DOI: 10.1007/s10967-007-6816-9 *Journal of Radioanalytical and Nuclear Chemistry, Vol. 273, No.2 (2007) 479–484*

The effect of additives on radiation-induced grafting of AA and SSS onto HDPE

Jianhua Zu,[1]* Zhiqiang Hu,[1] Weitao Wang,[1] Jianqiu Zhang,[1] E. S. Pino,[2] Jianzhong Gu,[1] Long Tong[1]

[1] *Shanghai Applied Radiation Institute, Shanghai University, Shanghai 201800, P.R. China*
[2] *Instituto de Pesquisas Energeticas e Nucleares, IPEN/CNEN-SP, São Paulo, Brazil*

(Received September 28, 2006)

A kind of ion-exchange membrane with strong acid and weak acid groups was prepared by radiation-induced grafting of acrylic acid (AA) and sodium styrene sulfonate (SSS) onto high-density polyethylene membrane (HDPE). The effect of additives such as sodium acetate, sodium chloride on grafting yield was studied. It was found that for either pre-irradiation method or simultaneous radiation method, the weak acid salt of strong alkali sodium acetate had a complex effect on the grafting yield by "pH effect" and "ion pair effect", and the neutral salt sodium chloride was helpful to the increase of grafting yield by "ion pair effect".

Introduction

Polyethylene can be modified with polar monomers to change its polarity and obtain ion-exchange property by radiation-induced grafting, which is a simple and effective method that can enlarge the application field of polyethylene.

In our earlier work, we introduced the preparation method of ion-exchange membrane, which was synthesized by radiation induced grafting of acrylic acid and sodium styrene sulfonate onto high density polyethylene.[1] The effect of reaction conditions on grafting yield was also studied. The membranes with low electric resistance can be used as battery separator. The $-SO_3Na$ groups grafted onto membranes will be transformed into $-SO_3H$ by immersing them into acid solution, so these membranes can be used as catalysts for the hydrolysis of methyl acetate[2] and synthesis of methyl tertiary butyl ester.[3]

In the research of polymer modification by radiation-induced grafting methods, scientists tried to obtain higher grafting yield at lower costs by reducing monomers usage or radiation dose. Some researches indicated that the introduction of inorganic acid and metal salt in the radiation-induced grafting system could increase the grafting yield and a quite high grafting yield could be reached using lower radiation dose. In 1979, GARNETT and YEN[4] published a comprehensive review on the role of additives in radiation grafting to modify a wide variety of natural polymers such as wool and cellulose and also synthetic polymers like the polyolefins.[4] Since then, some of the theories covering the mechanism by which the additives work have been revised. For example, it was found that acids,[5,6] multifunctional acrylates,[7] inorganic salts,[8] and organic materials, like urea[9] could enhance grafting yield when reactions were initiated by ionizing radiation. As far as acrylonitrile grafting onto cellulose system was concerned, the introduction of zinc chloride can improve the grafting yield. When acrylic acid was grafted onto nylon, the grafting yield of the system with the addition of 1% amine ferrous sulfate was six times higher than that without that additive.

In this paper, the radiation induced grafting of acrylic acid (AA) and sodium styrene sulfonate (SSS) grafted onto high-density polyethylene membrane (HDPE) was investigated. The effect of additives such as sodium acetate, sodium chloride on grafting yield was studied using pre-irradiation or simultaneous radiation technique, respectively. The results showed that it would be promising to develop an effective and economical method for the improvement of the grafting yield at lower costs.

Experimental

Materials

HDPE membranes (15 μm) were supplied by Shanghai Dayu Plastic Membrane Co. Ltd., SSS was obtained from Zibo Xingzhiyuan Chemical Co. Ltd., AA was received from Shanghai Chemical Reagent Co. Ltd. and purified by vacuum distillation. Other chemicals were analytically pure and were used as received.

Grafting procedure

HDPE membranes were washed with acetone and dried in a vacuum oven at 50 °C until constant weight was reached. After washing, the membranes were laid together with nonwoven polypropylene and rolled as a cylinder on a glass stick, then immersed into the monomer solution, which was prepared at a given concentration and deaerated by bubbling nitrogen.

