Separation of Tc-99m by Means of Radiation-Grafted Membranes

H. KAMAL,[1] EL-SAYED A. HEGAZY,[1] K. EL-ADHAM,[2] M. ABDEL GELEEL[2]

[1] National Centre for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt

[2] National Centre for Nuclear Safety and Radiation Control, P.O. Box 29, Nasr City, Cairo, Egypt

ABSTRACT: The characterization and possibility of the practical use of different polymeric materials for the purpose of radioactive isotope separation from their wastes were studied. The influence of chemical treatment on the chelation or adsorption capacity at 25 °C was investigated. The equilibrium swelling of these polymers in distilled water at room temperature and the effect of solvent composition on the graft yield were also explored. In this study, the mechanical, chemical resistance and other properties for the grafted, untreated, and treated membranes were investigated. The performance of the membranes was studied as a function of time and degree of grafting. The effects of chemical treatment on the initial activity and separation of Tc-99m have also been examined. The base polymer and degree of grafting have great influence on the Tc uptake. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 1207–1215, 2001

Key words: gamma radiation; membranes; separation; low-level waste; technetium 99-m

INTRODUCTION

With different, increasing sources of radioactive waste, concern about the treatment of low-level radioactive waste is growing.[1] The synthesis of ion-exchange membranes by radiation grafting of acrylic acid (AAc) onto polyethylene and fluorinated polymers for adsorption of different metal ions from simulated waste solutions has been investigated.[2–8] Adsorbents containing amidoxime groups, which make chelate complexes with uranyl ions, are noted[9–11] for the recovery of uranium from seawater.

In this respect, radiation-induced graft copolymerization of an AAc and acrylonitrile (AN) comonomer system onto low-density polyethylene (LDPE), high-density polyethylene (HDPE), and polypropylene (PP) films was studied for preparing ion-exchange membranes, which can meet the requirements of separation of Tc-99m from their wastes. The different variables affecting the grafting reaction (including solvent and its composition, the addition of inorganic salts, and acids) were examined as well as the chemical treatment of the grafted carboxylic and nitrile groups. Characterization and some properties of the prepared membranes were carried out, such as swelling in water and chemical stability and mechanical properties.

EXPERIMENTAL

Materials

LDPE, HDPE, and PP films of thicknesses 70, 30, and 55 μm, respectively, were produced by El-

Nasr Co. for Medical Supplies, Egypt. AAc of purity 99% (Merck) and AN of purity 99.3% (Merck) were used as received. Other chemicals such as solvents, inorganic salts, acids, and other reagents were reagent grade.

Graft Copolymerization

The direct-radiation-grafting method was used as a technique. The irradiation was carried out using Co-60 γ rays at a dose rate 0.6 Gy/s in nitrogen atmosphere. After irradiation, the grafted films were removed and soaked in dimethylformamide (DMF) and then washed with hot distilled water to extract the residual monomers as well as the homopolymer. These films were then dried at 40–50 °C in an oven for 24 h to constant weight. The degree of grafting was calculated by percentage increases in weight as follows

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

where W_o 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 (3%), 1/1 alcoholic solution containing 3% hydroxylamine/HCl at pH 7 or with HCl (3 mol %) using a reflux system at 90 °C for 16 h. The treated films were then washed and immersed in distilled water for 24 h to remove the excess reagents and then dried in oven at 40–50 °C for 24 h. The treatment of the nitrile group with HCl converts it to the amide group, whereas the alkaline treatment with KOH and NH_2OH converts the nitrile to carboxylate and amidoxime groups, respectively.[11,12]

Swelling Measurement

The grafted and treated films were immersed in distilled water for different times at 25 °C, then removed, blotted quickly with absorbent paper to remove the water that attached on its surface, and finally quickly weighed. The degree of swelling was determined as follows

$$\text{Swelling (\%)} = \{(W_s - W_g)/W_g\} \times 100$$

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

Mechanical Properties

The measurements of tensile strength and elongation at break were performed by an Instron Model 1195, England. Dumbbell shaped specimens (length of 50 mm, with a neck width of 25 and 4 mm) were used in these tests, and the crosshead speed was 50 mm/ min.

