Ion-exchange Membranes for Metal Ions Separation

El-Sayed A. Hegazy¹, H. Kamal¹, N. A. Khalifa²(*) and Gh. A. Mahmoud¹

¹National Centre for Radiation Research and Technology, P.O. Box 29, Nasr City, Cairo, Egypt
²Faculty of Science, Helwan University, Helwan, Egypt

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ABSTRACT

A new synthetic membrane has been synthesized by direct radiation grafting of acrylonitrile and vinyl acetate in a binary monomers mixture onto low density polyethylene and isotactic polypropylene films. The effect of grafting conditions, such as comonomer composition and concentration on the grafting process, was determined. The graft copolymers, thus obtained, have been chemically treated to improve their ion-exchange and hydrophilic properties. To explore the applicability of the prepared membranes, their sorption capacity and selectivity towards different metal ions such as Cu, Co, Fe, Pb, Sr, Cd and Li were investigated. The degree of grafting had a considerable influence on the metal uptake of these membranes and it increased with graft yield. The prepared membranes have great affinity toward Fe³⁺ if compared with other metal ions investigated. For a mixture of metal ions such as Cu²⁺, Sr²⁺ and Pb²⁺ these membranes show ability to chelate these ions from their mixtures in the order of Cu²⁺ > Sr²⁺ > Pb²⁺. But for a mixture of Co²⁺, Cd²⁺ and Li⁺ the selectivity was in the order of Co²⁺ > Cd²⁺ > Li⁺.

Key Words: gamma - irradiation, grafting, membranes, metal separation

INTRODUCTION

Modification of chemical and physical properties of polymers via graft polymerization has been the subject of much interest and has made paramount contributions towards improved industrial, space and biochemical applications [1]. The grafting may be carried out into commercially available polymeric films, which offers an advantage in terms of producing membranes without problems associated with transforming the graft matrix into a thin foil. In this respect, it is possible to introduce membrane properties into a film without much influencing the important characteristics of the trunk polymer, such as thermal stability and chemical resistance [2–4]. The improvement in the properties of graft copolymers depends on the nature, amount and chain length of the grafted branches as well as on the type of distribution of the grafted monomers in the base polymer. The introduction of polar substituents as grafting chains onto a hydrophobic polymer surface is expected to give favorable modifications of the polymer properties [5].

(*) To whom correspondence should be addressed.
Mixed monomers can also be used in grafting onto polymers to introduce dual properties such as hydrophilicity and hydrophobicity since different types of polymer chains containing various functional groups can be introduced into the polymer structure.

Conditions of the grafting reactions can be also manipulated and graft copolymers of desired properties are obtained [6—9].

In the present work, the preparation of graft copolymers by the direct radiation grafting of acrylonitrile (AN) and vinyl acetate (VAc) in a binary monomer mixture onto low density polyethylene (LDPE) and isotactic polypropylene (PP) was studied. Some factors that influence the ion-exchange property of the prepared ion-exchange membranes toward some selected metal ions have been also investigated.

**EXPERIMENTAL**

Low density polyethylene (LDPE) films of thickness 80 µm and isotactic polypropylene (PP) films of thickness 30 µm were provided by El-Nasr Co. for Medical Supplies, Egypt. Reagent grade acrylonitrile (AN) of purity 99.3 % (Merck) and reagent grade vinyl acetate (VAc) of purity 99 % (Merck) were used as received. Other chemicals, such as solvents, inorganic salts, acids and other reagents were reagent grade of BDH type.

The direct radiation grafting method was used as a technique. The irradiation was carried out using Co-60 gamma rays at a dose rate ranging from 0.27–1.1 Gys in 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 at 40–50 °C in oven for 24 h to constant weight. The degree of grafting was calculated by percentage increase in weight as follows:

\[
\text{Degree of grafting(\%)} = \left( \frac{W_g - W_0}{W_0} \right) \times 100
\]

Where: \(W_0\) and \(W_g\) are the weights of blank and grafted films, respectively.
The improvement in the hydrophilic and ion-exchange properties of the graft copolymers was effected by treating them with aqueous KOH (5%) or with 1:1 alcoholic solution containing 5% hydroxylamine using a reflux at 90 °C for 16 h. The treated films were then immersed in redistilled water for 24 h to remove the excess reagents and then dried in oven at 40–50 °C for 24 h.

