

Transition of polymers from the fluid to the forced high-elastic and leathery states at temperatures above the glass transition temperature

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The transition from the fluid to the forced high-elastic (rubber-like or quasi-vulcanizate) state and then to the leathery state (that is between rubbery and glassy states**) has been systematically studied by increasing stresses and deformation rates, using an uncured high molecular-mass 1, 2-polybutadiene characterized by a rather high glass transition temperature (-18°C). Investigation of polymers in simple shear is possible up to critical stresses corresponding to the transition of fluid polymers to FHES. Uniaxial extension offers wide possibilities for characterizing polymers in FHES and FLS since it covers the range of 4-6 decades of deformation rates over the range of simple shear. The deformability of polymers is limited by their fracture even in FHES, and the fracture process is determined only by recoverable deformation. The failure envelope covering FHES and transition to FLS has been constructed and the long-term durability in the range of 7 decades of time measured. The maximum extensibility corresponding to the transition of the polymer to FLS is determined by the ultimate extensibility of macromolecular coils. Over a wide range of stresses the polymer behaves like a linear viscoelastic body. This makes it possible to correlate the data obtained for uniaxial extension and low-amplitude sinusoidal shear deformation, which is important for the prediction of fracture phenomena by means of the low amplitude non-destructive dynamic method.

Keywords Polymers; stress; deformation; extension; fracture; 1,2-polybutadiene; characterization

INTRODUCTION

Some 30 years after the principal features of the three physical states of polymers--the fluid, high-elastic (rubbery) and glassy states--had been determined^{1,2} investigators focused their attention mainly to the thermomechanics of the transition of polymers from one physical state to another. These transitions are most prominently manifested by linear polymers of high molecular mass (MM) and narrow molecular-mass distribution (MMD). With polymers of this type, in the region of temperatures exceeding the glass transition temperature (T_g), as the rate of deformation increases there can be observed transition from the fluid (FS) to the forced high-elastic (FHES) and the leathery states (FLS). These are relaxation transitions; the relaxation nature being responsible for the equivalence of the effect of temperatures and deformation rates.

Transition from the fluid to the forced high-elastic state is most easily detected³. These transitions manifest themselves externally in the fracture of polymeric systems as continuous media since in FHES they behave as

quasicured polymers whose deformability is invariably limited. Perhaps, this was first observed by Hutton⁴ who, however, examined the effect of the fracture of polymers during shear from the energy standpoint and did not tie in this effect with transition of the polymer to the rubbery state.

It is essential that linear polymers of high MM and narrow MMD behave, at least judging by viscosity measurements, as linear viscoelastic bodies at $T \gg T_g$ over a wide range of stresses. This has been established most convincingly⁵ with polybutadienes (PB) of narrow MMD over a wide temperature range.

The most important specific features of the behaviour of polymers of narrow MMD have been described for the homologous-polymer series of PB and polyisoprenes (PI) and concentrated solutions of these polymers, in research^{3,6-17} carried out in the Laboratory of Polymer Rheology of the Institute of Petrochemical Synthesis of the USSR Academy of Sciences. It has been shown in experiments using capillary rheometers that the transition of polymers from FS to FHES takes place at certain critical shear stresses which are practically independent of M and temperature. To the critical regimes of deformation of polymers there correspond certain

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** FHES and FLS in abbreviated form

characteristic phenomena. The manner in which they manifest themselves depends on the test method. When a constant pressure drop is specified, there is observed a sudden increase in the flow rate which may be thousand-fold and even greater for polymers of very high MM . This is the 'spurt' effect⁶. In the constant-rate method, there is corresponding to the spurt effect a sharp decrease of the pressure gradient in ducts⁷. The critical stresses constitute an important characteristic of homologous-polymer series.

Cinematographic recording of the process of deformation of the polymers under consideration in ducts has demonstrated^{8,9} that the spurt effect reveals itself as a break in the continuity of polymers within the zone of the highest stresses at the walls, which is regarded as the wall slippage. The spurt effect is thought to be the result of the transition of polymers from FS to FHES^{6,7}.

A phenomenon analogous to the spurt in capillary rheometers is also observed in instruments with coaxial cylinders¹⁰.

Since the transition of polymers from FS to FHES upon shear is accompanied by a break in the polymer continuity and by the loss of contact between the polymer and the confining walls, the investigation of the deformability and properties of polymers in FHES and, particularly in FLS, becomes impossible. Therefore, the study of the behaviour of polymers on extension is of prime importance. Especially important results are obtained in the simplest case of uniaxial extension under the conditions of constant deformation rates or true stresses (but not at constant rates of stress/strain). Under these conditions there have been easily realized draw ratios reaching 1700%.

The critical shear stresses at which a spurt is observed in the case of uniaxial extension correspond to the stresses at which there is observed a sharp decrease of the ability of polymers to undergo irrecoverable deformation. Under these critical extension conditions the specimens are fractured. It has been pointed out³ that this takes place at stresses of the order of 0.1–1 MPa.

In experiments with PB and PI of narrow MMD , which were obtained by anionic polymerization and which contained small amounts of 1,2 and 3,4 groups and had very low T_g , their behaviour was studied both in the region of the transition from FS to FHES and in the region of FHES^{15–17}. However, for the polymers now under discussion the conditions of their transition from FHES to FLS have not been established; we are here concerned with the solution of these problems.

Experiments involving oscillating shear of large amplitudes have shown that the transition from FS to FHES is governed not only by the rate but also by the amount of deformation¹⁰. Since in the region of transition from FS to FHES recoverable deformations become determinative, it would be expected that it is precisely these deformations which determine the conditions of polymer fracture. It will be shown below that this is actually the case. Taking this into account, one should determine how the fracture process is affected by the manner and sequence in which the recoverable deformations are specified.

It has been shown that high molecular-mass PB and PI with narrow MMD while in a FHES behave, up to fracture, as linear viscoelastic bodies^{15–17}. This suggests comparing the results of investigations of such polymers

under the conditions of low amplitude oscillating shear (harmonic vibrations) and uniaxial extension, the more so that from experiments carried out under steady shear flow conditions it is known that there is a quantitative correlation between the frequency dependence of the loss modulus and the dependence of shear stress on the rate of deformation⁷.

Considering the possibility of studying the transition of polymers from FHES to FLS, one should be able to construct a Smith failure envelope¹⁸ for uncured polymers.

In experiments involving the extension of monodisperse polystyrenes at temperatures above T_g there has been observed neck formation¹⁹, as also obtained in experiments with high density polyethylene²⁰ and polyisobutylene²¹. It has also been repeatedly noted that with increasing rate of deformation the deformation again becomes stable beyond the necking region²². The problem was to determine how general these phenomena are.

