INFLUENCE OF THE PRESSURE OF THE AMBIENT MEDIUM UPON THE VOLUME OF HIGH-POLYMER MATERIALS†

M. Rainer and R. Taxerman-Croser

UDC 532.135

A rheological analysis of the volume deformation of an amorphous high-polymer substance in the highly elastic state was made. It was shown that the dependence of the volume upon the hydrostatic pressure of the ambient medium can be formally expressed by models of Voigt —Kelvin and Maxwell bodies.

1. When an amorphous polymer is heated beyond the glass-transition temperature, the volume of the polymer changes in the course of time in dependence of the pressure of the ambient medium and the temperature. This well known fact has been described in Chapter 4.2 of the book by MacCalvey (1954) on the conversion of polymers. When at the time $t = t_0$ the pressure or the temperature is changed, the volume changes instantaneously from V_0 to V_1. This change continues in the course of time until the state of equilibrium volume V_e has been reached. As in the case of crystalline materials, the difference $V_i = V_1 - V_0$ results from changes in the intermolecular distances. The ensuing volume deformation is caused by time-dependent changes in the length of chain molecules. When the external pressure is removed at the time t^*, the volume decreases gradually to the initial value V_0.

2. Figure 1 shows the time dependence of the volume change and depends upon the actual process under consideration. The rheological aspect of the process can be discussed with two models. They are expressed by the structural formulas (Fig. 2) $I = H - K$ and $II = H/M$.

Let us discuss model I. The rheological equation of this model has the form

$$e = \frac{s}{2\mu_H} + e^{-\frac{\mu_K}{\eta}t}\left(e_0 + \frac{1}{2\eta}\int_0^t se^{\frac{\mu_K}{\eta}t}\,dt\right). \tag{2.1}$$

Differentiation with respect to time results in

$$\dot{e} = \frac{\dot{s}}{2\mu_H} + \frac{s}{2\eta} - \frac{\mu_K}{\eta}e^{-\frac{\mu_K}{\eta}t}\left(e_0 + \frac{1}{2\eta}\int_0^t se^{\frac{\mu_K}{\eta}t}\,dt\right). \tag{2.2}$$

When the expression of Eq. (2.1) is inserted in place of the term in parentheses, we obtain

$$\frac{\dot{s}\eta}{\mu_H} + s\,\frac{\mu_H + \mu_K}{\mu_H} = 2\eta\dot{e} + 2\mu_K e. \tag{2.3}$$

a. Let us consider the process after pressure has been removed from the body, i.e., when s and $\dot{s}$ have vanished at the time $t^* = 0$. Then, according to Eq. (2.3), we have

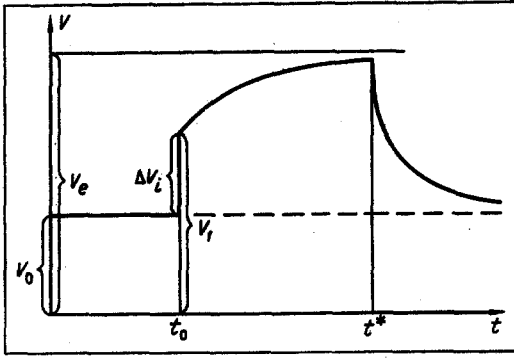$$\eta\dot{e} + \mu_K e = 0 \tag{2.4}$$

Fig. 1. Time dependence of the volume when hydrostatic pressure is applied at the time t_0 and removed at the time t*.

or

$$e = e^* \exp \left[-\frac{\mu_K}{\eta} t \right], \tag{2.5}$$

where e* denotes the deformation at t = t*.

Thus, the process can be characterized by the retardation time

$$T_{\text{ret}} = \frac{\eta}{\mu_K}. \tag{2.6}$$

b. Let us assume that the deformation is kept constant and amounts to e = e* after the time t = t* = 0, so that $\dot{e} = 0$. We obtain from Eq. (2.3):

$$\frac{\dot{s}\eta}{\mu_H} + s \frac{\mu_H + \mu_K}{\mu_H} = 2\mu_K e^* \tag{2.7}$$

or

$$s = \frac{2\mu_H\mu_K}{\mu_H + \mu_K} e + \left(s_0 - 2e^* \frac{\mu_H\mu_K}{\mu_H + \mu_K} \right) e^{-\frac{\mu_H + \mu_K}{\eta}t}. \tag{2.8}$$

This means that there exists a relaxation time

$$T_{\text{rel}} = \frac{\eta}{\mu_H + \mu_K}. \tag{2.8'}$$

Let us consider model II. This model has been used some time ago by Poynting and Thomson (1929). We have in this case

$$s + \dot{s} \frac{\eta}{\mu_M} = 2\mu_H e + 2\eta \frac{\mu_H + \mu_M}{\mu_M} \dot{e}. \tag{2.9}$$

a. As in the preceding section, we consider first the case

$$s = \dot{s} = 0 \tag{2.10}$$

or

$$\mu_H e + \eta \frac{\mu_H + \mu_M}{\mu_M} \dot{e} = 0. \tag{2.11}$$

Integration of this equation results in

$$e = e^* \exp \left[-\frac{\mu_M \mu_H t}{(\mu_M + \mu_H)\eta} \right]. \tag{2.12}$$

