

Effect of Molecular Weight on the Breaking Time of a Glassy Polymer

T. K. KWEI, *Bell Telephone Laboratories, Incorporated,
Murray Hill, New Jersey 07971*

Synopsis

An analysis of the dependence of the breaking time t_b of a glassy polymer under constant stress on the molecular weight of the polymer is made with the use of the theories by Bueche and by Cohen and Turnbull. It is concluded that $\log t_b$ is proportional to the degree of polymerization x when x is small but becomes independent of x at large values of x .

It is well known that the breaking time of a polymer under constant stress is shorter for a low molecular weight sample.¹ However, to my knowledge, no theoretical consideration has been proposed to explain the dependence of breaking time t_b on the degree of polymerization x of a polymer. It occurs to me that a combination of Bueche's theory² of breaking time and the transport theory of Cohen and Turnbull³ leads to an expression which relates breaking time to molecular weight.

In Bueche's treatment of the breaking time of a glassy polymer t_b is related to the segment jump frequency φ by eq. (1):

$$\ln t_b = -\ln \varphi - (V/kT)\sigma + \ln (2F^2/\pi^2\sigma^2V'^{1/3}) \quad (1)$$

where σ is the applied stress, and V is the volume of a segment which can hold a load F . A segment, as meant here, may contain many repeating units which participate in the chain relaxation process as one statistical entity. The jump frequency φ may be expressed in terms of the free volume by the theory of Cohen and Turnbull:

$$\varphi = \varphi_0 \exp \{ -V^*/V_f \} \quad (2)$$

where V_f is the average free volume per polymer unit, V^* is the critical amount of free volume necessary to permit the jump process to take place, and φ_0 is the pre-exponential factor.

If the dependence of V_f on molecular weight is written in a way similar to that used by Fox and Loshaek⁴ for the specific volume, one obtains:

$$V_f = [(x - 2)/x]V_i + (2/x)V_e \quad (3)$$

where V_e is the free volume associated with each terminal unit of the polymer chain, and V_i is that of the internal units. The quantity V_e is usually

considered to be much larger than V_t . A combination of eqs. (1), (2), and (3) yields:

$$\ln t_b = \frac{V^*x}{2V_e + (x-2)V_t} - \ln \varphi_0 - \frac{V}{kT} \sigma + \ln \frac{2F^2}{\pi^2 \sigma^2 V^{2/3}} \quad (4)$$

According to eq. (4), $\ln t_b$ is proportional to x when x is small and $2V_e \gg (x-2)V_t$. At very large values of x , $(x-2)V_t \gg 2V_e$, and $\ln t_b$ becomes independent of x .

In the application of the free volume formulation to the transport properties of a polymer in the glassy state, it is necessary to consider V_f as the local free volume which can be redistributed. Although eq. (4) gives a functional dependence of $\ln t_b$ on x , its numerical application is handicapped by the fact that very little is known about the magnitude of the free volume in the glassy state.

References

1. E. Gaube, *Kunststoffe*, **49**, 446 (1959).
2. F. Bueche, *Physical Properties of Polymers*, Interscience, New York, 1962, Chap. 11.
3. M. H. Cohen and D. Turnbull, *J. Chem. Phys.*, **31**, 1164 (1959).
4. T. G. Fox and S. Loshaek, *J. Polymer Sci.*, **15**, 371 (1955).

Résumé

Une analyse de la dépendance du temps de rupture t_b d'un polymère vitreux sous tension constante en fonction du poids moléculaire du polymère a été faite en utilisant la théorie de Bueche et de Cohen et Turnbull. On en conclut que le $\log t_b$ est proportionnel au degré de polymérisation x lorsque x est petit et devient indépendant de x pour de grandes valeurs de x .

Zusammenfassung

Eine Analyse der Abhängigkeit der Bruchdauer t_b eines glasigen Polymeren unter konstanter Spannung vom Molekulargewicht des Polymeren wird mit den Theorien von Bueche sowie von Cohen und Turnbull durchgeführt. Man kommt zu dem Schluss, dass $\log t_b$ bei kleinem Polymerisationsgrad x proportional zu x ist, jedoch bei grossen Werten von x unabhängig von x wird.

Received May 9, 1966
Prod. No. 1404