From experiments with amorphous glassy and crystalline polymers it is well known how the fracture of materials is affected by the liquid medium²³ and it is interesting to investigate the extension of PB in various liquid media. For this purpose convenient media are propyl and isopropyl alcohols.

All the problems put forth above are most conveniently studied with a polymer of relatively high T_g . Accordingly, we chose, for our investigation, PB containing a large number of 1,2-groups.

EXPERIMENTAL

Materials

For this investigation we used a specimen of polybutadiene (PB) produced with a sec-butyllithium catalyst: the polymer contained 84.5% of 1,2-units. The viscosity average molecular mass (determined from the intrinsic viscosity in toluene²⁴) was 1.70×10^5 and the polydispersity ratio \bar{M}_w/\bar{M}_n (determined by g.p.c.) was 1.7. The glass transition temperature was -18°C from data provided by dynamic investigation carried out at a frequency of 1 c/s. The polybutadiene did not crystallize either when deformed or when cooled.

Experimental techniques

Uniaxial extension was carried out at a constant rate of deformation ($\dot{\epsilon}$) and at a constant true stress (σ) over a temperature range of -10° to $+50^\circ\text{C}$. The instruments used have already been described^{25,26}. We made use of logarithmic measures of strain according to Hencky: $\epsilon = \ln l/l_0$, $\epsilon_e = \ln l/l_f$, $\epsilon_f = \ln l_f/l_0$, where ϵ is the total deformation; ϵ_e and ϵ_f are its recoverable and irrecoverable components; l_0 is the initial and l and l_f are the total and irrecoverable components of the specimen length at a given moment of time. The total deformation was resolved into the irrecoverable and recoverable components in the same manner as reported in the literature²⁷. The dynamic characteristics on low-amplitude deformation were determined by means of the mechanical spectrometer²⁸ and the flow curves on shear were measured on a constant-pressure capillary viscometer²⁹.

The experiments were carried out in water (an inert medium), propyl and isopropyl alcohols. According to the

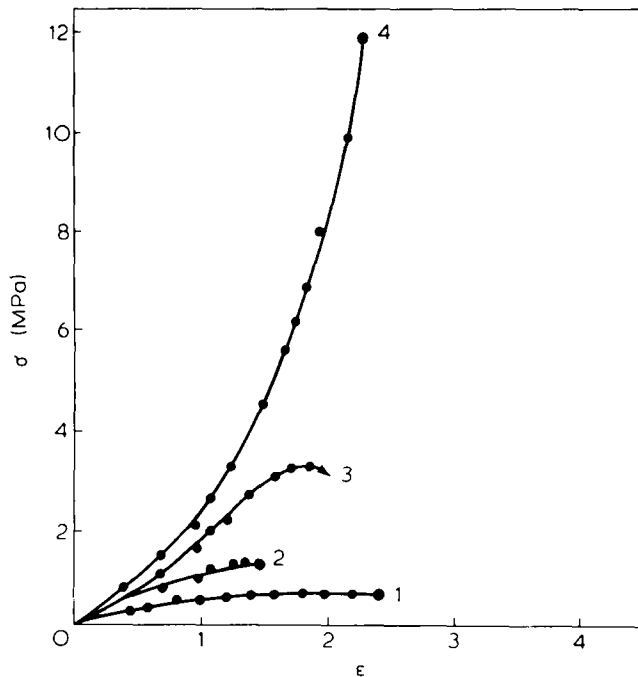


Figure 1 Dependence of true stress on total deformation for polybutadiene (the rate of total deformation is equal to $5 \times 10^{-2} \text{ s}^{-1}$) at various temperatures: 1, +50; 2, +25; 3, +10; 4, 0°C

results of equilibrium swelling at temperatures of +10 and +25°C the polybutadiene contained not more than 1–2% of the alcohols.

RESULTS AND DISCUSSION

Strain characteristics of 1,2-polybutadiene

The investigation of PB under the $\dot{\epsilon} = \text{constant}$ regimes has shown that its behaviour is strongly dependent on temperature. Four cases of deformation of PB are observed, as seen from the data presented in Figure 1: (1) with increasing amount of deformation there is attained a steady flow at which σ does not depend on the value of $\dot{\epsilon}$ (50°C); (2) with increasing amount of deformation the specimen undergoes fracture before a constant value of σ is attained (25°C); (3) when a certain value of σ is reached, the uniform deformation of the specimen is disturbed because of the neck formation the region of the maximum on the $\sigma(\epsilon)$ curve for 10°C; (4) the $\sigma(\epsilon)$ dependence observed at 0°C is characterized by the uniform extension are a strong dependence of stress with deformation by the brittle rupture of the polymer.

The experiments carried out under isothermal conditions at various rates of extension show that the increase of $\dot{\epsilon}$ (Figure 2) has the same qualitative effect on the mode of deformation of PB as the fall of temperature (Figure 1).

Creep of PB

Under the creep conditions $\sigma = \text{constant}$ depending on the specified value of σ , there was also observed the attainment of the steady-state deformation regimes, neck formation and brittle fracture. Necking during the deformation of 'fluid' polymers has been reported in the literature^{19,20,21}.

In the case of linear viscoelasticity³⁰,

$$\sigma(t) : \dot{\epsilon} = 3 \int_{-x}^{+x} \theta H(\theta) (1 - e^{-t/\theta}) d \ln \theta \quad (1)$$

where $H(\theta)$ is the relaxation time spectrum on shear. From this it follows that the deformation curves for linear viscoelastic bodies can be generalized (master curves are thus obtained) when represented in the coordinates $\sigma/\dot{\epsilon}\lambda_0$ vs. $t a_T$. Here λ_0 is the initial value of extensional viscosity at the test temperature; $t = \epsilon/\dot{\epsilon}$, where $\dot{\epsilon}$ is the specified constant rate of deformation; a_T is the temperature shift factor. As will be shown below, the value of the parameter a_T is determined in all the cases under consideration by the temperature dependence of the initial viscosity. The values of λ_0 are taken from Figure 3 which was plotted according to the data of creep measurements under the $\sigma = \text{constant}$ conditions, the viscosity being equal to $\sigma/\dot{\epsilon}_f$, where $\dot{\epsilon}_f$ is the rate of accumulation of irrecoverable deformation. In Figure 3 and all the subsequent figures the half-filled points correspond to the beginning of the necking process. From the data presented in Figure 3 follows the constancy of extensional viscosity up to high values of σ , of the order of 0.1–2.0 MPa, which is typical of high molecular-mass polymers which are not highly polydisperse. The values of $H(\theta)$ were determined by the Ninomiya-Ferry method³¹ from the frequency

