

Evaluation of Anionic- and Cationic-Supported Hydrogel Membranes for Sorption of Th(IV) and U(VI) Ions from Nitric Acid Medium

E. A. Hegazy,¹ B. El-Gammal,^{1,2} F. H. Khalil,¹ T. M. Mabrouk¹

¹National Center for Radiation Research and Technology, Nasr City, Egypt

²Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt

Received 8 August 2005; accepted 10 November 2005

DOI 10.1002/app.23816

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Functionalized membranes were obtained by radiation-induced graft copolymerization (RIGP) of acrylamide-acrylic acid (AAM-AAc) and acrylamide-4-vinyl pyridine (AAM-4VP) binary monomers on both low-density polyethylene and polypropylene films. The supporting conditions as inhibitor concentration, irradiation dose comonomer compositions and concentrations were studied and optimized. The prepared membranes were characterized using SEM, DTA-TG, and FTIR. They proved that supporting the selected hydrogels on the base films have modified their structure and enhanced their thermal and mechanical char-

acteristics. The sorption characteristics of Th(IV) and U(VI) on the different membranes were studied. The amount of ions sorbed at equilibrium was found to increase with increase in the degree of graft at certain conditions. The kinetics of sorption was also studied and found to obey the Lagergren and Morris-Weber kinetic models. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 320–332, 2006

Key words: LDPE; PP; acrylamide-acrylic acid; acrylamide-4-vinyl pyridine; membranes; preparation; characterization; sorption; U(VI) and Th(IV)

INTRODUCTION

Graft polymerization¹ and crosslinking² are well-known reactions in radiation processing of polymers. These reactions were initialized by high-energy irradiation of γ -ray or electron beam toward the polymer. Thus, the radiation-induced graft polymerization (RIGP) can be applicable to the conventional polymers having various shapes such as membrane,³ fabric,⁴ and fiber.⁵ The radiation-induced crosslinking can be carried out in solid⁶ and liquid state.⁷ Polymers modified by grafting and crosslinking have been widely industrialized as battery separators, heat shrinkable materials, and wound dressing.⁸ Other applications have been directed to their use in the removal of some heavy metal ions.^{9,10}

On the emphasis on vinyl polymers, graft copolymerization of mixtures of vinyl monomers is important since different types of polymer chains containing various functional groups can be introduced into the structure of trunk polymers used, that may influence the extent of grafting of individual monomer onto the substrate polymer, especially when synergism occurs

during such reaction.^{11–13} Such grafting reactions can also give more economical grafts under the most favorable reaction conditions.¹⁴

Although grafting of AAc-AAM onto low-density polyethylene (LDPE) and polypropylene (PP) have been intensively studied by different authors^{15–19} as cationic membranes, a little attention has been shown to study the grafting of AAM-4VP as anionic membranes. In this connection, a study has been made for the preparation and characterization of the prepared graft copolymers and the possibility of their practical application in adsorption and separation of some radioisotopes. Cationic and anionic membranes were prepared by the direct radiation-induced graft copolymerization of AAc-AAM and AAM-4VP binary monomers onto LDPE and PP films. Many factors affecting the radiation grafting process of binary comonomer mixture, such as the inhibitor, comonomer concentration, and composition of monomers mixture and total exposure radiation dose were studied. These factors are considered and determined so that a reasonable grafting yield with homogenous distribution in the graft copolymer can be obtained

Correspondence to: B. El-Gammal (belalegammal@yahoo.com).

EXPERIMENTAL

LDPE and PP films of thickness 60 and 35 μm , respectively, were produced by El Nasr Chemical, Egypt.

Acrylic acid (AAc) and acrylamide (AAM), purity 99.9% and 4-vinyl pyridine (4VP), purity >96%, were supplied by Merk, Germany. The other chemicals were Spec-pure grade and used without further purification.

The ionic graft copolymerization was prepared by the direct radiation grafting of AAc-AAM and AAM-4VP as cationic and anionic graft copolymer, respectively. Strips of 1 g of the LDPE and PP films were washed with acetone, dried at 50°C in vacuum oven, weighed and immersed in a glass tube containing 10 mL of binary monomers/solvent solution mixture, and subjected to Co-60- γ -rays in N₂ gas atmosphere. The grafted films were removed and washed thoroughly with acetone to extract the residual monomers and the remaining homopolymers that may be accumulated in the film. The films were dried in vacuum oven at 50–60°C for 24 h and weighed. The degree of grafting (%) was determined by the percentage increase in weight as follows

$$\text{Degree of Grafting} = \left(\frac{W_g - W_o}{W_o} \right) \times 100$$

where W_o and W_g represent the weights of initial and grafted films, respectively.

Shimadzu DTA-TGA system of type DTA-TGA 60 (Japan) was used for the measurements of the phase transformations and weight loss as a function of temperature of the sample at a heating rate of 10°C/min in the presence of nitrogen gas to avoid thermal oxidation of the polymer sample.

The IR spectra were measured for the base and grafted films using Perkin-Elmer 398 FTIR spectrometer.

The surface topography of the different membranes was tested using SEM technique after sputtering the specimens with gold using JEOL-TSM-5400 Instrument, Japan.

The prepared membranes were used in this investigation to evaluate them for sorption of Th(IV) and U(VI) ions from nitrate medium. Twenty milliliter of 10⁻³M solution of these ions was used and added to 0.1 g of the membrane so that the v/m value was 200 mL/g, and the % sorption was estimated at different time intervals using the following equation

$$\% \text{ Sorption} = \left(\frac{A_i - A}{A_i} \right) \times 100$$

where A_i and A are the initial and final concentrations in milligram per liter in the solution, respectively, and the distribution coefficients K_d of both ions were determined as a function of the concentration at equilibrium using the specified v/m values according to the following equation

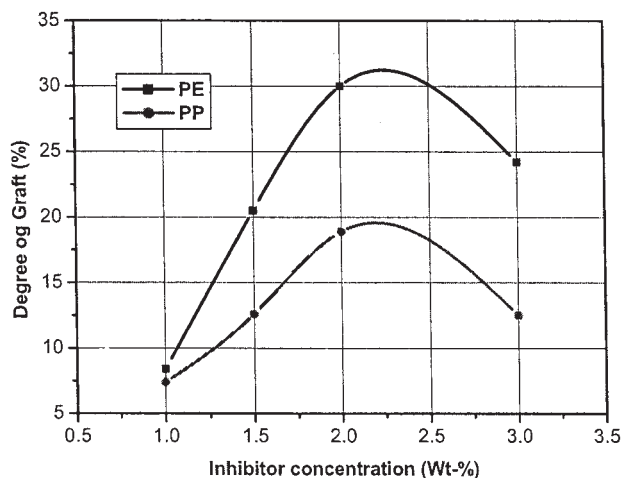


Figure 1 Effect of inhibitor concentration on the degree of grafting of AAM-AAc on polyethylene and polypropylene films using 20 wt % comonomer concentration, 50:50 wt % comonomer composition at 20 kGy irradiation dose.

$$K_d = \left(\frac{A_i - A_{eq}}{A_{eq}} \right) \times \frac{v}{m}$$

where, A_i and A_{eq} are the initial and equilibrium concentrations of the specified ions in solution. Th(IV) and U(VI) concentrations were determined at the specified time intervals and at equilibrium using Arsenazo-III as spectrophotometric reagent²⁰ by means of a Milton Roy Spectronic 1201 in the range from 190 to 900 Å and by using a chemistry Analyzer RA-50.

RESULTS AND DISCUSSION

Preparation of bifunctional grafted copolymers

In this study, different anionic and cationic membranes were prepared by direct irradiation-induced graft copolymerization of AAM-4VP and AAM-AAc binary monomers onto PE and PP sheets. The grafting process was optimized in terms of the maximum yield that was affected by inhibitor concentration, composition of the comonomer mixture, and total exposure to radiation dose.

