GENERALIZATION OF THE TEMPERATURE-STRAIN CHARACTERISTICS FOR POLYVINYL CHLORIDE UNDER TENSION

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A universal temperature-time characteristic of the stress-strain relation has been derived for polyvinyl chloride under uniaxial tension.

An evaluation of test data in terms of referred variables yields universal temperature-time characteristics of various properties of polymers, and the data obtained in the laboratory can thus be used for analyzing the behavior of polymers under processing conditions (temperature, strain, and rate of strain). Referred variables are reliable, however, only in describing linear strain modes in polymers. The feasibility of extending the temperature-strain characteristics of polymers to the nonlinear range has generally not been ascertained and must, for the time being, be considered individually for each specific case.

T. L. Smith [2] has obtained universal stress-strain curves for polyisobutylene under uniaxial tension within the nonlinear range 1.6-1.7 over a wide range of strain rates and temperatures. J. R. Meissner [3], however, has used the same referred variables as T. L. Smith without being able to obtain universal strain curves for threaded polyethylene at 150°C and at various constant strain rates.

Our aim here was to establish the feasibility of obtaining universal temperature-strain characteristics for polyvinyl chloride (PVC) under tension, up to large strains and within a wide range of strain rates and temperatures.

The objects of this study and the experimental technique have been described in an earlier article [1]. As before, we obtained curves of true stress (P) versus time (t) for PVC fibers under a constant elongation rate (v_c) and under a constant strain rate ($\dot{\varepsilon}_c$). The elongation rate is $v = dl/dt$. The strain rate is $\dot{\varepsilon} = v/l$, $\dot{\varepsilon}_0 = (dl/dt)(1/l)_{t \to 0}$. The instantaneous strain rate, expressed in terms of $\dot{\varepsilon}_0$, is equal to $\dot{\varepsilon}_0/\alpha$ with $\alpha = l/l_0$ denoting the total elongation factor. Correspondingly, $(\alpha - 1) = v_c t/l_0 = \dot{\varepsilon}_0 t$ and $v = l_0 \dot{\varepsilon}_c = \exp(\dot{\varepsilon}_c t)$.

Simultaneous stress relaxation and strain retention occurred in specimens subjected to elongation under various strain modes. The relaxation modulus was defined as $E_t = P/(\alpha - 1)$.

The test results could not be interpreted within a better than 95% confidence level.

It has been noted earlier [1] that the elongation characteristics, namely the true tension versus deformation curves for PVC at $v = v_c$ = const and with $\dot{\varepsilon} = \dot{\varepsilon}_c$ = const within the 90-160°C temperature range pass through maxima. The rate of increase in stress (modulus), the coordinates of the maximum tension point, and the elongation factor at fiber rupture all depend on the temperature and on the elongation rate cycle. The dependence of the mechanical properties of polymers on the test conditions has to do with the relaxation mechanism of polymer deformation and with the change in the polymer structure due to large deformations. The same factors affect also the trend of relaxation processes which occur after the deforming force has been removed at various elongation levels. The relevant results shown in Fig. 1 indicate that, at a given temperature and at given elongation levels lower than $\alpha_{p=\max}$ (corresponding to the maxima of the $P(\alpha)$ curves), the value of E_t does not deviate from the average by more than 10-15%.

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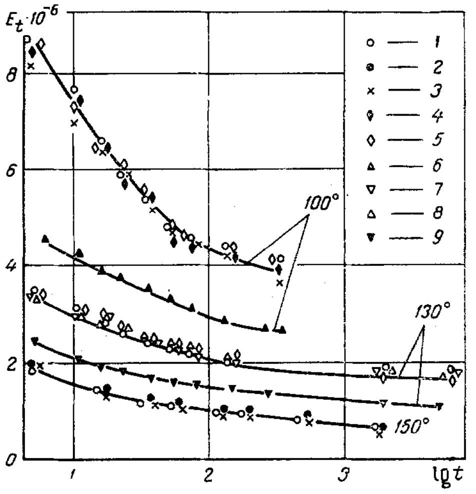

