Dialysis Membranes from Polyethylene Films Grafted with Acrylic Acid

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ABSTRACT: Low-density polyethylene-*g*-poly(acrylic acid) membranes were prepared by the direct radiation grafting of aqueous acrylic acid solutions (containing Mohr's salt) onto low-density polyethylene films and were irradiated at two different irradiation doses (2 and 3 Mrad) at a dose rate of 0.02 Mrad/h. Two series of polyethylene-*g*-poly(acrylic acid) membranes with 100 and 150% grafting were obtained. The free carboxylic acid groups in the grafted films were converted into the corresponding acrylates by reactions with different metal salts. The swelling (water uptake) and dialysis permeability of glucose and urea through the grafted membranes in different metal-ion forms were investigated. The prepared membranes showed good permeability to both solutes, which increased as the hydrophilicity of the membrane increased. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 10–14, 2004

Key words: graft copolymers; membranes; polyethylene (PE); radiation; swelling

INTRODUCTION

Although membrane separation processes have been studied for more than a century, they have only recently attracted interest for many industrial separations. Today, their applications range from the purification and concentration of fluids, to the desalination of saline water and hemodialysis (artificial kidneys), to the separation and fractionation of gases or micromolecular mixtures.[1,2]

Graft polymerization provides a convenient method for the synthesis of semipermeable membranes because commercially available polymer film can be used as substrates.

A number of researchers[3–6] have used this technique to modify the properties of existing membranes or a polymer before the casting of the membranes.

Much effort has been devoted to the production of permselective membranes through the grafting of various hydrophilic monomers onto polyethylene, polypropylene, and fluorinated polymers, which have been used as base polymers.[7–9] The grafting of some functional groups of hydrophilic monomers onto hydrophobic polymers seems to meet all the requirements because such grafting can induce hydrophilicity and good electrochemical properties.

Fang et al.[10] prepared polypropylene dialysis membranes with γ-radiation by directly grafting 2-hydroxyethyl methacrylate. The influence of the degree of grafting and the grafting temperature on the permeabilities of polypropylene-*g*-2-hydroxyethyl methacrylate membranes to urea and creatinine was studied.

Anion-exchange membranes were prepared by the radiation-initiated graft copolymerization of 4-vinyl pyridine onto low-density polyethylene and poly(tetrafluoroethylene).[11] Some of the basic characteristics, such as the water content and specific electric resistance, of these anion-exchange membranes were studied with respect to the grafting degree of 4-vinyl pyridine.

Gupta et al.[12] studied the influence of the synthesis conditions on the development of membranes through the radiation grafting of acrylamide onto polyethylene films.

The radiation-induced grafting of acrylic acid onto polyethylene has been studied by many workers[13,14] with both the direct grafting method and the preirradiation method.

In this study, the direct grafting method was used to graft acrylic acid (as a hydrophilic monomer)onto low-density polyethylene films. The swelling properties and dialysis permeabilities of the grafted films with respect to two molecular species (glucose and urea) were examined to develop improved dialysis membranes.

EXPERIMENTAL

Materials

Low-density polyethylene films (120 μm thick) were commercially available from Hema Plast Co. (Cairo, Egypt). Cellophane was obtained in the form of uncoated sheets 20 μm thick. The sheets were supplied by Misr Rayon Co. (Kafr El-Dawar, Egypt) and were

TABLE I
Water Swelling Properties of Different Polyethylene-*g*-Poly(metal acrylate) Membranes

Membrane type	Water content(%)		Expansion in surface area(%)	
	100% graft	150% graft	100% graft	150% graft
$-K^+$	67.7	71.0	120	133.2
$-Na^+$	62.5	66.8	84.3	110.4
$-Li^+$	31.7	43.7	31.2	41.8
COOH	28.0	36.2	24.3	34.7
Cellophane	46.0		25.0	

used as a control films in the dialysis permeability experiments. Acrylic acid (99% pure; BDH Chemicals) was used as received. Other chemicals were reagent-grade and were used without further purification.