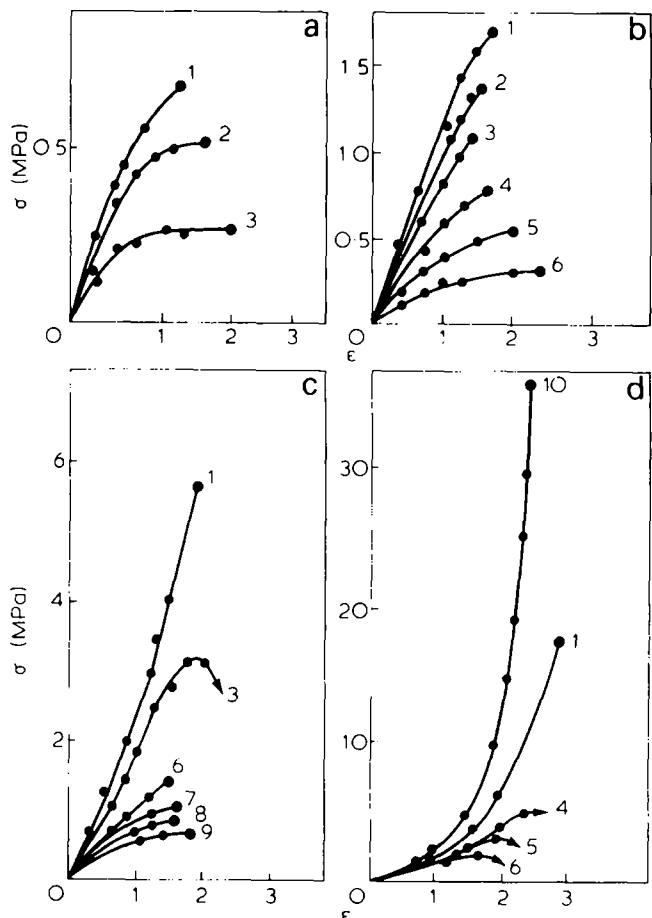


Figure 2 Dependence of true stress on total deformation for polybutadiene at different temperatures: a, +50; b, +25; c, +10; d, 0°C; and rates of total deformation: 1, 2×10^{-1} ; 2, 1×10^{-1} ; 3, 5×10^{-2} ; 4, 2×10^{-2} ; 5, 1×10^{-2} ; 6, 5×10^{-3} ; 7, 2×10^{-3} ; 8, 1×10^{-3} ; 9, 5×10^{-4} ; 10, $4 \times 10^{-1} \text{ s}^{-1}$

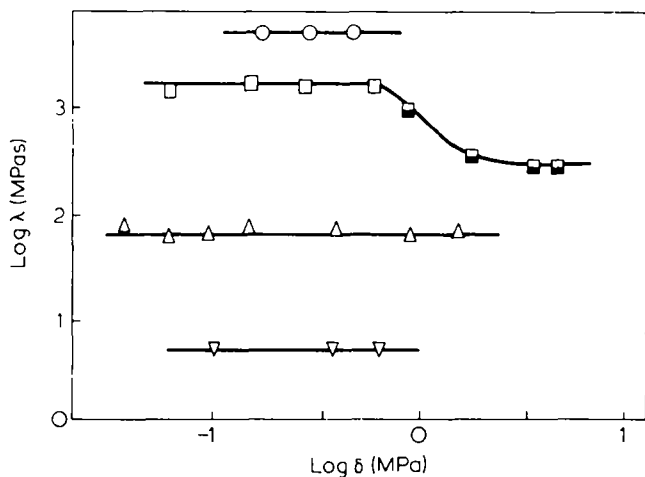


Figure 3 Dependence of extensional viscosity on stress at different temperatures: \circ , 0°C ; \square , $+10^\circ\text{C}$; \triangle , $+25^\circ\text{C}$; ∇ , $+50^\circ\text{C}$. The half-filled points here and in the subsequent figures correspond to the moment of neck formation

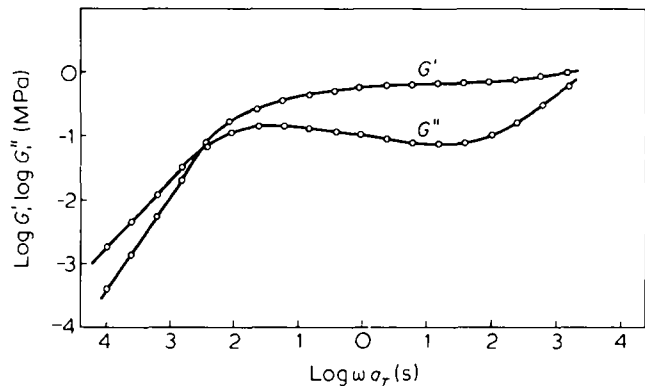


Figure 4 Frequency dependence of loss and storage moduli for polybutadiene. The reduction temperature here and in the subsequent figures is equal to $+25^\circ\text{C}$

dependences of the loss modulus (G'') and the storage modulus (G') given in Figure 4.

The master curve for extension apparent viscosity normalized by its initial value. Figure 5 presents the master time curve of the parameter $\sigma/\dot{\epsilon}\lambda_0$, where $\dot{\epsilon}$ is the rate of total deformation. In Figure 5 and all subsequent figures data corresponding to fracture are designated by filled points. Because of the large number of rates of deformation used, it is impossible to single out in Figure 5 the data for each of them by using a separate symbol.

From Figure 5 it follows that the points for different temperatures and rates of deformation are concentrated on the curve calculated in accordance with equation (1), which is evidence of the linear viscoelastic behaviour of PB up to the moment of fracture or neck formation during extension over a wide range of $\dot{\epsilon}$.

Fracture and 'spurt' process in 1,2-PB

Transition to the conditions of deformation under which PB undergoes brittle rupture causes a departure from the linear viscoelastic behaviour. This departure proves to be the more considerable as the higher is the rate of deformation itself and the closer the test temperature is to the glass temperature of the polymer. What has been said corresponds to the points located on the broken

curves in the left bottom part of the graph. It should be noted here that the strongest departure from the linear behaviour is typical at stresses exceeding 10 MPa.