Effect of inhibitor concentration

Figure 1 shows the effect of FeCl₃ in the reaction mixture containing bidistilled water as a solvent that acts as an inhibitor for polymerization during the grafting process of AAM-AAc binary mixture on PE and PP supports. The yield increased by increasing the inhibitor concentration of about 2.25 wt % followed by an effective decrease at higher concentrations, which may be assigned to prevention of the graft process by migration of the individual ions onto the substrate surface and blocking the active points that can be

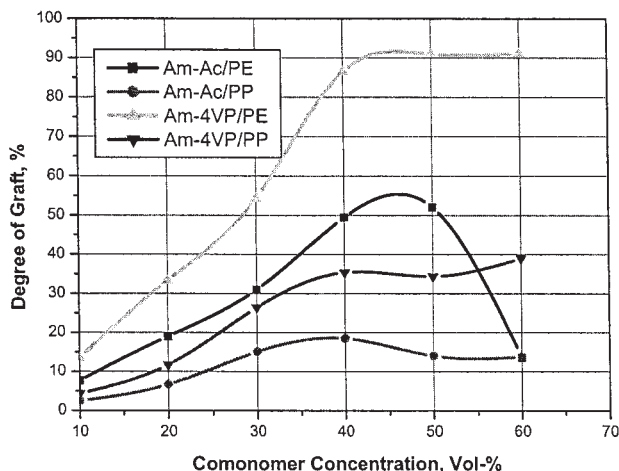


Figure 2 Effect of comonomer concentrations on the degree of grafting of AAm-AAc and AAm-4VP on polyethylene and polypropylene films using 50:50 wt % comonomer composition, 2.25 wt % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 20 kGy irradiation dose.

considered as targets for copolymerization as well as inhibition of homopolymer formation.^{17,21} Such effect was not considered when AAm-4VP was selected for grafting.¹⁷

Effect of comonomer concentration

The influence of comonomer dilution in bidistilled water on the grafting yield on the surfaces of PE and PP sheets using 50:50 wt % of AAm-AAc and AAm-4VP compositions was studied and is represented in Figure 2. When PE and PP films are grafted with AAm-AAc binary mixture, the grafting yield increases with increasing the comonomer concentration so that maximum yields are produced using about 49 and 40 wt % in both cases, respectively. At higher concentrations, the yield is lowered due to the homopolymerization acceleration at the expense of graft induction. On the other hand, the optimum comonomer concentrations from AAm-4VP to graft PE and PP may extend to 60 wt %, due to the low possibility of homopolymerization.²²

Effect of comonomer composition

Figure 3 illustrates the relation between AAm-AAc and AAm-4VP comonomers composition with the degree of grafting on PE and PP films. The degree of grafting increases as the AAm content increases to reach a maximum at 40:60 wt % in case of AAm:AAC composition and 60:40 wt % for AAm:4VP composition, thereafter, it tends to level off. This may be attributed to the formation of dense homopolymer at higher Am concentration on the expense of grafting yield.^{23,24}

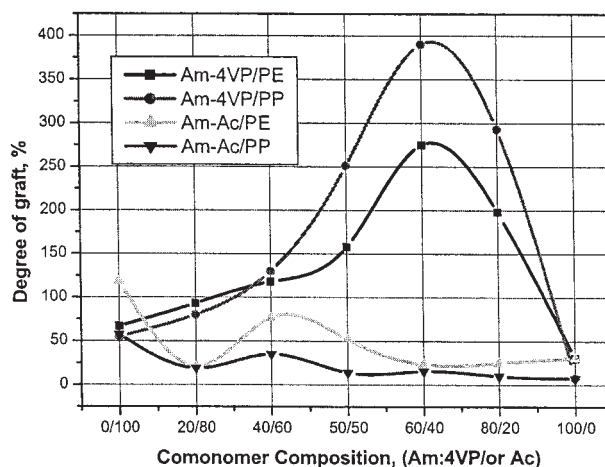


Figure 3 Effect of comonomer composition on the degree of grafting of AAm-AAc and 4VP on polyethylene and polypropylene films using 20 wt % comonomer concentration, 2.25 wt % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 20 kGy irradiation dose.

Effect of irradiation dose

Graft copolymerization of AAm and its binary mixture with AAc and 4VP on PE and PP films has been studied as a function of irradiation dose, and represented in Figures 4–7. In case of PE films grafted with AAm-AAc binary comonomers, the degree of grafting is enhanced when the radiation dose increases at different monomer concentrations; the highest degree of grafting (84%) is obtained at 30 kGy using 50 wt % concentration. At higher concentration, the degree of grafting is nearly unchanged and reaches only 11%. This may be assigned to the enhanced homopolymerization at expense of the grafting process.

In case of PP films grafted with AAm-AAc, the degree of grafting increases with increase in the irra-

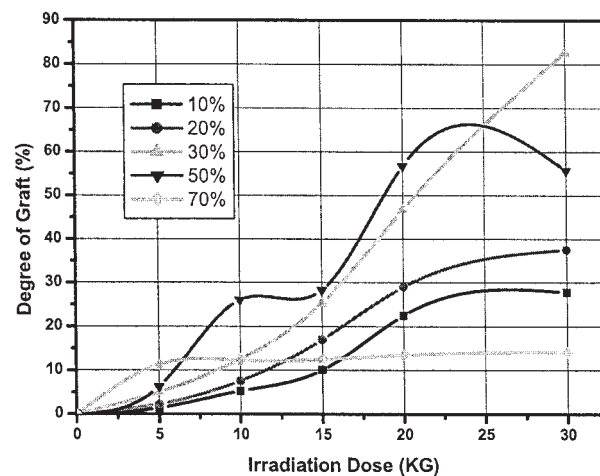


Figure 4 Effect of irradiation dose on the degree of grafting of AAm-AAc having different monomer concentrations on polyethylene films using 40:60 wt % comonomer composition, 2.25 wt % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

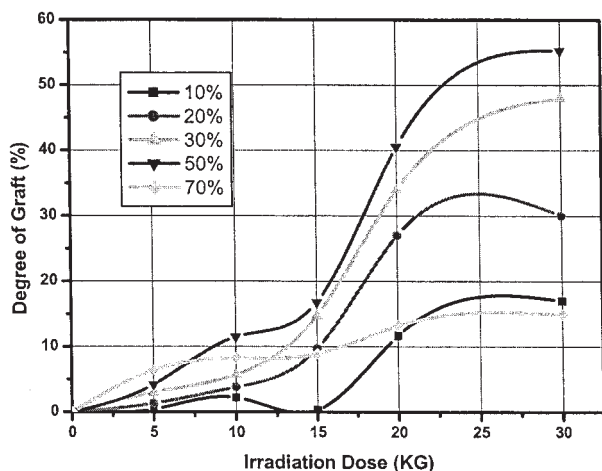


Figure 5 Effect of irradiation dose on the degree of grafting of AAm-AAc having different monomer concentrations on polypropylene films using 40:60 wt % comonomer composition, 2.25 wt % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

diation dose and maximum grafting value is obtained at for 50 wt % of monomer concentration at 30 kGy irradiation dose. Also higher monomer concentration will decrease the degree of grafting dramatically due to the enhanced homopolymerization.

