

Criterion of ultimate strength of fluid high polymers in uniaxial extension

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With increasing deformation rate, fluid high polymers lose, more or less sharply, their ability to accumulate irrecoverable deformations¹ and their behaviour becomes similar to that of cured rubbers². This is accounted for by the transition of polymers to the forced high-elastic state¹. From dynamic experiments involving large amplitudes of oscillating shear deformations it follows that such a transition is governed not only by the rate but also by the amount of deformation³. These features of the viscoelastic properties of high polymers reveal themselves most distinctly in the case of samples of narrow molecular mass distribution (*MMD*). Experiments devoted to the uniaxial extension of high polymers of narrow *MMD* have shown that the transition from the fluid to the forced high-elastic state occurs with certain combinations of deformation rates and deformations (see *Figure 12* in ref 4).

In the forced high-elastic state, the deformations are invariably limited, recoverable deformations being of decisive importance. The accumulation of a certain amount of recoverable deformation is accompanied by the rupture of high polymers. The relation between the rupture stress and the rupture recoverable deformation must be determined by the lower branch of the Smith failure envelope, independently of the loading conditions⁶.

To verify what has been said above, a series of experiments were carried out on 1,2-polybutadiene. Its molecular mass was 1.35×10^5 , $M_w/M_n = 1.75$. It contained 84% of 1,2- units and 7.8% of *trans* 1,4- units. The glass temperature of the polymer was -18°C .

The results of the experiments are shown in *Figure 1*, where the rupture stress σ^* is plotted along the ordinate and the rupture recoverable deformation ϵ_e^* (according to Hencky) along

the abscissa (see ref 7 for the estimation of ϵ_e). As seen from the *Figure*, in contrast to cured rubbers, fluid high polymers become capable of being ruptured only after the attainment of the 'critical' recoverable deformation, ϵ_e^{**} is reached. In the case under consideration $\epsilon_e^{**} = 0.44$. If the value ϵ_e^{**} was not attained in the experiments, we succeeded in providing the maximum possible degrees of extension (17-fold) on the apparatus used without rupture of the polymer. The conditions of rupture of fluid high polymers are determined as follows:

$$\frac{\sigma}{\epsilon_e - \epsilon_e^{**}} = E^* = \text{const} > 0$$

Here, E^* corresponds to the angular coefficient of the straight line (*Figure 1*) which expresses the invariant dependence of the stress on the rupture elastic deformation. Although σ and ϵ_e in the above relation are determined by the relaxation characteristics of the material and the time regime of deformation, from the data of the present work it however follows explicitly that the Deborah number alone cannot predict the critical deformation regimes leading to the rupture of non-cured high polymers.

The results obtained point to the fundamental importance of the failure envelope for non-cured linear flexible-chain polymers, which characterizes their strength properties, independently of the loading conditions. Another point of interest here is the determination of the components of total deformation, primarily the recoverable deformation, the importance of which was stressed since the first publications by Vinogradov *et al.*, which were devoted to the problems of extension of polymers^{7,8}.

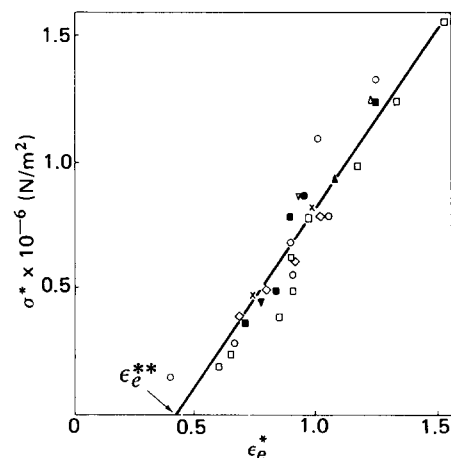


Figure 1 Fracture stress σ^* versus the fracture recoverable deformation, ϵ_e^* , under various loading conditions: \square = constant true stress, $t = +25^\circ\text{C}$; \blacksquare = $t = +10^\circ\text{C}$; \diamond = $t = +50^\circ\text{C}$; \circ = constant rate of extension deformation, $t = +25^\circ\text{C}$; \bullet = $t = +10^\circ\text{C}$; \times = constant rate of extension, $t = +25^\circ\text{C}$; \triangle = constant force, $t = 25^\circ\text{C}$; Complex loading conditions at $t = +25^\circ\text{C}$: ∇ = $\dot{\epsilon}_1 = 2 \times 10^{-3} \text{ sec}^{-1}$ for 30 sec = relaxation at constant deformation for 60 sec; $\dot{\epsilon}_2 = 0.5 \times 10^{-2} \text{ sec}^{-1}$ up to rupture. ∇ = $\dot{\epsilon}_1 = 0.5 \times 10^{-2} \text{ sec}^{-1}$ = relaxation at constant deformation for 60 sec; $\epsilon_1 = 2 \times 10^{-2} \text{ sec}^{-1}$ for 30 sec = relaxation at constant deformation for 30 sec. $\epsilon_2 = 2 \times 10^{-2} \text{ sec}^{-1}$ up to rupture

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