Polymer Bulletin 1, 737–741 (1979)

Polymer Bulletin

Environmental Stress Relaxation Studies of Polymers: Effect of Ketones on Polyethylene and Its Temperature Dependence

Mizuho Nisizawa*

Department of Chemistry, Defense Academy, Yokosuka, Japan

ABSTRACT

The method of stress relaxation has been used to study the effect of ketones on polyethylene as it changes with temperature. From the observation of the stress relaxation in polyethylene under ketones and its temperature dependence, the activation energy of penetrant-enhanced relaxation of polyethylene caused by ketones were obtained and the effect of ketones on polyethylene were discussed.

INTRODUCTION

Stress failure of polymers such as polyethylene caused by the environment such as benzene-series hydrocarbons, alcohols and ketones(Decoste, et al, 1951; Grams and Granbe, 1955; Carey, 1954; Hittmair and Ullman, 1962; Renfrew and Morgan, 1960; Nisizawa, 1969a; Nisizawa, 1969b). Since the penetrant-enhanced relaxation of polymers caused by ketones as well-known penetrants poses a problem of considerable interest, it was therefore decided to investigate the effect of ketones on polyethylene and its temperature dependence. The ketones used in this work were acetone, methyl ethyl ketone and cyclohexanone, since these ketones are well-known ketone. The determination can be followed by measuring the stress decay of the polyethylene under ketones at various temperature(Nisizawa, 1969a; Nisizawa, 1969b).

EXPERIMENTAL

Materials

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, methyl ethyl ketone and cyclohexanone used were commercial-grade ketones.

---

* Correspondence should be addressed to my home address (Mizuho Nisizawa, Hashirimizu 2 - 21 - 1 - 31, Yokosuka, Japan) after August 1, 1979.

0170-0839/79/0001/0737/$01.00

Apparatus and Procedure

The apparatus used in this work was shown in Figure 1.

Polyethylene film(1) was set in the clamps(2,3) in the inner vessel containing ketones(4), preheated in the unstrained state for 15 min then extended. The determination was followed by measuring with a balance the residual stress as a function of time in this film sample(1) held at constant extension in a thermostated vessel containing ketones(4) at various temperature.

RESULTS

The changes with time in stress of the polyethylene film under ketones(such as acetone, methyl ethyl ketone or cyclohexanone) at various temperature were studied with a 50 % elongation. Figure 2-a shows one of the results. Figure 2-b shows the relaxation of polyethylene under ketones at 30°C. From these results, the relaxation of polyethylene under ketones was found to be approximate the following equation:

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

where τ is the relaxation time. If the relaxation time can be considered as the reciprocal of a rate constant for penetrant-enhanced relaxation in polyethylene caused by ketones, the rate constant ($1/\tau$) can be indicate an activity of the penetrant-enhanced relaxation of polyethylene caused by ketones and the values of the activity are given in Table 1 for comparison. On the other hand, as the value of rate constant of relaxation of polyethylene under ketone shows in Figure 2-a is plloted versus the temperature, the relationship shown in Figure 3 is obtained. From this relationship the activation energy for the penetrant-enhanced relaxation of polyethylene caused by the ketone was obtained and the

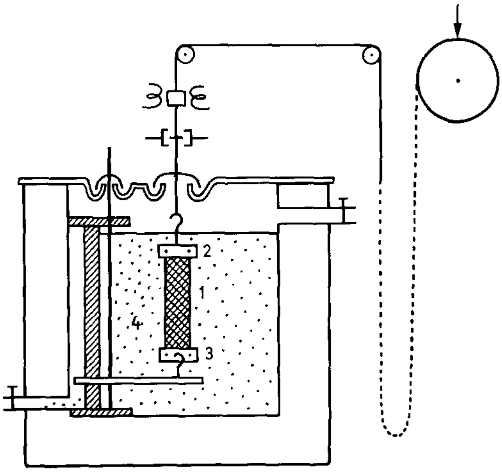

Fig.1. Schematic diagram of stress relaxation apparatus. (1) sample, (2,3) clamps and (4) environments(ketones).

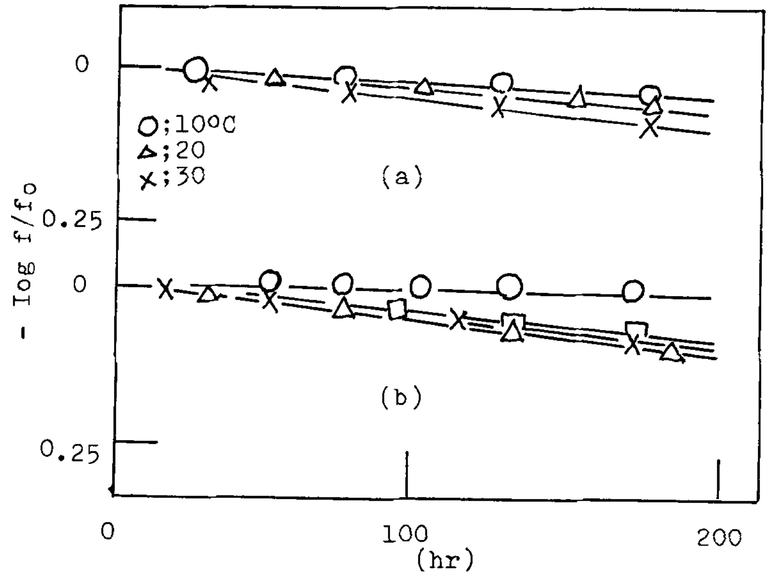

Fig.2. Stress relaxation of polyethylene under ketones. (a) methyl ethyl ketone, (b) o;air, △;acetone, x; methyl ethyl ketone and □;cyclohexanone at 30°C.

