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## CALCULATION OF STRESS -- STRAIN CURVES FROM RELAXATION
## DATA IN THE RUBBERY - FLOW REGION

BY

## M. NARKIS

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# CALCULATION OF STRESS - STRAIN CURVES FROM RELAXATION DATA IN THE RUBBERY - FLOW REGION

BY

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## FOREWORD

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# CALCULATION OF STRESS - STRAIN CURVES FROM RELAXATION DATA IN THE RUBBERY - FLOW REGION

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## ABSTRACT

Stress relaxation curves for polysulfone and Lexan  polycarbonate are only time dependent at a constant temperature if strain is defined as $\epsilon_H = \ln(\ell/\ell_o)$ and the "true" cross-sectional area $A = A_o/(1+\epsilon)$ is used.  The strain independent stress relaxation curves can be used to calculate stress-strain curves at different rates of strain according to the linear viscoelastic theory.  The agreement between experimental and calculated stress-strain curves is good at least up to about 60% strain in the range of 0.01 to 0.2 in/min rate of extension if an average rate of strain defined by $\bar{\epsilon}_H = 1/t \, \ln(\ell/\ell_o)$ is used.

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# CALCULATION OF STRESS - STRAIN CURVES FROM RELAXATION DATA IN THE RUBBERY-FLOW REGION

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## Introduction

A linear viscoelastic body, Maxwell-Wiechert body [1], under a constant rate of strain $\dot{\epsilon}$ is described by the following equation:

$$f(t) = \dot{\epsilon} \int_{-\infty}^{\infty} \tau H(\tau) \, (1 - e^{-t/\tau}) \, d \ln \tau \qquad (1)$$

where $f(t)$ is the stress at time $t$, $\tau$ is the relaxation time which varies between zero and infinity, and $H(\tau)$ is the distribution of relaxation times. Differentiation of Equation (1) with respect to time yields [2, 3, 4],

$$\frac{df(t)}{dt} = \dot{\epsilon} \int_{-\infty}^{\infty} H(\tau) e^{-t/\tau} \, d \ln \tau = \dot{\epsilon} \, E_r(t) \qquad (2)$$

or

$$f(t) = \dot{\epsilon} \int_{0}^{t} E_r(t) \, dt = \dot{\epsilon} \int_{-\infty}^{\ln t} t \, E_r(t) d \ln t \qquad (3)$$

Another form of equation (2) was given by Smith [5],

$$E_r(t) = F(t) \, [1 + \frac{d \log F(t)}{d \log t}] \qquad (4)$$

where $F(t) = f(t)/\dot{\epsilon} t$ and $E_r(t)$ is the relaxation modulus. Smith studied Equation (4) by analyzing experimental data on NBS polyisobutylene and SBR elastomer.

Tensile measurements carried out by using the Instron machine are done under constant extension rate. If the instantaneous rate of strain is defined by $\dot{\epsilon} = 1/\ell \cdot d\ell/dt$, the strain $\epsilon_H$ (Hencky strain) and the average rate of strain $\bar{\dot{\epsilon}}_H$, when the sample is extended from $\ell_0$ ($t = 0$) to $\ell$ in a time interval $\Delta t = t$, are given by $\epsilon_H = \ell n (\ell/\ell_0)$ and $\bar{\dot{\epsilon}}_H = 1/t \, \ell n (\ell/\ell_0)$ respectively.

The logarithmic definition of strain was found appropriate for the experimental data shown in this paper, this strain definition was also recently used by Vinogradov et al. [6] for polystyrene at 130°C. Ballman [7] studied the stress-strain curves of polystyrene at 300°F and at different rates of strain. The rate of strain $d\ell n (\ell/\ell_0)/dt$ in his experiments was kept constant. The cross-sectional area A decreases with the extension and assuming a constant volume then $A = A_0/(1 + \epsilon)$ where $A_0$ is the initial cross-section area and $\epsilon = \Delta \ell/\ell_0$.