In case of using AAm-4VP as a hydrogel supported on PE and PP films, the grafting process is highly preferred rather than homopolymerization compared with AAm-AAc. This may be attributed to the nature of 4VP that retards the homopolymerization, regardless the presence of any inhibitor of homopolymerization. However, the maximum grafting yield was determined at 30 wt % comonomer concentrations and 40 kGy irradiation dose. Taking into consideration the irradiation dose, it is recommended carrying out the

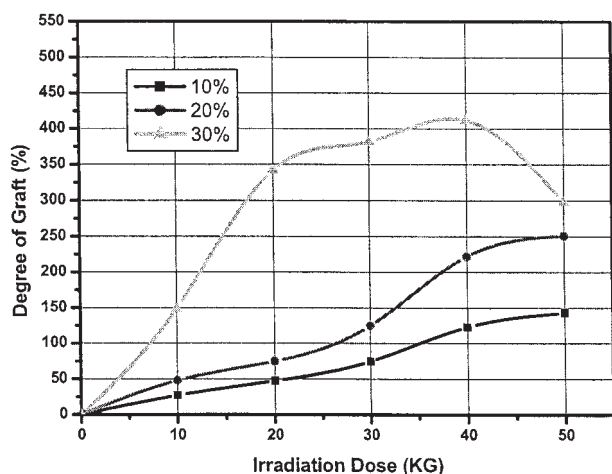


Figure 6 Effect of irradiation dose on the degree of grafting of AAm-4VP having different monomer concentrations on polyethylene films using 50:50 wt % comonomer composition, 2.25 wt % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

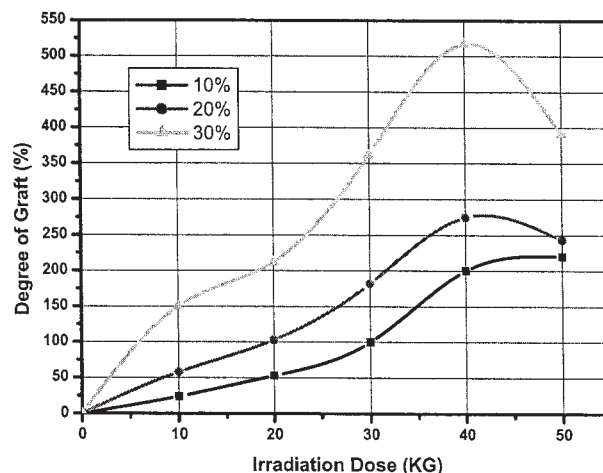


Figure 7 Effect of irradiation dose on the degree of grafting of AAm-4VP having different monomer concentrations on polypropylene films using 50:50 wt % comonomer composition, 2.25 wt % $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$.

grafting process at 30 wt % and 30 kGy in case of PP films because of their degradation.²¹

Characterization of the prepared membranes

The prepared membranes were characterized with different advanced analytical techniques that can participate in their application.

FTIR

Infrared spectroscopy was used to characterize the structure of the different membranes. Figure 8 shows that the infrared analysis was made for the original LDPE films and LDPE-g-p(Am-Ac) and LDPE-g-p(Am-4VP). From the spectra it is clear that the characteristic bands of LDPE appeared at around 2900, 1470, and 720 cm^{-1} . Strong bands at 3200 and 3500 cm^{-1} are corresponding to $-\text{NH}$, $-\text{OH}$ banded groups, respectively, corresponding to the grafted acrylamide acrylic onto LDPE films. The intensity of these bands depends on the graft yield, it can be seen that an absorption band at 1720 cm^{-1} corresponding to the carbonyl group of Ac of LDPE-g-p(AAm-4VP). A characteristic band for $-\text{NH}$ group for 4VP was observed at 3500–3000 cm^{-1} .

Figure 9 shows the infrared spectra for PP films and PP-g-(AAm-AAc) and PP-g-(AAm-4VP) films, the spectra show the characteristic band for PP around 2775–3075 cm^{-1} corresponding to methyl group, also the same band appeared in the case of LDPE.

Topography of the membranes

Figure 10 shows the SEM of the blank PE and PP films and grafted with both AAm-AAc and AAm-4VP. The

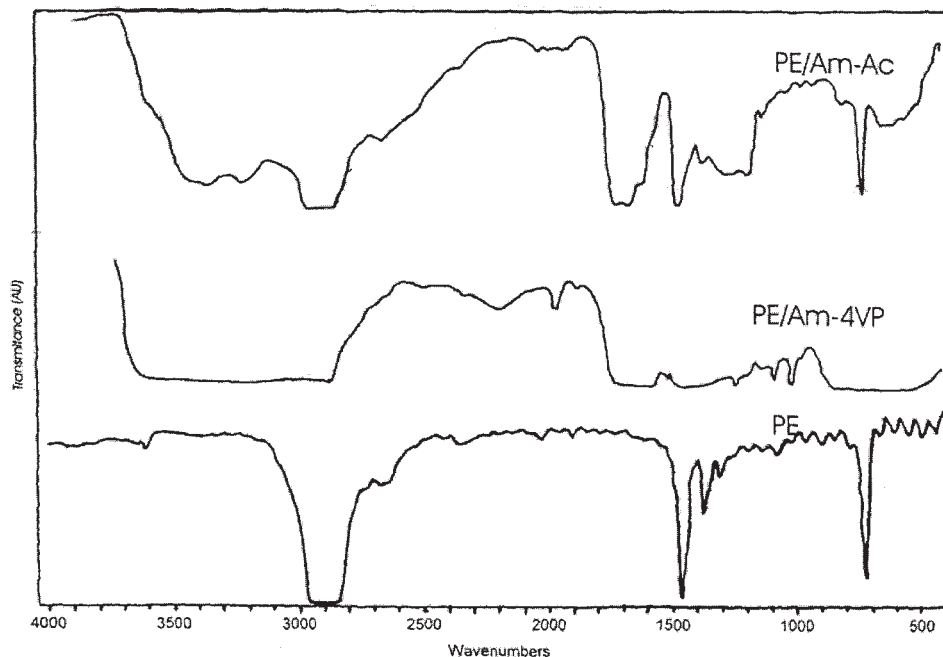


Figure 8 FTIR spectra of polyethylene grafted with AAm-AAc and AAm-4VP binary mixtures.

surface of the blank films of PE and PP, which are irradiated, seems to be smooth with continuous phase as most semicrystalline polymers. However, grafting with AAm-AAc binary monomers, the surface is completely changed. In case of AAm-AAc as gel supported on PE film, the surface becomes heterogeneous having interconnected groves of different widths that can enhance the swelling character of the original

membranes and forces the ingoing ions to be accumulated within their structure. For PP films grafted with AAm-AAc, no groves were observed rather than cotton balls of different sizes. The average size of these domains lies in the range of 6–11 μm .

In case of using AAm-4VP, two different surface textures appear depending on the blank films. For PE grafted with AAm-4VP, the groovy structure predom-

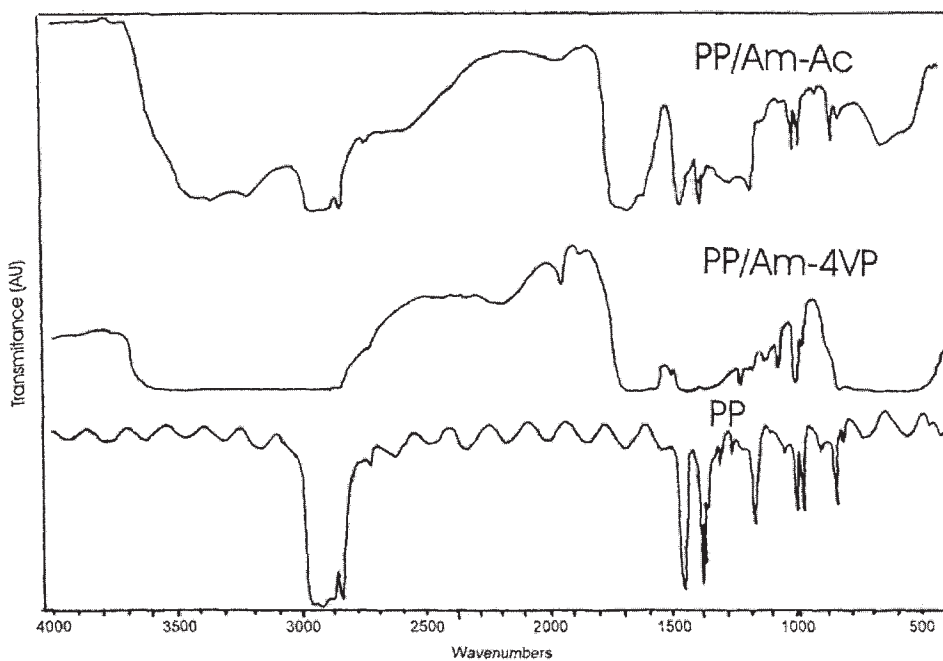


Figure 9 FTIR spectra of polypropylene grafted with AAm-AAc and AAm-4VP binary mixtures.

