Study of Radiation-Induced Graft Copolymerization of Vinyl Acetate onto Ethylene-*co*-propylene Rubber

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SYNOPSIS

The radiation-induced graft copolymerization of vinyl acetate (VAc) onto ethylene-*co*-propylene rubber (EPR) has been studied in methanol with radiation of cobalt-60. The effects of irradiation dose, dose rate, concentration of monomer, Cu^{++} concentration, and temperature on the degree of grafting were investigated. The dependence of the initial grafting rate on dose rate, monome, and Cu^{++} concentration were found to be 1.0, 1.95, and 0.5 order, respectively. The apparent activation energy was calculated to be 49 kJ/mol. Mechanical properties of the grafted polymer were investigated as a function of the grafting percentage. The tensile strength increases and elongation of break decreases with the increase of the degree of grafting in the region of low grafting percentage (≅10%). © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The radiation-induced grafting polymerization is a well-known important method for modification of the chemical and physical properties of polymeric materials. So far, it has been used to prepare hundreds of interesting materials, some of them on a large scale. Many studies on the radiation grafting of vinyl monomers such as styrene, acrylic acid, methyl methacrylate, NVP, and vinyl acetate onto polyethylene or polypropylene using simultaneous or postradiation grafting techniques have been reported.[1-6]

Dessouki studied the grafting of vinyl acetate onto LDPE[5] or PTFE[6] for obtaining membranes with new properties. Reverse-osmotic properties of the membranes were examined in detail in the case of vinyl acetate grafting. The mechanical and electrical properties of membranes as well as desalting of aqueous solutions were investigated.

A. J. Restaino and W. N. Reed[7] studied the grafting copolymerization or vinyl acetate to different polymer matrices, but the grafted yield was very low. The grafting of vinyl acetate onto silicone rubber in different solvents was reported by Hua fengjui and coworkers.[8] The effects of various factors on the grafting have been investigated in detail and the results have been kinetically analyzed.

The present work is to study the grafting of vinyl acetate onto EPR (which has excellent chemical stability and mechanical properties) by simultaneous radiation grafting technique, for obtaining new materials with desired properties.

EXPERIMENTAL

Materials

EPR was purchased from Daqing rubber plant. Vinyl acetate, manufactured in Shanghai Heli chemical industry plant, was separated from hydroquinone inhibitor by distillation before it was used. Methanol, benzene, and cupric nitrate (all analytical grade) were used without further purification.

Grafting Procedure

Weighted EPR was dissolved in benzene at 60°C with constant stirring. The solution was filtered and poured on a glass dish. The dish was maintained at

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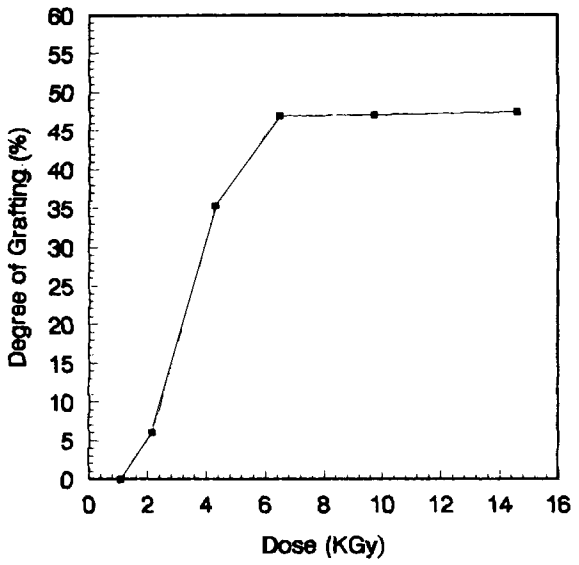

Figure 1 Effect of dose on the degree of grafting. Grafting conditions: monomer conc. 5.4 mol/L; Cu^{++} conc. 5 $\times$ 10^{-4} mol/L; dose rate 72.02 Gy/min; grafting temp. 26°C.

room temperature until the solvent was removed completely. After about three days, membranes with 100 μm thickness were obtained.

Samples of the obtained membranes (30 $\times$ 26 mm) were dried at 60°C under vacuum (10 mmHg) for 7 h. The initial membrane weight, W_0 was measured. The samples were immersed in grafting solution (mixture of methanol and with certain weight Cu^{++}) in grafting vessels, bubbled with N_2 gas (99.5%) for 7 min to remove oxygen, and then irradiated in a 60,000 ci Co-60 source at different grafting conditions.