Equation (3) is applied to the experimental data as follows:

$$f(t) = (1 + \epsilon) \, f_s(t) = \ell n(\ell/\ell_0)/t \int_{-\infty}^{\ell nt} t \, E_r(t) d\ell nt \qquad (5)$$

where $f(t)$ is the stress calculated on the initial cross-section area. The cross-section area correction and the logarithmic strain were also applied to the stress relaxation data.

## EXPERIMENTAL

Stress relaxation and stress-strain data were obtained for polysulfone (1700 Union Carbide) and Lexan polycarbonate ($\overline{M}_w$ = 29,000, General Electric). Sheets of polysulfone and polycarbonate were compression molded and strips, about 0.1 in. thick and 0.75 in. wide, were cut from them. The distance between the grips was 3 in.

In stress relaxation experiments samples were extended at 2 in/min to a certain elongation and force-time curves were recorded. Force-elongation curves were studied at three rates of extension, namely, 0.01, 0.05 and 0.2 in/min.

Stress relaxation curves were obtained at several temperatures and shifted to 187°C and 160°C for the polysulfone and polycarbonate, respectively. Stress-strain curves were studied at 187°C and 160°C for the polysulfone and polycarbonate, respectively.

At least two samples were tested in each case.

## RESULTS AND DISCUSSION

A relaxation curve which is time dependent at a constant temperature and does not depend on strain can be converted into stress-strain data by using Equation (5). The dependence of the relaxation modulus upon strain was studied at four different strains. Results for polysulfone are shown in Figure 1 where four stress relaxation curves are plotted at 5, 10, 20 and 40% strain, the effect of strain on these curves is very significant. In figure 1 a stress relaxation curve, where $E_r(t)$ is calculated on the "true" cross-section area and the Hencky strain is used, is also shown. In this case, the stress relaxation curve is practically independent of strain at least up to 40%. Similar results were found for the Lexan polycarbonate and the strain

independent stress relaxation curves were used for further calculation of stress-strain curves with the aid of Equation (5). The possibility of separation of time and strain dependence of the stress for other polymers was shown by other researchers [5,8].

The range of rates of extension that was studied is 0.01 to 0.2 in/min. Experimental and calculated stress-strain curves for the polysulfone are shown in Figure 2. At very slow rates of extension the experiment extends to long times and since high temperatures are involved the stability of the polysulfone becomes an important factor and expecially in experiments that are carried out under air. Shifted stress relaxation data from lower temperatures become more important for calculated stress-strain curves at higher rates of extension, thus, the additional error due to shifting results in predicted stress-strain curves that are less accurate. Figure 2 shows that in the range of 0.01 to 0.2 in/min., the agreement between calculated curves and experimental data is good.

In Figure 3 stress relaxation curves at three different temperatures are shown for Lexan polycarbonate ($\overline{M}_w$ = 29,000). The curves for 154 and 170°C were shifted to the 160°C curve. By using the shift factors and a modified WLF equation for polycarbonate given by Tobolsky, et. al. [9] a value of $T_i$ = 147°C was obtained. $T_i$ values of 150 and 155°C for 40,000 and 90,000 molecular weight Lexan polycarbonate, respectively, were given by Tobolsky, et. al. In Figure 3, the 160°C relaxation curve is also represented by plotting $t\,E_r(t)$ versus log t, thus the value of the integral in Equation (5) can be graphically obtained.

Stress-strain behavior was studied at 160°C at three different constant extension rate experiments. The data are shown in Figure 4 and compared with calculated curves.

Figure 4 shows that stress-strain curves for the Lexan polycarbonate can be predicted from relaxation data with reasonable accuracy at least up to strain of 60%. Tobolsky, et. al. [9] , by measuring the relaxation curve at three different strains, have shown that practically for Lexan polymer ($\overline{M_w}$ = 40,000) $E_r$ (t) does not depend on strain at least up to 25% elongation.