Radioactive Waste Treatment

Technetium (Tc)-99m waste was introduced from the hospitals of Ain Shams University. The activity of the radioactive liquid waste was measured using a Multichannel Analyzer Model-800 A. The grafted treated membrane was immersed in the radioactive liquid waste, and the remaining activity was then measured after removing the membrane. Therefore

$$\text{Tc-99m Uptake (\%)} = \{(I_0 - I)/I_0\} \times 100$$

Table I   Effect of Different Solvents on the Grafting of AAc and AAc/AN (50/50) Binary Monomers onto LDPE, HDPE, and PP Films of Thicknesses 70, 30, and 55 μm, Respectively (Irradiation Dose: 20 kGy, AAc and AAc/AN Concentration: 30 wt %)

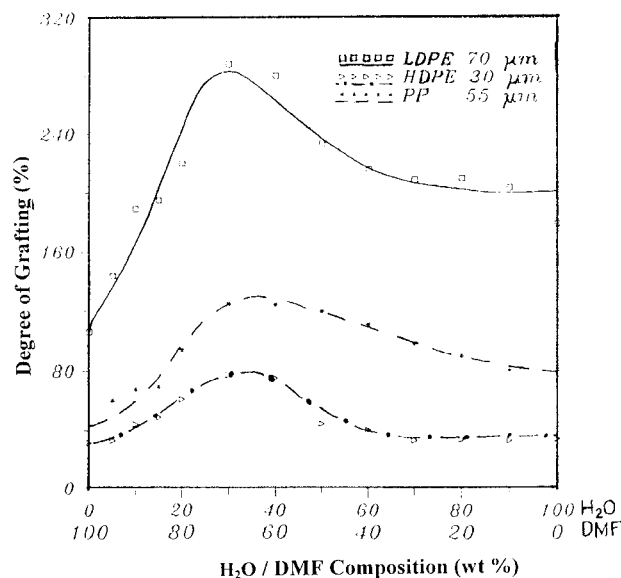| | Degree of Grafting (%) | | | | | |
| | AAc | | | AAc/AN | | |
Polymer Substrate	H_2O	H_2O/MeOH (70/30 wt %)	MeOH	H_2O	H_2O/DMF (50/50 wt %)	DMF
LDPE	26.3	19.4	3	29.8	217.8	94.9
HDPE	37.4	13.6	3.9	50.6	38.8	49.5
PP	7	4.3	3	41.5	122.1	87.3

Figure 1 Effect of H_2O/DMF composition on the degree of grafting of AAc/AN 50/50 (wt %) (comonomer concentration: 30 wt %, irradiation dose: 20 kGy).

where I_0 and I represent the initial and the remaining activity, respectively.

RESULTS AND DISCUSSION

Preparation of the Grafted Membranes

Effect of Solvent

Table I summarizes the effect of different solvents on the degree of grafting of AAc and AAc/AN comonomer onto LDPE, HDPE, and PP films. The maximum degree of grafting was obtained when water was used as a diluent for AAc, and the decrease in water content, that is, increase in MeOH content, leads to a decrease in the degree

of grafting. However, in the AAc/AN comonomer system the maximum grafting extent was obtained when a H_2O/DMF mixture of composition (50/50 wt %) was used as a solvent, whereas the minimum grafting extent was obtained in the absence of DMF.

The apparent increase in the grafting of AAc in the unitary system and its mixture with AN in the binary system in the presence of H_2O and H_2O/DMF, respectively, may arise from the increased diffusivity of AAc and AAc/AN into the polymer matrix. This leads one to believe that the presence of these solvents may reduce the G value of these monomers by chain transfer. This would result in aiding graft polymerization and retarding the homopolymerization processes. Therefore, water was selected to be the suitable diluent for the grafting of AAc, whereas H_2O/DMF was used for the AAc/AN comonomer.

Effect of Solvent Composition

The influence of the H_2O/DMF mixture composition on the grafting yield of AAc/AN (50/50 wt %) was determined and is graphically represented in Figure 1. The degree of grafting increases as the water content increases in the solvent mixture until it reaches its maximum value at 30/70 (wt %) of the H_2O/DMF mixture. Thereafter, the addition of more H_2O results in a reduction of the graft copolymerization yield.

The aforementioned results suggest that the increase in DMF content is required to enhance the diffusivity of AN with AAc because DMF is a good solvent for AN, as reported in literature.[13] However, a higher H_2O content results in the hinderance of the diffusion of AN and facilitates only the diffusion of AAc as a result of the less hydrophilic properties of AN as compared with that of AAc, which is highly hydrophilic. The pre-

Table II Effect of Inorganic Salts on the Degree of Grafting of 30 wt % of Aqueous AAc and AAc/AN (50/50 wt %) in H_2O/DMF (30/70 wt %) as Solvent onto LDPE, HDPE, and PP Films (Comonomer Concentration: 30 wt %, Irradiation dose: 20 kGy, Inorganic Salt Concentration: 0.5 wt %)