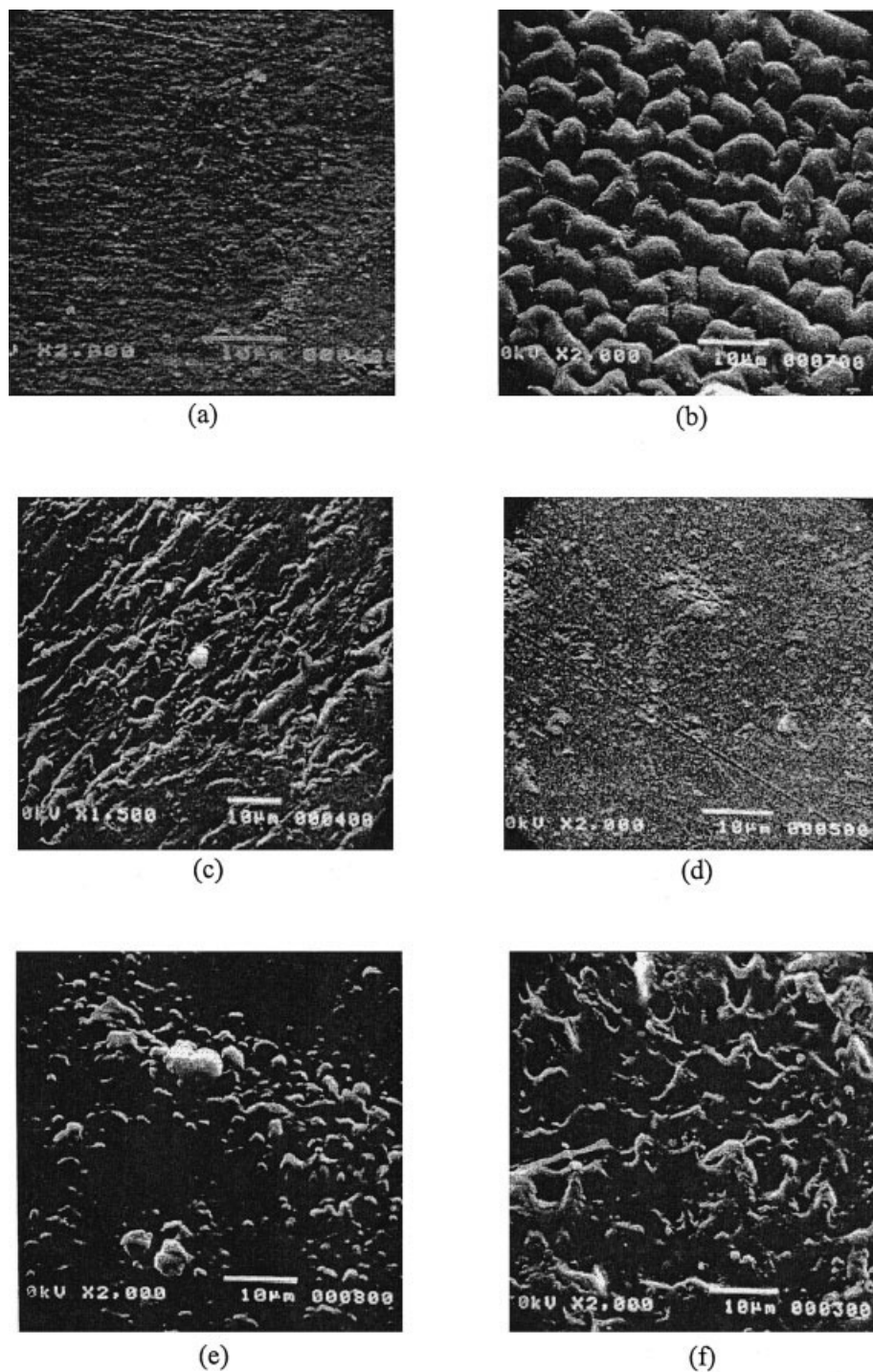


Figure 10 Scanning electron micrographs of different PE and PP membranes. (a) PE, (b) PE/AAm-AAc, (c) PE/AAm-AAc, (d) PP, (e) PP/AAm-AAc, (f) PP/AAm-4VP.

inates which is characteristic of the PE films. On the other hand, with the use of PP films as support membrane, cavities and crests appear in the micrographs. With increase in the concentration or irradiation dose, the roughness and deformation of the surfaces are observed, due to either phase separation or degradation in case of PP membranes.

Thermal analysis of the films

Figure 11 shows the variation of residual weight fraction (%), as a measure of the weight loss of PP, PP-g-p(AAm-AAc) as a cationic membranes and PP-g-p(AAm-4VP) as an anionic membranes. It is shown in a comparison between the anionic and cationic mem-

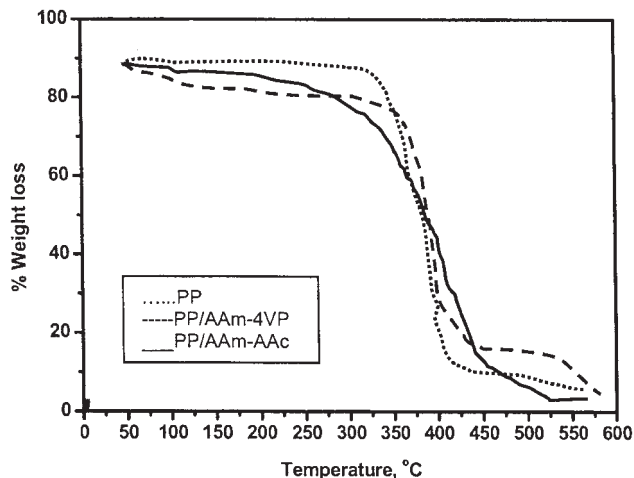


Figure 11 TGA thermograms of polypropylene grafted with AAm-AAc and AAm-4VP binary mixtures.

brates that the ungrafted PP samples start to decompose at about 320°C. The PP-g-p(AAm-4VP) shows weight loss in two stages, the first begins at 80°C, which could be attributed to the removal of physisorbed water molecules. The second step begins 320–325°C. In case of PP-g-p(AAm-AAc), the first weight loss begins at about 80°C, while the second stage begins at 210, probably due to intermolecular interaction between adjacent —COOH groups and dehydration decomposition is observed above 300°C.

On the other side, the TGA thermograms of LDPE and its grafting derivatives (cf. Fig. 12) are different. In case of LDPE-g-p(AAm-AAc), a slower step of weight loss takes place at about 200–400°C, while a faster one takes place above 400°C. It is possible that in case of chains grafted with acrylic, dehydration reaction takes

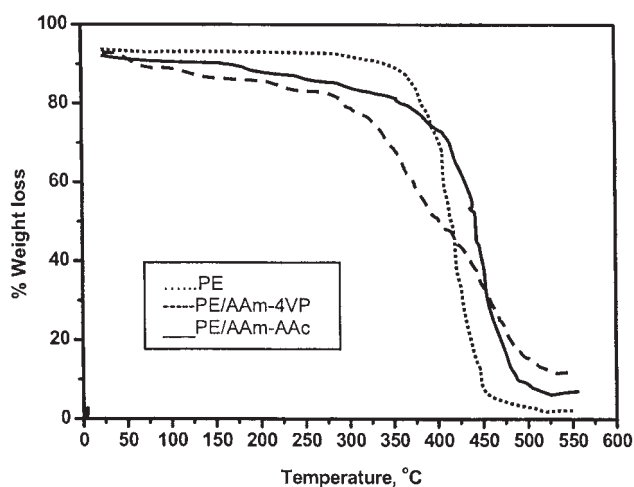


Figure 12 TGA thermograms of polyethylene grafted with AAm-AAc and AAm-4VP binary mixtures.