Grafting procedure

Low-density polyethylene-*g*-poly(acrylic acid) membranes were prepared by the direct (mutual) radiation grafting of a 25% aqueous acrylic acid solution containing 2.5 wt % Mohr's salt (a homopolymerization inhibitor for acrylic acid) onto low-density polyethylene films and were irradiated with two different γ-irradiation doses of 2 and 3 Mrad from a ^{60}Co source at a dose rate of 0.02 Mrad/h. After they were thoroughly cleaned in warm water, the films were dried under reduced pressure at 60°C for 24 h.

The degree of grafting was calculated from the weight increase of the original polyethylene films.

Dialysis permeability measurements

A laboratory dialysis cell was used for determining the permeability of the membranes to various compounds, as a function of time, at room temperature. The cell consisted of two compartments (150 cm^3 each). A membrane was clamped between the two compartments with suitable supporting devices. One compartment was filled with distilled water, and the other was filled with an aqueous solution containing a mixture of two solutes: urea (0.5 wt %, weight-average molecular weight = 60) and glucose (0.5 wt %, weight-average molecular weight = 180). Both compartments were stirred during the permeability measurements. The permeability of the solutes through the membranes was analyzed spectrophotometerically[15–18] at different time intervals. The permeability percentages were then calculated according as follows:

$$\text{Permeability (\%)} = \frac{C}{C_0} \times 100$$

where C is the concentration of the solute in the filtrate and C_0 is the concentration of the solute in the initial solution.

Water content determination

The membranes were immersed in distilled water for several days, and the water on the membrane surfaces was blotted off before the membranes were weighed. The weights of the dry membranes were determined by the membranes being dried to constant weights at about 100°C. The water content was expressed as the ratio of the weight of water in the water-swollen membrane to that of the water-swollen membrane.

RESULTS AND DISCUSSION

Two different series of polyethylene-*g*-poly(acrylic acid) films with degrees of grafting of about 100 and 150% were prepared at two γ-irradiation doses of 2 and 3 Mrad, respectively. The free carboxylic acid groups of some grafted films in the two series were converted into the corresponding acrylates by reactions with different metal salts such as KOH, NaOH, and LiCl.

For the evaluation of the obtained grafted films as potential membranes, their swelling behavior and the dialysis permeabilities were determined for two molecular species (glucose and urea) and compared to the permeabilities of cellophane control films to determine the relative significance of the results. The results are given in Table I and Figures 1 and 2.

Swelling properties

Table I shows the effect of the degree of grafting and the metal-ion type on the swelling properties (the water content and expansion of the film surface area upon swelling in water). The sequence of the swelling properties was in the order —$COOK^+ > COONa^+ > COOLi^+ >$ COOH, and all the values increased with an increasing percentage of grafted acrylic acid in the films. Moreover, the conversion of free carboxylic

