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Environmental Stress Relaxation Studies of Polymers

Rate of Penetrant-Enhanced Relaxation of the γ-Irradiated Polyethylene-Ketone System

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ABSTRACT

Polyethylene films were irradiated by ^{60}Co gamma-rays, and the effect of ionizing radiation on polyethylene - ketone system was studied by the method of stress relaxation. An empirical equation for the rate constant of penetrant-enhanced relaxation in the polyethylene - ketone system was obtained.

INTRODUCTION

Stress failure of polymers caused by liquid environment (Decoste, et al, 1951; Grams and Gaube, 1955; Carey, 1954; Hittmair and Ullman, 1962; Renfrew and Morgan, 1960; Nisizawa, 1969; Nisizawa, 1979; Singleton et al, 1977; Shanahan and Schultz, 1976; Shanahan and Schultz, 1980) and also, the action of ionizing radiation on polymers resulted in chain fracture or cross-linking between the polymer chains (Charlesby, 1960; Chapiro, 1962; Siegel and Coughlin, 1970; Besmann and Greer, 1975; Jenkins and Keller, 1975; Patel and Keller, 1975; Patel etal, 1978). Since the penetrant-enhanced relaxation of irradiated polymers caused by liquid environment poses a problem of considerable interest, it is considered desirable to study the effect of radiation on the penetrant-enhanced relaxation in polyethylene - ketone system. The ketones used in this work were acetone and cyclohexanone, since these ketones have been used in the studies on the effect of ketone on polyethylene(Nisizawa, 1979). The stress decay of irradiated polyethylene with varying radiation dose under the influence of ketone was measured(Nisizawa, 1969; Nisizawa, 1979).

EXPERIMENTAL

Materials

The polyethylene used in this work was limited to a commercial polyethylene film having a density of 0.922 g/cc, a melt index of 2 and a thickness of 0.0024 cm.

The acetone and cyclohexanone used were of commercial grade.

Apparatus and Procedure

The polyethylene films were irradiated by ^{60}Co gamma-rays

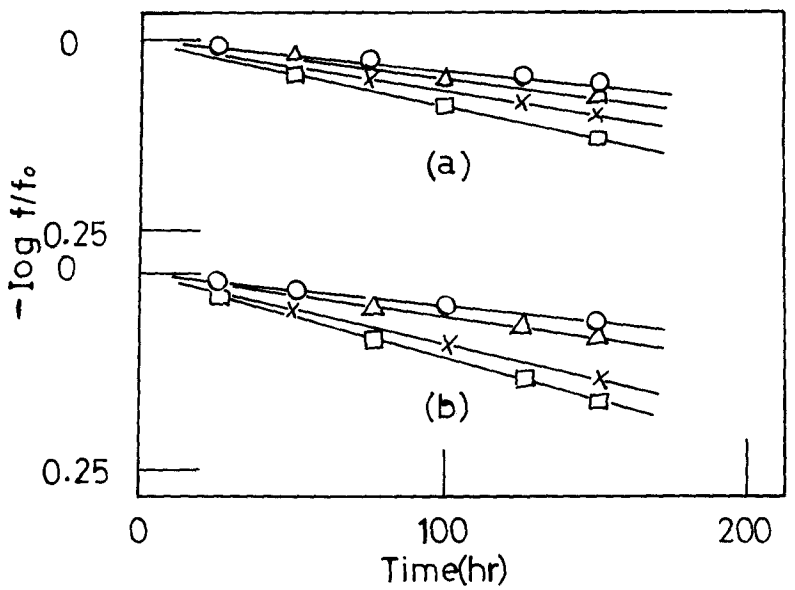

Fig.1. Stress relaxation of irradiated polyethylene - ketone system. (a) acetone, (b) cyclohexanone, o, 0 R; △, 10^5 R; x, 10^6 R and □, 10^7 R