* E-mail: zujianhua1999@163.com

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The reaction was carried out in a temperature-controlled bath, which was placed beside a ^{60}Co γ-ray radiation source when simultaneous radiation method was used. After reaction was carried out for a period of time, these membranes were taken out from the monomer solution, washed thoroughly with 70 °C distilled water, and soaked in it overnight to remove the residual monomers and the homopolymers. At last, they were dried in vacuum oven at 70 °C until reached constant weight. As far as the pre-irradiation method was concerned, the HDPE membranes were sealed in polyethylene bags with 99.99% purity nitrogen gas and irradiated with a dose of 100 kGy using ^{60}Co γ-rays as the radiation source. After irradiation, the grafting reaction was carried out in a temperature-controlled bath. The rest were the same as those in simultaneous radiation method. When AA and SSS were grafted onto HDPE, the overall grafting yield (G_t) was defined as:

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

where W_g is the weight of grafted HDPE, W_0 is the weight of ungrafted HDPE, G_a denotes the grafting yield of acrylic acid onto HDPE. As far as AA and SSS grafted onto HDPE system was concerned, G_a could be calculated by the following equation: $G_a = G_t - G_s$. When AA was grafted onto HDPE, G_a was defined as:

$$G_a = \frac{W_g - W_0}{W_0} \times 100\%$$

Measurement of grafting yield of SSS onto HDPE (G_s)

When the grafted membranes were immersed into 1 mol/l HCl solution, $-SO_3Na$ would be transformed into $-SO_3H$. After the membranes were taken out and washed with distilled water until pH 7.0 was achieved, they were immersed in 5% NaCl solution for 24 hours with stirring. The resulted HCl was titrated with NaOH solution. G_s and the ion-exchange capacity (IEC) can be calculated according to:

$$G_s = \frac{C_{\mathrm{NaOH}} \cdot V_{\mathrm{NaOH}} \cdot 206}{1000 \cdot W_0}$$

$$\mathrm{IEC\,(mmol/g)} = \frac{C_{\mathrm{NaOH}} \cdot V_{\mathrm{NaOH}}}{W_g}$$

where C_{NaOH} is the concentration of NaOH (mol/l), V_{NaOH} is 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 comes from its ionization can restrain the ionization of –COOH.

Results and discussion

The effect of NaAc additive on grafting yield when AA was grafted onto HDPE using simultaneous method

When acrylic acid was grafted onto HDPE using simultaneous method, NaAc additive which is a weak acid salt of a strong alkali has a complex effect on grafting yield by "pH effect" and "ion pair effect".The relations between G_a and NaAc concentrations were shown in Fig. 1. At the beginning without NaAc, G_a is 63.4%. With the increasing of NaAc concentration, G_a goes down gradually until NaAc concentration reached 0.19 mol/l, then increases gradually and reach a maximum, and goes down again as the beginning. "pH effect" dominates at the beginning when the concentration of NaAc is very low. The pH value of solution increases with the increasing of NaAc concentration. Acylic acid and its grafted chains are easy to be ionized and they are negatively charged due to the increasing of pH. Then their same negative charges could repulse them apart and lead to slower diffusion rate of monomers, compared to lower pH. So G_a decreases. However, if more NaAc are added to the grafting system (>0.27 mol/l), besides the value of pH still keeps increasing, more Na^+ from the ionization of NaAc could congregate around the grafted chains which have $-COO^-$ groups. As a result, the repulsion force between acylic acid monomers and grafting chains is weakened, which could facilitate the penetration of monomers into the bulk of the membrane. So G_a increases in the range of NaAc concentration of 0.27–1.09 mol/l. We call this phenomenon as "ion pair effect". At last, when NaAc is over 1.09 mol/l and still keeps going up, G_a decreases just as at the beginning when NaAc concentration is lower than 0.27 mol/l. "pH effect" dominates the trend of *Ga* changes again.