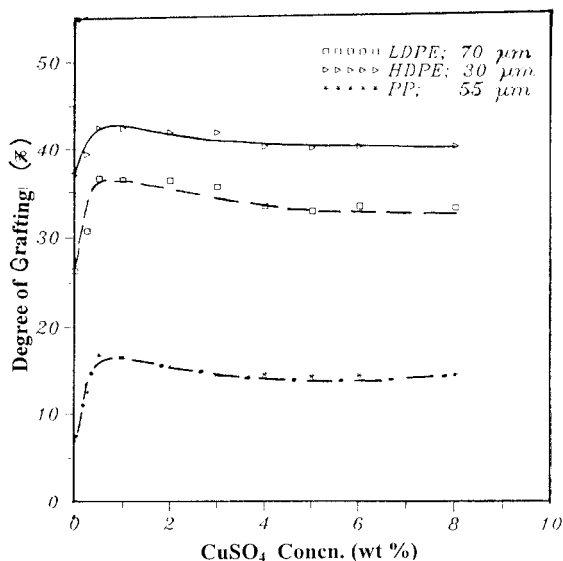| Polymer Substrate | Degree of Grafting (%) | | | | | |
| | Salts—Free | | CuSO$_4$ | | FeSO$_4$ | |
	AAc	AAc/AN	AAc	AAc/AN	AAc	AAc/AN
LDPE	26.5	92.4	31.6	117.8	31.9	87.9
HDPE	36	39.8	37	55.8	43.2	48.4
PP	7	83.3	13.8	102.1	13	77.4

Figure 2 Effect of copper sulfate concentration on the degree of grafting of AAc (30 wt %) in H_2O as a solvent (irradiation dose: 20 kGy).

vious data indicate that the most suitable H_2O/ DMF mixture composition is 30/70 (wt %).

Effect of Inorganic Salts Addition

Although the direct method of radiation grafting is the most efficient one, because the radicals can
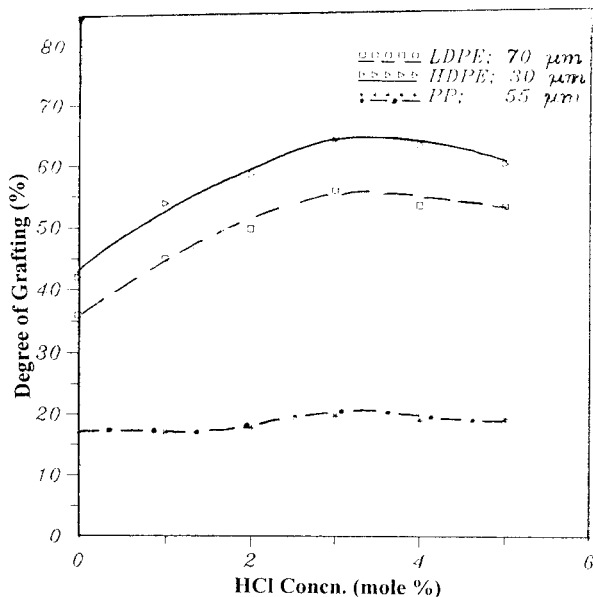

Figure 3 Effect of HCl concentration on the degree of grafting of AAc (30 wt %) in water as a solvent and in presence of 0.5 wt % $CuSO_4$.

Table III   Effect of Addition of 3 mol % HCl on the Grafting of AAc/AN (50/50 wt %) Binary Monomers onto LDPE, HDPE, and PP Films in H_2O/DMF (30/70 wt %) As a Solvent and in Presence of 0.5 wt % $CuSO_4$

Polymer Substrate	Degree of Grafting (%)	
	In Absence of HCl	In Presence of HCl
LDPE	117.8	287.8
HDPE	55.8	75.8
PP	102.1	122.1

react as fast as they are formed, excessive homopolymerization is encountered competing with the grafting reaction. Therefore, the grafting system, that is, the monomer and the substrate to be grafted, should be selected carefully in such a way that the sensitivity of both moieties toward γ radiation is comparable. Generally, it is much better that the radical yield (G value) of the substrate to be grafted is higher than that of monomer so the homopolymerization is minimized.

Inorganic salts such as $CuSO_4$ and $FeSO_4$ were added to the reaction mixture in an attempt to optimize the grafting conditions of AAc and the AAc/AN mixture onto LDPE, HDPE, and PP films. The results are listed in Table II.

The grafting process is affected by the addition of such inorganic salts. Such effects are different and varied depending on the type of salt and also
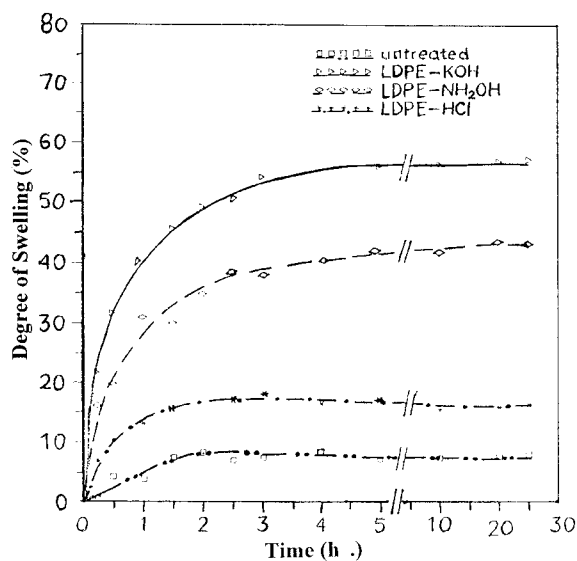