Fig. 1

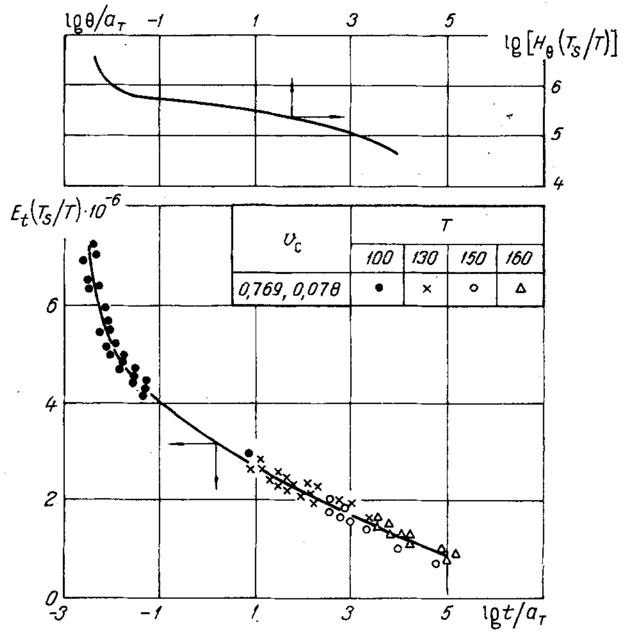

Fig. 2

Fig. 1. Relaxation modulus (N/m^2) as a function of the relaxation time, at a constant strain: 1) α = 3.3; 2) 4.5; 3) 5.5; 4) 9.0; 5) 10.0; 6) 11.5; 7) 12.5; 8) 14.0; 9) 16.5.

Fig. 2. Universal relations of relaxation modulus (N/m^2) and of relaxation spectrum (N/m^2 · sec) versus relaxation time, at constant elongation levels and temperatures.

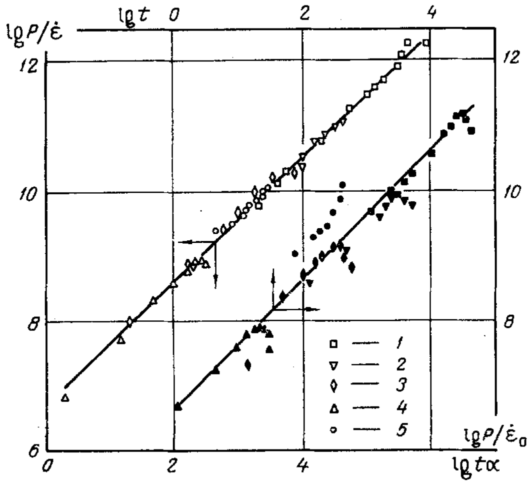

Fig. 3. Referred strain-**stress** (N/m^2) curves. Deformation temperature 130°C: 1) elongation rate v_c = 0.0079; 2) 0.078; 3) 0.769; 4) 8.33; 5) $\dot{\varepsilon}_c$ = 0.002. Black symbols refer to the same parameter values.

Relaxation slows down when $\alpha > \alpha_{p=\max}$, as is indicated by a comparison of the 100°C curve and the 130°C curve in Fig. 1. This confirms an earlier hypothesis that the transition through a maximum of the P(α) relation is due to stress relaxation as a result of a breakdown of the spatial linkage network, especially near the glass temperature.

This study of PVC deformation covered the explicitly nonlinear ranges. Furthermore, the relaxation moduli were determined after a momentary deformation as well as after a more or less prolonged deformation. Even though at a given temperature the $E_t(t)$ relations are invariant with respect to the elongation level, if $\alpha < \alpha_{p=\max}$, it is at least formally permissible to use the theory of linear viscoelasticity for calculating the relaxation spectrum by the integral equation

$$E_t = \int_{-\infty}^{\infty} H \exp(-t/\theta)\, d\ln\theta, \tag{1}$$

with t denoting the time through which relaxation is observed. Accordingly, the relaxation spectrum was calculated in the so-called first approximation, under the assumption that

$$H = -\left.\frac{dE_t}{d\ln\theta}\right|_{\theta=t}. \tag{2}$$

A universal curve of relaxation modulus versus time is shown in Fig. 2 along with a relaxation spectrum. These graphs represent data based on measurements of stress relaxation which has occurred at $\alpha = \alpha_{p=\max}$. The PVC specimens were deformed at elongation rates of 0.078 and 0.769 mm/sec at temperatures from 100 to 160°C. With 130°C as the reference temperature, the temperature coefficient a_T

