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

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Abstract Radiation-induced grafting of sodium styrene sulfonate and acrylic acid onto HDPE membranes was studied by pre-irradiation technique. Grafting was carried out using electronic beam from 2MeV accelerator at room temperature. The effects of pre-irradiation atmosphere, monomers concentration and storage time of pre-irradiationed HDPE membranes on grafting yield were investigated. An easy control over the grafting yield could be achieved by proper selection of reaction conditions. Infrared spectroscopy analysis of the grafted membrane confirmed the existence of sulfonate and carboxylic acid groups in the grafted membranes. Thermal and chemical properties of the cation-exchange membranes were investigated. The effectiveness of $–SO_3Na$ containing membranes was conformed in inducing high resistance to oxidative degradation. Char residue of the grafted HDPE is greater than that of ungrafted HDPE. It shows that the branch chains including $–SO_3Na$ and –COOH groups give a catalytically impetus to the charring.

1. Introduction

Radiation-induced grafting of hydrophilic monomers onto polyethylene has frequently been used to prepare ion-exchange membranes for various application[1-2]. This technique has been found to be convenient because the grafting yield can be controlled by proper selection of grafting conditions. Furthermore, the grafting may be carried out into commercially available polymeric membranes, which offers an advantage in terms of producing membranes without problems associated with transforming the grafted matrix into a thin foil. Many studies have been published on grafting of a weak acid functionality such as acrylic acid onto polyethylene membranes[3-4], but only a few on the grafting of a strong acid such as sulphonic acid.

Shkolnik et al[5] have reported the difficulties in direct grafting of SSS onto HDPE membranes by radiation-induced grafting because of the incompatibility between the highly ionized sulphonic acid groups with its hydration sphere and the polymer backbone. In the published article about the preparation of ion-exchange membranes bearing sulphonic acid groups two-step grafting method was used. Styrene are grafted onto polymers membranes using pre-irradiation method or simultaneous radiation method, and the graft copolymer is subsequently sulphonated[6].

In our studies, grafting of sodium styrene sulfonate and acrylic acid onto HDPE membranes was investigated using one step method. The effects of grafting conditions such as irradiation dose, monomers concentration and storage time of pre-irradiationed HDPE membranes on the grafting yield were investigated. The thermal and chemical stability of the cation-exchange membranes were evaluated.

2. Experiment

2.1 Material

HDPE membranes (15μm) were supplied by Shanghai Shilong Scientific Co. Ltd. SSS was bought from Zibo Longda Chemical Co. Ltd. AA was bought from Gaoqiao Chemical Plant and purified by decompression distillation. Other chemicals were reagent grade and were used as received.

2.1 Grafting Procedure

Rectangle HDFE membranes (13 cm ×7cm) were washed with acetone and dried in a vacuum oven at 50℃ to constant weight. The HDPE membranes were packed in polyethylene bags after the atmosphere was replaced by 99.99% pure nitrogen gas. The packed HDPE membranes were irradiated by passing them under the electron beams of accelerator with beam energy of 1.8Mev and a current of 1.5mA.The irradiated membranes were put together with polypropylene non-woven and rolled into cylinder using glass stick as axes, then immersed in the monomer solution which was prepared at the given concentration and deaerated by bubbling nitrogen. The reaction was carried out in the temperature-controlled bath. After reacting for a period of time, grafted membranes were taken out from the monomer solution in the glass tubes and washed thoroughly with 70°C distilled water, then soaked into it overnight to extract the residual monomers and the homopolymer in the membranes. After being dried in vacuum oven at 70°C until a constant weight the membranes were weighted. The overall grafting yield (G_t) was defined as:

$$G_t = \frac{Wg\ -\ Wo}{Wo} \times 100\%$$

Where W_g= weight of grafted HDPE, W_o= weight of ungrafted HDPE

2.2 Measure of Grafting Yield of SSS onto HDPE (Gs)

The grafted membranes were immersed in 1mol/L HCl solution, at the same time -SO_3Na was transformed into -SO_3H. After being taken out and washed with distilled water until to a pH of 7.0, the membranes were immersed in 5% NaCl solution for 24 hours in the situation of stirring. The replaced HCl was titrated with NaOH solution. G_s can be calculated according to the following equation:

$$G_S = \frac{C_{NaOH} \cdot V_{NaOH} \cdot 206}{1000 \cdot W_o} \times 100\%$$

C_{NaOH}: the concentration of NaOH (mol/L) V_{NaOH}: the volume of NaOH (ml)

The ionization of -COOH in 5% NaCl solution can be ignored. Because -SO_3H is a strong acid, the H^+ that come from its ionization can restrain the ionization of –COOH.

2.3 Measure of Membrane Resistance

The grafted membranes were soaked in KOH solution for 24hr to transform –COOH and –SO_3Na to –COOK and -SO_3K respectively. The resistance of the membrane was measured by the AC impedance instrument.