The effect of NaCl additive on grafting yield when acrylic acid was grafted onto HDPE using the simultaneous method

In order to prove our assumption about "pH effect", the effect of NaCl additive on G_a was investigated and the results are shown in Fig. 2. It can be seen that G_a increases with the increase of NaCl concentration. G_a reaches 122.2% when the concentration of NaCl is 0.78 mol/l, which is twice as much as the result without NaCl. There are no pH changes for NaCl, which is a neutral salt and different from NaAc. It can be assumed that only "ion pair effect" exists. The higher the NaCl concentraion is, the stronger the "ion pair effect". Therefore, we conclude that the intensity of "ion pair effect" is also affected by the valence of cation.

When the valence of cation is higher, the affinity between $–COO^–$ coming from the ionization of –COOH in grafting chains and cations from the ionization of neutral salt is stronger. From Fig. 3 we can see that G_a increases more quickly when $AlCl_3$ is added to the monomer solution than with NaCl at the same concentration.

The effect of NaAc additive on grafting yield when AA and SSS were grafted onto HDPE using simultaneous method

From Fig. 4 we can see that changes of G_t with the increase of NaAc are almost the same as that of G_a in Fig. 1. G_s is very small due to low concentration of SSS (total monomer concentration is 3 mol/l and the molar ratio of SSS to AA is 1:3). With the increase of NaAc concentration, there is no change of G_s as shown in Fig. 4. We can see that the change of G_t ($G_t = G_a + G_s$) are the same as that of G_a in Fig. 1.

The effect of NaCl additive on grafting yield when AA and SSS were grafted onto HDPE using simultaneous method

Figure 5 shows that G_t and G_s increase rapidly with the concentration of NaCl. The result is the same as at the HDPE-g-AA system that we have discussed. More NaCl can only strengthen the "ion pair effect". As a result, G_t and G_s increase rapidly.

The effect of additive NaAc on G_a when acrylic acid was grafted onto HDPE using pre-irradiation method

From Fig. 6 we can see that G_a declines markedly when only a little of NaAc is added. G_a drops off 90%. For pre-irradiation method, the amount of radicals which can initiate graft reaction is decided by different pre-irradiation dose. The pH of grafting system increases with the addition of NaAc. As mentioned above, high pH results in the lower rate of monomer diffusion, so a lot of grafting chains deactivated by reaction with other grafting chains around before the monomer can react with it. As far as the simultaneous radiation method is concerned, the polymer matrix is irradiated during the period of monomer reacting with polymer matrix. Matrix radicals which can initiate the graft reaction are generated at anytime during the whole period of reaction, so G_a does not decline obviously when NaAc is added.

The effect of NaAc additive on G_a when SSS was grafted onto HDPE -g-AA membranes using pre-irradiation method

From Fig. 7 we can see that G_s increases remarkably with the addition of NaAc. That is "pH effect" which is mentioned above, because SSS is a neutral salt and only the addition of NaAc can change the pH of the grafting system. Na^+ coming from the ionization of NaAc diffuses into the vicinity of grafting chains and neutralizes the negative charge of $–COO^–$ or $–SO_3^–$ groups by "ion pair effect". The "ion pair effect" intensifies with the increase of NaAc, so G_s increases obviously. When the concentration of NaAc is 3.74% wt., G_s can reach 453.7%, that is ten times as high as that without NaAc. This result is higher than that of SHKOLNIK et al.[10] (G_s = 49%) by two-step grafting method. Using two-step grafting method, we obtained the ion exchange membrane with high G_s by adding NaAc to the grafting system. The ion-exchange capacity is 3.98 meq when G_s is 453.7%. The results of Fig. 7 afford us an effective method for the preparation of high ion-exchange capacity resins. MIZOTA et al.[11] reported that the grafted polymer including $–SO_3H$ groups prepared by radiation induced graft copolymerization showed a higher hydrolytic activity for sucrose, compared to the polystyrene chain cross-linked with divinylbenzene, because of the absence of steric hindrance.

