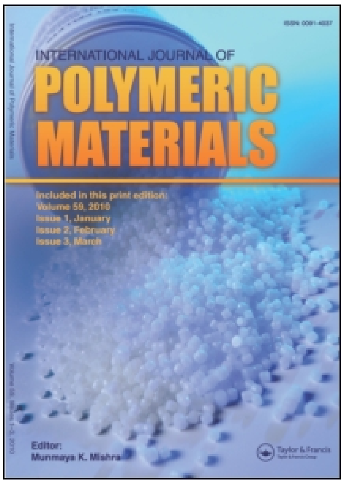

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Deformation and Strength Properties of 1, 2-Polybutadiene in Uniaxial Extension†

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It has been shown that the deformation-strength properties of 1,2-polybutadiene are determined at temperatures above the glass-transition temperature by its transition from the fluid state to the forced high-elastic and glassy states with increasing rate of deformation and stress. Here the determining role in the fracture of 1,2-polybutadiene is played by the high-elastic strain stored in it, and the regularities of its fracture are similar to those for rubbers.

INTRODUCTION

Investigators have become greatly interested over the last several years in the study of the extensional deformation and limiting fracture characteristics of linear polymers at temperatures above the glass-transition or melting temperature.[1–3] Such investigations enable one to examine the behaviour of polymers upon transition from the fluid state to the high-elastic and glassy states under the influence of the rate of deformation or the applied normal stress.[4] The majority of works on uniaxial extension have been carried out on polymers with a low glass-transition temperature (T_g), which complicates the attainment of the forced glassy state. The present work is devoted to the

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investigation of the deformation-strength properties of a polymer with a relatively high glass-transition temperature.

EXPERIMENTAL

We have investigated polybutadiene rubber (PB) produced with a butyllithium catalyst. The content of 1,2-units in the polymer is 84.5%, its viscosity-average molecular mass is 1.7×10^5, and the polydispersity ratio $\bar{M}_w/\bar{M}_n = 1.70$. According to the data of dynamic measurements at a frequency of 1 Hz the glass-transition temperature of PB is $-18°C$. The rubber did not crystallize either on deformation or on cooling.

Extension was carried out at a constant rate of deformation ($\dot{\varepsilon}$) and at a constant true stress (σ) over the temperature range from $-10°C$ to $+50°C$ on a device described earlier.[5] The dynamic characteristics were determined on the mechanical spectrometer DXП-2.[6]

RESULTS AND DISCUSSION

The extension of PB under the $\dot{\varepsilon}$ = const régime has shown that its behaviour depends, to a large extent, on the rate of deformation and temperature. As can be seen from Figure 1, which is a plot of stress versus strain at various temperatures and a single rate of deformation, with rise of temperature there are observed four different cases of the deformation of PB: 1—($+50°C$) with increasing deformation ε (the logarithmic measure of strain according to

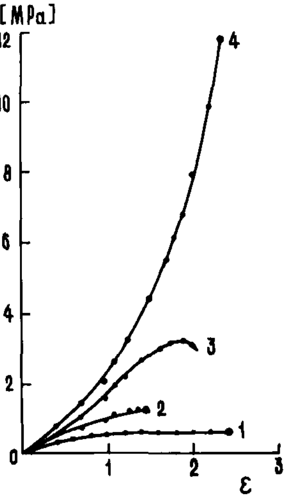

FIGURE 1 Stress versus strain for 1,2-polybutadiene at $\varepsilon = 5 \times 10^{-2} C^{-1}$ and at various temperatures: 1 = $+50°C$; 2 = $+25°C$; 3 = $+10°C$; 4 = $0°C$.

Hencky) there are established steady flow conditions under which σ is independent of deformation; 2—(+25°C), with increasing deformation the specimen is fractured before a steady flow is attained; 3—(+10°C), when a certain value of ε is reached, the specimen ceases to be uniform because of necking (shown by an arrow); the 4th case, which is observed at low temperatures (0°C), is again chacterized by the uniformity of extension and a strong dependence of stress on strain and ends up with a brittle rupture of the polymer. Tests conducted under isothermal conditions at various rates of deformation show that the increase of $\dot{\varepsilon}$ has the same qualitative effect on the character of deformation as the decrease of temperature. Under the conditions of constant true stress there were observed the same effects as at constant $\dot{\varepsilon}$.