Now considering the fracture of PB, Figure 6 is a plot of the true fracture stress and the stress corresponding to the beginning of neck formation versus the reduced rate of deformation (reduced to 25°C). Figure 6 also shows the dependence of shear stress (τ) on the rate of shear ($\dot{\gamma}$) marked by crosses and a broken line. The horizontal portion of the $\tau(\dot{\gamma})$ curve corresponds to the beginning of development of a spurt^{6,7}. The 'spurt'—a sharp increase of the flow rate in movement of the polymer in the duct, occurs as a result of the fracture of the polymer in the wall layer, which is regarded as the slippage of the polymer relative to the duct walls.

Attention should be focused on the fact that the $\tau(\dot{\gamma})$ curve is shifted relative to the true position so that at $\dot{\epsilon} = \dot{\gamma}$ the condition $3\tau = \sigma$ is satisfied.

An increase in the rate of deformation leads to a monotonic increase of the stress causing the fracture of PB or corresponding to the beginning of neck formation. From the data given in Figure 6 it is seen that under

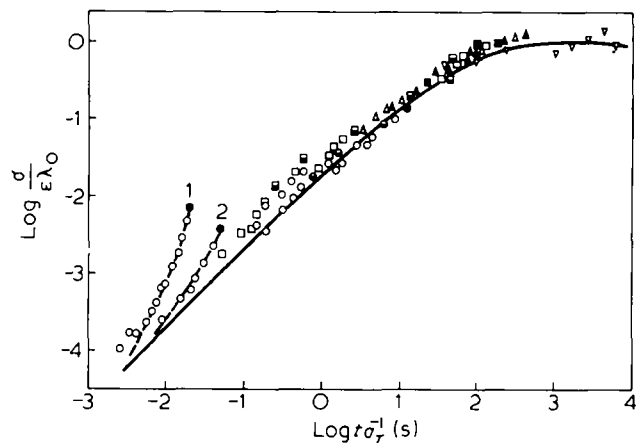


Figure 5 Dependence of reduced true stress on reduced time under prestationary and steady-stage (unfilled points), fracture (filled points) regimes and under the conditions of neck formation on extension as compared with the linear viscoelastic deformation of polybutadiene (the solid line). Broken line 1 corresponds to 0°C and $\dot{\epsilon} = 4 \times 10^{-1} \text{ s}^{-1}$; 2, 0°C , $\dot{\epsilon} = 2 \times 10^{-1} \text{ s}^{-1}$. The temperature designations are the same as in Figure 3

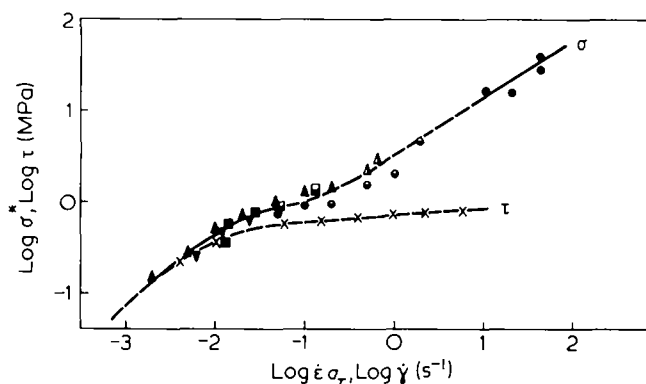


Figure 6 Dependence of the true fracture stress on the rate of total deformation. The designations are the same as in Figures 3 and 5. The dependence of shear stress on the rate of shear (broken line)

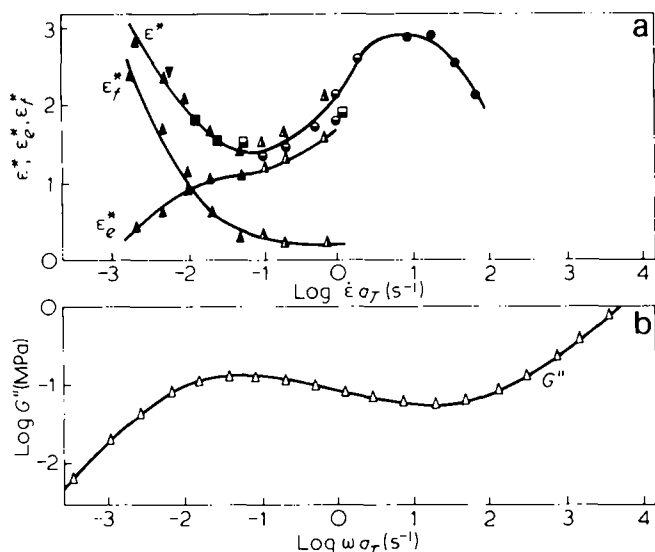


Figure 7 Dependence of total fracture deformation and its recoverable and irrecoverable components on the rate of total deformation. The designations are the same as in Figures 3 and 5; (b) the dependence of loss modulus on frequency

extension conditions the behaviour of the polymer can be traced at stresses which exceed by a factor of thousands and tens of thousands those stresses corresponding to the development of a spurt during shear.

Figure 7a shows the dependence of the total fracture deformation and its recoverable and irrecoverable components on the rate of deformation. The data of Figure 7a cover a wide range of $\dot{\epsilon}$ from the critical values corresponding to the development of fractures in the specimen and neck formation to the brittle fracture, which is evidence of the transition to FLS. Such a relationship has been obtained for the first time for uncured polymer. As has been shown³, such a change of the deformations on extension is associated with the transition of the polymer from the fluid state to FHES and FLS.

The transition from FS to FHES is connected with the suppression of the fluidity of the polymer with increasing $\dot{\epsilon}$ and with development of large recoverable deformations, which are, however, always limited in magnitude, leading to fracture of the polymer. The rapid decrease of the irrecoverable component (ϵ_f^*) and the increase of the recoverable component (ϵ_e^*) of fracture deformations are responsible for the appearance of a minimum on the $\epsilon^*(\dot{\epsilon}a_T)$ curve. Further transition to FLS makes difficult the development of viscoelastic deformations, as a result of which a maximum appears on the $\epsilon^*(\dot{\epsilon}a_T)$ curves and the fracture deformation decreases.

Correlation of extension and low amplitude dynamic data

As regards the maximum of high values of $\dot{\epsilon}$, this is typical of cured elastomers¹⁸. It should also be noted that the maximum on the $\epsilon^*(\dot{\epsilon}a_T)$ curve was obtained for melts of monodisperse polystyrenes¹⁹.

In the case of shear deformation of high-molecular-mass polymers of narrow *MMD* the transition from the fluid (FS) to the forced high-elastic state (FHES) is expressed as a correlation between the flow curves and the frequency dependence of the loss modulus up to the maximum G''_{max} . Here it is assumed that the circular frequency is equal to the shear rate under steady flow conditions.