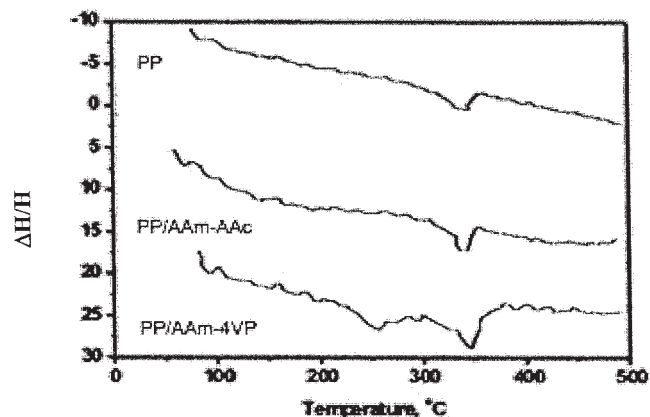


Figure 13 DTA thermograms of polypropylene grafted with AAm-AAc and AAm-4VP binary mixtures.

place between the adjacent carboxylic groups, resulting in some changes in the physical properties of the polymers.

The DTA thermograms for PP-g-p(AAm-AAc) and PP-g-p(AAm-4VP) (c.f. Fig. 13) and LDPE-g-p(AAm-AAc) and LDPE-g-p(AAm-4VP) (cf. Fig. 14) illustrate the behaviors of the radiation grafted films as cationic and anionic membranes. Some authors reported that the properties of the resulting membranes are dependent on base polymer.^{25,26} In a crystalline polymer, the melting point of the membrane depends on both the size of the individual crystallites and limited by the presence of branches, since smaller crystallites usually melt at lower temperatures than the larger crystallites, also, the presence of branches will reduce the melting temperature of polymers.

From the obtained records, the endothermic peaks characteristic for the melting are clear in case of LDPE

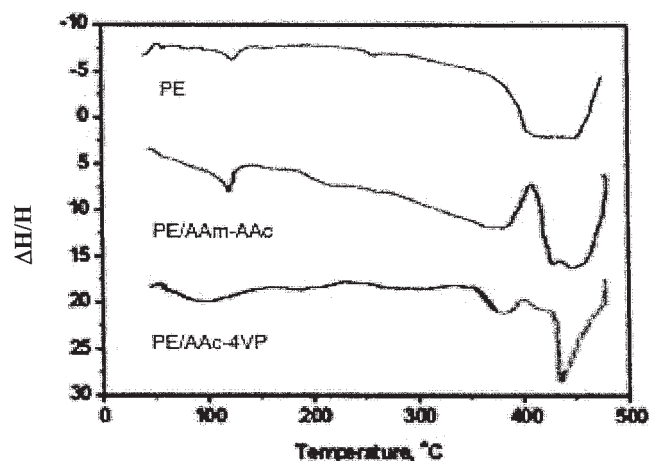


Figure 14 DTA thermograms of polyethylene grafted with AAm-AAc and AAm-4VP binary mixtures.

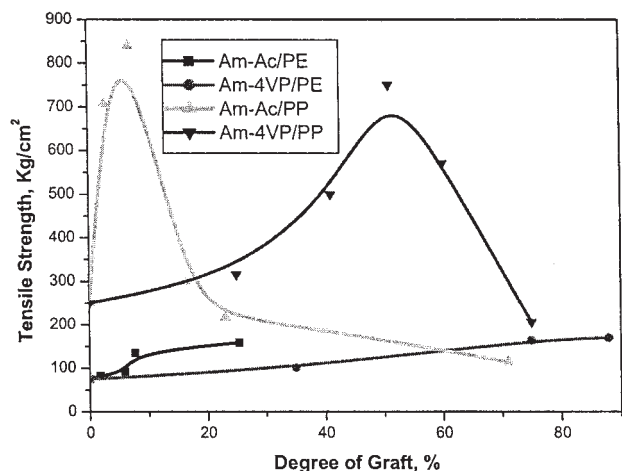


Figure 15 Effect of the degree of graft on the tensile strength of different membranes

and its grafted derivatives (cf. Fig. 14), however, they are not sufficiently clear in PP and its derivatives. The endothermic peaks associated with dissociation are clearly observed in all cases.

The melting temperature, T_m for PP, PP-g-p(AAm-AAc) and PP-g-p(AAm-4VP) are varying between 125 and 170°C; and decomposition temperature between 175 and 200°C, which is higher than those of the pure PP. The T_m for and LDPE-g-p(AAm-AAc) and LDPE-g-p(AAm-4VP) varying between 100 and 120°C and their decomposition temperature ranges between 400 and 500°C).

Mechanical properties of the prepared membranes

Figures 15 and 16 show the mechanical characteristics including the change in the tensile strength and %

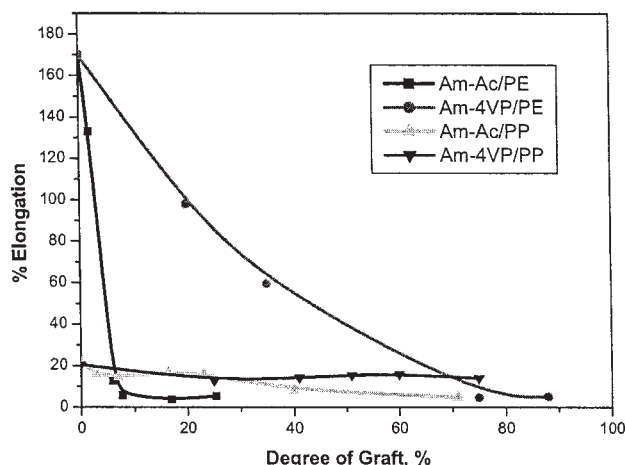


Figure 16 Effect of the degree of graft on the % elongation of different membranes.

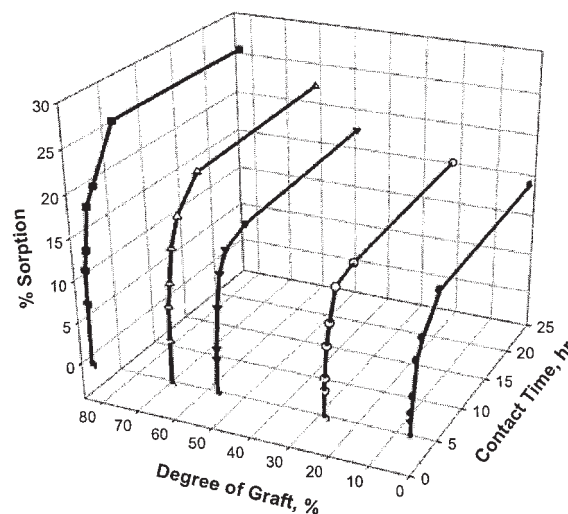


Figure 17 Effect of contact time on the sorption of Th(IV) on polyethylene membranes grafted with different amounts of AAm-AAc.

elongation at break for LDPE and PP grafted with AAm-AAc and AAm-4VP binary mixtures. It can be seen from the figures that the tensile strength increases gradually with increase in the degree of graft on LDPE grafted with AAm-AAc and AAm-4VP, while the % elongation decreases exponentially. This may be assigned to the increase in rigidity of the membranes at higher irradiation doses, so that they can maintain loads to 100 kg/m². On the other hand, the tensile strengths of the membranes based on PP grafted with AAm-AAc and AAm-4VP have different characters on exposure to radiation doses. Maximum tensile strength of about 750 and 675 kg/m² were obtained, followed by leveling off to 200 kg/m². This phenomenon could be explained by either homopolymerization and or degradation of the PP films at higher doses. Hence, the peak is shifted to the right hand side in case of grafting with AAm-4VP, due to the nature of the selected binary mixture that hinders the homopolymerization route. However, the % elongation of the tested membranes remains nearly constant over the entire range of grafting. This may be assigned to the more rigid and crystalline structure of PP rather than the LDPE.