The grafted membranes were extracted in methanol for 24 h. The extracted membranes were dried at 60°C under vacuum for 7 h, and the grafted membrane weight (W_g) was determined. The degree of grafting was calculated using the following equation:

$$\text{degree of grafting } (\%) = (W_g - W_0)/W_0 \times 100$$

Measurement of Mechanical Properties

The measurements of tensile strength (T_b) and elongation percent (E_b) at break were carried out using a versatile tensile tester (model DCS-5000, U.S.A.) with crosshead speed of 100 mm/min and load of 5 kg.

RESULT AND DISCUSSION

Effect of Irradiation Dose

The effect of irradiation dose on the direct graft of vinyl acetate onto EPR is shown in Figure 1. Grafting was carried out at dose range from 1.0 to 15.0 kGy, other conditions were kept constant. It can be observed that the degree of grafting rapidly reached a maximum at 6.2 kGy. Beyond 6.2 kGy, the grafting curve appears to level out. This may be due to the grafting system becoming almost depleted of monomer. Further grafting is insignificant.

Effect of Dose Rate

In most simultaneous irradiation systems, the degree of grafting increases with decreasing dose rate, which is the same as the result of our experiment (Fig. 2). At higher dose rates, short grafting branches were formed during the reaction. At lower dose rates vinyl acetate diffused into the EPR membrane, and longer grafting branches were formed, resulting in a larger degree of grafting. Figure 3 shows the logarithmic plots of the grafting rate against irradiation dose rate. A linear relationship was obtained. The dependence of the grafting rate on the dose rate was found to be of 1.0 order.

Effect of Monomer Concentration

The effect of monomer concentration on the degree of grafting is shown in Figure 4. The result shows

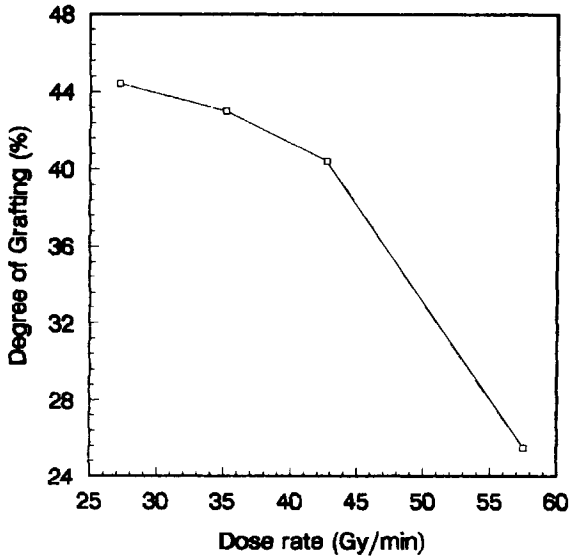

Figure 2 Effect of dose rate on degree of grafting. Grafting conditions: dose, 4.14 kGy; monomer conc. 5.4 mol/L; Cu^{2+} conc. 5.0 $\times$ 10^{-4} mol/L; grafting temp. 26°C.

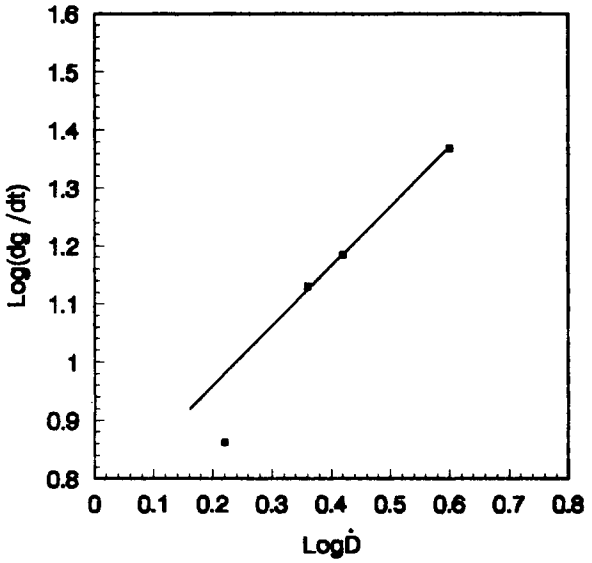

Figure 3 Logarithmic plots of grafting rate versus dose rate. Grafting conditions: monomer conc. 4.8 mol/L; Cu^{++} conc. 5.0×10^{-4} mol/L; grafting temp. 26°C.