From the data of Figure 7a and b it is seen that there is a correlation between the $\epsilon^*(\dot{\epsilon}a_T)$ and $G''(\omega a_T)$ dependences. The maximum of the $G''(\omega a_T)$ dependence corresponds closely to the minimum at the $\epsilon^*(\dot{\epsilon}a_T)$ curve. The minimum on the $G''(\omega a_T)$ curves corresponds to the maximum on the $\epsilon^*(\dot{\epsilon}a_T)$ curve. From the comparison of the data presented in Figures 7 and 4 it is seen that the maximum of the function $\epsilon^*(\dot{\epsilon}a_T)$ corresponds approximately to the midpoint of the high elasticity plateau and the initial stage of the transition of the polymer to the leathery state (FLS).

Unfortunately, the sample of 1,2-PB used was of rather wide *MMD*. This must have been responsible for the maximum and minimum being not too sharp on the $G''(\omega a_T)$ curve and for the modest correlation between the functions $G''(\omega a_T)$ and $\epsilon^*(\dot{\epsilon}a_T)$. A much better correlation between the functions in question, at any rate, for the maximum of the function $G''(\omega a_T)$ and for the minimum of the function $\epsilon^*(\dot{\epsilon}a_T)$ is seen in Figure 8 which presents data for polyisoprenes of narrow *MMD*^{6,16,17}.

In the linear viscoelastic approximation, under the transition regimes of extension at $\dot{\epsilon} = \text{constant}$ the dissipating part of the work of deformation up to fracture is determined by the following expression^{3,2}:

$$W_{dis} = 3(\dot{\epsilon})^2 \int_{\theta}^{\infty} \theta^2 H(\theta) [t:\theta - 3/2 + 2 \exp(-t:\theta) - 1/2 \exp(-2t:\theta)] d \ln \theta \quad (4)$$

When $t > \theta$, the above equation reduces to

$$W_{dis} = 3(\dot{\epsilon})^2 \int_{\ln t}^{\infty} \theta H(\theta) d \ln \theta \quad (5)$$

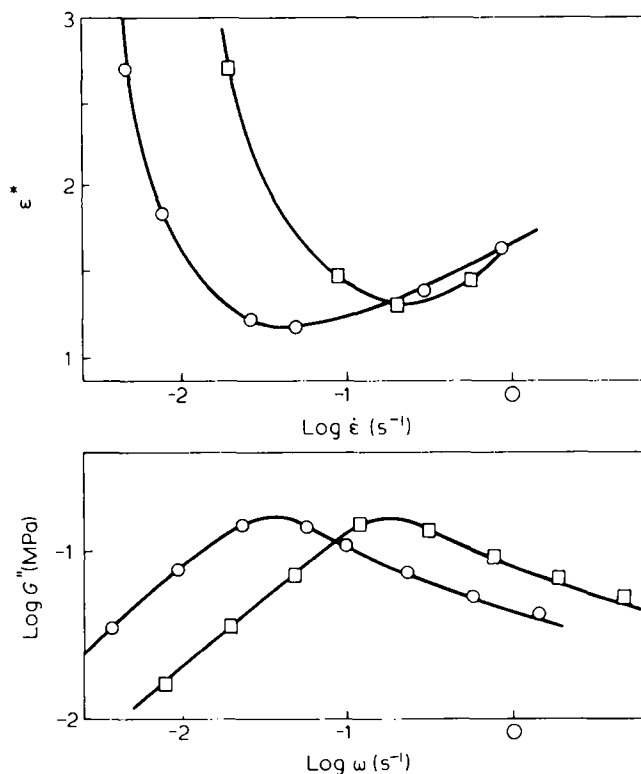


Figure 8 Dependence, at 25°C, of total fracture deformation on the rate of total deformation and of the loss modulus on frequency for polyisoprenes with the following molecular masses: O, 5.75×10^5 ; □, 3.8×10^5

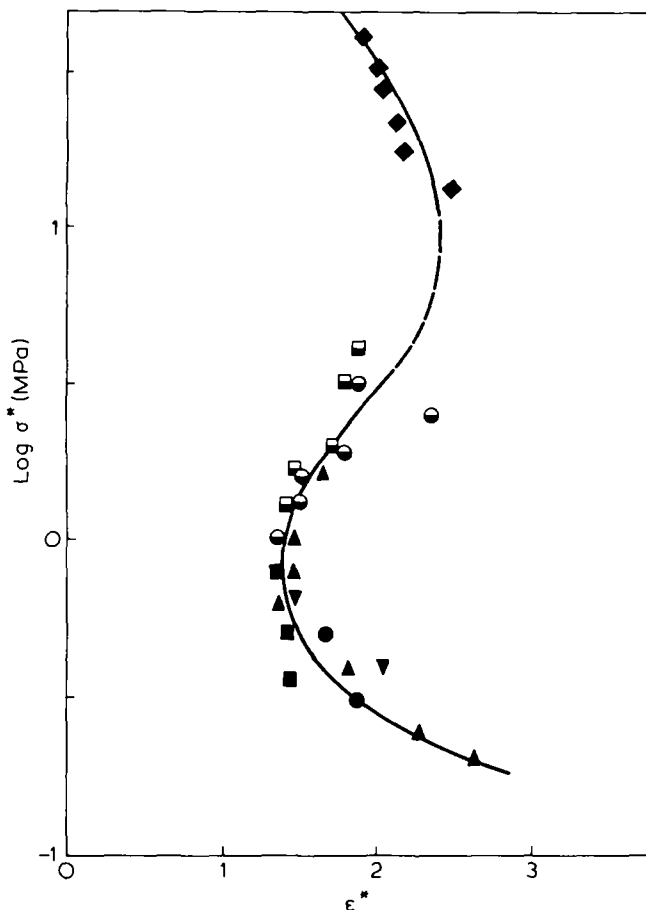


Figure 9 Dependence of true fracture stress on total fracture deformation, \blacklozenge , -10°C . The other designations are the same as in Figure 3

Further, on the assumption that

$$\int_{\ln \tau}^{\infty} \theta H(\theta) d \ln \theta \quad (6)$$

is equal to the dynamic viscosity on shear (η') we get

$$W_{\text{dis}} 3(\dot{\epsilon})^2 t \eta' = 3(\epsilon^*)^2 G'' \quad (7)$$

From this it follows that if W_{dis} is a constant quantity or a weak monotonic function of $\dot{\epsilon}$, which is adopted by a number of authors³² for vulcanized elastomers, then ϵ^* must in fact undergo an extreme change (a minimum) with rate of deformation as the quantity G'' passes through a maximum with frequency and *vice versa*. This correlation allows one to predict the condition for the transition of high-molecular-mass polymers of narrow *MMD* from FHES to FLS and also makes it possible to estimate the extension regimes, under which neck formation is observed, from the results of their low-amplitude deformation on shear.