Figure 4 The equilibrium swelling of untreated LDPE-*g*-(AAc/AN) and treated ones.
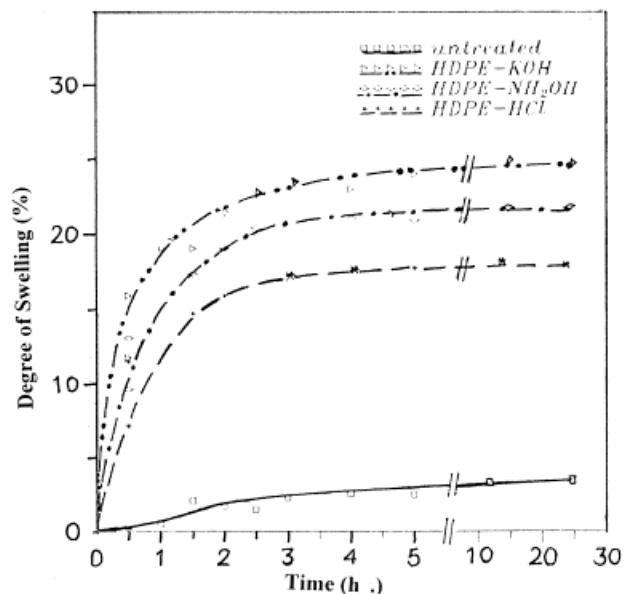
Figure 5 The equilibrium swelling of untreated HDPE-*g*-(AAc/AN) and treated ones.

on the polymer substrate. The maximum degree of grafting was obtained when $CuSO_4$ was used as an additive and the film looks to be homogeneous and smooth.

Effect of $CuSO_4$ Concentration

Figure 2 shows the effect of varied $CuSO_4$ concentrations on the grafting of AAc onto LDPE,
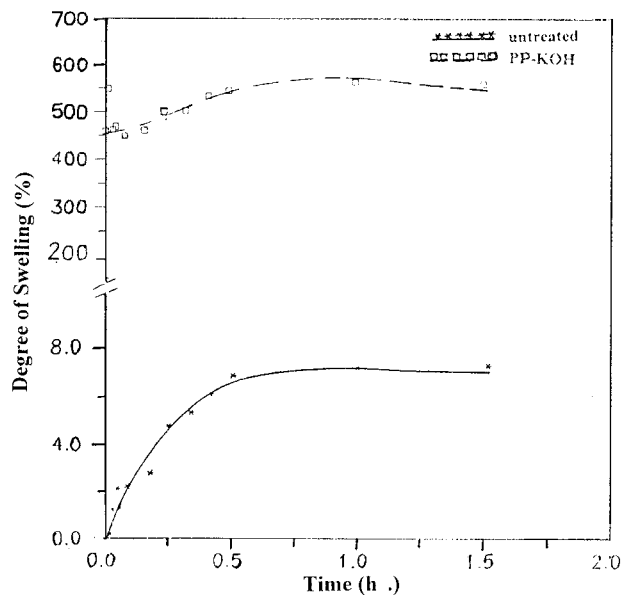

Figure 6 The equilibrium swelling of untreated and treated PP-*g*-(AAc/AN) film.
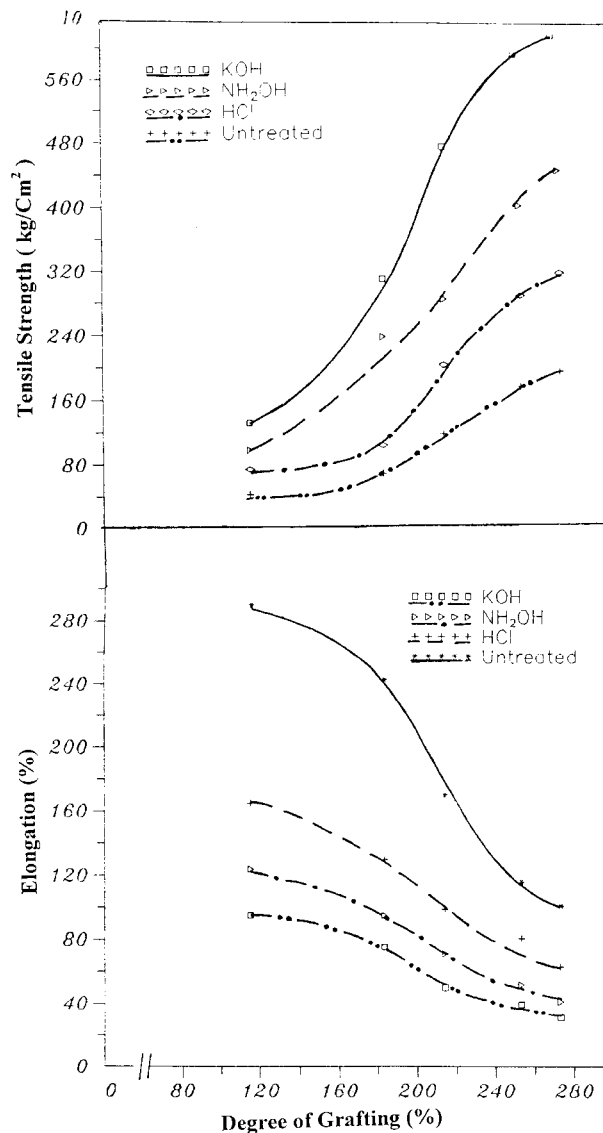

