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One step graft copolymerization of acrylic acid and sodium styrene sulfonate onto high-density polyethylene film by preirradiation method

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Abstract High-density polyethylene (HDPE) films were irradiated by ^{60}Co gamma ray with a dose of 100 kGy in air and then immersed in aqueous solution of acrylic acid (AA) and sodium styrene sulfonate (SSS) at different temperature. The effects of grafting conditions such as temperature, reaction time, Mohr's salt concentration, and total concentration of monomer on grafting yield were studied. Both grafting yield of AA and SSS onto HDPE respectively increases with total concentration of monomers. The highest grafting yield was observed at 3 mol/L monomers where the grafted PE swelled to the largest extent in the monomers mixture. The grafting yield increases with reaction time and then levels off. At higher temperature, the grafting yield decreases with Mohr's salt concentration, but increases at low temperature when Mohr's salt concentration is 0.083%. Which can be interpreted that in the presence of Fe^{2+} diperoxides and hydroperoxides may decompose at low temperature to form radical which can initiate the grafting. The physical and chemical properties of grafting films were also investigated.

Keywords High-density polyethylene, Preirradiation graft, Acrylic acid, Sodium styrene sulfonate

CLC numbers O631.3^{+}4, O621.3^{+}92 A

1 INTRODUCTION

Graft copolymerization is a well-known method for modification of chemical and physical properties of polymeric materials. It can be achieved by ionizing radiation, ultraviolet light or chemical initiators. Of these, radiation grafting is one of the most promising methods because of its deep penetration in polymer matrix and uniform formation of active sites for initiating grafting throughout the matrix, and the modification of polymers can be accomplished not only at the surface but also throughout the interior of polymers.

Many studies on the grafting of weak acid on PE have been published[1~4], but very few on the grafting of strong acids such as derivatives of sulfonic acid have been reported. In order to increase the ion-exchange capacity and to reduce film resistance, our work

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focuses on synthesizing bifunctional ion exchange film containing sulfo and carboxyl. In the past the sulfonation of PE was prepared by fuming sulfonic acid[5], but that considerably drastic reaction condition would damage the mechanism properties of the film. An indirect method for grafting of sulfonic group onto PE by gamma irradiation grafting, chlosulfonating and finally hydrolyzing has been reported by Chen *et al*[6]. Direct graft polymerization of the vinyl sulfonates onto PE film is difficult, because -SO_3^- groups with their hydration sphere are incompatible with hydrophobic PE and can not diffuse into the PE bulk. In order to make it easy, we introduce binary mixture system, the co-grafting of SSS and AA onto PE. In this system AA grafted onto PE and the hydrophilicity of films increased, then SSS could be grafted onto HDPE. So the sulfonic groups were introduced onto HDPE by a one-step method. The grafting film possesses high ion-exchange capacity and electrolytic conductivity, which makes it useful for a separator in alkaline batteries and catalysts for hydrolysis of methyl acetate[7].

2 EXPERIMENT

2.1 Materials

HDPE films were supplied by Xinyi branch of SNTC. SSS was bought from Zibo-Longda Chemical Co. Ltd. and not purified before using. AA was bought from Gaoqiao Chemical Plant and purified by decompression distillation.

2.2 Grafting procedure

HDPE film was irradiated in air at a dose of 100 kGy for 18 hours. The irradiated films were put together with polypropylene felt and rolled into cylinder using glass stick as axes, then were immersed in the monomer solution which was prepared at the given concentration of monomers and Mohr's salt and deaerated by bubbling nitrogen. The reaction was carried out in the temperature-controlled bath. After reacting for a period of time, grafted films were taken out from the monomer solution and washed thoroughly with hot distilled water, then soaked overnight to extract the residual monomers and the homopolymer in the films. After being dried in oven at 40°C until a constant weight, the films were weighted. The overall grafting yield (G_t) was defined as

$$G_t = (W_e - W_o)/W_o \times 100\%$$

Where W_e=weight of grafted HDPE and W_o= weight of ungrafted HDPE.