Sorption behavior of Th(IV) and U(VI) on different membranes

Testing of LDPE- and PP-supported hydrogels as membranes for radioactive waste elements was carried out in terms of their cation removal, distribution coefficients, and detection of the mechanism using different kinetic models.

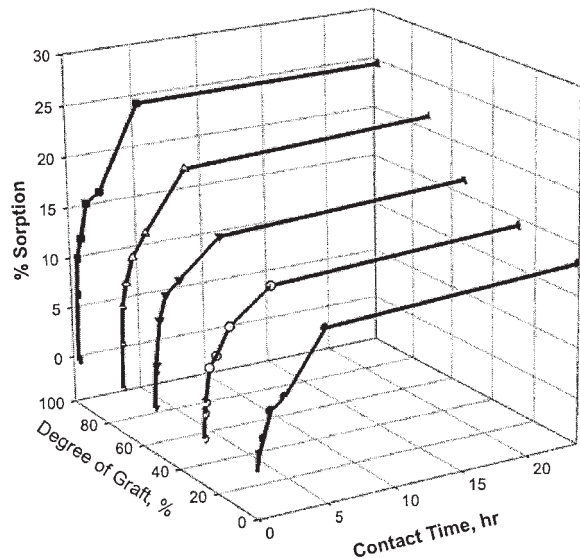


Figure 18 Effect of contact time on the sorption of Th(IV) on polyethylene membranes grafted with different amounts of AAm-4VP.

Distribution studies of Th(IV) and U(VI) on different membranes

Figures 17–24 show the effect of contact time on the % sorption of Th(IV) and U(VI) onto the selected membranes. In general, the % uptake increases with duration of time till equilibrium is maintained. In case of sorption of Th(IV) on PE grafted with AAm-AAC, the removal process is slightly greater and faster than that in case of using AAm-4VP for grafting the base films. The % sorption is enhanced with increase in the degree of grafting. This can be explained on the nature of the grafted gels that can act as either cationic mem-

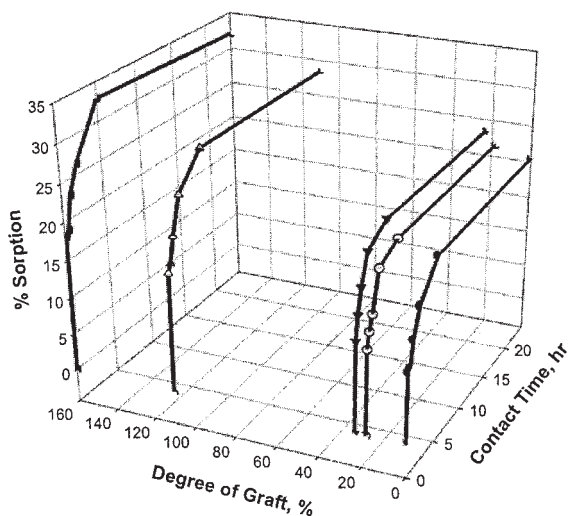


Figure 19 Effect of contact time on the sorption of Th(IV) on polypropylene membranes grafted with different amounts of AAm-AAC.

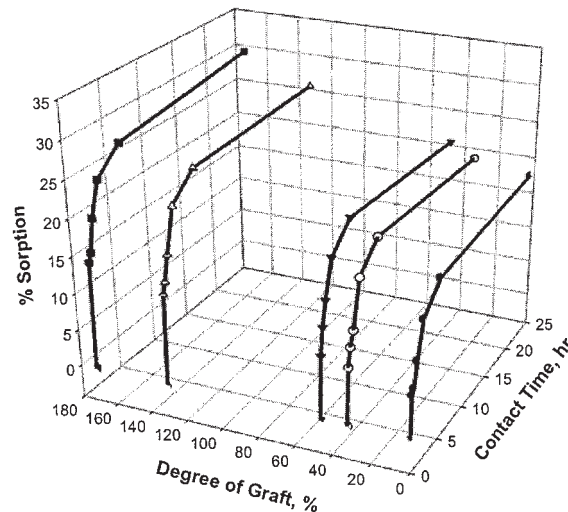


Figure 20 Effect of contact time on the sorption of Th(IV) on polypropylene membranes grafted with different amounts of AAm-4VP.

branes or sorption of the used metal species in their internal structure, due to their increased hydrophilic and swelling character, as augmented by their scanning electron microscopy. However, on transfer from Th(IV) to U(VI) case, the removal of the ions is raised, which may be attributed to the alteration of charge from state (IV) to state (VI).

On using PP as a blank support for grafting with AAm-AAC and AAm-4VP hydrogels, the situation changes. In case of thorium species adsorption on the membranes, equilibrium increased with 5–7 h. While longer times are required to attain equilibration in uranium species adsorption. The whole kinetics is considered in the following sections.

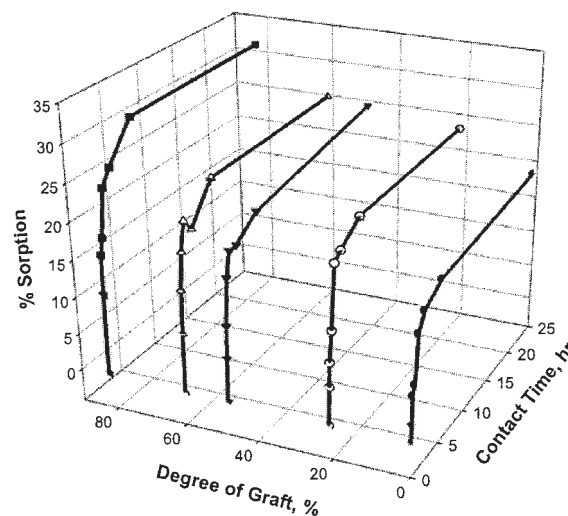


Figure 21 Effect of contact time on the sorption of U(VI) on polyethylene membranes grafted with different amounts of AAm-AAC.

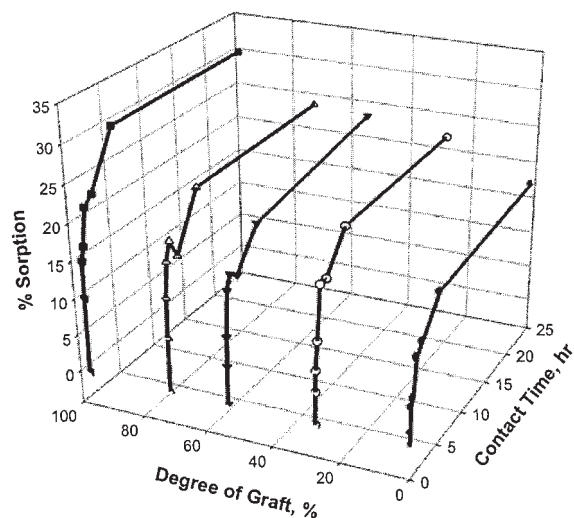


Figure 22 Effect of contact time on the sorption of U(VI) on polyethylene membranes grafted with different amounts of AAm-4VP.

