Radiation-Induced Grafting of Acrylic Acid and Sodium Styrene Sulfonate onto High-Density Polyethylene Membranes. II. Thermal and Chemical Properties

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ABSTRACT: Strong acid cation-exchange membranes were obtained by radiation-induced grafting of acrylic acid and sodium styrene sulfonate onto high-density polyethylene (HDPE). 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. The 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 catalytic impetus to the charring. The crystallinity of the grafted membranes was decreased when increasing the grafting yield. It was assumed that the decreased crystallinity was due to collective effects of the inherent crystallinity dilution by the amorphous grafted chains and the crystal distortion of the HDPE component. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 99: 3396–3400, 2006

Key words: radiation-induced grafting; acrylic acid; sodium styrene sulfonate; high-density polyethylene membranes

INTRODUCTION

In the past, commercialized cation-exchange membranes containing sulfonate groups were basically prepared by adding ion-exchange components to polymer matrixes. There are two defects: the ion-exchange groups' distribution in the membranes is not uniform and there is not enough intensity in the membranes, which confines their applications. An improved method is to coat a mixture of styrene and divinyl benzene on the surface of support materials such as poly(vinyl chloride) and polypropylene membranes, heat them to form the matrix membranes, and then immerse the matrix membranes in concentrated sulfuric acid or chlorosulfuric acid at an elevated temperature.[1,2] These preparation methods induce deterioration of the physical strength. In addition, the conductivity and ion selectivity of the prepared membrane will decrease because of the existence of the support material.

There are reports on preparing cation-exchange membranes containing sulfonate groups by radiation grafting of high-density polyethylene (HDPE) membranes. One way is HDPE grafted with styrene by the radiation-induced method, and then the grafted membrane is immersed in chlorosulfonic acid or sulfuric acid at higher temperature to introduce sulfonate groups into the benzene ring. This method will decrease the mechanism intensity of the membranes because of strong reaction conditions. Another method is HDPE is first grafted with acrylic acid (AA) or other monomers to attain hydrophilic performance, and then it is grafted with monomers containing a vinyl sulfonate group.[3] This method is complicated and expensive.

We used the one-step irradiation grafting method to prepare cation-exchange membranes containing —SO_3Na and —COOH groups. The effect of various factors on the grafting yield were studied in detail, and the results were analyzed in the first article of this series.[4] The present study evaluates the thermal and chemical stability of the cation-exchange membranes.

EXPERIMENTAL

Sodium styrene sulfonate (SSS) was purchased from Zibo Longda Chemical Co. Ltd. HDPE membranes were provided by Shanghai Shilong Science and Technology Co. Ltd. Irradiation was performed at ambient temperature by means of an electron accelerator.

The preparation of grafted membranes and measures of the grafting yield were described in Part I of

this series.[4] The variable G_t is the total grafting yield of AA and SSS onto HDPE, and G_s is the grafting yield of SSS.

The grafted membranes were soaked in KOH solution for 24 h to transform —COOH and —SO$_3$Na to —COOK and —SO$_3$K, respectively. The resistance of the membrane was measured by an ac impedance instrument. The membrane resistance (R) can be calculated as follows:

$$R = R_m - R_0$$

where R_0 and R_m represent the resistance of the grafted and ungrafted membranes, respectively.

The crystallinity and thermal behavior changes induced by grafting were evaluated by a synthetical thermal analysis instrument (NETZSCH STA 409PC). Samples were loaded into a combination differential scanning calorimetry thermogravimetric analysis (DSC–TGA) system at 20°C, and thermograms were run in a temperature range of 20–700°C under a nitrogen atmosphere at a heating rate of 20°C/min. The heat of fusion values of the membrane (ΔH_{mem}) were obtained from the area under the thermogram. The heat of fusion of the HDPE component (ΔH_{HDPE}) was obtained by correcting ΔH_{mem} for the HDPE fraction in a membrane according to the following equation:

$$\Delta H_{HDPE} = \Delta H_{mem}/W_h$$

where W_h is the weight fraction of the HDPE component in the membranes, which was obtained from the following relationship:

$$W_h = F/(F + G)$$

where F is the weight of the HDPE component and G is the weight of the grafting component. The weight fraction of the grafting component in the membranes (W_x) can then be calculated by the next equation:

$$W_x = 1 - W_h$$

The crystallinity of the grafted membranes was obtained by the following expression:

$$\text{crystallinity (\%)} = \frac{\Delta H_{mem}}{\Delta H_{crys}} \times 100\%$$

where ΔH_{crys} is the heat of fusion of 100% crystalline PE (70.4 cal/g).

