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

\[
e = \frac{s}{2\mu_H} + e^{-\frac{\mu_K}{\eta}} \left( e_0 + \frac{1}{2\eta} \int_0^t e^{\frac{\mu_K}{\eta}} dt \right).
\]

(2.1)

Differentiation with respect to time results in

\[
e = \frac{s}{2\mu_H} + \frac{s}{2\eta} - \frac{\mu_K}{\eta} e^{-\frac{\mu_K}{\eta}} \left( e_0 + \frac{1}{2\eta} \int_0^t e^{\frac{\mu_K}{\eta}} dt \right).
\]

(2.2)

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

\[
\frac{3\eta}{\mu_H} + s \frac{\mu_H + \mu_K}{\mu_H} = 2\eta e + 2\mu_K e.
\]

(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

\[
\eta e + \mu_K e = 0
\]

(2.4)

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

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

We have in this case

\[ s + \dot{s} = 2\mu_H e + 2\eta \frac{\mu_H + \mu_K}{\mu_M} \dot{\epsilon}. \]  

(2.9)

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

\[ s = \dot{s} = 0. \]  

(2.10)

or

\[ \mu_H e + \eta \frac{\mu_H + \mu_M}{\mu_M} \dot{\epsilon} = 0. \]  

(2.11)

Integration of this equation results in

\[ e = e^* \exp \left[ -\frac{\mu_H \mu_M}{\eta} t \right]. \]  

(2.12)

Consequently, there exists a retardation time

\[ T_{rel} = \frac{\eta (\mu_M + \mu_H)}{\mu_M \mu_H}. \]  

(2.13)

b. When we assume

\[ e = e^*, \dot{\epsilon} = 0, \]  

(2.14)

we obtain with Eq. (2.9)

\[ s + \dot{s} = 2\mu_H e^*. \]  

(2.15)

This differential equation has the solution

\[ s = 2\mu_H e^* + (s_0 - 2\mu_H e^*) \exp (-\eta/\mu_M) \]  

(2.16)

and the retardation time

\[ T_{rel} = \frac{\eta}{\mu_M}. \]  

(2.17)