2.3 Measurement of grafting yield of SSS onto HDPE (G_s)

The grafted films were immersed in 1 mol/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 films 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:

$$G_S = [C_{NaOH} \cdot V_{NaOH} \cdot 206/(1000 \cdot W_0)] \times 100\%$$

here C_{NaOH} is the concentration of NaOH (mol/L) and 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 come from its ionization can restrain the ionization of -COOH.

2.4 Degree of swelling and alkali absorption in KOH

After the dry dimensions (S_0=width×length) were determined, the grafted films were soaked in 30% KOH solution for 24 hours, then the surface water was removed, the dimensions (S) and weight (W_J) were remeasured. For each film, degree of swelling (ΔS) and alkali absorption (C) were calculated as follows:

$$\Delta S = (S - S_0)/S_0 \times 100\%$$

$$C = (W_J - W_g)/W_g \times 100\%$$

2.5 Film electrolytic resistance

First, the grafted film was treated with 30% KOH to convert carboxyl group into its potassium salt. The electrolytic resistance of it was measured in 30% KOH solution at 25°C using an alternating current low impedance instrument.

3 RESULTS AND DISCUSSION

3.1 The effect of Mohr's salt concentration on the grafting yield in different temperature

When HDPE film was irradiated in air, free radicals formed in amorphous regions and a part of radicals formed in the crystalloid regions. Some radicals may react with oxygen to form peroxiodes such as diperoxides (R-O-O-R) and hydroperoxides (R-O-O-H), which can initiate graft reaction in the presence of monomer only at high temperature[8]. Compare Fig.1 to Fig.2 and Fig.3, we find the grafting yield increases with the increasing of temperature without the addition of Mohr's salt, because of the higher temperature, the more rapid rate of monomers diffusion and peroxides decomposition. When Mohr's salt is added, for different reaction temperature the change of grafting yield is different. For 35°C Fig.1 shows G_s and G_t increases with the Mohr's salt concentration and the highest yield of grafting is obtained at the Mohr's salt concentration of 0.083%. At this temperature, the contribution of thermally decomposed peroxides should be very low. It can be expected that in the presence of a few Mohr's salt diperoxides and hydroperoxides may decompose even at a lower temperature to form radicals which can initiate the grafting. This can be explained by reaction Fe^{2+} + R-O-O-R or R-O-O-H $\rightarrow RO^{\bullet} + Fe^{3+} + OH^-$ or RO^-. Subsequently the decrease of grafting yield for different temperature at a higher Mohr's salt concentration can be explained by the reaction $Fe^{2+} + \text{-}R^{\bullet} \rightarrow \text{-}R^- + Fe^{3+}$. This reaction suggests that a part of the growing chain radicals ($\text{-}R^{\bullet}$) was deactivated. As seen in Fig.2 and Fig.3, the temperature is higher, the reduction of grafting yield is more obvious. That may be attributable to the decay of matrix and growing chain radicals more quickly at 50°C or 70°C than 35°C, because high temperature is beneficial to diffusion of Fe^{2+} into matrix.

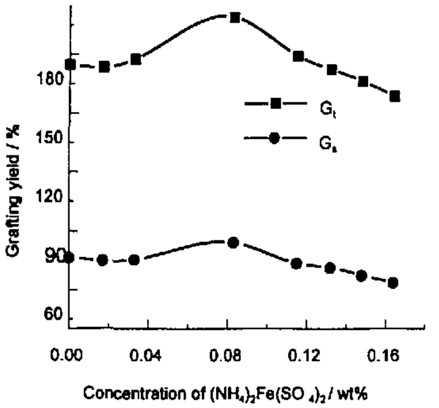

Fig.1 Effect of $(NH_4)_2Fe(SO_4)_2$ quantities on the grafting yield
Preirradiation dose: 100kGy,
Total concentration: 3 mol·L^{-1},
Molar ratio of SSS to AA: 1:2, Grafting temperature: 35°C, Grafring time:24h.
G_t: The overall grafting yield G_s: Grafting yield of SSS onto HDPH