Figure 7 Change in tensile strength and elongation percent with degree of grafting for the untreated and treated LDPE-*g*-P(AAc/AN) films.

HDPE, and PP. The grafting yield increases with $CuSO_4$ concentration to reach a maximum value at 0.5 wt % of $CuSO_4$ and the homopolymerization is reduced to a minimum. Further increase in $CuSO_4$ concentration is accompanied by a monotonic decrease in the grafting yield.

The addition of such a salt may affect the chain-transfer process of AAc monomer and/or the chain transfer of its growing graft-chain radicals, leading to somewhat hgher grafting yield and lower homopolymer formation. On the other hand, at high $CuSO_4$ concentration the Cu ions may form a complex with AAc monomer; there-
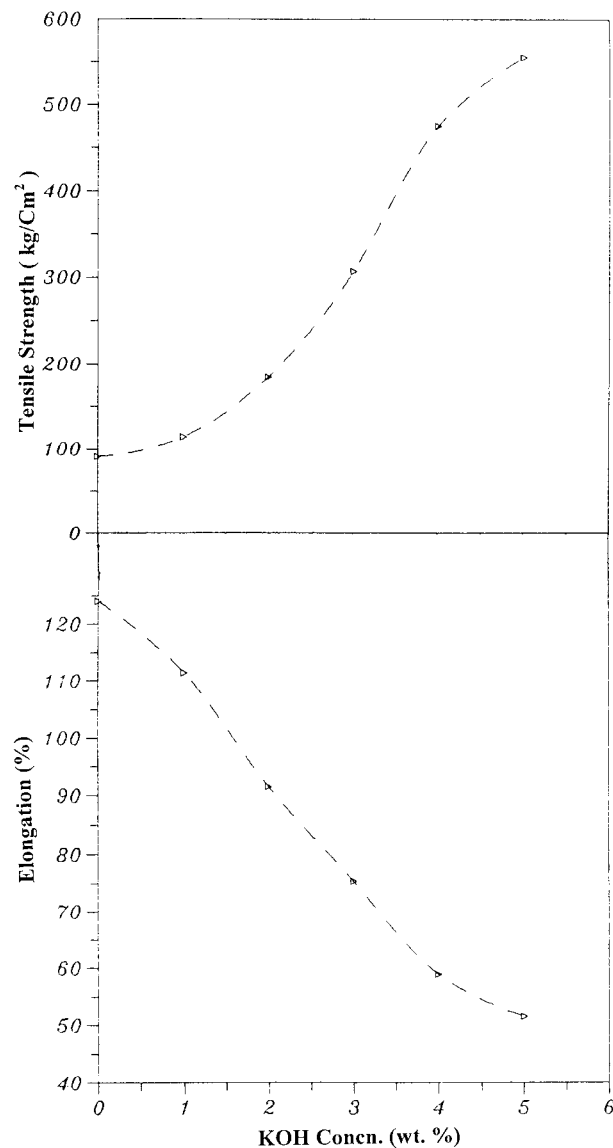
Figure 8 Change in tensile strength and elongation percent with KOH concentration for LDPE-*g*-P(AAc/AN) films (graft percent: 323%).

fore, the diffused CuSO$_4$ is negligible, and its effect on the grafting process is not very significant.

Effect of Acid Addition

Figure 3 demonstrates the effect of HCl concentration on the grafting yield of AAc onto LDPE, HDPE, and PP in the presence of water as a solvent. The grafting yield increases with increasing HCl concentration to reach its maximum value at about 3 mol %. Further increase in the HCl concentration is accompanied by a small decrease in the grafting yield, and it nearly levels off.

For the grafting of AAc/AN comonomer, the addition of 3 mol % of HCl to the reaction medium

was tested, and the results are listed in Table III. It is obvious that the grafting yield is enhanced in the presence of HCl in the reaction medium.

Properties of the Grafted Membranes

The properties that might be incorporated into the base polymer are determined by the evaluation of various parameters, for example, swelling behavior, mechanical properties, and chemical stability.

