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Preparation of strong acid cation-exchange membrane using radiation-induced graft polymerisation

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Abstract

Polyethylene (PE) sheet modified with acrylic acid (AA) was grafted with *p*-vinyl benzene sulphonic acid sodium salt hydrate (SSS) using ^{60}Co γ-rays in a direct grafting method in the presence of air at ambient temperature. It was observed that increasing dose results in increase of SSS grafting. Changes in surface area, thickness, ion-exchange capacity and water uptake with respect to dose were also evaluated. The grafting was confirmed by FTIR studies. The ion-exchange capacity of the grafted membrane under the conditions was 5.5–5.8 milli equivalent per gram (meq/g) which is better than most of the commercially available membranes.

Keywords: Cation-exchange membranes; Radiation-induced grafting; Acrylic acid; *p*-vinyl benzene sulphonic acid sodium salt hydrate; Polyethylene; γ-rays; ^{60}Co

1. Introduction

An ideal ion-exchange membrane should exhibit a high electrical conductivity combined with a high ionic permeability, so as not only to promote productivity, but also to reduce the operational cost.

Radiation-induced grafting is one of the methods used for modification of physical and chemical properties of the polymer materials (Satoshi et al., 1991; Kim et al., 1991). UV light, γ radiation or electron beam have been used to initiate the reaction instead of the chemical initiators. Cation-exchange membranes having strong acid functional groups such as sulphonic acid have applications in the field of electrodialysis method of water desalination, electrolysis in fuel cell, etc., due to their wider pH range working characteristic (Sata et al., 1996). Most of the commercially available cation-exchange membranes consist of styrene (St) grafted onto the polymer substrate and subsequent modification by conventional chemical method such as sulphonation to introduce the strong acid ion-exchange moieties (D'Agostino et al., 1977; Momose et al., 1986). Studies on preparation of ion-exchange membranes by radiation-induced graft polymerisation (RIGP) have been reported in the literature (Ang et al., 1982; Gupta and Chapiro, 1989; Vigo et al., 1981). Preparation of strong acid cation-exchange membranes having sulphonic acid groups by radiation-induced co-grafting method has been reported (Satoshi et al., 1995). In this case, pre-irradiation method at a very high dose with electron beam was used and an ion-exchange capacity of 2.5 milli equivalent per gram (meq/g) was obtained.

The objective of this work is to prepare strong cation-exchange membranes using γ radiation without going into the sulphonation step, which is quite cumbersome. We are reporting here a method to introduce sulphonic acid groups onto polyethylene (PE) sheet using γ

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radiation by simultaneous grafting method in presence of air at room temperature, under atmospheric pressure at low doses.

In this method, a PE sheet is suitably modified by acrylic acid (AA) and subsequently *p*-vinyl benzene sulphonic acid sodium salt hydrate (SSS) grafted at relatively low doses resulting in high ion-exchange capacity.

2. Experimental

2.1. Materials

PE sheet with the thickness of 100–110 μm, density 0.89–0.91 $g\,cm^{-3}$ was supplied by Indian Petrochemical Ltd (IPCL) grade no. 1070LA17. Reagent grade acrylic acid (AA) and ferrous ammonium sulphate were obtained from SD Fine Chemicals (India) Ltd, SSS was obtained from Lancaster (England) Ltd with purity of 90% and was used as received.

2.2. Estimation of the degree of grafting

The degree of grafting was calculated gravimetrically and expressed as a percentage of the grafting monomer weight by the following Eq. (1)

$$\text{Percentage of grafting} = \frac{P - P_0}{P_0} \times 100, \quad (1)$$

where P_0 and P are the weight of PE before and after grafting, respectively.

2.3. Grafting of AA on PE

A PE sheet of size 6 cm × 4 cm was washed with soap water followed by ethanol and dried at 50 °C under vacuum for 12 h. AA and water were mixed in equal ratio by weight and Mohr's salt 1% (w/w) was added as an inhibitor for homopolymerisation. The PE sheet was kept in the above AA solution at room temperature for 24 h. After this, the sample was irradiated with γ rays from ^{60}Co source at ambient temperature to total dose of 6 kGy at dose rate of 0.5 kGy/h. The sheet was removed and washed with hot water to remove excess of monomer and homopolymer. The AA-grafted PE (PE-g-AA) sheet was dried in vacuum oven at 50 °C for 12 h. Similarly grafting of AA on to PE was carried out at 8 and 10 kGy and degree of grafting was determined as per Eq. (1) to be approximately 60%, 80% and 120%, respectively.

2.4. Grafting of SSS on PE-g-AA

In order to optimise the requirement of the acrylic acid percentage on PE, we have carried out the following experiment. Three PE-g-AA sheets having 60%, 80% and 120% AA grafting were kept separately in 1 M SSS aqueous solution for 24 h at room temperature. The samples were irradiated with γ rays from ^{60}Co source for the total dose of 6 kGy at a dose rate of 0.5 kGy/h at atmospheric pressure and ambient temperature. The sheets were removed from the solution and the grafting percentage of SSS on the above three AA-grafted PE sheets was estimated by using Eq. (1). It is seen from Table 1 that there is no significant increase in percentage grafting of SSS when the AA-modified PE sheet with 120% AA grafting was used, in comparison to the modified PE sheet with 80% AA grafting, whereas when the PE sheet having 60% AA grafting was used, the SSS grafting was much less. Therefore, in all further experiments a modified PE sheet having 80% AA grafted was used for grafting SSS.

Table 1
Grafting of SSS on AA modified PE

Details of the sample	Dose in kGy	% Grafting of SSS on AA-modified PE
PE-60% AA grafted	6	4.5
PE-80% AA grafted	6	15.1
PE-120% AA grafted	6	17.2

A 1 M SSS aqueous solution was prepared and the PE-g-AA sheet was kept in this solution for 24 h at room temperature. The sample was then irradiated with γ rays from ^{60}Co source for various doses at dose rate of 0.5 kGy/h at ambient temperature. The PE sheet was then removed and washed repeatedly with hot distilled water and dried in vacuum oven at 50 °C for 12 h. The percentage of SSS grafting was calculated by using Eq. (1).

2.5. Estimation of percentage change in area and thickness of PE-g-AA after and before SSS grafting

The area change after grafting SSS on PE-g-AA was calculated using Eq. (2). Results are given in Table 2.

$$\text{Percentage area change} = \frac{A_1 - A_0}{A_0} \times 100, \quad (2)$$

where A_0, A_1 are the areas of the membranes before and after SSS grafting in a wet condition. The area of the membrane was calculated by using Eq. (3).

$$\text{Area} = \text{length} \times \text{width}. \quad (3)$$

The change in the thickness of membrane before and after SSS grafting was calculated by measuring the initial and final thickness of the membranes when dry by using thickness gauge (Mitutoyo, Japan).