All the cases of deformation of PB are illustrated by the curves of fracture deformation ε^* (Figure 2a) versus the temperature-reduced rate of deformation $\dot{\varepsilon}a_T$. This figure also shows the components of total fracture deformation, the recoverable component ε_e^* and the irrecoverable component ε_f^*. The $\varepsilon^*(\dot{\varepsilon}a_T)$ curve has an extremal character which is due to the successive transition of the polymer with increasing rate of deformation from the fluid to the forced high-elastic state (the region of the minimum—a sharp decrease of ε_f^*) and then to the forced glassy state (the region of the maximum—a brittle rupture of the polymer). The right portion of the curve with a maximum is

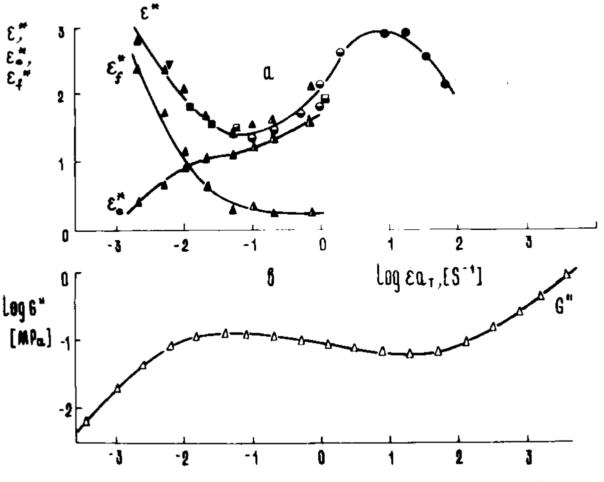

FIGURE 2 The fracture deformation ε^* and its recoverable and irrecoverable components, ε_e^* and ε_f^*, versus the rate of deformation (a); and the loss modulus versus frequency (b). The reduction temperature is +25°C. The signs used here and in the other figures correspond to the various test temperatures, and the half-filled signs represent the regions of neck formation.

similar to the well-known Smith fracture envelope obtained by Smith for rubbers.[7]

Lying between the minimum and the maximum of the $\varepsilon^*(\dot{\varepsilon}a_T)$ curve are the points corresponding to the deformations at which there begins a nonuniform extension of the specimen—the formation of a neck (half-filled signs). According to our data, this corresponds to the stress range of 1 to 10 MPa. The nonuniform deformation is probably associated with the decrease of the viscosity of PB, which directly precedes the necking.

It is also interesting that the $\varepsilon^*(\dot{\varepsilon}a_T)$ curve correlates qualitatively with the frequency dependence of the loss modulus on low-amplitude deformation (Figure 2b). The maximum of $G''(\omega)$ in Figure 2b corresponds to the transition of PB from to the forced high-elastic state, and the minimum to the transition to the glassy state. The correlation indicated is interesting from the standpoint of the possibility of predicting the variation of the fracture characteristics of a linear polymer on the basis of the results of dynamic low-amplitude tests.

The measurement of the dependence of the durability of the polymer under investigation, t^* (the time from the onset of deformation at constant stress up to the fracture of the specimen) on the stress (Figure 3) has shown that in a wide range of times and temperatures it is described well by the relation:

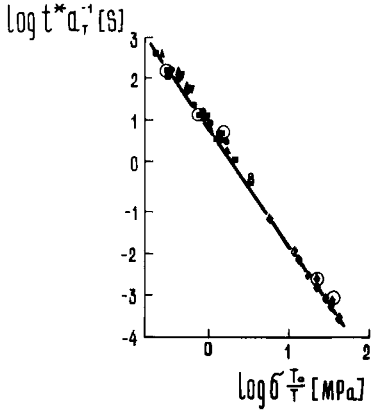

FIGURE 3 The durability of PB against stress. The reduction temperature is +25 °C.

$$t^* = k\sigma^{-\alpha}$$

which is well known to hold for rubbers; here $\alpha = 2.7$. It is characteristic that the results corresponding, with respect to time, to the beginning of neck formation are also described by this curve. This is evidence in favour of the general relaxational factors responsible for the fracture on uniform deformation and necking in linear polymers.