Consequently, there exists a retardation time

$$T_{\text{ret}} = \frac{\eta(\mu_M + \mu_H)}{\mu_M \mu_H}. \tag{2.13}$$

b. When we assume

$$e = e^*, \quad \dot{e} = 0, \tag{2.14}$$

we obtain with Eq. (2.9)

$$s + \dot{s} \frac{\eta}{\mu_M} = 2\mu_H e^*. \tag{2.15}$$

This differential equation has the solution

$$s = s\mu_M e^* + (s_0 - 2\mu_H e^*) \exp(-\eta t/\mu_M) \tag{2.16}$$

and the relaxation time

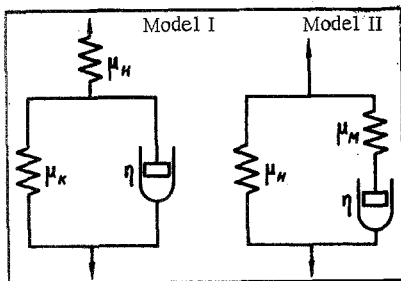$$T_{\text{rel}} = \frac{\eta}{\mu_M}. \tag{2.17}$$

Fig. 2. Rheological models for the volume deformation of polymers.

A comparison of Eqs. (2.3) and (2.9) allows us to establish a relation between the parameters of the two models in the form

$$\mu_H^{II} = \frac{\mu_H^I \mu_K^I}{\mu_H^I + \mu_K^I}$$

$$\mu_M^{II} = \frac{(\mu_H^I)^2}{\mu_H^I + \mu_K^I} \qquad (2.18)$$

$$\eta^{II} = \frac{\eta^I (\mu_H^I)^2}{(\mu_H^I + \mu_K^I)^2}$$

In analogous fashion, μ_K^I, μ_H^I, and η^I can be expressed by μ_H^{II}, μ_M^{II}, and η^{II}. This means that there exists a certain freedom to use either model I or model II.

3. In order to determine the influence of the pressure of the ambient medium upon the volume, we use model I. In our ensuing discussion, we will use Henke's definition (1931) of volume deformation:

$$e_V = \ln(V/V_0), \qquad (3.1)$$

where V_0 denotes the volume under atmospheric pressure ($p_0 = 0$). The rheological equation of model I can be expressed by Eq. (2.1), i.e.,

$$e_V = \frac{p}{k_H} + \frac{e^{-\int k_K \, dt/\zeta}}{\zeta} \int p e^{\int k_K \, dt/\zeta} \, dt. \qquad (3.2)$$

In our case $e_{V_0} = 0$.

We will assume that the quantity k is constant and that the parameter ζ is a function of p. This function will be determined below. Naturally, the quantity ζ is also a function of t. By differentiating Eq. (3.2), we obtain

$$\frac{\dot{p}}{k_H} + \frac{p}{\zeta}\left(1 + \frac{\dot{\zeta}}{k_H} + \frac{k_K}{k_H} \cdot \frac{\zeta - \zeta t}{\zeta}\right) = \dot{e}_V + e_V\left\{\frac{\dot{\zeta}}{\zeta} + \frac{k_K}{\zeta^2}(\zeta - \zeta t)\right\}. \qquad (3.3)$$

Let us assume that the dependence of η upon the free volume has the same form as the dependence of the shearing viscosity ζ upon the free volume, the dependence having been derived in 1951 by Doolittle. We are of the opinion that the mechanism of viscosity changes is the same in both cases. The dependence is expressed by the formula

$$\ln\left(\frac{\zeta}{\zeta_0}\right) = B\left(\frac{1}{f} - \frac{1}{f_0}\right), \qquad (3.4)$$

where ζ_0 denotes the viscosity under atmospheric pressure. Furthermore, we have

$$f = V_f/V. \qquad (3.5)$$

The pressure dependence of f is given by the differential equation

$$\frac{df}{dp} = \frac{d(V_f/V)}{dp} = -\beta_f + \beta f, \qquad (3.6)$$

where β_f and β are material constants given by the relations

$$-\frac{1}{V} \cdot \frac{dV_f}{dp} = \beta_f; \quad -\frac{1}{V} \cdot \frac{dV}{dp} = \beta \qquad (3.7)$$

at constant temperature.