3. Results and Discussion

3.1 Pre-irradiation Atmosphere

As can be seen from Fig.1 that the grafting yield increases gradually with increase of irradiation dose within the limits of the studied values (10-100kGy). This behavior can be attributed to the increase in the number of radicals formed in the grafting system. Fig. 1 also shows that the grafting yield for HDPE membranes was higher when they were pre-irradiated in air rather in nitrogen. This might be interpreted in the follow way: (1) Monomer can diffuse more easily in polymer pre-irradiated in air than in polymer pre-irradiated in nitrogen because the gel fraction of HDPE irradiated in nitrogen is markedly large than that of HDPE irradiated in air. These results indicate that HDPE chains crosslink in nitrogen but do so only rarely in air, and consequently the diffusion of monomer in polymer matrix appears to be higher in HDPE pre-irradiated in air. (2) Free radicals formed in the amorphous regions and some of those which migrated form the crystalline region to its surface, may react with oxygen to form peroxides such as diperoxides (R-O-O-R) and hydroperoxides (R-O-O-H), which can initiated the grafting reaction in the presence of monomers at an elevated temperature (70℃) used in our grafting system. As a result, the grafting yield for air-irradiated HDPE is always more than those for N_2-irradiated ones.

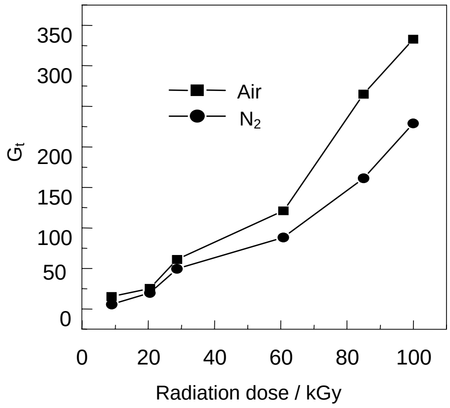

FIG.1. Effect of radiation dose on grafting yield at different irradiation atmosphere. Total concentration: 3mol • L^{-1}, Grafting time: 15h, Molar ratio of SSS:AA: 1:2, Grafting temperature: 70 ℃

3.2 Monomers Concentration

Fig.2 shows the variation of grafting yield with monomers concentration. The grafting yield is fund to increase dramatically with the increase of total concentration of monomers at a range of 0.5-3mol/L. Since, the grafting depend largely on the monomers availability to the radicals sites within the membrane, at higher monomers concentration, the AA and SSS availability into membranes increases. One of the important requirements for the monomers diffusion into the bulk of the membranes is its high swelling in the grafting medium. If the dilution of monomers has impact on swelling of the grafted matrix, monomers diffusion rate will be influenced accordingly. Fortunately grafted copolymers chains swell in deioned water which used as dilution of monomers. As a result, this also benefits to the increase of grafting yield.

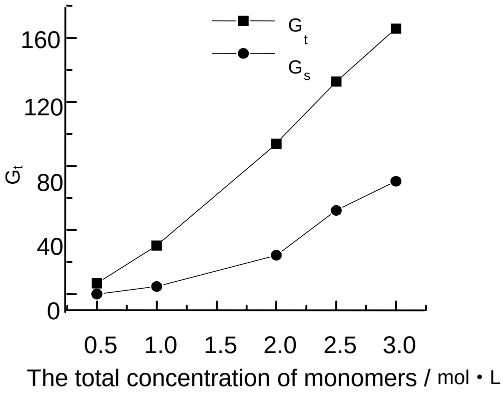

FIG.2. Effect of monomers concentration on the grafting yield
Total concentration: 2mol·L^{-1}, Molar ratio of SSS: AA: 1:2, Grafting temperature: 40ºC, Grafting time: 10h

3.3 Storage after Pre-irradiation

It well known that grafting activity of pre-irradiationed polymers decreases with the storage of the irradiated HDPE because of the decay of radicals, and that the higher the storage temperature, the larger the decreasing rate. The plot of grafting yield against storage time at -4℃ is shown in fig.3. At first G_t and G_s decrease remarkably with time, and then remain almost constant through the duration of storage. G_t declines 30% during two months.