Failure envelope of uncured elastomer

One of the most important characteristics of vulcanized rubbers is Smith's failure envelope¹⁸. It gives the dependence of ϵ^* on fracture stresses. In FHES, uncured rubber behaves like a quasivulcanized rubber and thus a failure envelope can be constructed for 1,2-PB. This failure envelope is presented in Figure 9 where the data

given cover the region from the start of the transition of the elastomer in FHES to unstable regimes of deformation characterized by neck formation and to brittle fracture in FLS.

Recoverable deformation and fracture of uncured elastomer

In the introduction it was noted that the fracture of uncured polymers at $T \gg T_g$ and, hence, the true fracture stresses, must unambiguously be determined by the recoverable deformation. The relevant data are given in Figure 10 for 1,2-PB studied in the present work (line I) and for polyisoprenes (line II) described in the literature^{16,17}. From Figure 10 it follows that there exist the lowest (critical) values of recoverable deformation ϵ_e^{**} , the exceeding of which must necessarily be accompanied by the fracture of polymer specimens. The values of ϵ_e^{**} are characterized by the intersection of the straight $\sigma^*(\epsilon_e^*)$ line with the dashed line determining the dependence of stress on recoverable deformation under steady flow conditions. It should be remembered that the highest extension ratio attainable on the setup used in the present work was 17-fold. So, the condition for fracture of polymers at $T \gg T_g$ is given by the following relation:

$$\sigma^*/(\epsilon_e^* - \epsilon_e^{**}) = E^* = \text{constant} \quad (8)$$

The value of E^* is an important characteristic of homologous polymer series.

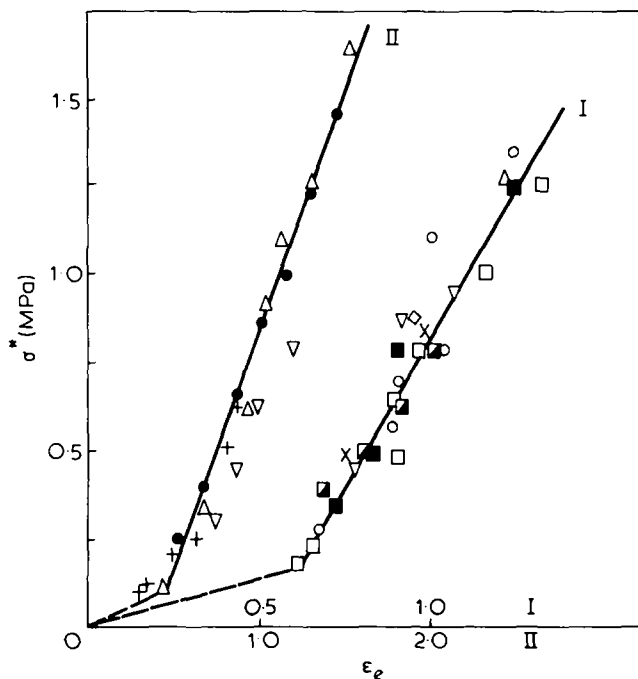


Figure 10 Dependence of true fracture stress on the high elastic component of fracture deformation for polybutadienes (I) and polyisoprenes (II) under various deformation regimes: PB—deformation regimes: $\sigma = \text{constant}$ (\blacksquare = $+10^\circ\text{C}$, \square = $+25^\circ\text{C}$, \blacksquare = $+50^\circ\text{C}$) $\dot{\epsilon} = \text{constant}$ (\diamond = $+10^\circ\text{C}$, \circ = $+25^\circ\text{C}$); the constant rate of extension (\times , $+25^\circ\text{C}$); the constant force (Δ , $+25^\circ\text{C}$); the stepwise loading conditions at 25°C (∇_1 , deformation at $\dot{\epsilon}_1$, $2 \times 10^{-3} \text{ s}^{-1}$) for 30 s, relaxation at constant deformation for 60 s, deformation at $\dot{\epsilon}_2 = 5 \times 10^{-3} \text{ s}^{-1}$ up to fracture; ∇_2 , deformation at $\dot{\epsilon}_1 = 5 \times 10^{-3} \text{ s}^{-1}$ for 180 s, relaxation at constant deformation for 60 s, deformation at $\dot{\epsilon}_2 = 2 \times 10^{-2} \text{ s}^{-1}$ up to fracture; ∇_3 , deformation at $\dot{\epsilon}_1 = 2 \times 10^{-2} \text{ s}^{-1}$ for 30 s, relaxation at constant deformation for 30 s, deformation at $\dot{\epsilon}_2 = 2 \times 10^{-2} \text{ s}^{-1}$ up to fracture). II—PI at 25°C , the $\dot{\epsilon} = \text{constant}$ regime (the molecular mass M : ∇ , 3.75×10^5 ; \bullet , 5.75×10^5 ; Δ , 8.3×10^5); the σ , constant regime, $M = 5.75 \times 10^5$ (+)

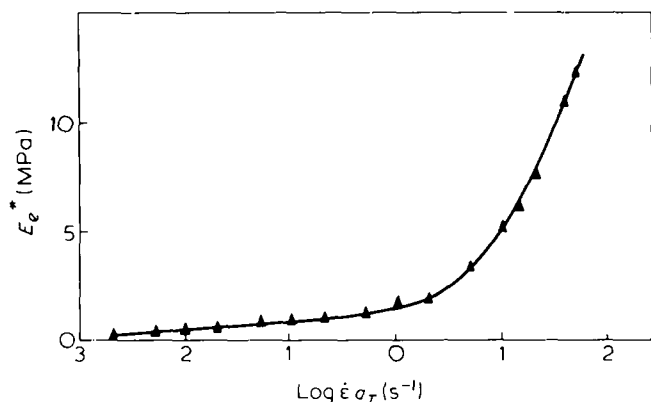


Figure 11 Dependence of the high-elasticity modulus E_e^* of polybutadiene on the rate of total deformation at the moment of fracture of the specimens

The values of ϵ_e^{**} for PB and polyisoprenes are approximately equal to 0.5. To the values of ϵ_e^{**} there also correspond the minimal value of strength of uncured elastomers (σ^{**}). Taking into account the linear viscoelastic behaviour of PB, for which the Young and Newton laws are valid, it is not difficult to show that the quantity $\sigma^{**} = E_0 \epsilon_e^{**} \approx 0.5 E_0$, where E_0 is the initial value of high-elasticity modulus. The critical value of the rate, $\dot{\epsilon}_{cr}$, at which the steady flow of the polymer becomes unattainable, is determined as

$$\dot{\epsilon}_{cr} \theta_0 = \epsilon_e^{**} \approx 0.5 \quad (9)$$

Here $\theta_0 = \lambda_0 / E_0$ is the characteristic relaxation time and λ_0 is the initial value of viscosity.