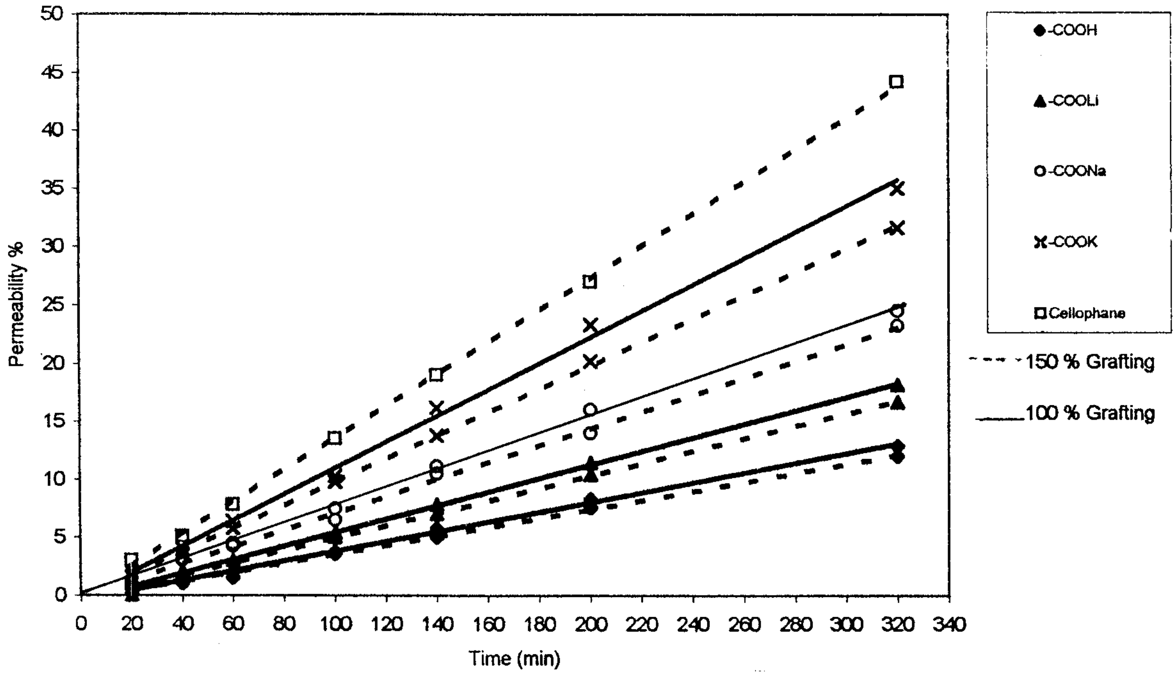

Figure 1 Permeability of urea through polyethylene-*g*-poly(metal acrylate) membranes.

groups of poly(acrylic acid) chains into metal acrylates increased the hydrophilic properties of the grafted membranes. These results may be understood from the point of view of the hydration of metal ions.[19] The hydration energy of K^+ and Na^+ was lower than that of the Li^+ metal ions.

Another explanation could be the state of the water molecules (free or bound) in the water-swollen membranes. In a study of a similar sort, Wycisk and Trochimczuk[20] determined the free and bound water contents in polyethylene poly(methacrylic acid-*co*-divinyl benzene) interpolymer-type carboxylic membranes by

