Preparation of cation-exchange membrane containing bi-functional groups by radiation induced grafting of acrylic acid and sodium styrene sulfonate onto HDPE: Influence of the synthesis conditions

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Electron beam radiation induced grafting of acrylic acid (AA) and sodium styrene sulfonate (SSS) onto high-density polyethylene (HDPE) membranes was investigated by the pre-irradiation method, and a cation-exchange membrane containing bifunctional groups was synthesized. The effects of grafting conditions such as monomer concentration, radiation dose and temperature on grafting yield were studied. The dependence of grafting yield on pre-irradiation dose and monomer concentration was found to be 0.54 and 2.21, respectively. The activation energy for the grafting was calculated to be 22.2 kJ/mol. Infrared spectroscopy analysis of the grafted membrane confirmed the existence of sulfonate and carboxylic acid groups.

Introduction

High-energy radiation can change the property of polymers through radiation grafting, and polymers modified by radiation grafting can be used as ion-exchange membrane in the fields of separation and electrochemistry,1–3 or as haemocompatible biomaterials.4 Applications of HDPE membranes are limited because of their weak hydrophilicity. After grafting with some polar monomers such as acrylic acid by radiation, the hydrophilicity of the membranes is improved.5,6 Cation-exchange membranes prepared by radiation-induced graft copolymerization of acrylic acid (AA) onto all kinds of polymers are widely used in batteries as separators. In order to improve the ion-exchange capacity of cation-exchange membranes, authors have tried to introduce sulfonic acid groups onto the polymer matrix.7,8 The highly ionized SO3– can easily form sphere-hydrated ions, which are incompatible with hydrophobic HDPE membranes, so it is impossible to introduce vinyl monomers containing sulfonic acid groups directly onto HDPE membranes. Almost all of the studies on the preparation of cation-exchange membranes containing sulfonic acid groups involved more than one preparation step.9–11 Introduction of sulfonic acid group was finished after grafting of the monomers such as styrene.

In order to simplify the grafting procedure, we have introduced a binary mixture system by which co-graft AA and sodium styrene sulfonate (SSS) onto HDPE membranes. At the beginning of the grafting reaction, AA could be grafted onto the surface of HDPE and the hydrophilicity of the surface was improved. Then SSS and AA were co-grafted onto HDPE, sulfonate groups were introduced onto HDPE by a one-step method.

Electron beam has been selected as radiation source because of it gives higher dose rate compared to γ-rays.

In this paper, electron beam radiation induced grafting of AA and SSS onto HDPE membranes was investigated by the pre-irradiation method. The effects of grafting conditions such as monomer concentration, radiation dose and temperature on grafting yield were studied.

Experimental

Materials

HDPE membranes of 15 μm thickness were supplied by Shanghai Dayu Plastic Membrane Co. Ltd.; AA was obtained from Shanghai Chemical Reagent Co. Ltd.; SSS was bought from Zibo Longda Chemical Co. Ltd. All materials were used as supplied.

Grafting procedure

HDPE membranes were cut into strips (13×7 cm²), then washed with acetone and dried under vacuum at desired temperature before weighing. The dried membranes were put into HDPE bags and subsequently flushed with nitrogen several times to drive away the air in the bag. After sealed the bags were irradiated using an electron beam of accelerator (GJ-2 Dynamit Electron Accelerator, Shanghai Xianfeng Electric Manufacturing Factory) with a beam energy of 1.8 MeV and a current of 3 mA. The HDPE membranes were irradiated in steps in order to avoid the increase of temperature in the irradiated HDPE. The radiation dose per step was 20 kGy. The irradiated membranes were put together with polypropylene nonwoven fabrics and rolled together around a glass stick, then they were immersed in the monomer solution which was deaerated by...
During the period that the HDPE membranes were taken from the sealed bags and immersed into the monomer solution, the membranes were inevitably exposed to air, but this exposure was limited as much as practical.

**Measurement of the total grafting yield**

After the desired reaction time the membranes were taken out and washed with distilled water, then soaked therein overnight to remove homopolymers. Finally, the grafted membranes were dried at 60 °C until a constant weight was attained, and the total grafting yield was determined by the weight increase according to the following equation:

\[ G_t = \frac{W_t - W_0}{W_0} \times 100 \%
\]

where \( W_0 \) and \( W_t \) are the weight of ungrafted and grafted membranes, respectively.

**Result and discussion**

**Effect of grafting time on the total grafting yield for various doses**

The total grafting yield at 60 °C versus different pre-irradiation doses is shown in Fig. 1. From it we can see that \( G_t \) increases with the increase of the pre-irradiation doses. At the beginning of grafting reaction, the total grafting yields did not differ much at radiation doses of 120, 160, 200 kGy. The explanation is that the initial grafting reaction was controlled by the diffusion rate of monomers into the polymer matrix. After the grafting reaction continues for half an hour, the higher the radiation dose, the higher is the grafting yield. Such behavior may be attributed to the fact that at higher dose, the number of radicals generated in the polymer matrix also increases. The grafting yield is very low at 80 kGy. This can be ascribed to the following factors: (1) the concentration of trapped radicals is lower at dose of 80 kGy than 200 kGy; (2) most of trapped radicals decay by recombination at 60 °C before monomers diffuse into the polymer matrix and react with the trapped radicals.

**Effect of grafting time on the total grafting yield for various monomer concentrations**

From Fig. 2, it is obvious that the total grafting yield increases with the increasing monomer concentration then levels off after 2 hours grafting time. The increase of total grafting yield can be reasonably attributed to the increase of the monomers diffusion rate and their concentration in the grafting layers. When grafting reaction continues 2 hours the high viscosity of the system influences the diffusion rate of the monomers to the substrate radicals and ultimately result in the levelling off of grafting yield.

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*Fig. 1. Variation of the total grafting yield with reaction time at various irradiation doses. Total monomer concentration 2.5 mol/L; molar ratio of AA to SSS: 2:1; reaction temperature: 60 °C*