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Environmental Stress Relaxation Studies of Polymers: Effect of Temperature on Polyethylene–Alcohol System

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Synopsis

The method of stress relaxation has been used to study the plasticizing effect of sorbed alcohols on polyethylene as it changes with temperature. From the observation of the stress relaxation in polyethylene under alcohols at various temperatures, the activation energy of penetrant-enhanced relaxation of polyethylene caused by alcohols was obtained.

INTRODUCTION

Stress cracking or stress failure of polymers such as polyethylene is caused by alcohols as the environment.[1-4] Since the penetrant-enhanced relaxation of polymers caused by alcohols as well-known penetrants poses a problem of considerable interest, it was therefore decided to investigate the effect of temperature on the stress decay behavior in polymer–alcohol systems. The polymer and alcohols used in this study were polyethylene, methyl alcohol, ethyl alcohol, and isopropyl alcohol, since these alcohols have previously been used in studies of the effect of alcohols on polyethylene.[4] The determination can be followed by measuring the stress decay of the polyethylene under the alcohols as a function of temperature.[5,6]

EXPERIMENTAL

Materials

The polyethylene, methyl alcohol, ethyl alcohol, and isopropyl alcohol used in this work were the same as those described in a previous paper.[4]

Apparatus and Procedure

The apparatus and procedure used in this work were the same as those described in previous papers.[5,6]

RESULTS

The changes with time in stress of polyethylene films under methyl alcohol, ethyl alcohol, or isopropyl alcohol at various temperatures were studied with a 50% elongation. The results are shown in Figures 1 to 3. From these results, the relation of polyethylene under alcohols at various temperatures was found to approximate the following equation[4]:

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

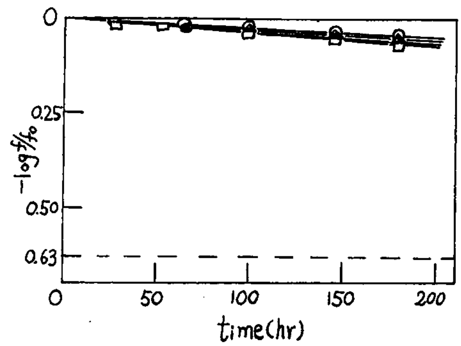


Fig. 1. Stress relaxation of polyethylene–methyl alcohol system: (O) 30°C; (Δ) 40°C; (◐) 50°C; (□) 55°C.

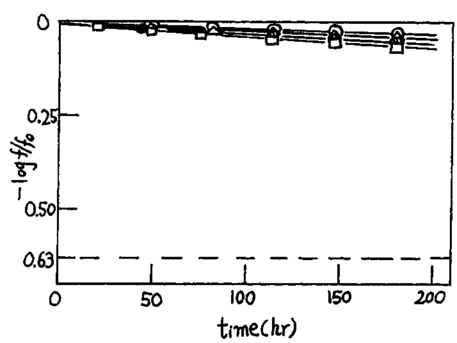


Fig. 2. Stress relaxation of polyethylene–ethyl alcohol system: (O) 30°C; (Δ) 40°C; (◐) 50°C; (□) 60°C.

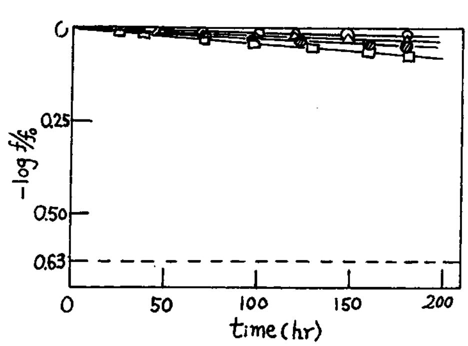


Fig. 3. Stress relaxation of polyethylene–isopropyl alcohol system; (O) 30°; (Δ) 40°C; (◐) 50°C; (□) 60°C.

where τ is the relaxation time. If the relaxation time τ can be considered as the reciprocal of a rate constant for penetrant-enhanced relaxation in polyethylene caused by alcohol and the rate constants are plotted versus the temperature, the relationships shown in Figures 4 to 6 are obtained.