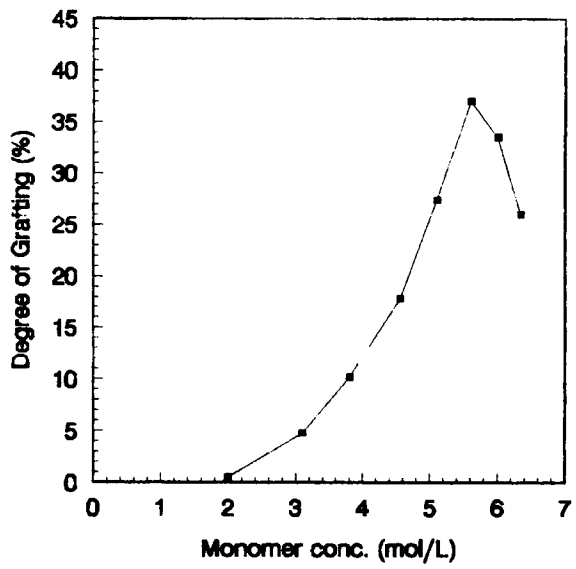

Figure 4 Effect of monomer conc. on degree of grafting. Grafting conditions: dose, 3.6 kGy; dose rate, 3.0 kGy/h; Cu^{++} conc. 5.0×10^{-4} mol/L; temp. 20°C.

that when monomer concentration is below 5.6 mol/L, the degree of grafting increases rapidly with monomer concentration. Beyond 5.6 mol/L, the degree of grafting was lowered. With higher monomer concentration, a large amount of homopolymers of vinyl acetate was formed in the grafting solution; the grafting system becomes very viscous due to gel formation. The gel is present to inhibit the diffusion of unreacted monomer to the grafting chains at the membrane. In addition, the gel effect enhances the rate of polymerization in the grafting solution, thus depleting further the monomer available for EPR membrane grafting. Therefore, the degree of grafting decreases with increasing monomer concentration. This behavior is typical of this reaction, in which the kinetics are critically controlled by the rate of diffusion of monomer in the membrane. Figure 5 shows the logarithmic plots of the initial grafting rate against concentration of vinyl acetate in methanol. A linear relationship was obtained. The dependence of grafting rate on monomer concentration was found to be of 1.95 order.

Effect of Cu^{++} Concentration

The effect of Cu^{++} concentration on the degree of grafting in the system methanol/EPR/vinyl acetate is shown in Figure 6. The result indicates that the degree of grafting increases with Cu^{++} concentration and reaches the highest point about 5×10^{-4} mol/L. Cu^{++} was the selective inhibitor which reduces the rate of homopolymerization without interfering too severely with the grafting process. Figure 7 shows the logarithmic plots of the grafting rate against Cu^{++} concentration. From this figure it is obvious that the grafting rate is proportional to 0.5 order of Cu^{++} concentration, if Cu^{++} concentration in the graft solution is below 5×10^{-4} mol/L.

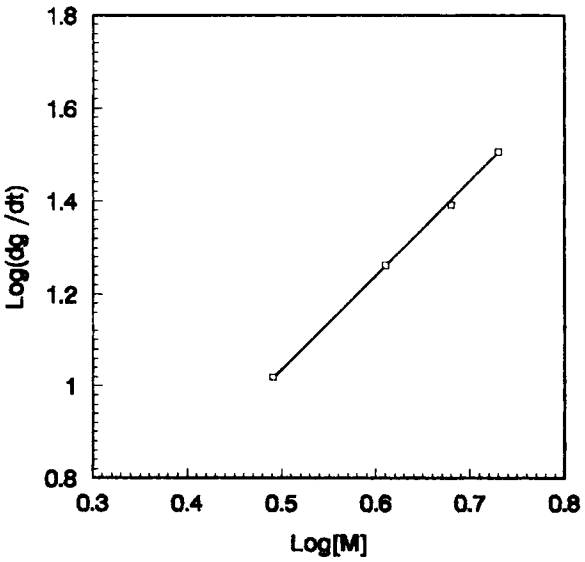

Figure 5 Logarithmic plots of grafting rate versus monomer concentration. Grafting conditions: Cu^{++} conc. 5.0×10^{-4} mol/L; dose rate, 2.743 kGy/h; temp. 26°C.