If the "true" experimental tensile stress is divided by the integral term in Equation (3), the value of $\dot{\epsilon}$ is obtained. Table 1 shows that $\dot{\epsilon}$ decreases with time as $\overline{\dot{\epsilon}}$ does. One of the major reasons for this behavior can be attributed to the non-constant rate of strain experiments under constant extension rates, where high strains are involved.

In summary, stress relaxation data on a polysulfone and Lexan polycarbonate are appropriate for calculation of their stress-strain behavior in the rubbery-flow regions, according to the linear viscoelastic theory and by using proper definitions of strain and rate of strain and correcting for the cross-section area change with strain.

## Acknowledgment

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TABLE I. COMPARISON OF $\dot{\epsilon}$ CALCULATED BY USING STRESS–STRAIN AND RELAXATION DATA, WITH $\bar{\epsilon} = \ln(\ell/\ell_0)$

| t | $\int_0^t E_r(t)dt$ $\times 10^{-9}$ | 0.2 in/min | | | 0.05 in/min | | | 0.01 in/min | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | $f(t)$ $\times 10^{-6}$ | $\dot{\epsilon} \times 10^3$ | $\bar{\dot{\epsilon}} \times 10^3$ | $f(t)$ $\times 10^{-6}$ | $\dot{\epsilon} \times 10^4$ | $\bar{\dot{\epsilon}} \times 10^4$ | $f(t)$ $\times 10^{-6}$ | $\dot{\epsilon} \times 10^5$ | $\bar{\dot{\epsilon}} \times 10^5$ |
| min | $\frac{\text{dyne·sec}}{\text{cm}^2}$ | $\frac{\text{dyne}}{\text{cm}^2}$ | $\frac{1}{\text{sec}}$ | $\frac{1}{\text{sec}}$ | $\frac{\text{dyne}}{\text{cm}^2}$ | $\frac{1}{\text{sec}}$ | $\frac{1}{\text{sec}}$ | $\frac{\text{dyne}}{\text{cm}^2}$ | $\frac{1}{\text{sec}}$ | $\frac{1}{\text{sec}}$ |
| 1 | 3.25 | 3.6 | 1.10 | 0.97 | 0.83 | 2.55 | 2.46 | – | – | – |
| 2 | 5.40 | 5.7 | 1.05 | 0.95 | 1.39 | 2.57 | 2.46 | – | – | – |
| 5 | 10.7 | 10.1 | 0.94 | 0.87 | 2.74 | 2.56 | 2.41 | 0.60 | 5.60 | 5.1 |
| 10 | 17.6 | 14.5 | 0.82 | 0.77 | 4.15 | 2.35 | 2.32 | 0.99 | 5.65 | 5.1 |
| 20 | 29.6 | – | – | – | 6.00 | 2.03 | 2.20 | 1.57 | 5.30 | 5.0 |
| 40 | 43.5 | – | – | – | 7.40 | 1.70 | 1.95 | 2.35 | 5.40 | 4.8 |
| 60 | 58.5 | – | – | – | – | – | – | 2.94 | 5.03 | 4.7 |
| 80 | 70.0 | – | – | – | – | – | – | 3.40 | 4.85 | 4.6 |
| 125 | 86.0 | – | – | – | – | – | – | 3.82 | 4.45 | 4.35 |