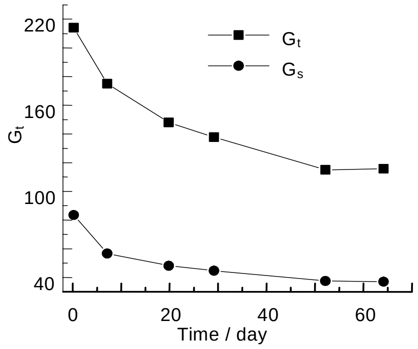

FIG.3. Relationship between grafting yield and storage time
Total concentration: 3mol·L^{-1}, Grafting time: 30h, Molar ratio of SSS:AA: 1:2, Grafting temperature: 25 ℃, HDPE stored temperature: -4 ℃

It shows that the radicals formed by pre-irradiation of HDPE are stable at -4℃. This is the advantage of pre-irradiation grafting technique compared to simultaneous technique. Therefore, a bulk of HDPE membranes may be irradiated once and stored at low temperature before carrying out grafting. Another advantage of pre-irradiation grafting is low homopolymer yield.

3.4 Grafted Membrane Identification

IR spectra of HDPE and ion-exchange membranes modified with the sulfonate（$-SO_3Na$）and carboxylic acid (-COOH) groups are shown in Fig.4. When the IR spectrums of Fig.4a and Fig.9b are compared, it is seen in the spectrum of Fig.4b some new absorption appear, one at 1715 cm^{-1} due to the absorption of C=O, and one at 1128 and 1037cm^{-1}due to ν_sS=O and ν_{as}S=O. A strong peak at 836 cm^{-1} compared with the small peak at 778cm^{-1}indicated that the monomers added to HDPE is para styrene sulfonate.

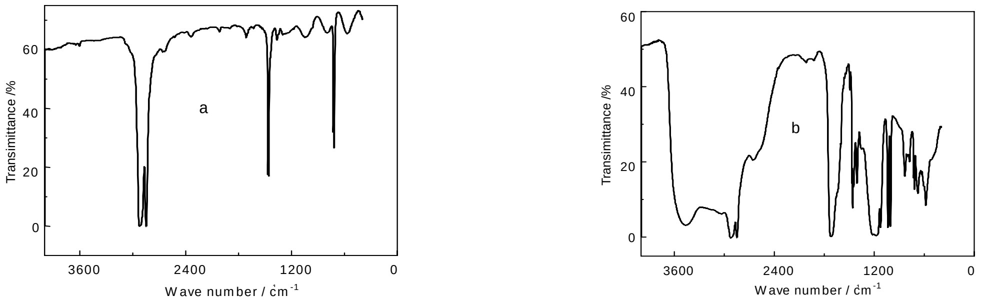

FIG.4. Infrared spectrum of the ungrafted HDPE membrane (a) and grafted HDPE membrane (b)

3.5 Membrane Resistance

Membrane resistance, determined by ac impedance measurements, as a function of grafting yield is presented in Fig.5. Initially, the membrane resistance shows a sharp decrease and then a transition point at a certain grafting yield of 55%, beyond that the membrane resistance does not show any appreciable change. It means that, the grafting reaction occurs on the surface

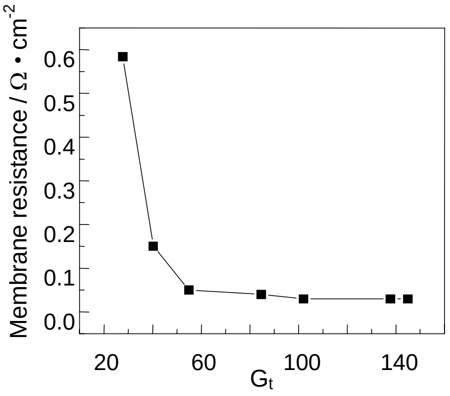

FIG.5. Electric resistance vs. G_t

layer of HDPE membrane at low grafting yield. With the increasing of the grafting yield, the monomers diffuse into the inner part of HDPE and react with it, leads to the decrease of the membrane resistance. When the grafting yield was beyond 55%, –COOK and -SO_3K groups were uniformly distributed at different position of grafted membrane, so the membrane resistance became stable.

3.6 Chemical Stability

Fig.6 shows the weight loss of grafted membranes after soaked in 3% H_2O_2 solution corresponding to grafting yield. The higher the grafting yields, the more the weight loss. From fig.6 we can see that the weight loss reach 11.3% at grafting yield 27.8%. From the reference [4], for HDPE-g-AA membrane, at the same condition, the weight loss is 17.4% while grafting yield is 21%, which proves that the introduction of sulfonate groups increase the anti-oxidation property of grafted membrane. A major function of HDPE-g-AA-SSS membrane has been used as separator in batteries or fuel cells. Due to the severe condition especially in fuel cells, the problem of membrane lifetime is by far important. So the grafted membranes should have sufficient chemical stability to avoid the oxidative degradation.

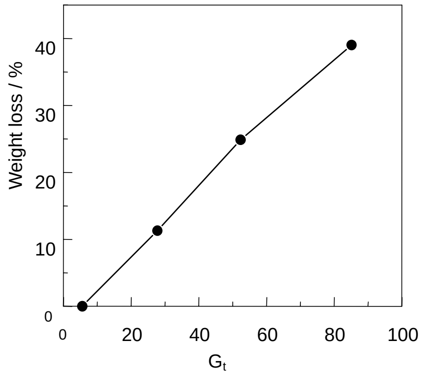

FIG.6.Chemical stability of the grafted membrane.