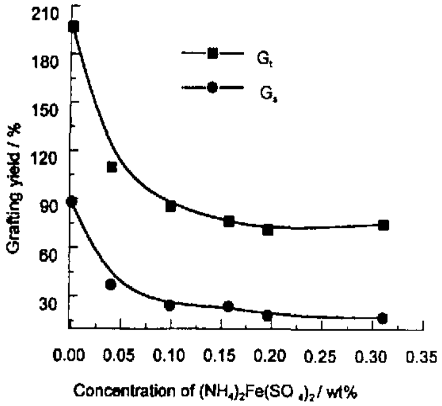

Fig.2 Effect of $(NH_4)_2Fe(SO_4)_2$ quantities on the grafting yield
Preirradiation dose: 100kGy,
Total concentration: 3 mol·L^{-1},
Molar ratio of SSS to AA: 1:2, Grafting temperature: 50°C, Grafring time: 24h

3.2 The effect of monomers concentration on the grafting yield at different temperature

The grafting is controlled by monomer concentration and free radical concentration in polymer substrate. At 50°C (Fig.4) little peroxides can decompose and the decay rate of substrate radicals is constant, so the grafting yield is controlled by the diffusion rate of monomers into polymer matrix. At 70°C (Fig.5) the decompose of multitude peroxiodes results in the increase of substrate radicals, at the same time high temperature can be in favor of increasing diffusion rate of monomers, so the grafting yield increases markedly.

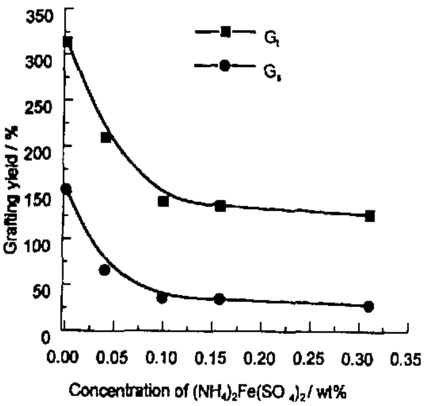

Fig.3 Effect of $(NH_4)_2Fe(SO_4)_2$ quantities on the grafting yield
Preirradiation dose: 100kGy,
Total concentration: $3\,mol{\cdot}L^{-1}$,
Molar ratio of SSS:AA:1:2, Grafting temperature: 70°C, Grafring time: 24h

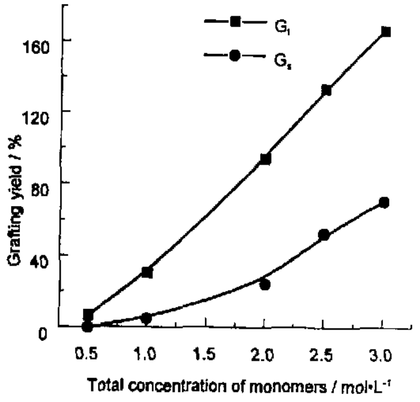

Fig.4 Effect of monomer concentration on the grafting yield
Preirradiation dose: 100kGy,
Grafting temperature: 50°C,
Grafting time: 24h,
Molar ratio of SSS:AA: 1:2

3.3 The effect of reaction time on the grafting yield

Fig.6 indicates that the grafting yield is proportional to reaction time in the initial stage. At this time the reaction rate is controlled by monomer diffusion, in the case of the less change of monomers molar ratio, the monomer concentration is nearly constant, so the diffusion rate and the reaction rate are constant. The reaction rate reduces with the time going on, and finally it tends to zero. Because the active centers that come from preirradiation are gradually consumed till they are exhausted.