Equilibrium Swelling

Figures 4–6 illustrate the degree of swelling as a function of time for different grafted treated and untreated membranes in distilled water at room
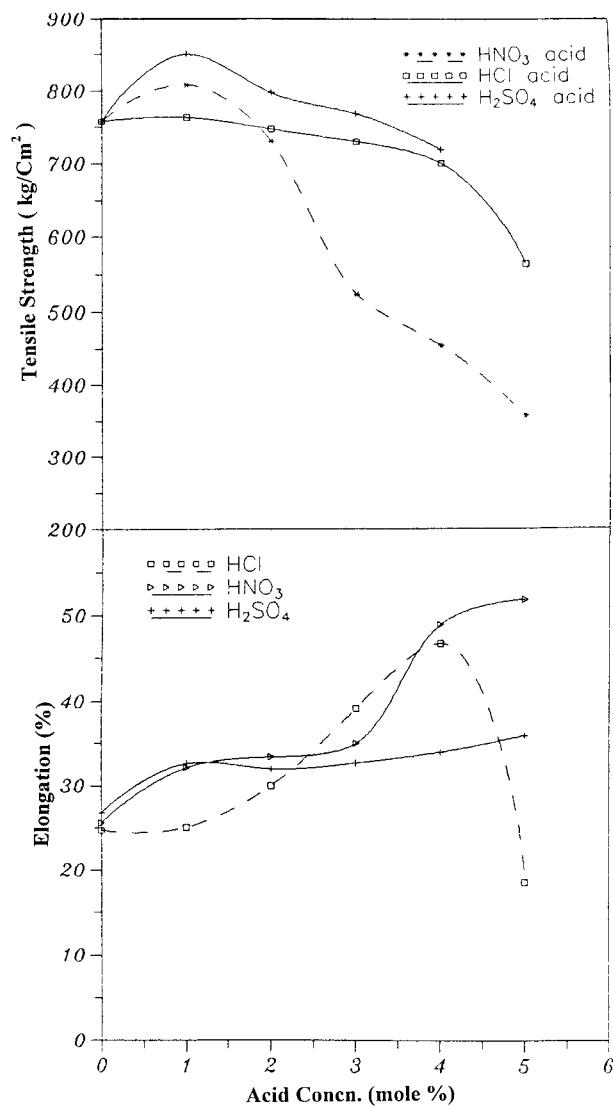

Figure 9 Change in tensile strength and elongation percent with acid concentration for LDPE-*g*-P(AAc/AN) films (graft percent: 323%).

Table IV   Effect of Time on the Uptake of Tc-99m Using PP-*g*-P(AAc/AN) Untreated and Treated Membranes (Degree of Grafting: 98%)

Time (min)	Tc Uptake	
	Untreated Membrane	KOH Treated
1	0.003	31.3
2	0.01	49.8
3	0.01	66.9
4	0.02	74.9
5	0.03	78.6
10	0.1	81.3
15	0.2	82.1
30	0.3	82.9
45	0.7	83.5
60	0.5	83.7
120	0.6	83.8

temperature (25 °C). The degree of swelling increases with time to reach a certain limiting value (equilibrium swelling) after 3 h. This behavior is obtained for LDPE and HDPE base polymers (Figs. 4 and 5). Also, the absolute values of swelling are very low for the grafted untreated membranes. However, the absolute values of equilibrium swelling for KOH-treated membranes are higher than those for NH_2OH- and HCl-treated membranes. For PP-grafted-untreated and KOH-treated membranes (Fig. 6), the equilibrium swelling is obtained after 30 min as its absolute value increases to ~500% for the KOH-treated membranes compared with 10% for the untreated one. This means that the hydrophilic nature of the treated membrane increases to a great extent leading to an increase in the water-absorbing capacity. The increase in the hydrophilicity of the membrane is expected to increase its adsorption of metal ions and radioactive isotopes.

Mechanical Properties

The changes in tensile strength (*Tb*) and elongation percent at break point (*Eb*) for the untreated and chemically treated membranes with various chemical reagents—KOH, NH_2OH, and HCl—were measured as a function of grafting yield, and the results are given in Figure 7. *Tb* increases and *Eb* decreases with a degree of grafting for the untreated and alkali- and acid-treated membranes. It is also obvious that the treatment medium has a strong influence on *Tb* and *Eb* and, consequently, on the mechanical properties. This

means that *Tb* and *Eb* depend not only on the degree of grafting but also on the nature of the functional groups.

The influence of alkaline and acidic media of various concentrations on *Tb* and *Eb* of the grafted-untreated membranes was investigated after soaking the membrane for ~24 h (Figs. 8 and 9). The curves of *Tb* and *Eb* for the membranes in alkaline media differ from the similar measurements in acid and oxidized media. *Tb* also increases and *Eb* decreases with KOH concentration indicating that the conversion of carboxylic acid groups to their salts, which are more polar, as well as their interactions increase the rigidity and *Tb* of the membrane; consequently, the *Eb* percent decreases.