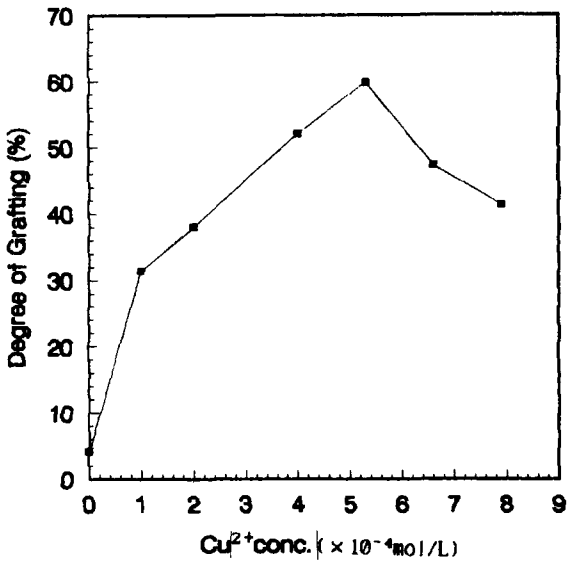

Figure 6 Effect of Cu^{++} conc. on degree of grafting. Grafting conditions: dose, 9.265 kGy; dose rate, 3.27 kGy/h; monomer conc. 5.4 mol/L; temp. 26°C.

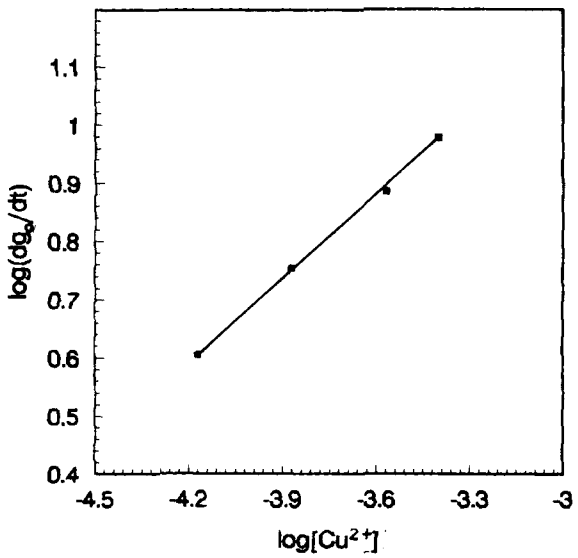

Figure 7 Logarithmic plots of grafting rate versus Cu^{2+} concentration. Grafting conditions: monomer conc. 5.2 mol/L; dose rate, 2.84 kGy/h; temp. 14°C.

Effect of Temperature

Figure 8 shows the degree of grafting–temperature curves for the grafting of vinyl acetate onto EPR membranes. The results reveal that the degree of grafting increases with temperature and reaches the highest value at 55°C, while over 55°C the degree of grafting tends to level off. The effect of temperature on the grafting process is very complicated. The increase in grafting temperature improves the diffusion of monomer into polymer matrix and the mobility of the chain segment, thus causing an increase in the initial grafting rate. However, the higher the temperature, the more homopolymer gels of vinyl acetate formed. These viscous gels hinder monomer diffusion toward the grafting region and decrease the degree of grafting.

Arrhenius plots for this graft copolymerization are shown in Figure 9. The average apparent activation energy was calculated to be 49 kJ/mol.

IR Spectrum Analysis

The IR spectra of EPR membranes are shown in Figure 10 (which was taken on a Shimadzu IR-440 spectrophotometer). When the IR spectra of Figure 10(a, b) are compared, it is seen that in the spectrum of Figure 10(b) the new absorption appears at 1720 cm^{-1} (ester carboxyl group). The result proves that vinyl acetate is grafting onto the EPR membrane.

Effect of Grafting on the Mechanical Properties

The tensile strength (TS) and elongation of the grafted membrane were measured as a function of the degree of grafting. The results are depicted in Figure 11. From this figure it is clear that TS value increases and elongation of break decreases with the increase of the degree of grafting in the region of low grafting percentage (≅10%). It is very interesting that

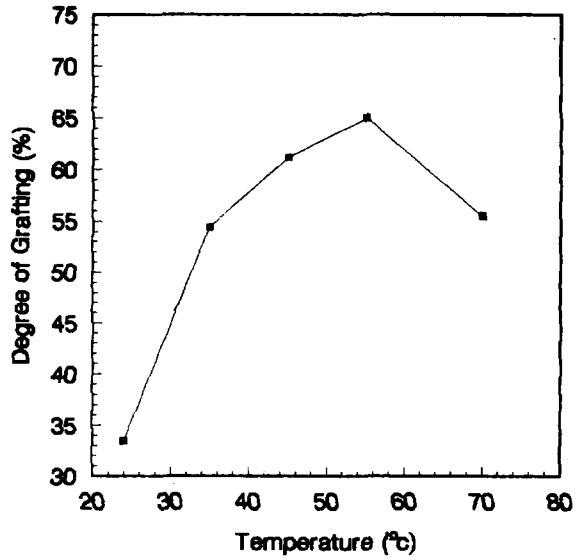

Figure 8 Effect of temperature on degree of grafting. Grafting conditions: monomer conc. 5.4 mpl/L; Cu^{2+} conc. 5.0×10^{-4} mol/L; dose, 3.454 kGy; dose rate, 3.46 kGy/h.