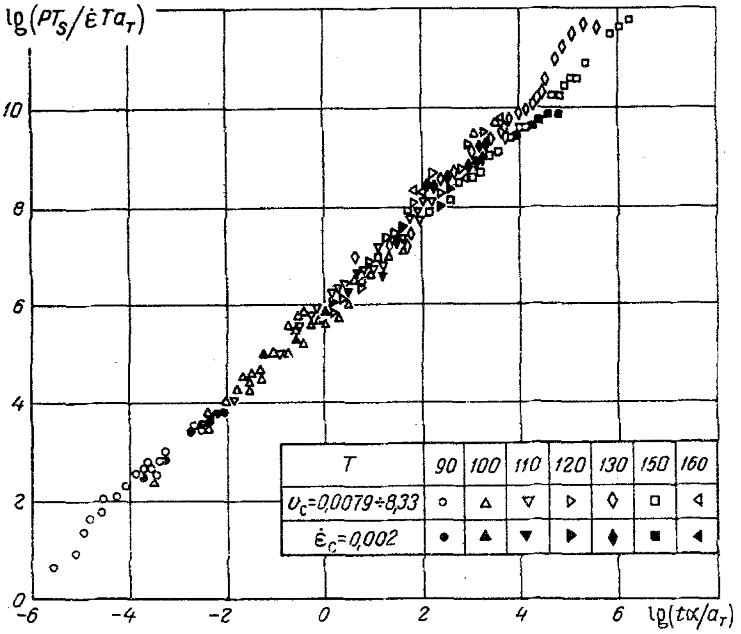

Fig. 4. Universal characteristic of PVC deformation modes in the superelasticity state.

was calculated by the VLF equation with universal values of the constants. According to Fig. 2, the relaxation spectrum of PVC is represented by a superelasticity plateau.

We will now analyze the stress-strain relation. According to the theory of linear viscoelasticity,

$$P/\dot{\varepsilon}_0 = \int_{-\infty}^{\infty} \theta H \left[1-\exp(-t/\theta)\right] d\ln\theta. \tag{3}$$

It follows from here that $P/\dot{\varepsilon}_0$ is a function of the deformation time. T. L. Smith has shown in [2] that, correspondingly, the empirical stress-strain relations can be described by a universal $P/\dot{\varepsilon}_0 = f(t)$ curve. Indeed, according to Fig. 3, the data for various rates v_c and small deformations fit this universal curve rather closely. The referred values of stress at strains larger than $\alpha_{p=\max}$ due to elongation at the rate v_c, as well as the values of $P/\dot{\varepsilon}_0$ at $\dot{\varepsilon}_0$, deviate appreciably from the universal relation. Considering that the strain rate changes during elongation at a rate v_c and that the total elongation factor varies with time differently in the v_c mode and in the $\dot{\varepsilon}_c$ mode of deformation respectively, it is worthwhile to represent Eq. (3) in the form

$$P/\dot{\varepsilon}_0\alpha = P/\dot{\varepsilon} = \int_{-\infty}^{\infty} \theta H \left[1-\exp(-t\alpha/\theta)\right] d\ln\theta. \tag{4}$$

According to Eq. (4), the relation between $P/\dot{\varepsilon}$ and $t\alpha$ should describe the test data in a form which is invariant with respect to the deformation mode. This has been made evident in Fig. 3.

With the aid of parameters $P/\dot{\varepsilon}$ and $t\alpha$ referred to the temperature, namely with $(P/\dot{\varepsilon})T_S/Ta_T$ and $t\alpha/a_T$, it is possible to derive a universal temperature-time relation for the referred stress. This is confirmed by the data in Fig. 4, which cover the variation of elongation rates through a factor of 1000 and a temperature range from 90 to 160°C. The results shown in Figs. 3 and 4 cover much higher values of the elongation factor (up to 15-17) than in [2] (1.6-1.7) and also data obtained with a constant strain rate.

NOTATION

P	is the true stress;
ε	is the strain;
l_0	is the initial length of specimen;
l	is the length of specimen at any instant of time;
α	is the total elongation factor;
$\alpha_{p=\max}$	is the elongation factor at maximum stress on $P(\alpha)$ curve;
v	is the elongation rate;

$\dot{\varepsilon}$	is the strain rate;
t	is the time;
T	is the absolute temperature;
E_t	is the relaxation modulus;
H	is the relaxation spectrum;
θ	is the relaxation time;
T_s	is the reference temperature, °K;
a_T	is the reference temperature coefficient.

LITERATURE CITED

1. V. D. Fikhman, V. M. Alekseeva, and G. V. Vinogradov, Inzh.-Fiz. Zh., 22, No. 4 (1972).
2. T. L. Smith, J. Polymer Sci., 20, 89 (1965).
3. J. R. Meissner, Reologica Acta, 8, 78 (1969).