3.4 Physical and chemical properties of the grafted films

The ion-exchange capacity, degree of swelling, alkali absorption in KOH solution and electrolytic resistance of some grafted films were measured, and the results were summarized in Table 1. From the table we can see that the value of G_s/G_t increased with G_a (G_a=G_t-G_s). That indicated the high hydrophilicity of grafted film was beneficial to SSS grafting onto HDPE. When G_t was 309.45%, G_s was 142.72%. This value was higher than the result of Shkolnik *et al.* (G_t =151%, G_s =49%) by a two-step method[9]. Ion - exchange capacity, degree of swelling and alkali absorption in KOH solution of the grafted film increased with an increasing of G_a and G_s. Ion-exchange capacity correspondes to ion-exchange resin containing sulfonic acid group when G_t is high. The Film resistance decreased with the increasing of grafting yield because of an increase in the amount of weak electrolyte (AA) and strong electrolyte (SSS). A high electric conductivity is an essential factor for the battery separator.

Table 1 Effect of grafting yield of monomers on chemical and physical properties of grafted films

Grafting yield/%		Ion-exchange capacity/meq·kg^{-1}	Degree of base absorption/%	Degree of swell in NaOH/%	Flim resistance /Ω·cm^{-2}
G_t	G_s				
0	0	0	0	0	∞
30.23	4.77	0.34	28.18	1.3	0.1
86.89	24.22	0.63	50.13	58.14	0.02
132.77	52.33	1.09	80.56	90.29	0.03
158.58	63.86	1.2	80.85	110.93	0.03
174.89	76.26	1.35	85.41	118.35	0.02
199.09	84.18	1.37	100.81	146.85	0.03
309.45	142.72	3.19	206.07	272.35	0.03

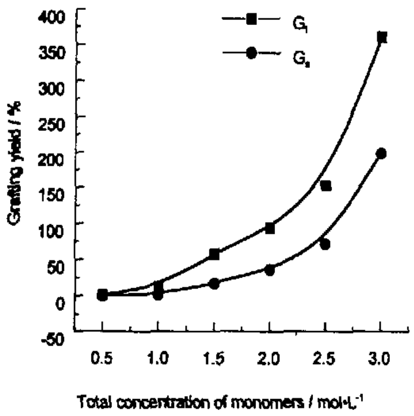

Fig.5 Effect of monomer concentration on the grafting yield

Preirradiation dose: 100kGy, Grafting temperature: 70°C, Grafting time: 24h, Molar ratio of SSS:AA: 1:2

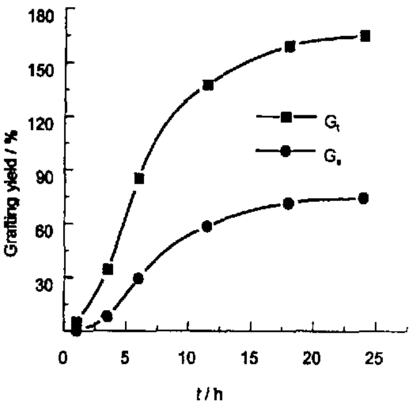

Fig.6 Effect of reaction time on the grafting yield

Preirradiation dose: 100kGy, Grafting temperature: 35°C, Total concentration of monomers: 3 mol·L^{-1},

Molar ratio of SSS:AA: 1:2

4 CONCLUSIONS

By introducing AA to the reaction system, sulfonation of PE can be prepared easily. At the presence of Fe^{2+} diperoxides and hydroperoxides may decompose at a low temperature to form radicals which can initiate grafting. Both grafting yield of AA and SSS onto HDPE respectively increases with total concentration of monomers. At the initial stage the grafting yield increases with reaction time and then levels off. High ion-exchange capacity and low electrolytic resistance make the grafted film be applicable to a battery separator and catalysts for hydrolysis of ester.

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