## LIST OF FIGURES
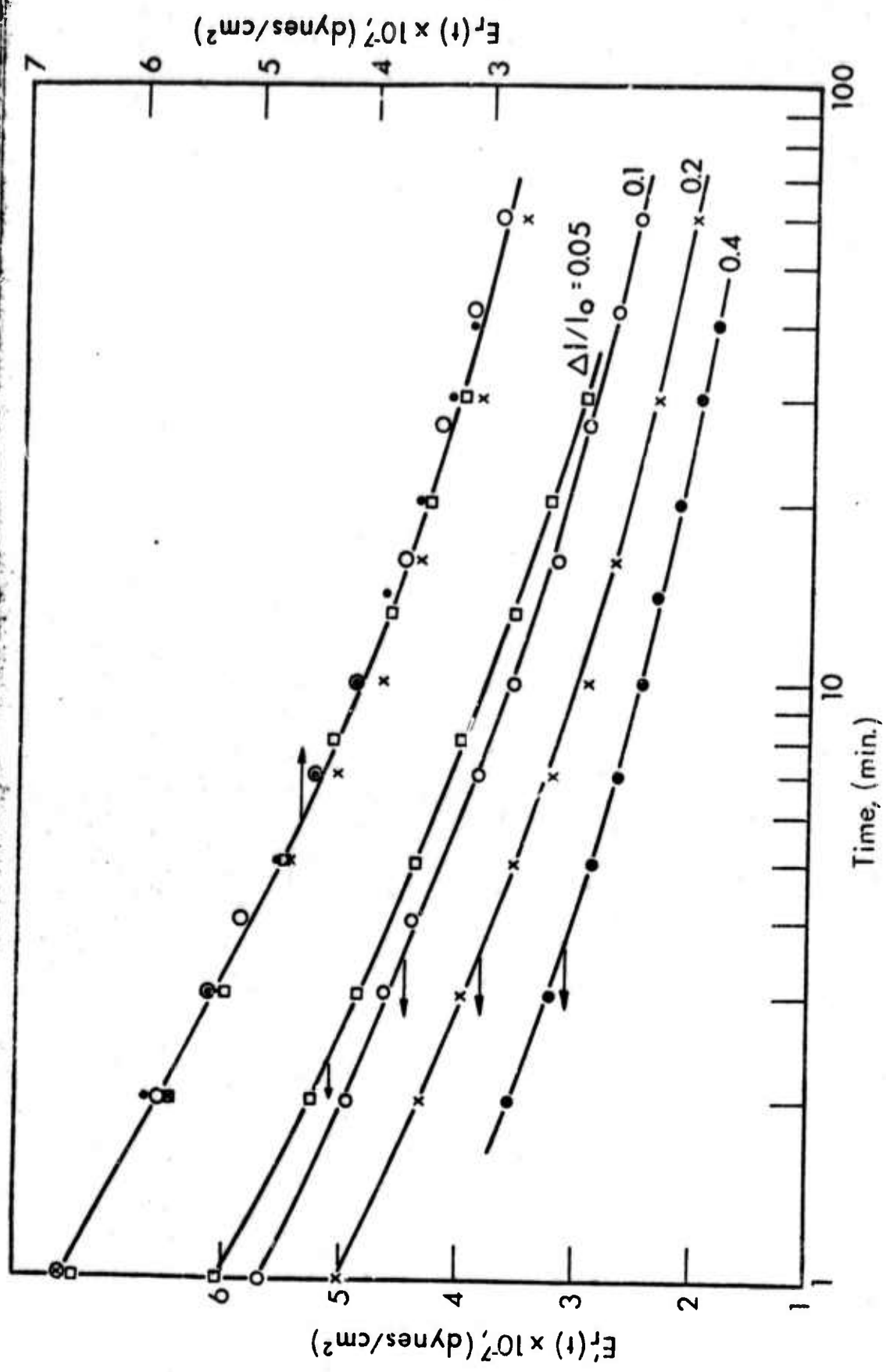
Fig. 1

POLYSULFONE   187°C                                    Fig. 2

The figure shows plots of $f(t)$, (dynes/cm$^2$) on the vertical axis (ranging from $10^6$ to above $10^7$) versus Strain, $(\Delta l / l_o)$ on the horizontal axis (from 0.1 to 0.6), for three crosshead speeds: 0.2 in/min, 0.05 in/min, and 0.01 in/min.
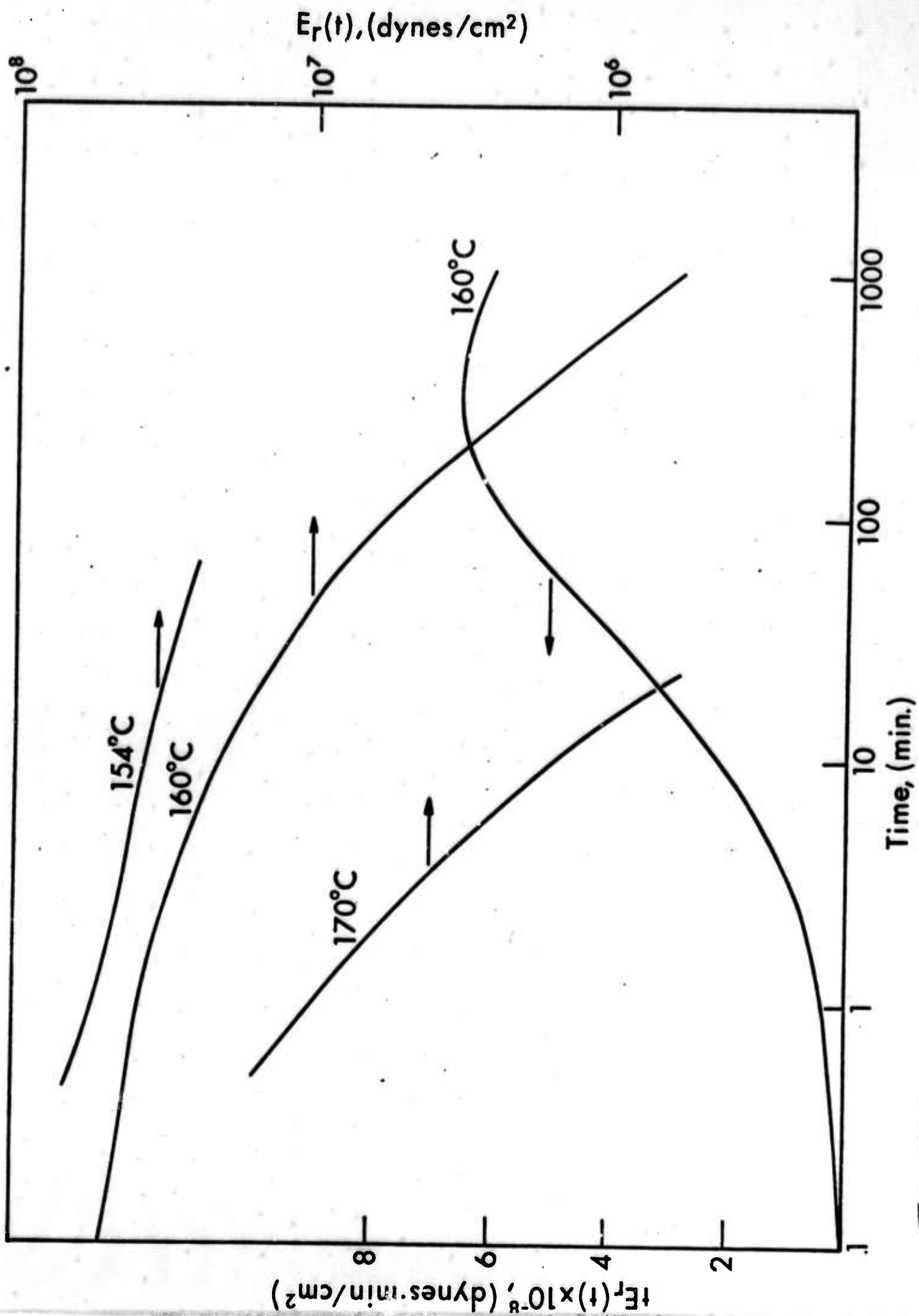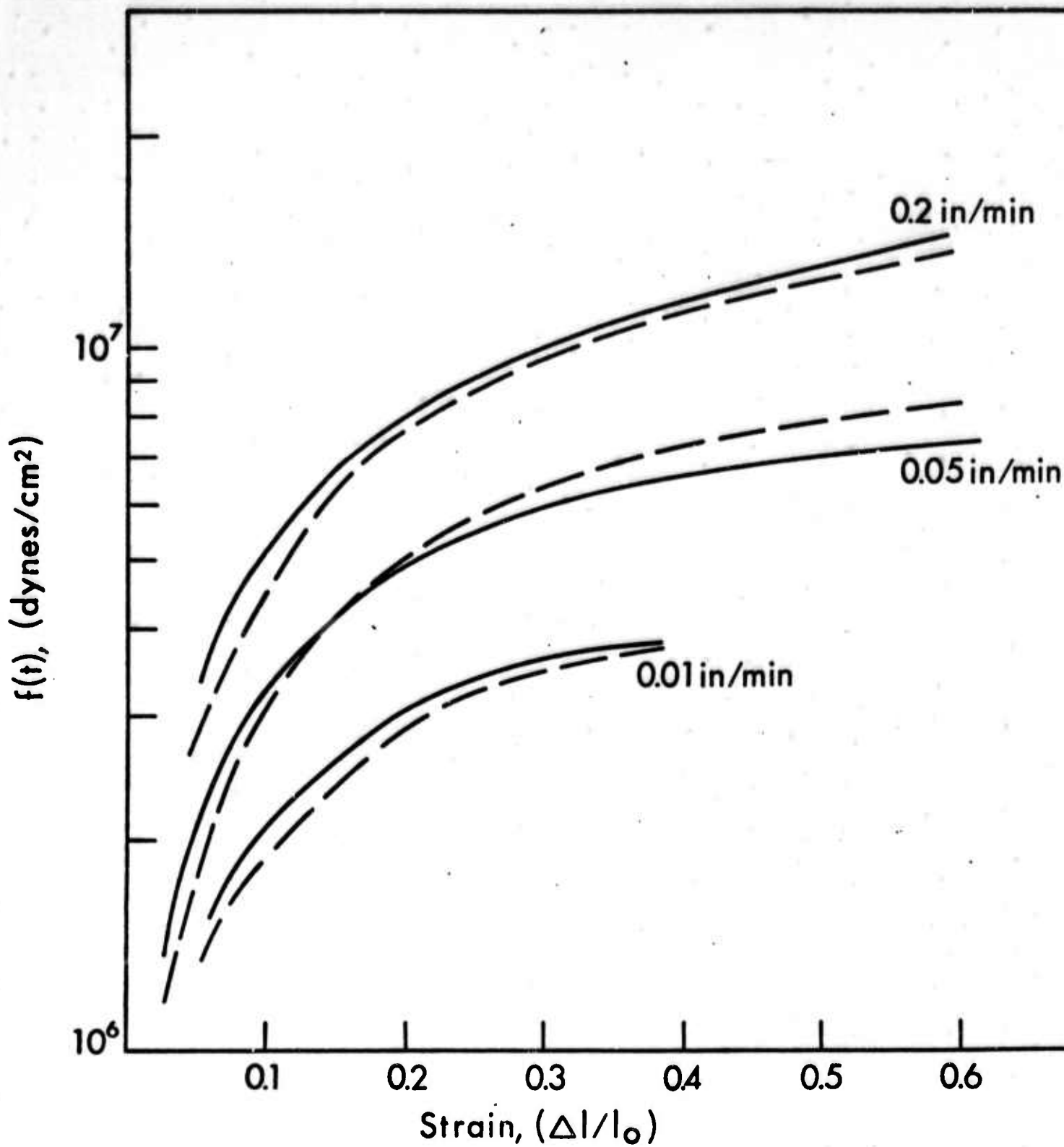
Fig. 3