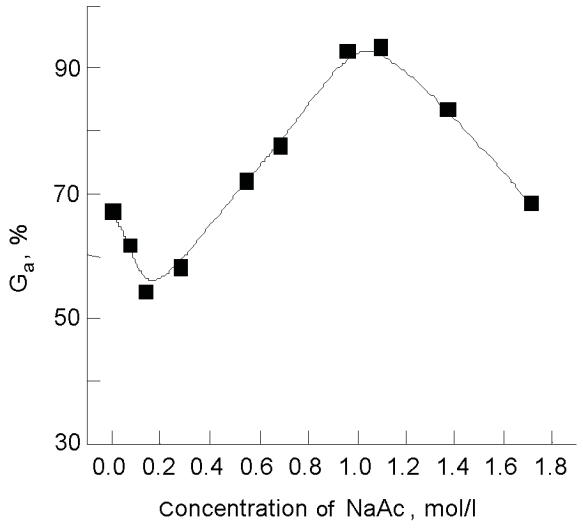

Fig. 1. Effect of the sodium acetate concentration on Ga when HDPE was grafted with AA using simultaneous method. Concentration of AA: 2 mol·l^{-1}, irradiation dose: 30 kGy, grafting temperature: 30 °C, grafting time: 18 hours

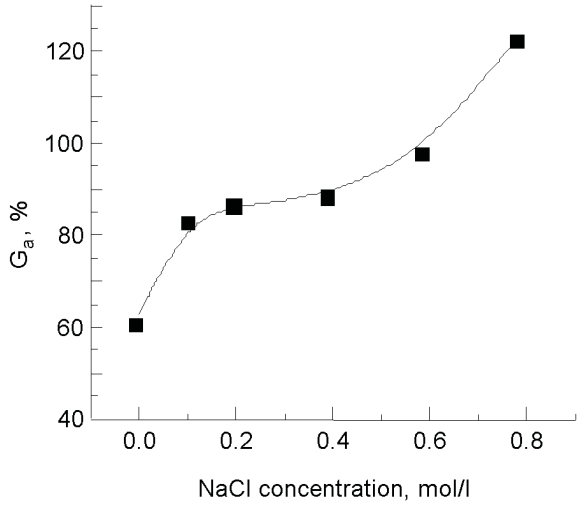

Fig. 2. Effect of the NaCl concentration on G_a when HDPE was grafted with AA using simultaneous method. The reaction conditions are the same as in Fig. 1

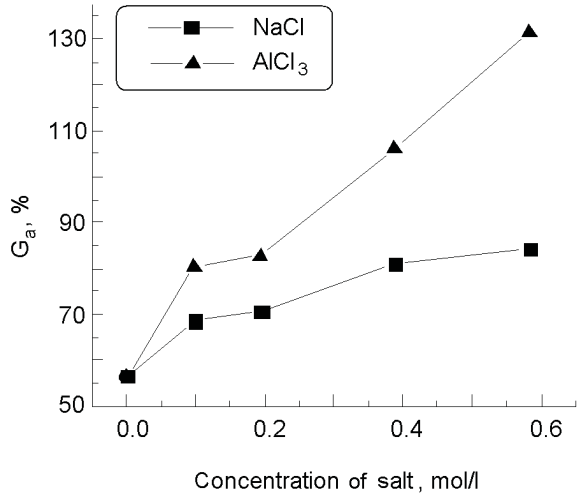

Fig. 3. Effect of the cationic salt concentration on G_a when HDPE was grafted with AA using simultaneous method. Concentration of AA: 2 mol·l^{-1}, Irradiation dose: 30 kGy, grafting temperature: 25 °C, grafting time: 17 hours

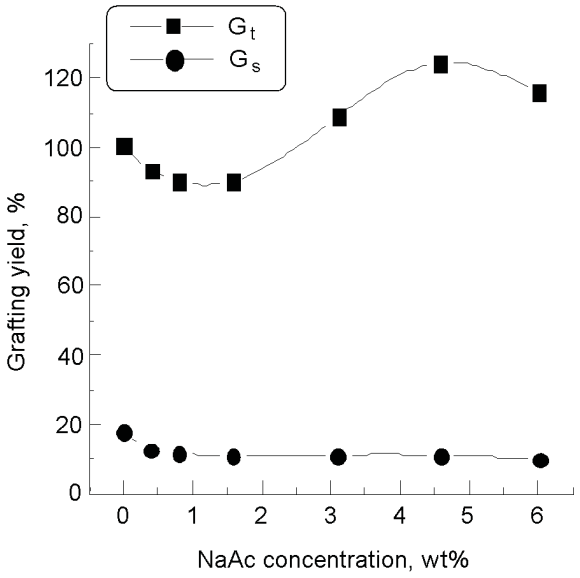

Fig. 4. Effect of the sodium acetate concentration on the grafting yield when HDPE was grafted with AA and SSS using simultaneous method. Total concentration: 3 mol·l^{-1}, molar ratio of SSS to AA: 1 : 2, irradiation dose: 30 kGy, grafting temperature: 30 °C, grafting time: 18 hours