Equation (9) is confirmed by a number of existing theories^{33,34,35} which predict, in this case for a linear viscoelastic liquid, a sharp increase of stress, which inevitably leads to its fracture.

Although the fracture characteristics of polymers are determined by the relaxation properties of polymers and the time factors of their deformation, from the present work it directly follows that the so-called Deborah number cannot by itself serve for predicting the critical conditions leading to the fracture of the polymers.

It should be noted that on the $\sigma^*(\dot{\epsilon}_T, \epsilon^* a_T)$ and $\epsilon^*(\sigma)$ curves presented in Figures 6, 7 and 9 there are concentrated the points (half-filled) corresponding to the stresses and deformations at which non-uniform extension of the polymer begins, the unstable deformation which is accompanied by the neck formation. From Figures 7 and 9 it is easily seen that necking starts in the region of deformation rates and stresses that lie between the minimum and maximum of the $\epsilon^*(\dot{\epsilon}_T)$ and $\sigma^*(\epsilon^*)$ curves.

Neck formation is observed at $\sigma > 1$ MPa and $\epsilon \geq 1.3$, which is consistent with the data available for other polymers²² and with predictions for viscoelastic bodies (based on Considere's approach) according to which necking starts at $\epsilon = 1.0$.

A neck appears in the region of the sharp decrease of irrecoverable deformations (Figure 7) and $\tan \delta$, which corresponds to the branch of the $G''(\omega)$ curve, which decreases after the maximum.

Under these conditions, the viscous flow is replaced by the deformation of the polymer as a solid body; this is a deformation regime where the viscous resistance becomes insignificant and the elasticity of the polymer is still rather

low. This is clearly illustrated by the data of Figure 11, which shows that the transition from necking to the stable deformation is accompanied by a very rapid increase of the high-elasticity modulus which is defined as $E_e^* = \sigma / \epsilon_e^*$.

An important problem is the detailed elucidation of the mechanism and the establishment of quantitative criteria for the appearance of unstable deformation accompanied by neck formation.

Long term durability of uncured elastomer

Fracture of polymers is strongly dependent on time. This is well known for solid polymers³⁶ and rubbers^{37,38}, and is observed for polymers at temperatures above the glass temperature^{15,17}. For the PB investigated in the present work, the time dependence of the strength is presented in Figure 12 which shows the temperature-invariant dependence of durability (t^* is the time from the beginning of deformation to the fracture of the polymer) on true stresses over a wide range of times (up to six decimal orders). This dependence is described by the relation

$$t^* = k \sigma^{-\alpha} \quad (10)$$

which is well known for vulcanized elastomers^{37,38}. In the case under discussion, $\alpha = 2.7$, which is close to the values of this parameter for polyisoprenes and 1,4-polybutadienes of narrow MMD ^{15,17}.

From the data given in Figure 12 it also follows that equation (10) describes well the dependence of the true stress on the time elapsed from the beginning of deformation to the moment when necking starts. This is indirect evidence of the unified (relaxation) mechanism of the fracture of polymers and of the loss of stability to deformation (neck formation).

To elucidate the mechanism of the fracture of linear polymers at temperatures above T_g , we studied the

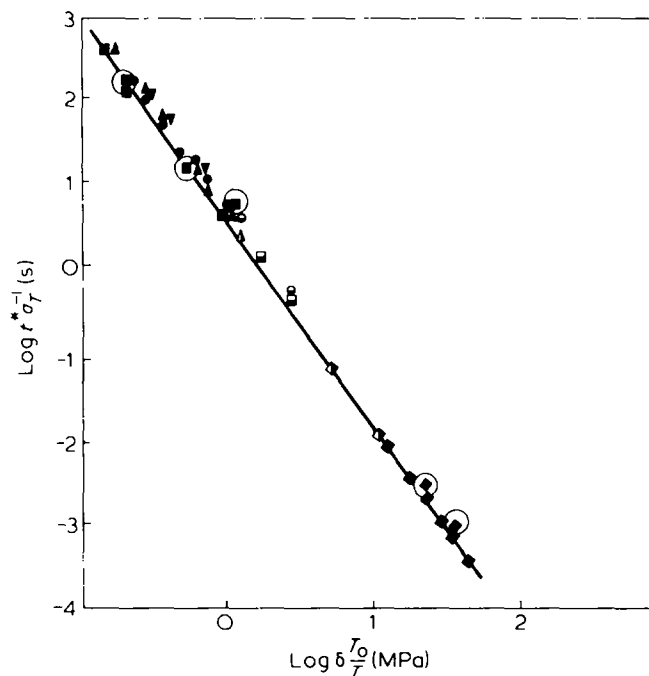


Figure 12 Dependence of long-term durability on the true stress under the $\sigma = \text{constant}$ regime. The designations are the same as in Figures 3, 5 and 9. The dots enclosed in circles correspond to the two-stage loading process. $T = \text{test temperature}$ $T_0 = 298\text{K}$

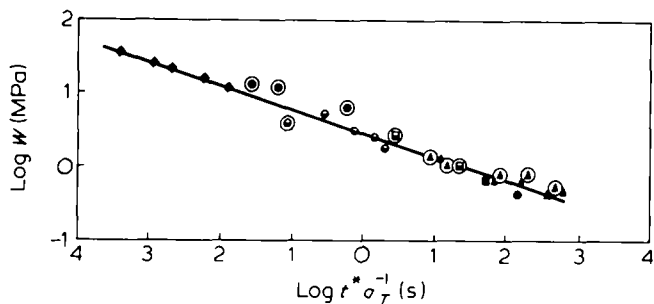


Figure 13 Relation between the long-term durability and the work of fracture of PB on uniaxial extension. Temperatures: \blacklozenge , -10°C ; \bullet , 0°C ; \blacksquare , $+10^\circ\text{C}$; \blacktriangle , $+25^\circ\text{C}$. The half-filled signs correspond to the moment when necking starts; the signs enclosed in circles correspond to the $\dot{\epsilon} = \text{constant}$ deformation regime; the other points correspond to the $\sigma = \text{constant}$ regime

durability of PB to which the stress was applied in two stages. At the first stage, the specimen was kept under stress during the time $0.5t^*$, where t^* is the durability at the specified stress. After this, the stress was removed and the specimens were allowed to relax at the test temperature, the relaxation time being varied over wide limits. Then, the same stress was applied to the specimens which were thus brought up to fracture. It has been found that the time of the repeated loading of the specimens practically coincided with the durability t^* . From Figure 12 it is seen that this result was attained over a wide range of specified stresses. From this it follows that when PB is loaded, no noticeable irrecoverable fractures of macromolecules accumulate in it. Only the recoverable rupture of intermolecular linkages occurs, i.e., fracture of uncured polymers at $T \gg T_g$ results from the relaxation processes.

