Use of Electron Beam in Pre-irradiation Grafting for Preparation of Ion Exchange Membrane and Application

Speaker: Jianhua Zu

6 June 2005

Shanghai Applied Radiation Institute, Shanghai University, Shanghai, 201800, China
Applications for radiation processing of materials

Introduction of radiation induced grafting and its application

Our work on the preparation of cation exchange membrane by pre-irradiation method
Applications for radiation processing of materials

- The physical and chemical properties of polymeric materials can be modified by treatment with ionizing radiation in the form of gamma rays, X-rays and electron beams.

- Polymerizing (curing), grafting, crosslinking and chain scissioning reactions can be initiated by irradiation.
Introduction of radiation induced grafting

- **Graft copolymerization**
  

  \[ \text{B}_n \quad \text{B}_m \]

- **Radiation-induced graft polymerization**
  - Simultaneous irradiation method
  - Pre-irradiation method

The pre-irradiation method has been given much attention because the homopolymer formation is little and the grafting can be carried out at any time.
Application of radiation induced grafting

- **Separation processes**
  - Dialysis and electrodialysis

- **Energy conversion applications**
  - Used as battery separator and solid polymer electrolytes

- **Solid-state applications**
  - Sensors and ion selective electrodes

- **Biomedical and biological applications**
  - Fixation of biological components

- **Environmental applications**
  - Removal of heavy metals

- **Miscellaneous applications**
  - Catalysis
Our work on the preparation of cation exchange membrane by pre-irradiation method
Introduction

Many studies have been published on grafting of a weak acid onto polymer membranes

- Only a few on the grafting of a strong acid such as sulphonic acid

- Ion-exchange membranes bearing sulphonic acid groups are prepared by two-step grafting method because of the incompatibility between the highly ionized sulphonic acid groups with its hydration sphere and the polymer backbone

- We used one step pre-irradiation grafting method to prepare cation-exchange membranes containing –SO₃Na and –COOH groups
Grafting procedure

- HDPE membranes were washed with acetone and dried in a vacuum oven at 50°C

- HDPE membranes were irradiated using electron beams from accelerator

- The reaction was carried out in the temperature-controlled bath

- Grafted membranes were washed, dried and weighted
Measure of the overall grafting yield ($G_t$) and grafting yield of SSS onto HDPE ($G_s$)

$$G_t = \frac{(W_g - W_0)}{W_0} \times 100\%$$

$W_g$ : weight of grafted HDPE, $W_0$ : weight of ungrafted HDPE

$$G_s = \frac{C_{NaOH} \cdot V_{NaOH} \cdot 206}{1000 \cdot W_0} \times 100\%$$

- $C_{NaOH}$: the concentration of NaOH (mol/L)  
- $V_{NaOH}$: the volume of NaOH (ml)
Results and discussion

- Effect of radiation dose on grafting yield at different irradiation atmosphere

Total concentration: 3mol·L⁻¹, Grafting time: 15h, Molar ratio of SSS:AA: 1:2, Grafting temperature: 70℃
Effect of monomers concentration on the grafting yield

Total concentration: 2mol·L⁻¹, Molar ratio of SSS: AA: 1:2, Grafting temperature: 40°C, Grafting time: 10h
Relationship between grafting yield and storage time

Total concentration: 3mol·L⁻¹, Grafting time: 30h, Molar ratio of SSS:AA: 1:2, Grafting temperature: 25°C, HDPE stored temperature: -4°C

Fig.3
Grafted membrane Identification

IR spectra of (a) without grafting HDPE; (b) grafted membrane, $G_t=27.8\%$, $G_s=4.5\%$
Membrane resistance

Electric resistance vs. $G_t$

Fig. 5
Chemical Stability of grafted membranes

Fig. 6

The grafted membrane were dipped in 3% H$_2$O$_2$ solution (Fe$^{2+}$, 4ppm) at 70 °C for 5h
Thermogravimetric Analysis of grafted membrane

TGA thermograms of ungrafted HDPE and grafted HDPE with different grafting yield

a: ungrafted HDPE; b: $G_t = 12.5\%$, $G_s = 1.3\%$; c: $G_t = 72.8\%$, $G_s = 17.8\%$; d: $G_t = 155.1\%$, $G_s = 60.7\%$
Differential scanning calorimetry analysis

DSC thermograms of ungraftd HDPE and grafted HDPE with different grafting yield

Fig. 8

a: ungrafted HDPE
b: $G_t = 12.5\%$
c: $G_t = 72.8\%$
d: $G_t = 155.1\%$
Variation of heat of fusion with $W_x$ in membranes
Variation of crystallinity with $G_t$

Fig. 10
Fig. 11 Scanning electron micrograph of surface of (a) ungrafted HDPE and (b) HDPE grafted with AA and SSS ($G_t = 30.57\%$,) and (c) cross section of HDPE grafted with AA and SSS ($G_t = 28.04\%$)
Conclusion

- We have investigated the radiation-induced grafting of sodium styrene sulfonate and acrylic acid into the HDPE using the pre-irradiation method. The grafting yield increases with the increase of total concentration of monomers at a range of 0.5-3mol/L. Radicals formed by pre-irradiation of HDPE is stable at temperature below -4°C, so we can once irradiate a bulk of HDPE membranes and store them at low temperature before carrying out grafting. High temperature is suitable for obtaining high grafting yield when HDPE irradiated at air atmosphere.

- The resistance of the grafting membranes decrease with the increase of grafting yields, then reach stable to the value 0.03-0.04 Ω·cm². This low value is favorable for using as battery separator to discharge at large current.

- The anti-oxidation property of the ion-exchange membranes increase after the introduction of sulfonate groups. Anti-oxidation property as well as low resistance is of importance. Due to the particular environment of membranes in fuel cell, membranes must have high oxidative stability.
The contribution of membranes made by radiation graft copolymerization techniques to main production of membranes prepared by conventional techniques is relatively small. This may be attributed to general reasons such as:

A. limited access of irradiation facilities among membrane workers due to their ownership by governmental institutions in most countries.
B. captivity of irradiation facilities to commercial routine work.
C. high cost of irradiation facilities required for mass production and lack of knowledge on radiation graft copolymerization among membrane researchers and manufacturers.

Today there is a number of commercial companies that produces radiation grafted ion exchange membranes of different types for various applications

Pall-RAI (USA), Asahi; Chlorine Engineers (Japan); De Morgan (France)

HDPE-g-acrylic acid membranes which are used as battery separator have produced in Shanghai Applied Physics institute since 1990
High-frequency and high-voltage electron accelerator in our institute

Control system
Steel canister

Beam energy 2.0 MeV; Max. beam power 20 kW; Beam current 10 mA
The equipment for radiation of wire and cable
Thanks for your attention