The grafted membrane were dipped in 3% H_2O_2 solution (Fe^{2+}, 4ppm) at 70˚C for 5h

3.7 Thermogravimetric Analysis

Thermal behavior of HDPE-g-AA-SSS membrane was evaluated by thermogravimetric Analysis (TGA). Thermograms of ungrafted HDPE and HDPE-g-AA-SSS membranes with various grafting yield are presented in Fig.7. As far as ungrafted HDPE is concerned (Fig.7a), there is no weight loss below 415℃. The biggest weight loss was found at 482℃, which was due to the degradation of main chains. The decomposed products mainly includes saturated and unsaturated C-H compounds from C_2 to C_{90}, finally the char residue is 3.01%. Fig.7b-7d is TGA thermograms of grafted HDPE. The first peak at 83℃ is the dehydration peak, the second peak at 265℃corresponding to elimination of carboxyl groups. The largest weight loss peak at 482℃, which is due to the decomposing of the main chains. The results in Fig.8. show that the higher the grafting yield, the higher is the char residue, which indicate that the branch chains including –SO_3Na and –COOH give a catalytically impetus to the charring.

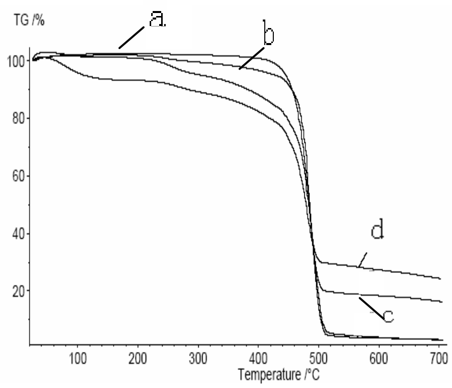

FIG.7. TGA thermograms of ungraftd HDPE and grafted HDPE with different grafting yield
a: ungraftd HDPE; b: G_t =12.5%, G_s= 1.3%; c: G_t =72.8%, G_s= 17.8%; d: G_t =155.1%, G_s= 60.7%

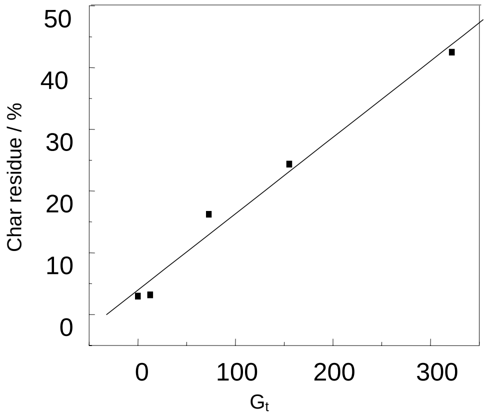

FIG.8.The relationship between grafting yield and char residue

4. Conclusions

We 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℃, so we can once irradiate a bulk of HDPE membranes and stored 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$\Omega\cdot cm^{-2}$. 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.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (project 50303009), Shanghai-Applied Materials Research and Development Foundation (project 0318), Shanghai Education Committee Foundation (project 03AQ96), which are gratefully acknowledged.

Reference

[1] Aydinli, B., Tinçer, T., Radiation grafting of various water-soluble monomers on ultra-high molecular weight polyethylene powder. Part II: Thermal, FTIR and morphological characterization. Radia. Phys. Chem. 62 (2001) 337.

[2] Taher, N H., Dessuoki, A M., El-Arnaouty, M B., Radiation initiated graft copolymerization of N-vinylpyrrolidone and acrylamide onto low density polyethylene films by individual and binary system. Radia. Phys. and Chem., 53(1998) 437.

[3] Kaur, I., Chauhan,G S., Misra, B N., Synthesis and characterization of grafted polyethylenes for use as membranes in water desalination. Desalination. 110(1997) 129.

[4] Ishigaki, I., Sugo, T., Senoo, K., Grafting polymerization of acrylic acid onto polyethylene fims by peirradiation method. I. effect of preirradiation dose, monomers concentration, reaction temperature and film thickness. J. Appl. Polym. Sci. 27(1982): 1033.

[5] Shkolnik，S., Behar，D.，Radiation-induced grafting of sulfonates on polyethylene. J. Appl. Poly. Sci. 27（1982）2189.

[6] Sara, D., Robert, C., Ivestigation of radiation grafted PVDF-g-polyethylene-sulfonic-acid ion exchange membrane for use in hydrogen oxygen membrane fuel cell. Solid State Ionics. 1997, 97(1997) 299.