**Fig. 4**

POLYCARBONATE 16(
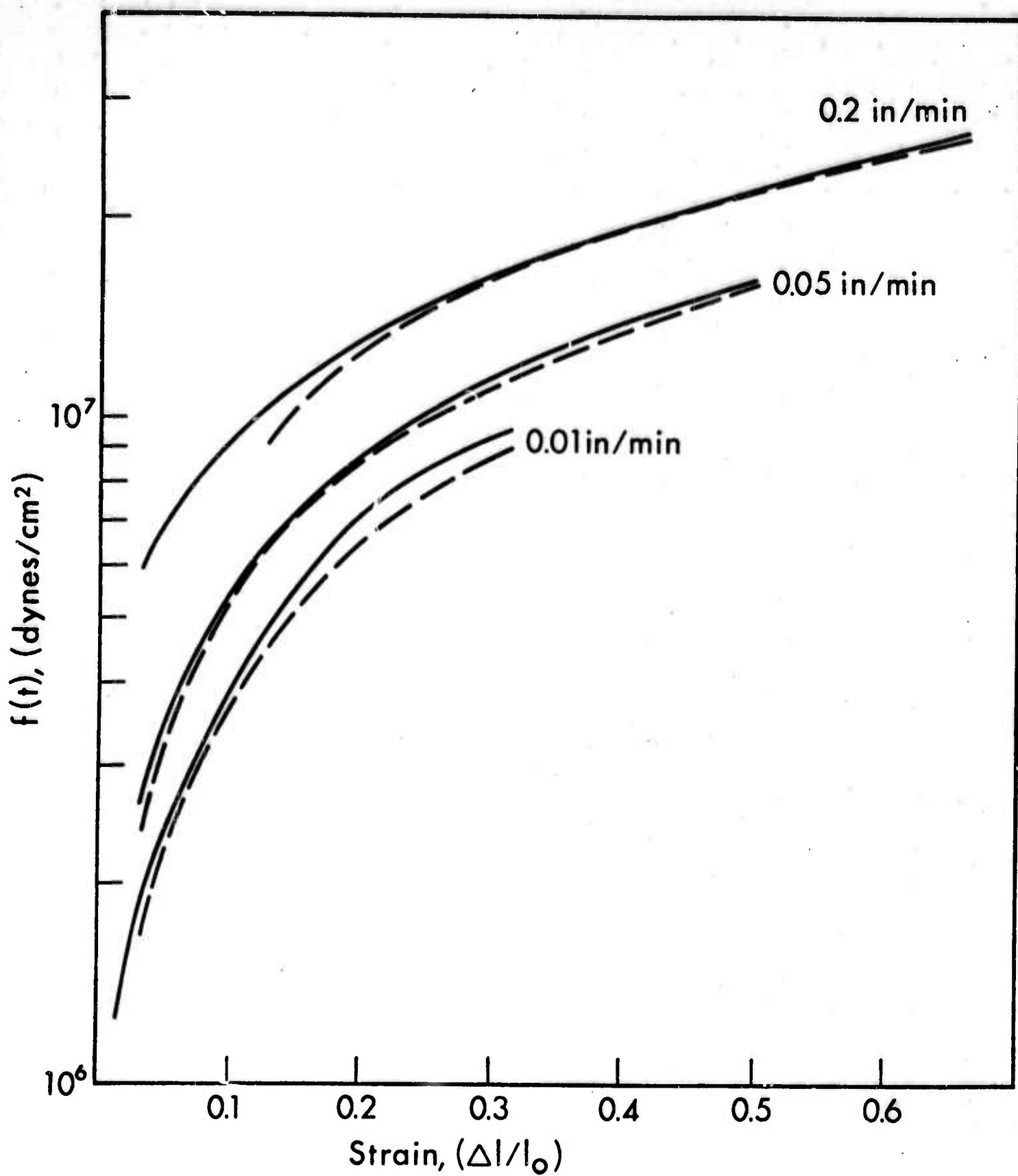
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**13. ABSTRACT**

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$epsilon(H) = \ln(\ell/\ell(o))$

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|---|---|---|---|---|---|---|
| | ROLE | WT | ROLE | WT | ROLE | WT |
| stress relaxation | | | | | | |
| polysulfone | | | | | | |
| polycarbonate | | | | | | |
| linear viscoelasticity | | | | | | |
| Maxwell-Wiechert body | | | | | | |

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