

THE RADIATION CROSSLINKING OF EPR/ SBR BLEND

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ABSTRACT

The radiation crosslinking of EPR/SBR blend has been studied. A relationship between sol fraction and radiation dose for the different weight ratio polymer blends and the method to calculate β_b value of EPR/SBR blend system have been established.

INTRODUCTION

The radiation crosslinking of polymer blend can produce many new kinds of materials with superior properties, e. g., heat shrinkable materials, so it attracts more scientists' attention for research. Few studies on the radiation crosslinking behavior of polymer blend have been reported in the literature^[1]. Since the crosslinking density of polymer influences their properties greatly, so it is very important to study the radiation crosslinking behavior. The relationship between sol fraction (S) and radiation dose (R) is usually used to characterize the crosslinking density and the crosslinking behavior^[2,3]. In this paper, we try to extend the relationship^[4] to EPR/SBR blend.

EXPERIMENTAL

Materials

EPR, which contains a small amount of diene-comonomer and ratio of propylene to ethylene is 2/3 by mole, is obtained from Japan Mitsui Polychemicals Co.

SBR in which content of butadiene monomer is about 85% by weight is obtained from Jilin Chemical Industry Corporation.

Irradiation and Preparation of EPR/SBR Blend

Dissolve ethylene-propylene rubber (EPR) and styrene-butadiene rubber (SBR) in xylene respectively, and the two solutions (concn. about 2%) were mixed and stirred vigorously. The solvent in the solution was distilled out at 50°C and dried at 90°C under vacuum. Then the polymer blends obtained were molded at 90°C under 150 atm. to form specimens in 1 mm thick sheet. The glasstubes containing EPR/SBR blend samples were evacuated, and sealed under vacuum and irradiated in a ^{60}Co -source.

Determination of gel content

Accurately weighed minced samples of 0.2 g were extracted under reflux with xylene for 36 hr. After cooling and washing with acetone, the samples were dried to constant.

RESULTS AND DISCUSSION

We have established a general expression relating sol fraction (S) to radiation

dose (R) for single linear polymer as follows:

$$R(S + \sqrt{S}) = 1/q_0 U_1 + p'_0 R^\beta / q_0 \quad (1)$$

where q_0 - crosslinking density, portion of unit crosslinked per unit dose; U_1 - initial number-average degree of polymerization; p'_0 - a constant. In addition, eq. (1) is valid only within certain limits of dose because eq. (1) is only an approach to sol-gel relation, assuming that degree of crosslinking and fracture are very small. If the conditions that q is proportional to dose R and p is proportional to R^β at $R \rightarrow \infty$ are satisfied, when p and q are very small, the assumptions are no longer satisfied^[4]. β is an exponent concerned with the structure of a polymer.

The glass transition temperature (T_g) is one of the polymer structure parameters, so there is relationship^[4] between β and T_g as follows:

$$\beta = 0.002T_g + 0.206 \quad (2)$$

The β value can be easily obtained from the above equation for single linear polymer, but it is difficult for polymer blend in which there appear two glass transition temperatures sometimes. For ideal blend system, T_g of the blend ($T_{g,b}$) can be calculated from Kelley-Bueche^[5-7] equation:

$$T_{g,b} = (T_{g1} + (KT_{g2} - T_{g1})\Phi_2) / (1 + (K-1)\Phi_2) \quad (3)$$

where $T_{g,b}$, T_{g1} and T_{g2} are glass transition temperature of polymer blend, component 1 and component 2 in the polymer blend respectively; Φ_2 - volume fraction of component 2; K is the ratio of difference of heat expansion coefficient above and under glass transition temperature for component 2 to one for component 1 ($K = \Delta\alpha_2 / \Delta\alpha_1$). Let β value of the blend be β_b . Then from equations (2) and (3), the following equation can be obtained:

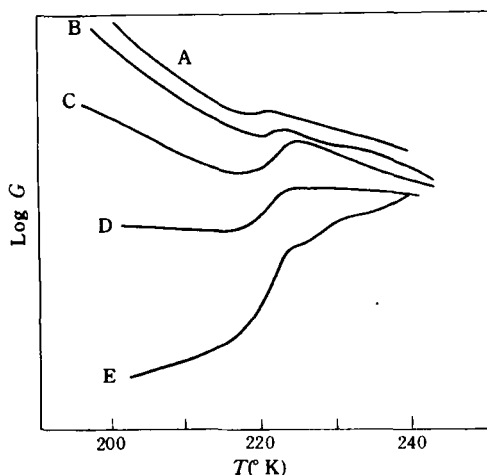


Fig. 1 DSC curve of EPR/SBR blend system

A) SBR=100%; B) SBR=89.3%; C) SBR=51.2%; D) SBR=11.4%; E) SBR=0 (EPR=100%)

$$\beta_b = (\beta_1 + (K' \beta_2 - \beta_1) \Phi_2) / (1 + (K' - 1) \Phi_2) \quad (4)$$

where β_1 and β_2 are the β value of components 1 and 2 in the blend respectively; K' - a parameter. Let EPR be component 1 and SBR be component 2. Then Φ_2 is approximate to W_2 (weight fraction) because specific gravity of SBR is approximately equal to one of EPR.