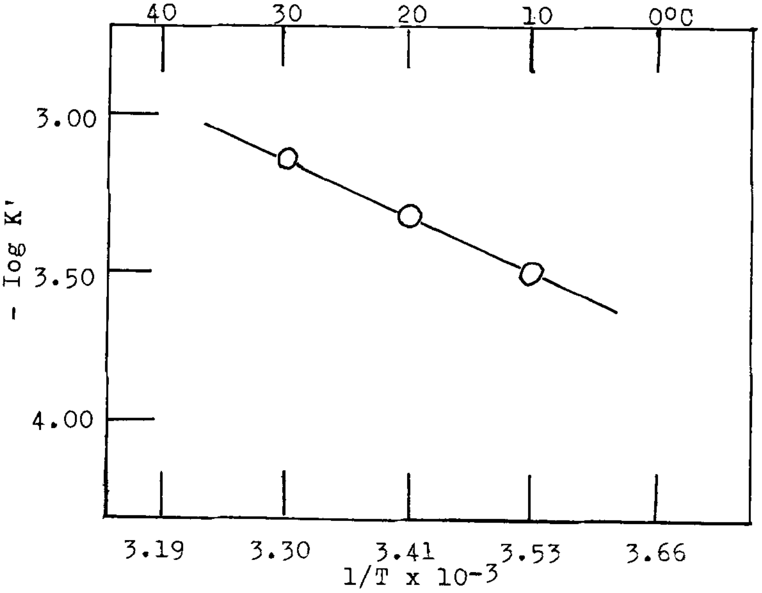

Fig.3. Temperature dependence of rate constant of polyethylene - methyl ethyl ketone system.

values of the activation energy are given in Table 1 for comparison. From these values it is clear that, in penetrant-enhanced relaxation of polyethylene - ketone system, the activity decrease and the activation energy increase with increasing the number of carbon atoms in the hydrocarbon attached to the carbonyl.

DISCUSSION

Stress failure of polymers such as polyethylene is caused by the environment such as benzene-series hydrocarbons, alcohols and ketones(DeCoste, et al, 1951; Grams and Granbe, 1955; Carey, 1954; Hittmair and Ullman, 1962; Renfrew and Morgan, 1960; Nisizawa, 1969a; Nisizawa, 1968b). A discussion of the effect of ketone on polyethylene and its temperature dependence follows. The penetrant-enhanced relaxation in polyethylene caused by ketones is estimated from the stress relaxation in polyethylene under ketones at constant temperature and various temperature. One of the results is given in Figure 2. The dependence of the rate constant for stress relaxation on the ketone is related to the dependence of the rate constant for penetrant-enhanced relaxation on the ketone. When the stress and the temperature are constant, a change in the hydrocarbon attached to the carbonyl results in a change in the enhanced relaxation for the penetrant; see Figure 2-b. In the polyethylene - ketone system the activity decrease and the activation energy increase with increasing the number of carbon atoms in the hydrocarbon attached to the carbonyl. These phenomena indicate that polyethylene become more sensitive to a ketones with a low number of carbon atoms in hydrocarbon attached to the carbonyl than with a high number of carbon atoms. Therefore, the activity and the activation energy of the penetrant-enhanced relaxation in polyethylene - ketone system are related to the number of carbon atoms in the hydrocarbon attached to the carbonyl; see Table 1.

Activity and activation energy of stress failure in polyethylene

TABLE 1

Ketone	Formula	Activity $1/\tau$, hr^{-1}	Activation energy E, Kcal/mole
Acetone	CH_3COCH_3	7.94×10^{-4}	2.9
Methyl ethyl ketone	$CH_3COCH_2CH_3$	7.36×10^{-4}	6.9
Cyclohexanone	$O{:}\underbrace{C(CH_2)_4C}H_2$	6.90×10^{-4}	9.3

The author wishes to thank Dr.N.Urata of Defense Academy for many helpful suggestions.

REFERENCES

DeCoste,J.B. et al., Ind.Eng.Chem., 43, 117(1951)
Grams,E. and E.Granbe, Angew.Chem., 67, 548(1955)
Carey,R.H., S.P.E.J., 10, 16(1954)
Hittmair,P. and R.Ullman, J.Appl.Polym.Sci., 6, 1 (1962)
Renfrew,A. and P.Morgan, Polythene, Iliff and Sons, London, 1960
Nisizawa,M., J.Appl.Polym.Sci., 13, 1921(1969)
Nisizawa,M., J.Appl.Polym.Sci., 13, 2506(1969)

Received July 12, 1979