Figure 9 shows the changes in *Tb* and *Eb* with acid concentration for different mineral acids: HCl, HNO_3, and H_2SO_4. At a lower acid concentration (less than 1 mol %), the *Tb* increases for membranes in HNO_3 and H_2SO_4, possessing a higher *Tb* than the unexposed membrane. Thereafter, *Tb* decreases at a higher acid concentration although no significant changes in *Tb* are apparent for membranes in various HCl concentrations up to ~4 mol % beyond which *Tb* decreases.

The increase in *Tb* at lower HNO_3 and H_2SO_4 concentrations is strongly influenced by chemical crosslinking. The decrease in *Tb* at a higher acid concentration is possibly due to chemical scission of the crosslinks in the graft side chains. Therefore, loosening of the graft copolymer structure might be responsible for the decrease in *Tb* of the graft copolymer films. The increase in *Eb* with acid concentration may be due to less entanglement in the graft copolymer chains in acidic media, which facilitate the sliding of these chains under strain.

Table V   Effect of Time on the Uptake of Tc-99m by Using LDPE-*g*-P(AAc/AN) Untreated and Treated Membranes (Degree of Grafting: 240%)

Time (min)	Tc Uptake (%)			
	Untreated Membrane	KOH Treated	NH_2OH Treated	HCl Treated
5	0.002	8.9	8.8	3.8
15	0.004	15.5	13.7	5.5
30	0.005	20.6	18.6	7.8
45	0.01	27.3	23.2	8.9
60	0.02	29.6	25.8	10
90	0.20	31.4	26.9	10.9
120	0.23	31.7	20.6	27.4

Table VI   Effect of Percent Graft on the Uptake of Tc-99m from Its Liquid Wastes

| | | Tc Uptake (%) | | | | | |
| | Degree of Grafting (%) | 5 min | | 60 min | | 120 min | |
		KOH	NH$_2$OH	KOH	NH$_2$OH	KOH	NH$_2$OH
	41	4.8	4.0	13.3	11.0	15.6	14.1
	51	5.3	4.7	14.9	12.5	18.0	15.3
HDPE	61.4	5.8	5.1	16.5	13.6	19.5	17.2
	73.8	6.8	5.9	17.7	14.9	20	18.5
	82.5	7.5	6.3	18.2	16.9	21.3	20
	155	10.3	8.9	31.4	29	33.8	32
	183	8.8	7.7	25.8	24	27.7	27.1
LDPE	219	8.9	7.8	26.9	25.1	29.8	28
	240	8.9	8.8	29.6	25.8	32.4	27.8
	273	8	7	26	24	29	26.9

Applications of the Grafted Membranes in Separation of Tc-99m from Its Wastes

Separation of Tc-99m from its liquid radioactive wastes, which is commonly used in most hospitals, was investigated by using the prepared membranes. The factors affecting the separation process include treatment time, degree of grafting and the initial activity.

Effect of Treatment Time

The time of treatment is a very important factor because of radiation safety, economics, and radiation exposure to the workers. Also, the efficiency of a membrane in waste treatment can be determined from the time required to adsorb the maximum capacity of radioisotopes by adsorption and/or chelation with its functional groups. The dependence of radioisotope uptake on the time for the prepared membranes is shown in Tables IV and V.

The results show that the activity decreases, that is, radioisotope uptake increases as the time increases very quickly to its maximum value, which is termed here as the maximum membrane capacity. The grafted KOH-treated PP-base membrane adsorbs most of the loaded radioisotopes quickly in the initial 0.5 h.

Effect of Degree of Grafting

The degree of grafting plays an important role in determining the isotope uptake from its wastes. Table VI summarizes the effect of different percent grafts on the uptake of Tc-99m at various immersion times by using LDPE and HDPE grafted with P(AAc/AN) and treated with KOH or NH$_2$OH.

Table VII   Effect of Initial Activity on Tc-99m Uptake from Its Liquid Wastes

| | Tc-99m Uptake | | | | | |
| | LDPE (% G; 240) | | | HDPE (% G; 51) | | |
Initial Activity (C/min)	Untreated Membrane	KOH Treated	NH$_2$OH Treated	Untreated Membrane	KOH Treated	NH$_2$OH Treated
18,326	4.5	22.5	17	4.2	17.8	15.6
20,516	4.9	24.4	21.5	4.2	18.4	16
25,285	5.4	26.8	22.6	4.2	18.9	16.8
30,228	5.8	29	24.4	4.3	19.3	17.3
32,416	6.4	28.4	26.1	5	19.8	18
35,325	7.1	32.4	27.8	5.6	20.2	18.6