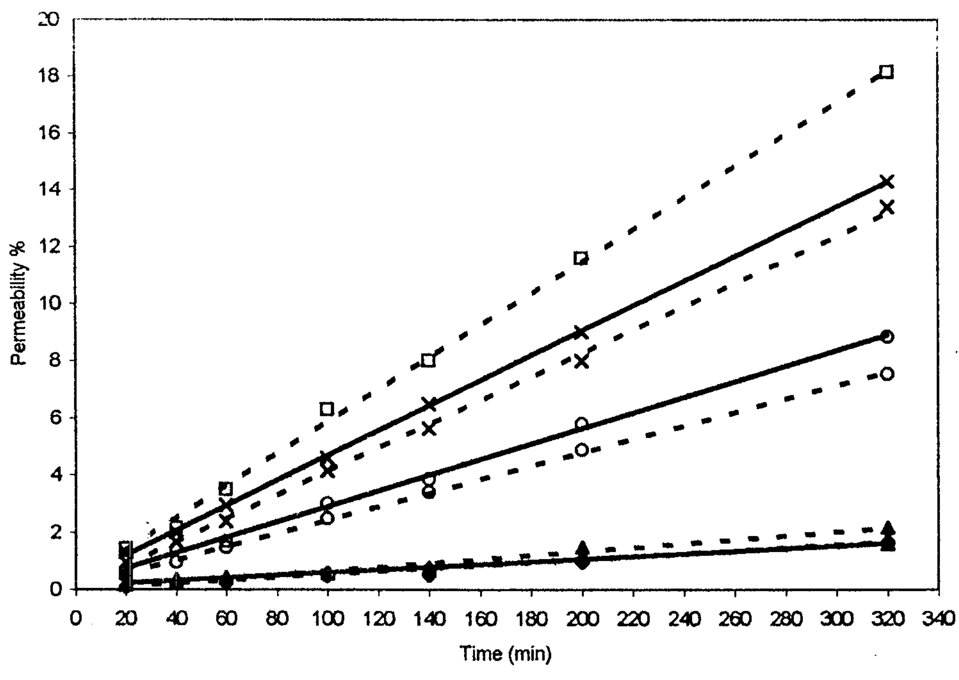

Figure 2 Permeability of glucose through polyethylene-*g*-poly(metal acrylate) membranes (see Fig. 1 for the definitions of the symbols used).

differential scanning calorimetry. Two series of membranes were investigated: membranes in COOH form and membranes in COONa form. It was shown that, for membranes in COOH form, nearly all the swelling water was in a nonfreezing bound water state, with free freezing water existing in minor amounts. For the membranes in COONa form, 50–80 wt % of the total swelling water was in the freezing water state.

According to these results, it was possible to arrange the amounts of free freezing water in the water-swollen membranes as follows:

$$-COOK^{+} > -COONa^{+} > -COO\,Li^{+} > -COOH.$$

The increase in the swelling properties of the membranes as the amount of grafted acrylic acid polymer increased from 100 to 150% was probably due to the insertion of the polar groups (—COOH) into the hydrophobic polyethylene films, which increased the hydrophilic character of the films.

Dialysis permeability

Figures 1 and 2 compare the results of the dialysis permeability of glucose and urea through various polyethylene-*g*-poly(metal acrylate) membranes and the permeability of cellophane films. The data show the following:

1. The values of the permeability (%) of glucose and urea increased linearly with increasing time for all the membranes and cellophane.
2. The sequence of permeability (%) of urea and glucose through the membranes was $-COOK^{+} > -COONa^{+} > -COOLi^{+} >$ COOH, the same order found for the water content and swelling properties of the membranes (see Table I). This relationship was not unexpected because the hydration and water swelling properties were the measures of base sheet accessibility, and it seemed reasonable that a correlation could be obtained between the swelling properties and dialysis permeability.
3. The cellophane films showed relatively higher permeability to both solutes, although they had lower water contents and swelling properties than those obtained for most grafted films (Table I). It was assumed that the water-soluble solutes diffused only through the water phases in the water-swollen membranes.[21,22] On the basis of the free-volume theory of diffusion, Yasuda et al.[21,22] indicated that the diffusive permeability of solutes through membranes could be explained by the water content. Many researchers[20,21,23] have reported different states of water molecules in water-swollen membranes (e.g., bound water, free water, and secondary bound water, or intermediate water). Currently, it is only clear that soluble solutes are difficult to diffuse through intermediate water regions and even more difficult to diffuse through bound water regions. It seems that the amount of free water allowing the diffusive permeation of solutes may have been less in all the polyethylene-*g*-poly(metal acrylate) membranes than in the cellophane films, although the total water content in most of the membranes was higher. However, further studies are needed to determine the relationship between the diffusive permeability of the solutes through the membranes and the state of water in them.
4. When the permeability values of the two solutes were compared, urea was found to be more efficient than glucose for permeation through the membranes. This could be explained by the fact that larger molecules such as glucose were hindered in penetrating the membranes more than smaller molecules such as urea because the macromolecular network was not sufficiently accommodating to allow such large molecules[24,25] to pass through.

CONCLUSIONS

This study suggests that the γ-radiation-induced grafting of acrylic acid can be performed successfully onto low-density polyethylene films. Our investigations of the swelling behavior and dialysis permeability of glucose and urea through various polyethylene-*g*-poly(metal acrylate) membranes have shown the possibility of their practical applications as promising dialysis membranes.

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