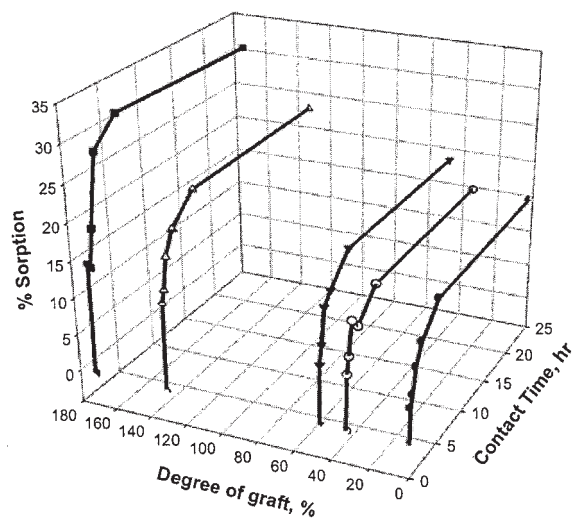


Figure 24 Effect of contact time on the sorption of U(VI) on polypropylene membranes grafted with different amounts of AAm-4VP.

Figures 25 and 26 show the distribution coefficients of uranium and thorium ionic species on the different membranes. The main species found in case of using uranyl nitrate solution in the adsorption of U(VI) on the different grafted membranes beside the hydroxyl and nitrate anions are $[\text{UO}_2]^{2+}$, $[\text{UO}_2\text{NO}_3]^+$, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$, and $[\text{UO}_2\text{OH}]^+$. Other cationic species such as $[(\text{UO}_2)_3(\text{OH})]^{5+}$ are possibly found. In case of using thorium nitrate for the adsorption of Th(IV) on various grafted membranes, $[\text{Th}]^{4+}$, $[\text{Th}(\text{OH})]^{3+}$, $[\text{ThNO}_3]^{3+}$, and $[\text{Th}(\text{OH})_2]^{2+}$ are coexistent at the ambient pH 2.5 at 30°C.²⁷

Generally, the selectivity of the different membranes towards the earlier mentioned species in-

creases with increase in the degree of grafting. However, the general order of selectivity is as follows.

In case of Th(IV), the order on AAm-AAc/PP > AAm-4VP/PP > AAm-AAc/PE > AAm-4VP/PE, meanwhile, for U(VI), the following order is obeyed: AAm/AAc/PP > AAm-AAc/PE > AAm-4VP/PE > AAm-4VP/PP. This order of selectivity may be explained by the cationic nature of AAm-AAc gels rather than AAm-4VP once. However, in case of using PP as a membranes support, it contributes itself to the sorption process, and in turn participates in increasing the selectivity in case of Th(IV) till 60% degree of grafting, beyond this limit, the order changes.

In considering the specific tendency for adsorption of the uranyl nitrate and thorium nitrate on the vari-

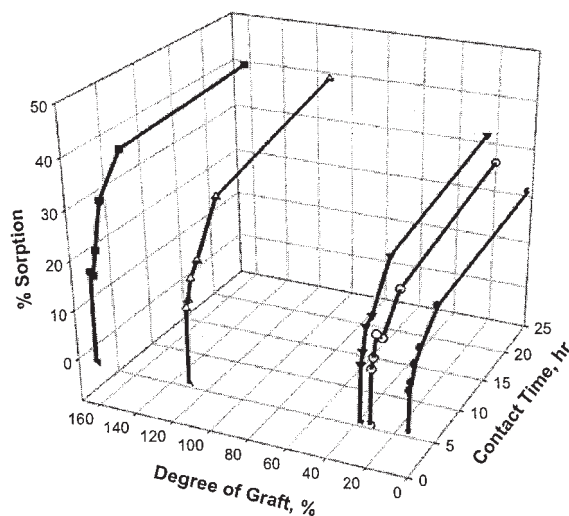


Figure 23 Effect of contact time on the sorption of U(VI) on polypropylene membranes grafted with different amounts of AAm-AAc.

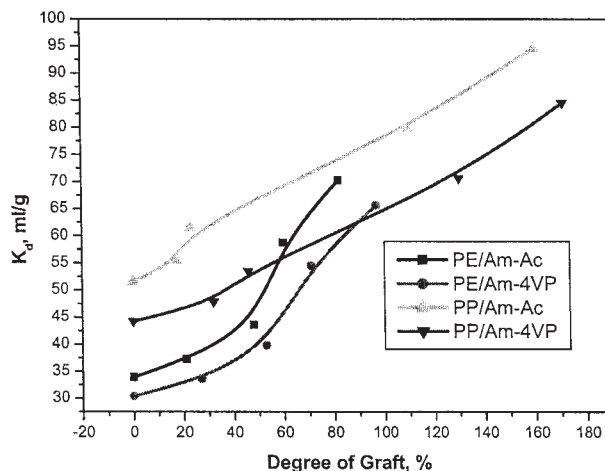


Figure 25 Effect of the degree of graft on the distribution coefficients of Th(IV) on polyethylene and polypropylene membranes grafted with different monomer types.

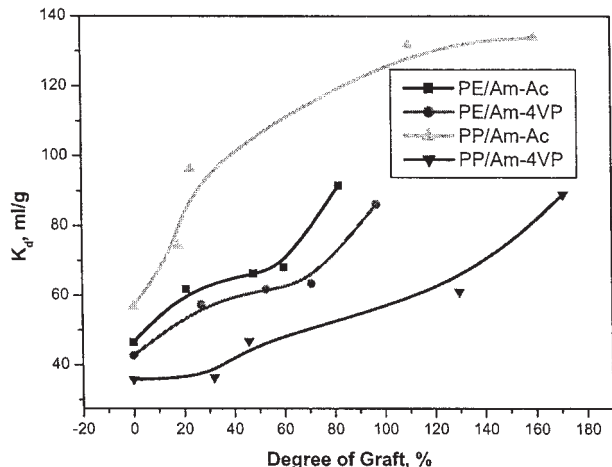


Figure 26 Effect of the degree of graft on the distribution coefficients of U(VI) on polyethylene and polypropylene membranes grafted with different monomer types.

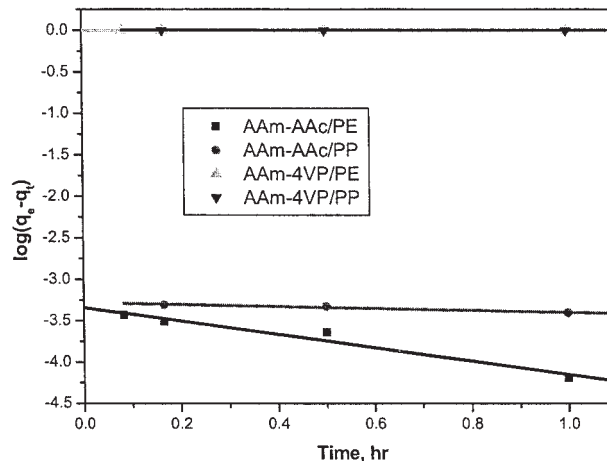


Figure 28 Lagergren relationships for U(VI) adsorption on polyethylene and polypropylene membranes grafted with different monomer types.

ous membrane types, it was found that uranyl cationic species are selectively adsorbed on AAm-AAc/LDPE, AAm-4VP/LDPE, and AAm-AAc/PP rather than the thorium ones. The distribution coefficients of Th(IV) and U(VI) on these membranes at 50% degree of grafting were found to be 47.5, 40, and 64 mL/g and 68, 60, and 108 mL/g, respectively. On the other hand, the selectivity order was reversed at same conditions and recorded as 53 mL/g for Th(IV) and 42 mL/g for U(VI) species on AAm-4VP/PP membranes.

