

Environmental Stress Relaxation Studies of Polymers: Effect of Alcohols on Polyethylene

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Synopsis

The method of stress relaxation has been used to study stress decay behavior in polyethylene-alcohol systems. The behavior of stress decay in polyethylene under alcohols was observed and the respective activity forward stress decay of alcohols on polyethylene was obtained.

INTRODUCTION

Stress cracking of polyethylene caused by alcohols is known to be due to interaction with the alcohol molecule.¹⁻³ Stress failure of polyethylene under alcohols poses a problem of considerable interest.

Stress relaxation experiments which measure the rate of stress decay of the polyethylene-alcohols system have been utilized, since they were studied in previous works.⁴⁻⁶ If the polymers fail, then similar rates of stress decay should be obtained for alcohols.

The alcohols used in this study were methyl alcohol, ethyl alcohol, and isopropyl alcohol.

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 methyl alcohol, ethyl alcohol, and isopropyl alcohol used were commercial-grade alcohols.

Apparatus and Procedure

The apparatus used in this work was the same as that used in previous works.⁴⁻⁶

Polyethylene film was set in the clamps in the inner vessel containing the alcohols, 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 which was held at constant extension in the thermostated vessel containing the alcohols.

RESULTS AND DISCUSSION

The changes with time in stress of the polyethylene film under the alcohols were studied with a 50% elongation at 30°C. The results are shown in Figures 1 to 3. From these results the relaxation of polyethylene under alcohols was found to approximate the equation

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

where τ is the relaxation time. The relaxation time τ is the time value at which the residual stress reached $1/e$ (equals 0.368) of its value at zero time, and it was obtained from the slope of log stress plotted against time. If

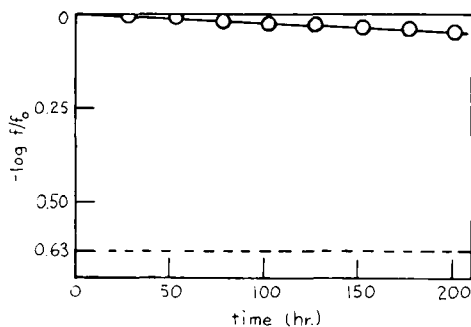


Fig. 1. Stress relaxation of polyethylene under methyl alcohol.

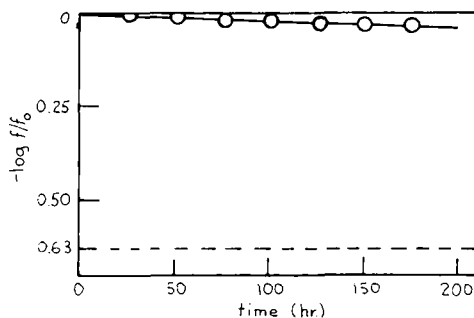


Fig. 2. Stress relaxation of polyethylene under ethyl alcohol.

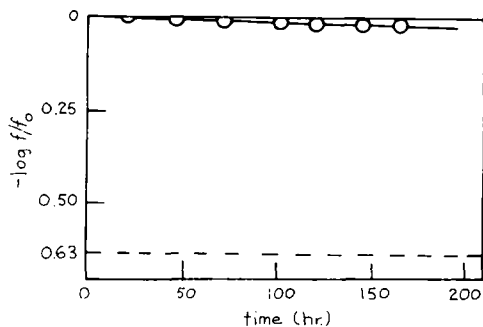


Fig. 3. Stress relaxation of polyethylene under isopropyl alcohol.

the relaxation time τ can be considered as the reciprocal of a rate constant for stress failure in this system, then the rate constant $1/\tau$ can indicate an activity forward stress decay of alcohols on polyethylene. These values were tabulated in Table I for comparison.

TABLE I
Activity^a of Stress Failure in Polyethylene

Alcohol	Formula	Structure	Relaxation time, hr	Activity $1/\tau$, hr ⁻¹
Methyl alcohol	CH ₃ OH	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	2.5×10^3	4.0×10^{-4}
Ethyl alcohol	CH ₃ CH ₂ OH	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{H} \end{array}$	3.4×10^3	2.9×10^{-4}
Isopropyl alcohol	(CH ₃) ₂ CHOH	$\begin{array}{c} \text{H} \quad \text{H} \\ \quad \\ \text{H}-\text{C}-\text{C}-\text{OH} \\ \quad \\ \text{H} \quad \text{C}-\text{H} \\ \\ \text{H} \end{array}$	5.7×10^3	1.8×10^{-4}

^a $1/\tau$ at 30°C.

From these values it is clear that stress failure tends to decrease the relaxation time, and that dependency increases with increasing activity of stress failure in polyethylene-alcohol systems.

In the present systems, an alkyl group attached to hydroxyl may be related to the stress failure observed.

References

1. J. B. DeCoste, F. S. Malm, and V. T. Wallder, *Ind. Eng. Chem.*, **43**, 117 (1951).
2. R. H. Carey, *S.P.E.J.*, **10**, 16 (1954).
3. P. Hittmair and R. Ullman, *J. Appl. Polym. Sci.*, **6**, 1 (1962).
4. M. Nisizawa, *J. Appl. Polym. Sci.*, **13**, 1621 (1969).
5. M. Nisizawa, *J. Appl. Polym. Sci.*, **13**, 2506 (1969).
6. M. Nisizawa, *J. Appl. Polym. Sci.*, **14**, 1381 (1970).

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