The sample was soaked in 3% H$_2$O$_2$ solution at 70°C for 5 h and then dried. The weight loss was used to characterize the antioxidation ability of the membrane.
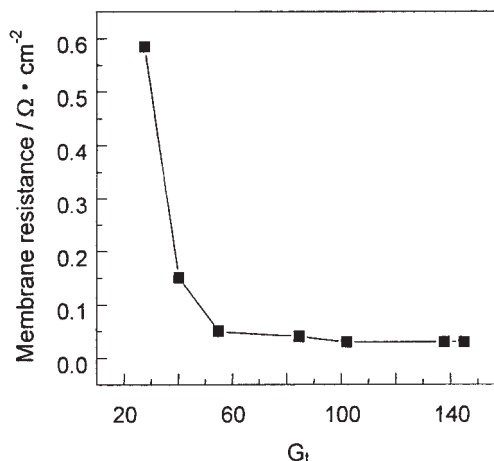

Figure 1   The electrical resistance versus G_t.

The water absorbability of the grafted membranes was determined by immersing dried membranes in H$_2$O and storing at 70°C for 24 h. The H$_2$O uptake per ionic site was measured according to the weight increase of the dry grafted membranes.

RESULTS AND DISCUSSION

Membrane resistance

The membrane resistance was determined by ac impedance measurements as a function of the grafting yield, and the results are presented in Figure 1. 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. This means that the grafting reaction occurs on the surface layer of the HDPE membrane at low grafting yield. With the increasing of the grafting yield, the monomers diffuse into the inner part of the HDPE and react with it, leading to the decrease of the membrane resistance. When the grafting yield was beyond 55%, —COOK and —SO$_3$K groups were uniformly distributed at different positions on the grafted membrane, so the membrane resistance became stable.

Chemical stability

Figure 2 shows the weight loss of grafted membranes after soaking in 3% H$_2$O$_2$ solution, which corresponds to the grafting yield. The higher the grafting yields are, the higher the weight loss. From Figure 2 we can see that the weight loss reaches 11.3% at a grafting yield of 27.8%. According to Ishigaki et al.,[5] for an HDPE-g-AA membrane under the same condition, the weight loss is 17.4% and the grafting yield is 21%, which proves that the introduction of sulfonate groups increases the antioxidation property of the
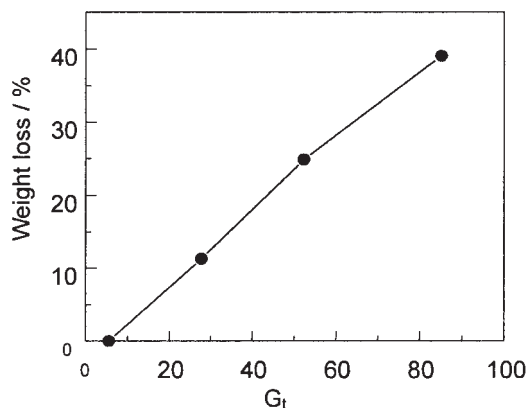
Figure 2 The chemical stability of the grafted membranes, which were dipped in 3% H_2O_2 solution (Fe^{2+}, 4 ppm) at 70°C for 5 h.

Figure 4 The relationship between the grafting yield and char residue.

grafted membrane. A major function of HDPE-*g*-AA-SSS membranes has been as separators in batteries or fuel cells. Because of severe conditions, especially in fuel cells, the problem of membrane lifetime is very important. Thus, the grafted membranes should have sufficient chemical stability to avoid oxidative degradation.

TGA

The thermal behavior of HDPE-*g*-AA-SSS membranes was evaluated by TGA. Thermograms of ungrafted HDPE and HDPE-*g*-AA-SSS membranes with various grafting yields are presented in Figure 3. There is no weight loss below 415°C in ungrafted HDPE (Fig. 3, curves a–c). The biggest weight loss was found at 482°C, which was due to the degradation of main chains. The decomposed products mainly included
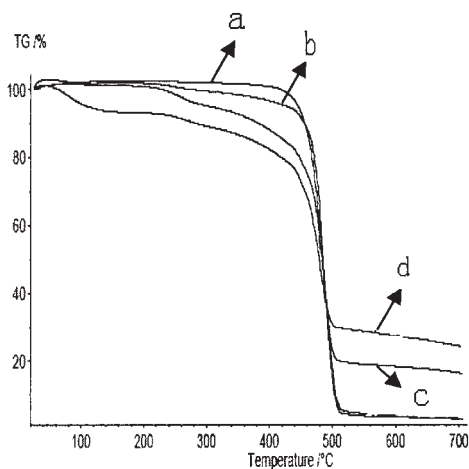
saturated and unsaturated C—H compounds from C_2 to C_{90},[6,7] and the char residue was 3.01%. Curves b–d in Figure 3 are TGA thermograms of grafted HDPE. The first peak at 83°C is the dehydration peak, and the second peak at 265°C corresponds to elimination of carboxyl groups. The largest weight loss peak at 482°C is attributable to the decomposition of the main chains. The results in Figure 4 show that the higher the grafting yield is, the higher the char residue, which indicates that the branch chains including —SO_3Na and —COOH provide catalytic impetus to the charring.