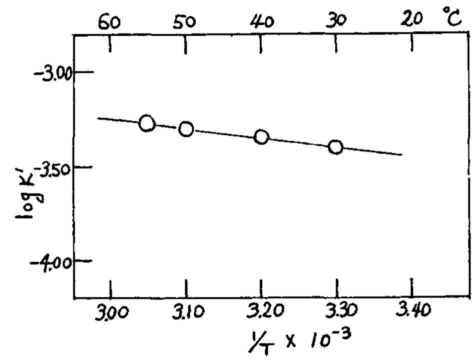


Fig. 4. Temperature dependence of rate constant of polyethylene–methyl alcohol system.

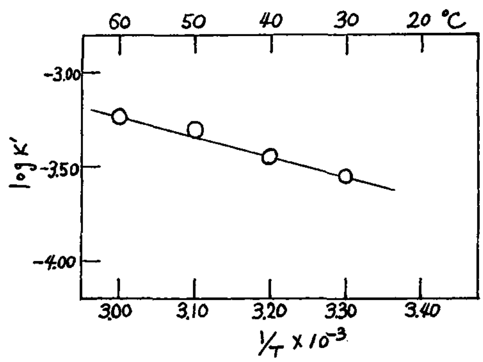


Fig. 5. Temperature dependence of rate constant of polyethylene—ethyl alcohol system.

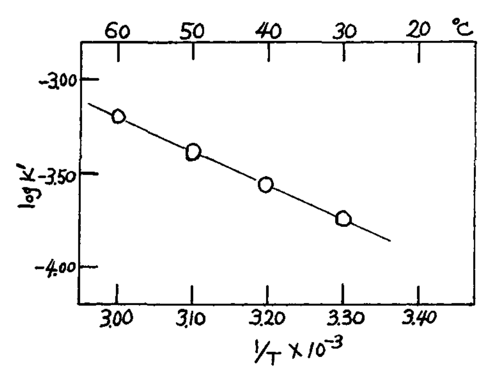
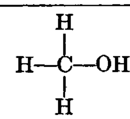
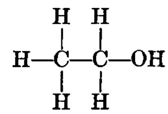
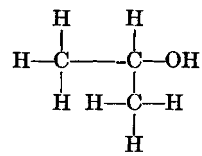


Fig. 6. Temperature dependence of rate constant of polyethylene–isopropyl alcohol system.

TABLE I
Activation Energy of Stress Failure in Polyethylene

Alcohol	Formula	Structure	Activation energy E, kcal/mole
Methyl alcohol	CH_3OH		0.6
Ethyl alcohol	CH_3CH_2OH		1.0
Isopropyl alcohol	$(CH_3)_2CHOH$		1.8

From these relationships, the activation energies for penetrant-enhanced relaxation of polyethylene caused by alcohols were obtained, and the values are listed in Table I for comparison. From these rates it is clear that the temperature dependence of polyethylene–alcohol systems and therefore the activation energy of the penetrant-enhanced relaxation increase with increasing number of carbon atoms in the alkyl group attached to hydroxyl.

DISCUSSION

As stated above, it is well known that stress cracking or stress failure of polymers such as polyethylene is caused by alcohols as the environment.[1–4] A discussion of the effect of temperature on penetrant-enhanced relaxation in polyethylene–alcohol systems follows. The penetrant-enhanced relaxation in polyethylene caused by alcohols at various temperatures is estimated from the stress relaxation in polyethylene under alcohols at various temperatures and is given in Figures 1 to 3. The dependency of the rate constant for stress relaxation on the temperature is related to the dependency of the rate constant for penetrant-enhanced relaxation by the alcohols on the temperature. When the stress and the alcohol are constant, a change in the temperature results in a change in the enhanced relaxation for the penetration by alcohol (see Figs. 1 to 6). The temperature dependency of polyethylene–alcohol systems increases with increasing number of carbon atoms in the alkyl group attached to the hydroxyl. This phenomenon indicates that polyethylene becomes more sensitive to an alcohol with a low number of carbon atoms in the alkyl group attached to the hydroxyl than to one with a high number of carbon atoms. Therefore the activation energy of penetrant-enhanced relaxation in polyethylene–alcohol systems is related to the number of carbon atoms in the alkyl group attached to the hydroxyl (see Table I). This also explains the enhancing effect of alcohols on the relaxation of polyethylene, as shown in an earlier work.[4]

References

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