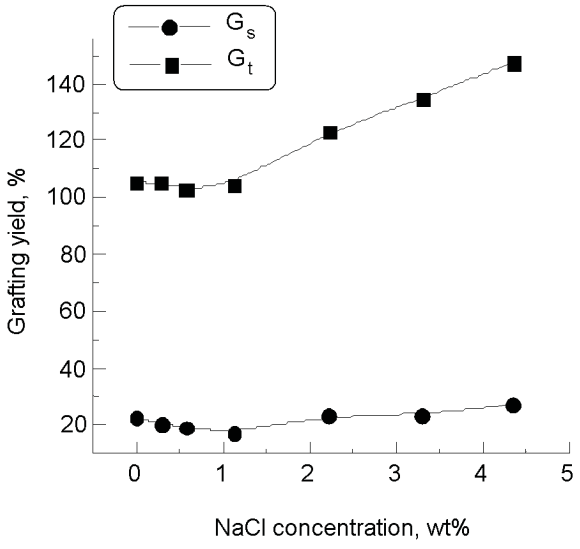

Fig. 5. Effect of the NaCl concentration on the grafting yield when HDPE was grafted with AA and SSS using simultaneous method. The reaction conditions are the same as in Fig. 1

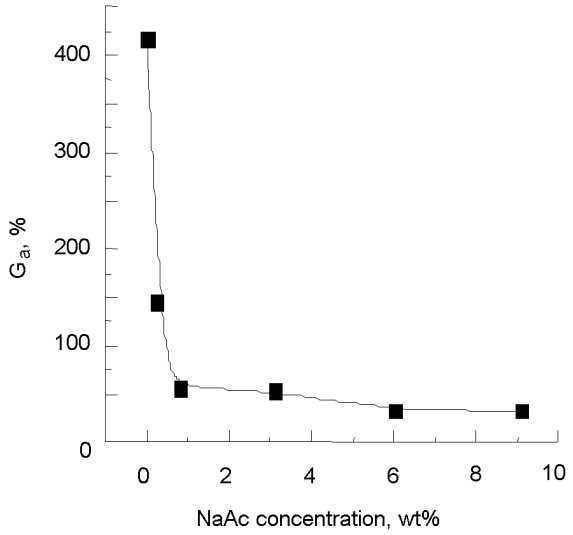

Fig. 6. Effect of the sodium acetate concentration on G_a when HDPE was grafted with AA using pre-irradiation method. Concentration of AA: 2 mol·l^{-1}, irradiation dose: 100 kGy, grafting temperature: 50 °C, grafting time: 24 hours

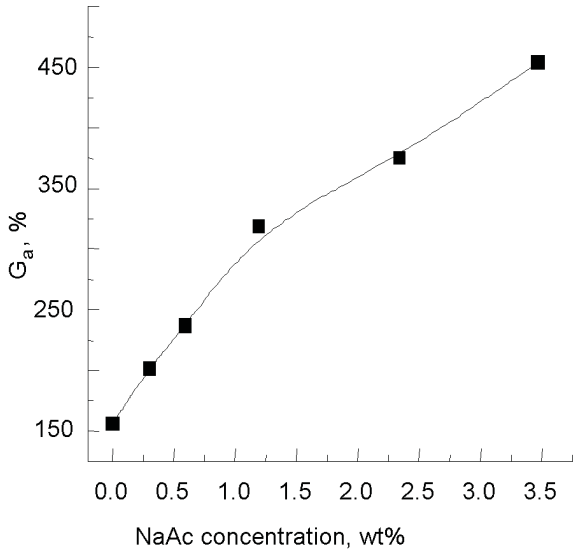

Fig. 7. Effect of the sodium acetate concentration on G_s when HDPE-g-AA was grafted with SSS using pre-irradiation method. Concentration of SSS: 0.75 mol·l^{-1}, grafting temperature: 50 °C, irradiation dose: 100 kGy, grafting time: 6 hours