Metal uptake of the grafted treated films was determined by atomic absorption spectrophotometer (Perkin Elmer model 2380). The selectivity of different prepared membranes towards Pb, Cd, Fe, Co, Cu, Sr and Li was determined. The effect of degree of grafting and initial feed concentration on the metal ion uptake was also investigated.

RESULTS AND DISCUSSION

Effect of Comonomer Composition

Figures 1 and 2 show the effect of comonomer composition on the grafting of AN/VAc onto LDPE and isotactic PP films, respectively in presence of DMF as a diluent. It can be seen that, the degree of grafting increases as AN content increases in the solution. On the other hand, the grafting yield decreases with increasing VAc content in the mixture until it reaches its lower value at 100% VAc. It seems that the presence of AN would enhance the grafting of VAc, as it was found in other binary graft copolymerization systems with different monomers [10,11].

It is important to note that the shape of curves in Figures 1 and 2 is different. At comonomer composition (50/50) in Figure 2, saturation grafting is observed then an acceleration of grafting is occurred at comonomer composition (70/30) (AN/VAc). At high content of VAc, the degree of grafting never goes above 40 wt % which indicates that the high VAc content prevents the diffusion of the comonomer from the solution phase to the bulk polymer and the grafting is only obtained on the isotactic PP surface. This effect decreases the total grafting yield, and hence saturation grafting is observed at 50/50 comonomer composition. The acceleration of grafting observed at comonomer composition (70/30) (AN/
VAc) is highly dependent on AN concentration. The appearance of such acceleration is dependent upon the polarity of AN and the preferential solvation of the growing radical chain by this polar monomer [12].

Individual radiation grafting of VAc onto LDPE and isotactic PP is very difficult, since the homopolymerization goes on rapidly, due to the high radical yield G(R') of VAc when subjected to gamma irradiation [13]. The presence of AN in the reaction mixture may reduce the G(R') of VAc during irradiation process by chain transfer effect and hence facilitates the diffusion of the reaction mixture into the bulk polymer. This leads to successive grafting and minimizing the homopolymerization.

Grafting of AN/VAc binary mixture onto LDPE and IPP, indicated that, the polymer morphology plays a great role in the grafting process due to its influence on the diffusivity of monomer and reactivity of formed radicals in the polymer matrix and their life time. It is well known that, isotactic PP is more crystalline than LDPE i.e., the crystalline domains in LDPE are less than that of isotactic PP structure. The diffusion of monomer is enhanced in the amorphous regions of the polymer chains; therefore, both the rate of grafting and the yield are higher for LDPE than those for isotactic PP films.

**Effect of Comonomer Concentration**

It is demonstrated in this study that the concentration of (AN/VAc) comonomers plays an important role in the grafting process. The effect of comonomer concentration on the grafting of (AN/VAc) mixture onto LDPE and isotactic PP films at comonomer composition 70/30 (wt%) is investigated and shown in Figures 3 and 4, respectively. It can be seen that, the degree of grafting increases with increasing the comonomer concentration i.e., with decreasing the solvent content in the reaction medium.

The increase in the grafting yield with comonomer concentration might be due to the increase in diffusion rate of the monomers into the bulk polymer. The higher concentration of monomers at the grafting sites favors propagation of growing chains and consequently, the grafting yield increased. Figures 3
and 4 show also an acceleration at comonomer concentration 60 (wt%), this leads one to believe that the" viscosity effect" plays an important role, at this high comonomer concentration, because it enhances the propagation process and retards the termination of the radicals because of the low mobility of the growing chain radicals. On the other hand, the decrease of grafting yield with dilution might be due to the lower ratio of propagation and more termination reactions, thus keeping the molecular weights of PAN and PVAc chains rather low.