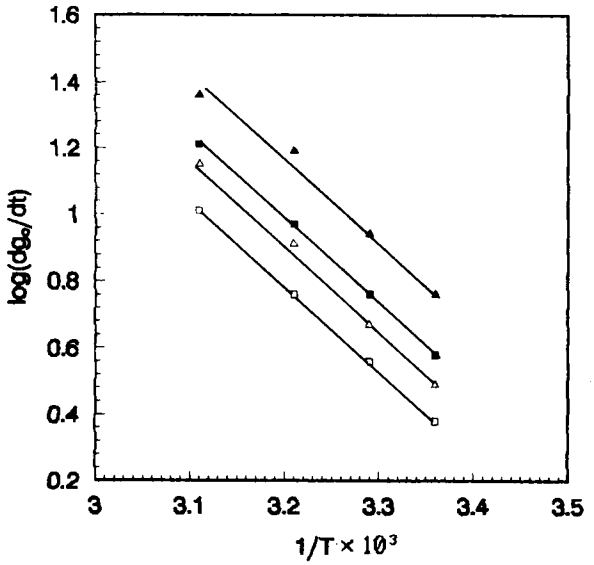

Figure 9 Arrhenius plots of grafting rate at various dose rate (kGy/h): (□) 1.665; (△) 2.288; (■) 2.629; (▲) 3.943. Grafting conditions: monomer conc. 4.8 mol/L; Cu^{2+} conc. 5.0×10^{-4} mol/L.

TS and elongation slightly change with the degree of grafting, if the degree of grafting is over 10%.

CONCLUSIONS

1. The degree of grafting reaches a maximum at 6.2 kGy irradiation dose.
2. Cu^{++} was the selective inhibitor which reduced the rate of homopolymerization without interfering too severely with the grafting process.

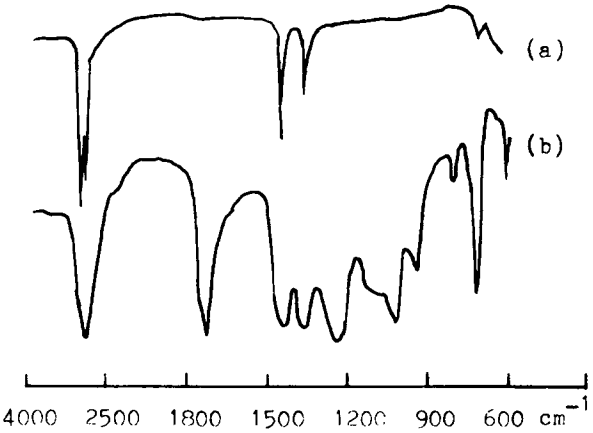

Figure 10 IR spectra of EPR (a) and modificated EPR (b). (a) 0% grafting; (b) 10% grafting.

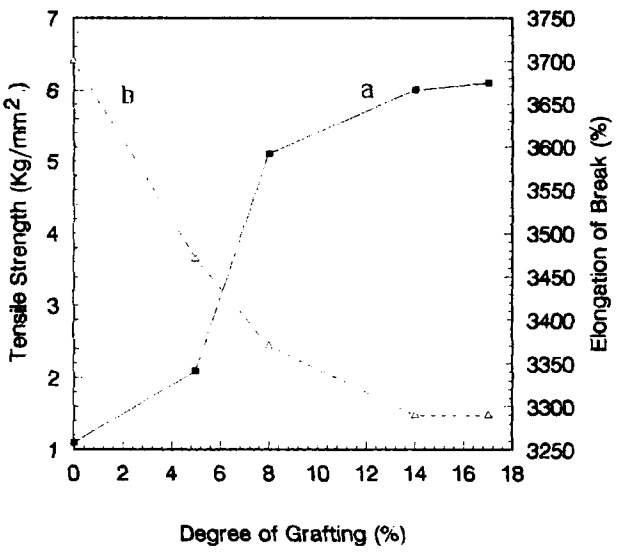

Figure 11 The relationships of tensile strength (a) and elongation of break (b) with the degree of grafting.

3. The dependence of the initial grafting rate on dose rate, monomer, and Cu^{++} concentration were found to be 1.0, 1.95, and 0.5 order, respectively. The apparent activation energy was 49 kJ/mol.
4. The tensile strength of grafted EPR membrane increases and elongation of break decreases with the increase of the degree of grafting in the region of low grafting percentage (≅10%).

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