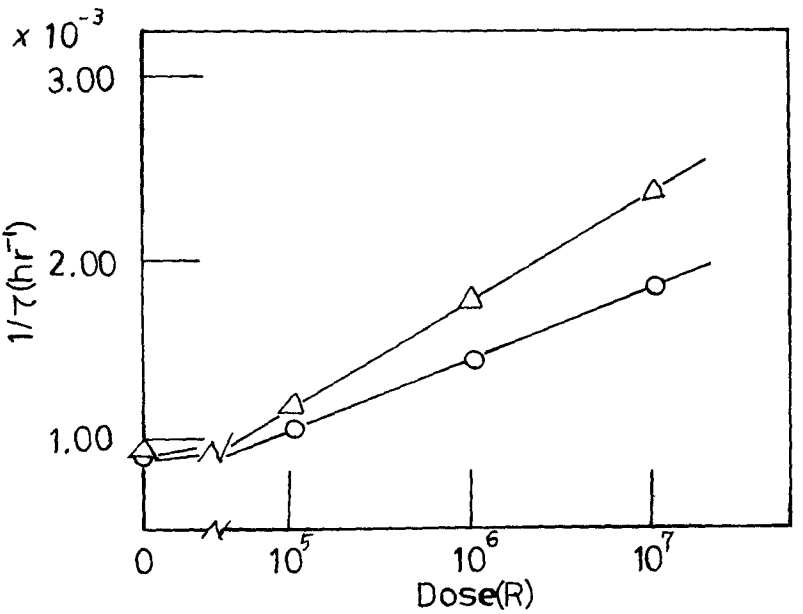

Fig.2. Dependence of radiation dose on rate constant for polyethylene - ketone system. o, acetone; △, cyclohexanone

in air at room temperature at the dose rates of 1.5×10^5 to 3.0×10^5 R/h.

The apparatus used in this work was the same as that described in the previous paper(Nisizawa, 1979).

The irradiated polyethylene film was set in the clamps in an inner vessel containing acetone or cyclohexanone, preheated in the unstrained state for 15 min and then, extended. The determination was followed by measuring with a balance the residual stress as a function of time in this film sample held at a constant extension in a thermostated vessel containing acetone or cyclohexanone.

RESULTS AND DISCUSSION

The changes with time in stress of irradiated(0 to 10^7 R) polyethylene films in ketone(acetone or cyclohexanone) were studied with a 50 % elongation at 40°C. The results are shown in Figure 1. From these results, the rate of relative stress decay f/f_0 of the irradiated polyethylene under ketones was found to follow the following equation:

$$f/f_0 = e^{-t/\tau}$$

where τ is the relaxation time. Since the relaxation time can be considered as the reciprocal of a rate constant for the penetrant-enhanced relaxation in irradiated polyethylene caused by ketone, the rate constant($1/\tau$) is plotted versus radiation dose and then, the relationships shown in Figure 2 are obtained.

Changes in the penetrant-enhanced relaxation in polyethylene - ketone system were estimated from changes in the stress relaxation in irradiated polyethylene in ketones, as shown in Figure 1. Figure 2 shows the relationships between the values of the rate constant and the radiation dose of the polyethylene. When the stress, the ketone and the temperature are constant, an increase of the radiation dose results in an increase of the rate constant. For the present system, the observed rate constant is related to the radiation dose R according to the following equation:

$$1/\tau = a + b \log R$$

The b-values in the formula are in inverse proportion to the radio-resistance of the polyethylene - ketone system(0.41×10^{-3} for polyethylene - acetone; 0.59×10^{-3} for polyethylene - cyclohexanone). In the system, if we assume that the principal changes in polyethylene caused by gamma radiation in air are both the destruction of crystalline structure and the formation of new chemical bonds, the irradiated and oxidized polyethylene is no longer highly crystalline. Therefore, the rate constant for the penetrant-enhanced relaxation in polyethylene - ketone system increases with increasing radiation dose.

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