Effect of Grafting Degree on Metal Ion Uptake

The degree of grafting i.e., the number of functional groups present in the membrane, plays an important role in determining the amount of metal uptake by the membrane. Figures 5–8 show the relation between the amount of metal ions uptake expressed in (mmol/g) and degree of grafting for different membranes. It can be seen that, the amount of metal ions uptake increases with increasing the graft percent for all kinds of membranes being investigated. This clearly

Table 1. Ion exchange selectivity of treated LDPE and isotactic PP membranes towards three metal ions present in a mixture for: Cu2+, Sr2+ and Pb2+ mix. at pH: 5 and Co2+, Cd2+ and Li+ mix. at pH: 6, treatment time: 8 h, temp.: 100 °C, initial feed concn.; 1000 ppm and grafting percent; 200%.

<table>
<thead>
<tr>
<th>Metal feed</th>
<th>Metal uptake (mmol/g)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>LDPE/ KOH</td>
</tr>
<tr>
<td>Cu2+</td>
<td>2.0</td>
</tr>
<tr>
<td>Sr2+</td>
<td>1.1</td>
</tr>
<tr>
<td>Pb2+</td>
<td>0.6</td>
</tr>
<tr>
<td>Co2+</td>
<td>1.50</td>
</tr>
<tr>
<td>Cd2+</td>
<td>0.09</td>
</tr>
<tr>
<td>Li+</td>
<td>0.20</td>
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</tbody>
</table>

* isotactic PP
confirms that the metal chelation or complexation is mainly dependent on the amount of functional reactive groups in the membranes. It is also observed that, for membranes having graft percent < 200%, the amount of metal ions uptake increases rapidly with increasing the graft percent, but for membranes having higher graft percent > 200 a slower metal uptake is observed.

The above results suggested that, the diffusion of the metal ion solution in the membrane (i.e., to the functional groups) plays an important role. In the membranes having high graft yield>200% the cross-linking formation would hinder the diffusion of metal ions and the metal ion uptake increased to a small extent with degree of grafting.

Effect of Initial Concentration of Metal Feed Solution

This study was carried out by equilibrating a series of initial metal ion concentrations with fixed amount of the sorbent membrane that can be removed from the solution when the chelating sites of the sorbent are saturated.

Figures 9–12 show that, increasing the initial metal ions concentration results in increasing the amount of metal ions uptake to reach a certain limiting value. Thereafter, it levels off at higher feed concentration (>1000 ppm). This behaviour is observed for all different membranes having various functionalized groups.

These results revealed that the chelating sites of the sorbent become saturated when the concentration of the feed solution is reached 1000 ppm, above which no more metal ions uptake occurred.

Membrane Selectivity Towards Different Metal Ions

The selectivity of different prepared membranes are investigated using mixtures of three metals in the same feed solution at suitable pH and the results are shown in Table I. The selectivity of membranes towards metal ions is interpreted by considering the uptake of metal ion by complexation and/ or chelation with the membrane functional groups. Consequently, the results can be reasonably explained by considering
metal ions namely: Cu$^{2+} + \text{Sr}^{2+} + \text{Pb}^{2+}$ mixture and Co$^{3+} + \text{Cd}^{2+} + \text{Li}^{+}$ mixture. It was observed that, the amount of Li extracted by the sorbent is negligible. Since Co and Cd ions have the same valence ($2^+$) with different ionic radii and the selectivity of the sorbent towards Co$^{2+}$ is higher than Cd$^{2+}$. This is possibly due to the smaller ionic radii of Co$^{2+}$. Meanwhile, in case of the other mixtures containing Cu$^{2+}$, Sr$^{2+}$ and Pb$^{2+}$, the selectivity towards Cu$^{2+}$ is higher than that for the other two metal ions for the same reason. These results indicated that the ionic radii are the effective factor in the selectivity of these metal ions.

**CONCLUSION**

It can be concluded that the prepared membranes have great affinity toward Fe$^{3+}$ if compared with the other metal ions investigated at the suitable pH. The trivalent Fe$^{3+}$ forms a more stable and strong complex with the functional groups of the treated grafted membranes. The selectivity of each membrane towards different metal ions, which exist in a mixture of three metal ions of different characteristics and of the same initial concentration, depends mainly on the valence, ionic radii and the stability of the formed complex. Results also showed that such kind of grafted copolymers might be of great interest in the application of wastewater treatment from heavy and toxic metals.

**REFERENCES**