DSC analysis

DSC thermograms of ungrafted HDPE membrane and HDPE-*g*-AA-SSS membranes are presented in Figure 5. Although the shape of the thermograms in all samples remains almost identical, the intensity of the peaks decreases with the increase of the grafting yield. The variations in the Dgr;H_{mem} and ΔH_{HDPE} with the

Figure 3 TGA thermograms of ungrafted (curve a) and grafted HDPEs (curves b–d) with different grafting yields: $G_t = 12.5\%$, $G_s = 1.3\%$ (curve b); $G_t = 72.8\%$, $G_s = 17.8\%$ (curve c); $G_t = 155.1\%$, $G_s = 60.7\%$ (curve d).
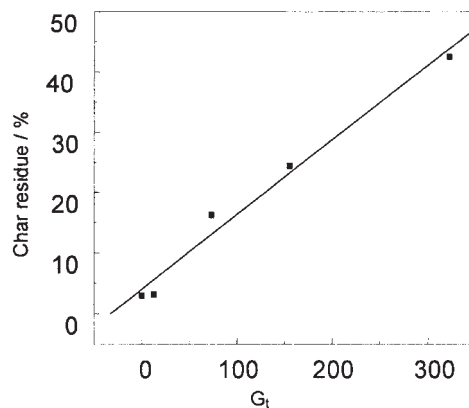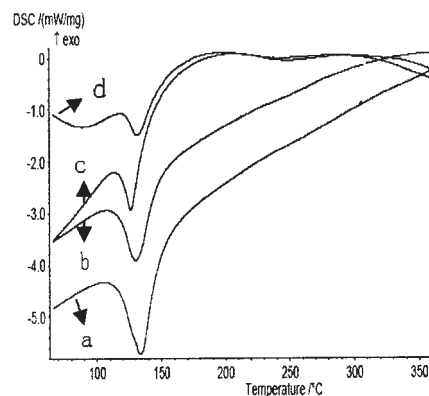

Figure 5 DSC thermograms of ungrafted (curve a) and grafted HDPEs (curves b–d) with different grafting yields: $G_t = 12.5\%$, $G_s = 1.3\%$ (curve b); $G_t = 72.8\%$, $G_s = 17.8\%$ (curve c); $G_t = 155.1\%$, $G_s = 60.7\%$ (curve d).
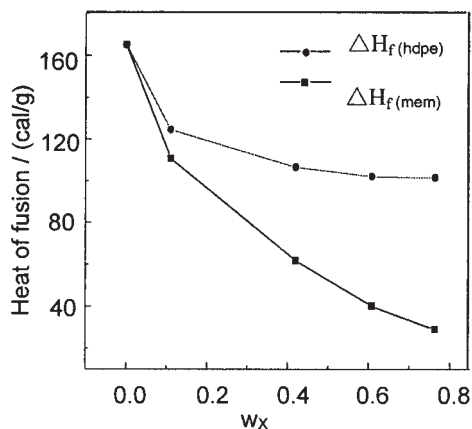
Figure 6 The variation of the heat of fusion with W_x in the membranes.

Figure 7 The variation of the crystallinity with G_t.