Results show that the adsorbed Tc by HDPE-grafted membrane increases with the degree of grafting as well as with increased immersion time. However, for LDPE-grafted membrane no significant change in the uptake percent of Tc with the degree of grafting, in the range of 155–273% presently investigated, is observed. However, it increases as the immersion time increases. This behavior is observed for all types of treatment. The adsorption capacity for KOH-treated membranes is slightly higher than the NH_2OH-treated membranes. For HDPE-base polymer, percent grafting of membrane utilized is less than 83%. At high degrees of grafting in the LDPE membrane, the content of crosslinked network structure is high, leading to no more Tc uptake because of the diffusion resrictions. Therefore, the adsorption ability of the grafted membrane decreased at graft perentage higher than 155%, which can be reasonably explained by considering that the content of crosslinked network structure formed at high degrees of grafting restricts the diffusivity and extraction of radioisotope.

These results suggest that the efficiency of these membranes is a function of the number of functional groups introduced in the grafted copolymer and their subsequent ability to adsorb or chelate ions. By introducing carboxylate groups via KOH treatment, the adsorption properties increased as well as the chelating ligands derived from these groups.

It has been noticed that low-molar-mass hydrophilic branches attached to the hydrophobic backbone provide optimal efficiency of the properties of the resultant membrane.[13] Ion exchange could then take place on as many sites as possible for a given percentage of grafted monomer. Having long polymer chains attached to a limited number of sites is not desirable for ion exchange because they would minimize the efficient use of monomer, giving far less potential for ion exchange to occur.[14]

Effect of Initial Activity

The reduction in initial activity of liquid radioactive waste is a very important factor because of its effects on the public and workers when exposed to the radiation. The efficiency of membranes in the treatment of radioactive liquid wastes can be determined from their ability to decrease the initial activity of radioactive liquid wastes.

Table VII shows the effect of initial activity on the uptake of Tc-99m by using different prepared membranes with different base polymers.

The aforementioned results reveal that the amount of isotope adsorbed by each membrane increased with the initial activity but that different

levels were recorded depending on the type of treatment and base polymer. Also, the KOH-treated membrane has a stronger ability to separate Tc-99m than the NH_2OH-treated membranes.

CONCLUSION

The prepared membranes possessed good properties of great interest in adsorption and/or chelation of Tc-99m from its liquid wastes. They possess good hydrophilic and mechanical properties, and they are mechanically stable against alkali and different acidic media. Therefore, membranes treated with KOH seem to possess a higher adsorption capacity, and the KOH-treated grafted PP is the most efficient membrane in reducing the activity of this radioactive liquid waste to a great extent. Such reduction in activity reaches to 83.8% of the initial activity of Tc-99m waste.

REFERENCES

1. El-Naggar, H. A.; Shenata, M. K.; Abdel-Sabour, M. F.; Ezz El-Din, M. R. 5th Conference on Nuclear Science & Applications; The Egyptian Society of Nuclear Sciences and Applications, Cairo, Egypt 1992; Vol. 2, pp 999–1000.
2. Lawler, J. P.; Charlesby, A. Radiat Phys Chem 1980, 15, 595.
3. Ishigaki, I.; Sugo, T.; Senoo, K.; Takayama, T.; Machi, S.; Okamoto, J.; Okada, T. Radiat Phys Chem 1981, 18, 899.
4. Guthrie, J. T.; Kotov, S. J Appl Polym Sci 1989, 37, 39.
5. Hegazy, E. A.; Abd El-Rehim, H. A.; Khalifa, N. A.; Atwa, S. M.; Shawky, H. A. Polym Int 1997, 43, 321–332.
6. Hegazy, E. A.; Abd El-Rehim, H. A.; Ali, A. M. I.; Nowier, H. F.; Aly, H. F. J Nucl Instrum Methods Phys Res 1999, B151, 393–398.
7. Abd El-Rehim, H. A.; Hegazy, E. A.; El-Hag, A. A. J Radioact Functional Polym 1999, 1.
8. Okamoto, J.; Sugo, T.; Katakai, A.; Omichi, H. J Appl Polym Sci 1985, 30, 2967.
9. Suito, K.; Yamada, S.; Furusaki, S.; Sugo, T.; Okamoto, J. J Membr Sci 1987, 34, 307.
10. Suito, K.; Yamaguchi, T.; Uezu, K.; Furusaki, S. J Appl Polym Sci 1990, 39, 2153–2163.
11. Kabay, N.; Katakai, A.; Sugo, T.; Egawa, H. J Appl Polym Sci 1993, 49, 599.
12. March, J. Advanced Organic Chemistry, 3rd ed.; Wiley Interscience: New York, 1985; Chapter 16, p 788.
13. Hegazy, E. A.; Ebaid, A. R.; Barakat, A. M.; Kamal, H.; Ally, H. F. J Nucl Sci Appl 1990, 23(2), 185.
14. Guthrie, J. T. J Appl Polym Sci 1989, 37, 39–54.