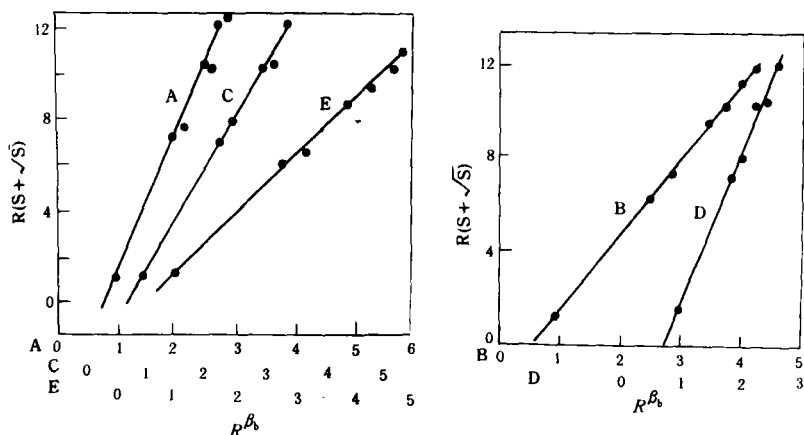
From DSC curve in Fig. 1, the glass transition temperature of EPR and SBR can be obtained. Their values are 222.4K and 221.9K respectively.

Substituting the experimental value of R and S of the blends into eq. (1), we can find out β value of experiment for the blend ($\beta_{b_{exp}}$) and the corresponding correlation coefficient (r) fitting eq. (1) by using mathematical regression method. The results are shown in Fig. 2 and listed in Table 1.

Substituting $\beta_{b_{exp}}$, β_1 and β_2 values obtained from eq. (2) into eq. (4), we can obtain a series of K' values and take an average value over these values as $\bar{K}'$ value of EPR/SBR blend ($\bar{K}' = 2.13$). Then again substituting $\bar{K}'$ into eq. (4), the relationship between β_b and composition (Φ_2) is obtained, shown as Fig. 3, so the value of β_b can also be calculated by eq. (4), which agrees closely with the experimental values (Tab. 1).

Table 1 β_b value of EPR/SBR blend system

Φ_2	$\beta_{b_{cal.}}$	$\beta_{b_{exp.}}$	r	K'
0.114	0.52	0.50	0.999	2.91
0.403	0.38	0.46	0.997	0.96
0.512	0.35	0.40	0.997	1.29
0.595	0.32	0.30	0.994	4.94
0.893	0.26	0.32	0.997	0.53



A) $\Phi_2 = 0.893$; B) $\Phi_2 = 0.595$; C) $\Phi_2 = 0.512$; D) $\Phi_2 = 0.403$; E) $\Phi_2 = 0.114$

Fig. 2 The relationship between S and R for EPR/SBR blend system.

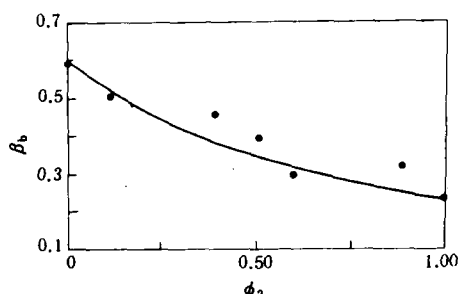


Fig. 3 The relationship between β_b and composition for EPR/SBR blend.
Experimental value — Value calculated from eq. (4)

From Fig. 3, it can be seen that the β_b values do not change abruptly through all composition range, which shows that there is almost no dependence between β_b and phase structure of the blend although EPR/SBR blend system is not an ideal blend system.

As stated above, the experimental data of radiation crosslinking for EPR/SBR blend fit well to equation (1) and show that eq. (1) and eq. (4) may characterize the radiation crosslinking behavior of EPR/SBR blend and the radiation crosslinking behavior of the blend is related to the structure of polymers in the blend.

Keywords:

Radiation crosslinking; Blend; Glass transition temperature; SBR; EPR.

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