The study of the components of the total fracture deformation of PB shows that its fracture is unambiguously determined by the stored recoverable high-elastic deformation ε_e^*. This is seen from the data presented in Figure 4, which is a graph of the true fracture stress (σ^*) against the recoverable deformation for PB. From Figure 4 it follows that there exists a critical value of recoverable deformation (ε_e^{**}), below which the polymer samples are not fractured and a steady flow can always be set up. The value of ε_e^{**} is found by the intersection of the straight line of σ^* versus ε_e^* with the line characterizing the dependence of the stress on the recoverable deformation under steady flow conditions. The value of ε_e^{**} is close to 0.5. From this it follows that at a linear viscoelastic approximation

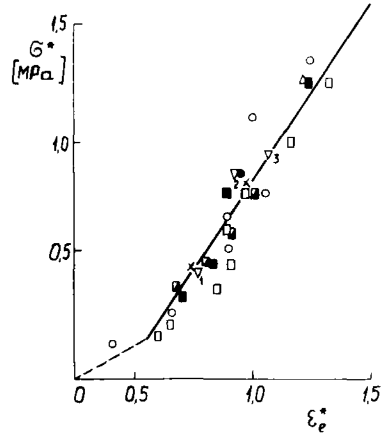

FIGURE 4 The dependence of the true fracture stress on the high-elastic component of fracture strain under various deformation conditions: σ = const (■ = +10°C; □ = +25°C; ◪ = +50°C); $\dot{\varepsilon}$ = const (◇ = +10°C; ○ = +25°C); the constant rate of extension (× = +25°C). and the constant force (△ = +25°C).

$$\dot{\varepsilon}_{cr}\theta_0 = \varepsilon_e^{**} \cong 0.5$$

where $\dot{\varepsilon}_{cr}$ is the critical value of the rate of deformation; when this critical value is reached, the steady flow régime becomes unattainable; $\theta_0 = \lambda/E$ is the characteristic relaxation time; λ and E are the initial values of viscosity and high-elasticity modulus on extension.

On the whole, the data obtained indicate that the deformation-strength properties of linear polymers at temperatures above the glass-transition temperature have a number of common features with the analogous properties of rubbers. Perhaps, these common features are due to the presence of a homogeneous fluctuating entanglement network in uncured rubbers, which is responsible for their deformation and strength properties, just as in the case of rubbers which have a network formed by chemical bonds.

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References

1. G. V. Vinogradov and A. Ya. Malkin, *Rheology of Polymers*, Khimiya, Moscow, 1977 (in Russian; an English translation will be available from Mir Publishers, Moscow, in 1980).
2. F. N. Cogswell, *Appl. Polym. Symp.*, **27**, 1 (1975).
3. A. N. Prokunin, N. G. Proskurnina, and O. Yu. Sabsai, *Mekhanika Polimerov*, **2**, 353 (1977).
4. G. V. Vinogradov, *Polymer*, **18**, 1275 (1977).
5. G. V. Vinogradov, V. D. Fikhman, and B. V. Radushkevich, *Rheol. Acta*, **11**, 286 (1972).
6. L. P. Ulyanov, V. M. Neimark, Yu. G. Yanovsky and S. I. Sergeenkov, *Zav. Lab.*, **11**, 1402 (1973).
7. F. R. Eirich and T. L. Smith, in: *Fracture. An Advanced Treatise* (edited by H. Libovitz), vol. 7, Academic Press, New York and London, 1972.
8. V. E. Gul', *Structure and Strength of Polymers*, Khimiya, Moscow, 1978.