Characterization of the grafting membrane

After the grafting reaction, the HDPE membranes were washed thoroughly with water, and then soaked into distilled water overnight to remove residual monomers and homopolymers or copolymers contained in the membrane. The membranes were analyzed by infrared spectroscopy (IR200, America Nicolit Co., Ltd.). Compared to the ungrafted HDPE membrane in Fig. 8a, there are some new absorption peaks in the 3450–2650 cm^{-1} region due to the O–H stretching vibration in Fig. 8b. At 1715 cm^{-1} there is an absorbance of C=O, at 1128 there is the absorbance of stretching vibration and 1037 cm^{-1} is the non-symmetrical stretching vibration of S=O. Since monomers or homopolymers might be attached on the HDPE surface, a comparative experiment was done. Under the same experimental conditions, the same procedures were followed for the treatment of un-irradiated HDPE membranes before the infrared spectrum test. We did not find the peaks of –COOH and –SO_3Na. So it was further proved that AA and SSS were grafted onto HDPE.

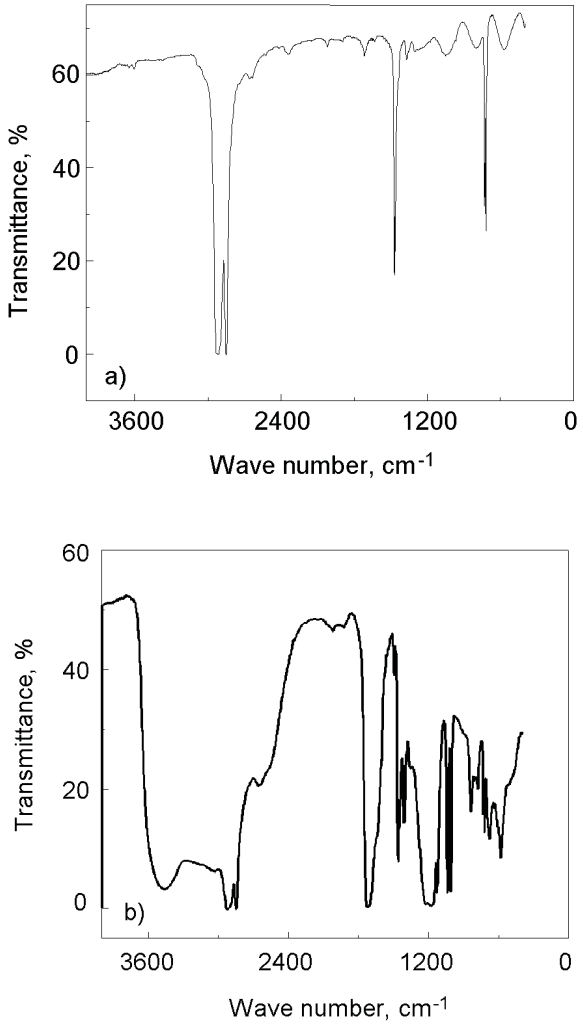

Fig. 8. Infrared spectrum of the ungrafted HDPE membrane (a) and grafted HDPE membrane (b)

Conclusions

AA and SSS were grafted onto high-density polyethylene membrane by the radiation grafting method. After the grafted membrane was immersed into HCl solution, $-SO_3Na$ was transformed into $-SO_3H$ and an ion-exchange membrane with strong acid and weak acid groups was got.

The effect of additives such as sodium acetate, sodium chloride on grafting yield was studied. It was found that in either pre-irradiation method or simultaneous radiation method, the NaAc which is a weak acid salt of a strong alkali had a complex effect on grafting yield by "pH effect" and "ion pair effect", and the neutral salt NaCl could increase the grafting yield by "ion pair effect".

The cationic salt played an important role in the radiation grafting process, which could change the diffusion rate of monomers and lower the required radiation dose or monomers concentration.

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This work was financially supported by National Natural Science Foundation of China (Project 50303009), Shanghai Science and Technology Foundation (Project 05dz12032), which are gratefully acknowledged.

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