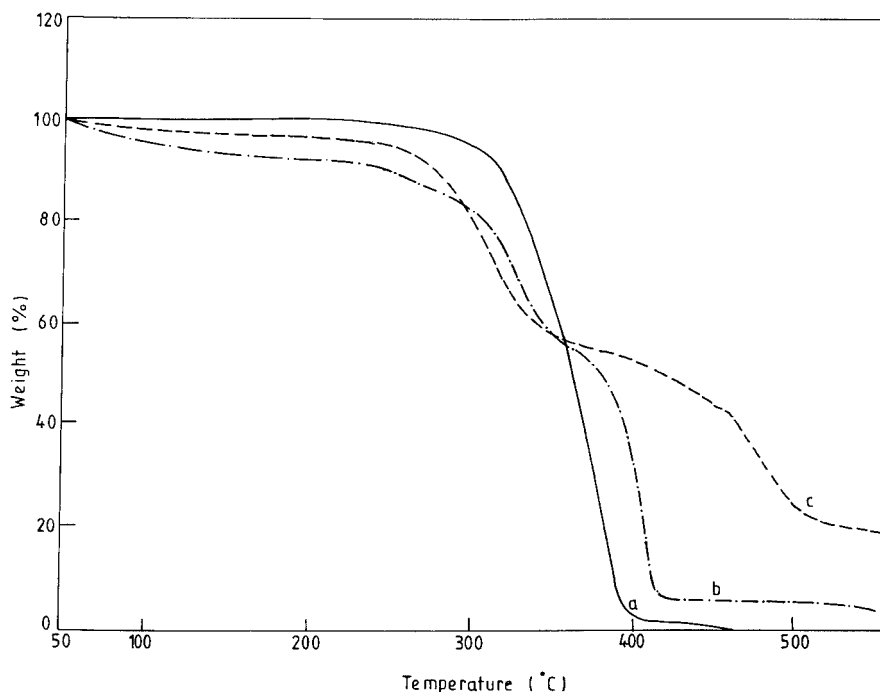


Figure 8 TGA thermograms of (a) PE, (b) PE-*g*-PAAm (percent grafting 100%), and (c) PE-*g*-PAAm-Hg membranes (percent grafting 100%). Heating ratio, 10°C/min; N₂ atmosphere.

shows clean single-step degradation with an IDT of 311°C. However, the thermograms of acrylamide-grafted PE membranes show a multistep degradation pattern, which may be divided into three distinct steps, that is, dehydration, PAAm degradation, and PE main-chain decomposition.²⁵ The thermogram of the mercury-loaded membrane, on the other hand, shows some distinct changes. The loss of moisture in the dehydration step is much lower (3.6%) as compared to the virgin membrane (7.8%). This may be attributed to the fact that once mercury is bound to the amide groups few free sites for interaction with water by hydrogen bonding are available. The weight loss in the second step corresponds to the PAAm component in the membrane. The loss in the subsequent step may be assigned to the main-chain degradation as observed in the grafted membrane. Interestingly, the IDT of this step is enhanced from 311°C for the virgin membrane to 440°C for the mercury-loaded membrane. A significant amount of residue is formed at the end of the thermogram. The high thermal stability of the mercury-loaded membranes may be ascribed to the crosslinking by metal ions. These observations suggest that mercury loading influences the copolymer degra-

ation by virtue of the interlinking of PAAm chains by metal ions and leads to an overall increase in the thermal stability of the graft copolymer membranes. Similar observations were made by Hegazy et al. for the PE membranes containing different metal ions.¹⁷ The authors found that the thermal stability strongly depended on the nature of the chelating ion.

FTIR Measurements

FTIR measurements on the different membranes are presented in Figure 9. The unmodified PE shows a doublet peak associated with C—H bonding in the range of 1400–1500 cm⁻¹. However, the spectrum of grafted PE membrane shows additional peaks in the range of 1550–1800 cm⁻¹. The peak at 1665 cm⁻¹ may be assigned to the C=O stretching vibration of the amide group.³⁰ These peaks may be attributed to the carbonyl stretching of amide groups, indicating the presence of grafted PAAm chains within the PE membrane matrix. It is interesting to see that in the mercury-bonded membrane the broadening of some peaks takes place and an additional peak arises at 1553 cm⁻¹. The peak at 1589 cm⁻¹ in the

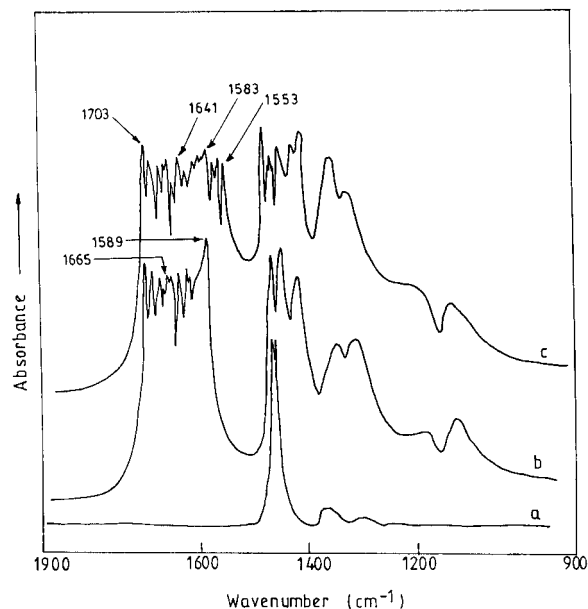


Figure 9 FTIR of (a) PE, (b) PE-g-PAAm (percent grafting 100%), and (c) PE-g-PAAm-Hg (percent grafting 100%) membranes.

grafted membrane broadens in the mercury-loaded sample. However, the shifting of the peak at 1589 cm^{-1} in the grafted sample to 1583 cm^{-1} in the mercury-loaded sample is also indication of the involvement of amide nitrogen in the coordination with the metal ions.

CONCLUSIONS

The graft polymerization of acrylamide into PE films leads to membranes which show good swelling in aqueous medium. Membranes with low electrical resistance ($\sim 200\text{ ohm cm}^2$) are produced at high graft levels. The membranes have an excellent ability to chelate mercury ions from the aqueous solution. The mercury-binding capacity of the membranes strongly depends on the degree of grafting. The higher the grafting, the higher is the mercury uptake. Mercury uptake as high as 6.2 mmol/g was achieved for a membrane having a 590% degree of grafting. The membranes are very effective in separating mercury from a solution of as low a concentration as 200 ppm. The metal binding capacity of the membranes is not affected by the pH of the solution in the range of 2.6 and 4.6, suggesting that there is no competition between the proton and mercury binding to the amide groups. The mercury-loaded

membranes show a different degradation pattern as compared to the virgin membrane. The higher thermal stability of mercury-loaded membranes may be an outcome of the crosslinking of PAAm chains by mercury ions. In an attempt to design membranes with additional functional groups, a partial hydrolysis was carried out to introduce carboxyl groups. The structure and metal binding capacity of such membranes will be presented subsequently.³³

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