Kinetic characterization of the sorption process

The kinetics of the sorption of Th(IV) and U(VI) species onto PE and PP films grafted hydrogels was investigated. To quantify the changes in the sorption of U(VI) and Th(IV) with time, an appropriate kinetic

model is required the first kinetic model tested for this purpose, was the first order Lagergren equation^{28,29}

$$\log(q_e - q_t) = \log q_r - \left(\frac{kt}{2.303} \right)$$

where q_e is the amount of metal ion sorbed at equilibrium (mol/g); q_t , the amount of the corresponding ion sorbed at time t (mol/g); and k , the overall rate constant (time⁻¹).

Figures 27 and 28 show that the sorption of Th(IV) and U(IV) ionic species followed the Lagergren equation over the entire range of shaking time explored from the slopes of these plots, the value of the first order rate constant k was evaluated and represented in Table I.

Table I shows that in case of uranium, the order of acceleration decrease in the following order

$$\begin{aligned} AAm-AAc/PE &> AAm-AAc/PP \\ &> AAm-4VP/PE > AAm-4VP/PP \end{aligned}$$

However, in case of tetravalent thorium, the following order is obeyed

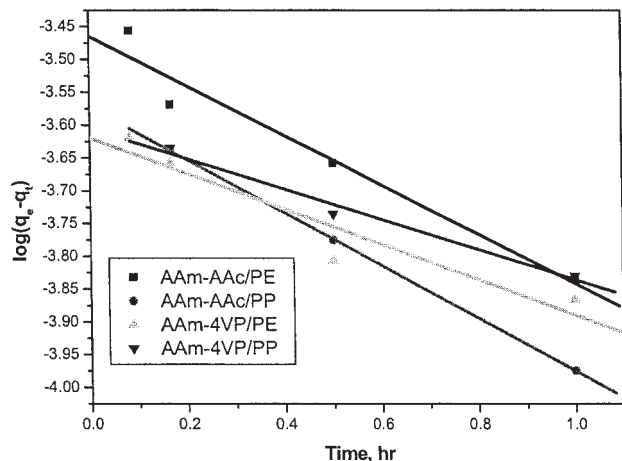


Figure 27 Lagergren relationships for Th(IV) adsorption on polyethylene and polypropylene membranes grafted with different monomer types.

TABLE I
Overall Rate Constant of Sorption of Uranium and Thorium on Different Membranes

Membrane	Rate constant (h ⁻¹)	
	Uranium	Thorium
AAm-AAc/PE	1.86087	0.868093
AAm-AAc/PP	0.272744	0.929053
AAm-4VP/PE	0.000632	0.622063
AAm-4VP/PP	0.000351	0.531325

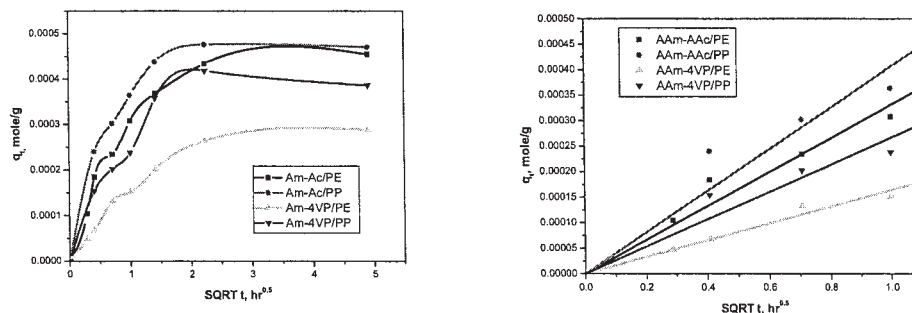


Figure 29 Morris–Weber relationships for Th(IV) adsorption on polyethylene and polypropylene membranes grafted with different monomer types.

$$AAm-AAc/PP > AAm-AAc/PE \\ > AAm-4VP/PE \gg AAm-4VP/PP$$

The membranes grafted with acylamide-acrylic acid comonomers showed higher reaction rates compared with those grafted with acylamide-4-vinyl pyridine. This behavior may be attributed to the strong cation exchange properties after alkali treatment with the conversion of the original carboxylic and amide groups to the corresponding carboxylic groups in their exchangeable potassium forms. Also, the membranes composed basically from polyethylene exhibited higher rates than those composed of polypropylene. Such behavior can be explained by the ability of LDPE films to be more grafted than the corresponding PP sheets (cf. Figs. 1 and 2)

The kinetic of sorption of Th(IV) and U(VI) on the different polymeric membranes was also evaluated by applying the Morris–Weber equation^{29,30,31}:

$$\bar{q}_t = k_s \sqrt{t}$$

where q_t (mol/g) is the amount of metal ions sorbed at time t (h) k_d is the rate constant of transport through the film ($\text{mol g}^{-1} \text{h}^{-1/2}$). According to this model, plotting a graphic of q_t versus \sqrt{t} , Figures 29 and 30 if a straight line is obtained passing through the origin,

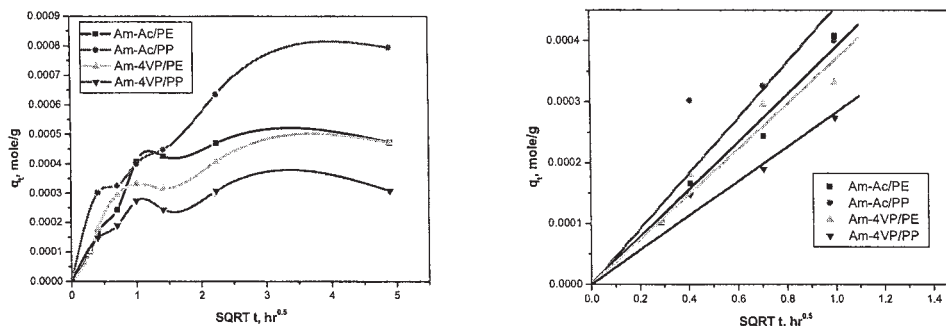


Figure 30 Morris–Weber relationships for U(VI) adsorption on polyethylene and polypropylene membranes grafted with different monomer types.

it can be assumed that the involved mechanism is a diffusion of the species through the membranes. The figures show that Morris–Weber relationship holds good to the first hour, only deviating at higher agitation times. The Morris–Weber constants of the different membranes were calculated and represented in Table II. The various membranes grafted with acrylamide-acrylic acid showed higher transport constants than the membranes grafted with acrylamide-4-vinyl pyridine and followed the following order

$$AAm-AAc/PP > AAm-AAc/PE \\ > AAm-4VP/PE > AAm-4VP/PP \text{ for U(VI)}$$

$$AAm-AAc/PP > AAm-AAc/PE \\ > AAm-4VP/PP > AAm-4VP/PE \text{ for Th(IV)}$$

Besides, the transport constants found in case of adsorption of U(VI) species are found to be greater than those obtained for Th(IV) ones. This phenomenon can be explained in terms of both the valency of the adsorbed ions and the species involved in the transport process in solution. The main species controlling the transport of uranium is mainly $[\text{UO}_2]^{2+}$ rather than $[\text{UO}_2\text{NO}_3]^+$, $[(\text{UO}_2)_2(\text{OH})_2]^{2+}$, $[\text{UO}_2\text{OH}]^+$, and $[(\text{UO}_2)_3(\text{OH})]^{5+}$ species through solid. In case of

TABLE II
Overall Transport Constant for Sorption of Uranium and Thorium on Different Membranes

Membrane	Transport constant (mol/(g h ^{-0.5}))	
	Uranium	Thorium
AAm-AAc/PE	3.87 E -04	3.31 E -04
AAm-AAc/PP	4.52 E -04	4.05 E -04
AAm-4VP/PE	3.68 E -04	1.64 E -04
AAm-4VP/PP	2.81 E -04	2.66 E -04

Th(IV), Th(OH)³⁺, [ThNO₃]³⁺, and [Th(OH)₂]²⁺ are expected to participate in the transport process beside the free [Th]⁴⁺.

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