The solution to Eq. (3.6) is

$$f = \frac{\beta_f}{\beta} + \left(f_0 - \frac{\beta_f}{\beta}\right) e^{-\beta p}. \qquad (3.8)$$

We obtain with Eq. (3.4)

$$\ln\left(\frac{\zeta}{\zeta_0}\right) = \frac{B\left(1 - e^{-\beta p}\right)\left(f_0 - \frac{\beta_f}{\beta}\right)}{f_0\left\{\frac{\beta_f}{\beta} + \left(f_0 - \frac{\beta_f}{\beta}\right)e^{-\beta p}\right\}} . \tag{3.9}$$

We have in the case $\beta p < 1$

$$e^{-\beta p} \simeq 1 - \beta p \tag{3.10}$$

and Eq. (3.9) transforms into

$$\ln\frac{\zeta}{\zeta_0} = \frac{\beta_p}{f_0\{f_0/(\beta f_0 - \beta_f)^{-p}\}} = \frac{p}{A(C-p)} . \tag{3.11}$$

This expression transforms into the formula of Ferry and Strutton (1960) for $\beta = 0$.

4. Let us consider three particular cases, namely:

a.

$$p = p_c \,(\text{const}). \tag{4.1}$$

Consequently,

$$\dot{\zeta} = \dot{p} = 0. \tag{4.2}$$

Then, according to Eq. (3.3), we have

$$\frac{p}{\zeta} \cdot \frac{k_H + k_K}{k_H} = \dot{e}_V - e_V \frac{k_K}{\zeta} . \tag{4.3}$$

The solution to this equation is

$$e_V = \frac{p_c}{k_H} + \frac{p_c}{k_K}\,(1 - e^{-k_K t/\zeta}). \tag{4.4}$$

Equation (4.4) expresses the dependence of the volume deformation upon the time when a constant pressure is acting.

b. Let us assume that the volume expansion is e_V^*. The pressure is assumed to decrease to atmospheric pressure, which is assumed to be zero:

$$p = 0. \tag{4.5}$$

We have in this case

$$\dot{\zeta} = 0, \quad \dot{p} = 0 \tag{4.6}$$

and obtain from Eq. (3.3)

$$\dot{e}_V - \frac{k_K}{\zeta_0}\,e_V = 0 \tag{4.7}$$

or, after integration,

$$e_V = e_V^* e^{-k_K t/\zeta_0} , \tag{4.8}$$

and the volume decreases with the retardation time:

$$T_{\text{ret}} = \zeta_0/k_K. \tag{4.9}$$

c. Let us assume that the volume expansion is e_V^* and is kept constant so that $\dot{e}_V = 0$. The pressure change $\dot{p}$ is in this case determined from Eq. (3.3):

$$\dot{p}\left\{\frac{p}{k_H}\,(1-A) + \frac{AC}{k_H} + e_V^* - \frac{k_K}{k_H}\,\frac{p}{\zeta}\,t - e_V^*\,\frac{k_K}{\zeta}\,t\right\} + \frac{A}{\zeta}\left\{1 + \frac{k_K}{k_H}\,(Cp + p^2)\right\} - \frac{k_K A}{\zeta}\,e_V^*\,(p - C) = 0. \tag{4.10}$$

Let us use this equation for extremely large pressures p, when $\zeta \to \zeta$ and $\dot{\zeta} = 0$, where ζ denotes the asymptotic value of ζ for $p = \infty$. Equation (4.10) assumes in this case the following form:

$$\frac{\dot{p}}{k_{\mathrm{H}}} + \frac{p}{\zeta}\left(1 + \frac{k_{\mathrm{K}}}{k_{\mathrm{H}}}\right) = e_V^* \frac{k_{\mathrm{K}}}{\zeta}. \tag{4.11}$$

We obtain after integration

$$p = \frac{k_{\mathrm{H}} k_{\mathrm{K}}}{k_{\mathrm{H}} + k_{\mathrm{K}}} e_V^* \left[1 - \exp\left\{-\frac{(k_{\mathrm{H}} + k_{\mathrm{K}})}{\zeta} t\right\}\right]. \tag{4.12}$$

The quantity p will decrease with the relaxation time:

$$T_{\mathrm{rel}} = \bar{\zeta}/(k_{\mathrm{H}} + k_{\mathrm{K}}). \tag{4.13}$$

CONCLUSIONS

It was shown that in an amorphous polymer, the rheological process of volume change produced by changes in the ambient pressure can be formally described by two equivalent models: model I = H − K and model II = H/M. The processes can be characterized by retardation and relaxation times, which, in turn, depend upon the absolute values of elasticity and viscosity.

NOTATION

A, B, C	are the material constants;
e	is the deformation;
e_V	is the volume expansion;
$\dot{e}$	is the deformation rate;
f	is the specific free volume;
$f_0 = f$	under atomospheric pressure;
H	Hooke;
K	Kelvin;
M	Maxwell;
s	is the stress;
$\dot{s}$	is the rate of stress change;
t	is the time;
T_{ret}	is the retardation time;
T_{rel}	is the relaxation time;
V	is the volume;
V_0	is the volume under atmospheric pressure;
V_f	is the free volume;
ζ	is the volume viscosity;
k	is the modulus of bulk elasticity;
μ	is the shear modulus;
η	is the coefficient of shear viscosity.