grafting yield are presented in Figure 6. The ΔH_{mem} and ΔH_{HDPE} decrease with the increase of the grafting yield. The result shows that ΔH_{mem} does not follow a linear decrease. Instead, the decrease is faster for the lower grafting yield compared to the higher grafting yield. Studies on the grafting of styrene onto HDPE carried by Gupta and Scherer[8] showed that the ΔH_{mem} was a function of the HDPE fraction in grafted membranes. They found that the grafting takes place by the incorporation of amorphous polystyrene chains in the noncrystalline region of the HDPE membrane. The grafted polystyrene chains thereby exert a dilution effect on the inherent crystallinity of the HDPE membrane. In our grafting system, the grafted AA and SSS monomers are hydrophilic. The decrease of $\Delta H_{f(mem)}$ is caused by two factors. On the one hand, the addition of amorphous grafting chains into the noncrystallinity region of the HDPE exerts a dilution effect on the inherent crystallinity of HDPE. On the other hand, the grafting reaction often takes place in the entire amorphous region of the HDPE matrix and some of the chains grow from the crystallite surface as well, because the monomer cannot interact with molecules inside the rigid crystalline phase. When —COOH groups are first grafted onto HDPE membranes, it may be assumed that some of the chains also grow from the crystallite surface. The grafted membrane absorbs water, and strain is created between hydrophilic grafting chains and the hydrophobic HDPE matrix. As a result, some of these chains are cleaved off, leading to crystal disruption.[9] At a higher grafting yield, the distribution of grafted chains is more homogenous. This leads to a more uniform swelling of the matrix. As a result, the influence of the "crystal disruption" in reducing the crystallinity slows down. The disruption of the crystalline region during sulfochlorination of PE membranes has also been reported by Zevin and Messalem.[10]

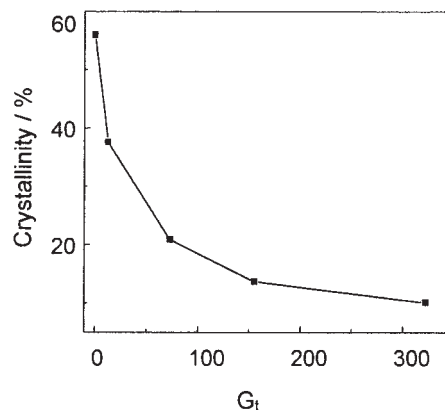The relationship between the degree of crystallinity and the grafting yield is shown in Figure 7. The degree

of crystallinity decreases with increases of the grafting yield. The cumulative influence of the diluting effect and crystal disruption is so high that the crystallinity in a membrane with 72.8% grafting yield decreases to almost one-third of its original value. Similar behavior was also observed in studies of methacrylic acid and 2-hydroxyethylmethacrylate grafting onto polypropylene.[11,12]

Water absorbability of grafted membranes

Figure 8 shows that the number of H_2O molecules per ionic site is considerably increased with the increase of the grafting yield. When the grafting increases from 5.6 to 158.3%, the hydration number rises from 0.8 to 5.8. These results may be understood from two factors: the increase in the hydrophilicity of the matrix, and the decrease in the crystallinity in membranes. The —SO_3Na and —COOH groups are hydrophilic in nature and remain randomly distributed in the HDPE matrix. This results in the enhancement of the fractional hydrophilicity of membranes as the grafting yield increases. At the same time, the crystallinity
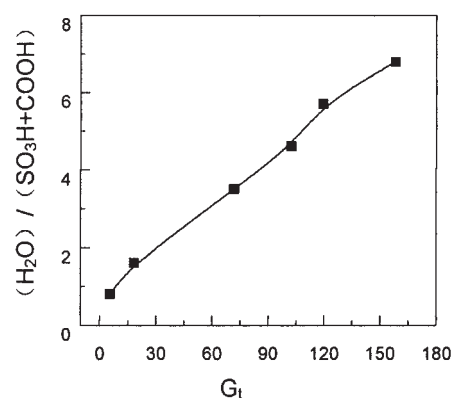

Figure 8 The influence of the grafting yield on H_2O/ionic site ratio in the membranes.

decreases with increasing grafting, as discussed earlier. On the one hand, the enhancement of the hydrophilicity makes the membrane structure more amenable to H_2O molecules. On the other hand, the decrease in crystallinity leads to the membrane structure being more permeable to diffusing species. As a result, the H_2O molecules absorbed per ionic site increases considerably at higher grafting yield.

CONCLUSIONS

The thermal and chemical properties of cation-exchange membranes were evaluated in this study, and the following conclusions were drawn:

1. The resistance of the grafting membranes decreased with the increase of grafting yields and then reached stable values of 0.03–0.04 Ω cm^{-2}. This low value is favorable for use in battery separators to discharge at large current.
2. The antioxidation property of the ion-exchange membranes was increased after the introduction of sulfonate groups. Both the antioxidation property and the low resistance are important. Because of the particular environment of membranes in fuel cells, membranes must have high oxidative stability.
3. The degree of crystallinity of grafted membranes containing —SO$_3$Na and —COOH groups decreased with the increase of the grafting yield. The mechanism was discussed.
4. At higher grafting yield, the water absorbability of grafted membranes was considerably increased.

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