Limiting extension of macromolecules at tensile deformation

In considering the properties of cured elastomers, wide use is made of the approach which relates strength to the energy consumed in the deformation process³⁹. Figure 13 gives the dependence of the durability of PB on the energy (W) consumed on deformation up to fracture. Its value was determined as $\sigma\epsilon^*$ under the $\sigma = \text{constant}$ deformation regimes and as

$$\int_0^{\epsilon^*} \sigma(\epsilon) d\epsilon$$

in the case of deformation at $\dot{\epsilon} = \text{constant}$.

Independent of the deformation regime, the value of W unambiguously determines the durability of the polymer and the time up to neck formation. The quantity W is composed of the accumulated elastic energy (W_e) and the energy dissipated in the process of deformation. Taking into account the small contribution of the irrecoverable component of the fracture deformation to the total value of ϵ^* at high values of σ and $\dot{\epsilon}$, we can state that the main contribution to W in this case is introduced by the quantity W_e . An increase of W_e lowers the durability of the polymers.

From the data of Figure 10 it follows that there exists a minimal value of W_e which corresponds to the transition from the regimes which result in the attainment of steady flow, to the unstable and fracture deformation regimes.

It is important to note that the maximal extension ratio of PB, $(l/l_0)_{\text{max}}$, corresponding to transition to the forced leathery state (FLS) and which is of a recoverable nature, is found to be close to the value of $L/(h_\theta^{-2})^{0.5}$, where L is the contour length and $(h_\theta^{-2})^{0.5}$ is the root-mean-square distance between the ends of the polymer chains. Thus, from Figures 7 and 9, in which the maxima of the fracture deformation curves are traced out quite distinctly, it follows that $(l/l_0)_{\text{max}} = 18$. At the same time, $L/(h_\theta^{-2})^{0.5} = 20.0$. In calculating this value it was assumed that the polymer under study contains 100% of 1,2-units. The value of $(h_\theta^{-2})^{0.5}$ used is equal to the value for atactic 1-polybutene which is similar in chemical constitution to 1,2-polybutadiene⁴⁰. This is a sufficient approximation since from the analysis of literature data⁴¹ it follows that for most vinyl polymers the values of $(h_\theta^{-2}/h_f^{-2})^{0.5}$ differ only by 10–20%. Here $(h_f^{-2})^{0.5}$ is the root-mean-square distance between the ends of the chain exhibiting free rotation about the C–C bonds in the principal chain. The value of L was found as pb , where p is the degree of polymerization and $b = 2.54 \text{ \AA}$ is the projection of the link onto the direction of the chain at an angle of 109° between the carbon–carbon bonds.

The largest recoverable deformations for uncured polymers may exceed those known for cured elastomers. This is associated with the fact that in high molecular-mass uncured polymers the largest recoverable deformations are close to those which correspond to the complete uncoiling of the macromolecules. This accounts for the considerable increase of the extension ratio with increase of molecular mass.

Effect of the nature of the liquid medium on the fracture of uncured elastomers

The relevant data are given in Figure 14. The curve showing the dependence of the fracture stress on the total deformation (Figure 14a) gives the lower portion of the

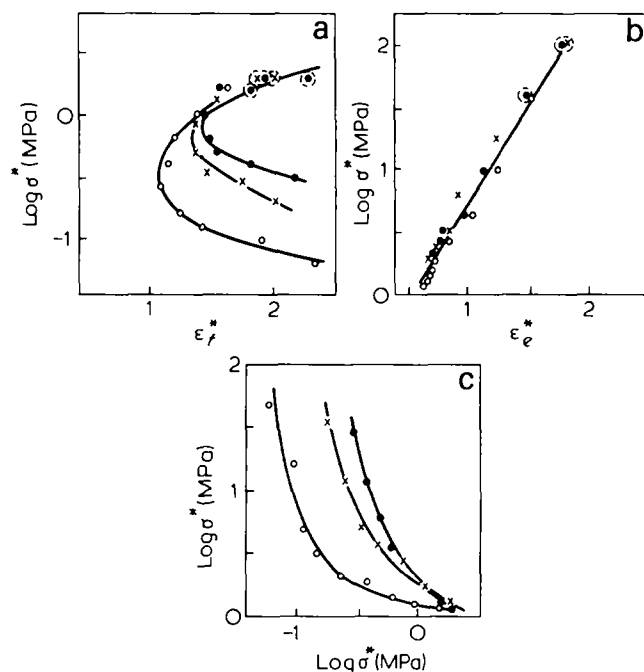


Figure 14 Dependence of true fracture stress in various liquid media at $+10^\circ\text{C}$ on (a) the total fracture deformation, ϵ_f^* ; (b) the recoverable fracture deformation, ϵ_e^* ; (c) the irrecoverable fracture deformation, ϵ_f^* . The media: \times , isopropyl alcohol; \circ , propyl alcohol; \bullet , water

Smith failure envelope. From this it is seen that in changing from water to propyl and isopropyl alcohols the fracture stress decreases by about four times. The most surprising point is that the recoverable deformation as a function of stress does not depend on the medium in which the extension is carried out (Figure 14b). As regards the accumulation of irrecoverable deformation, this varies strongly on the medium in which the experiments were carried out (Figure 14c).

CONCLUSION

In a wide range of stresses and rates of deformation, the polymer investigated behaves as a linear viscoelastic body. Assuming the equivalency of the circular frequency, the rate of shear and the rate of extension deformation, there is observed a clear-cut correlation between the frequency dependence of the loss modulus, and of the stress on the rate of shear and of the total deformation during uniaxial extension.

The maximum of the loss modulus corresponds to the transition of the polymer from the fluid to the forced rubbery state in which deformability of the polymer is always limited. This results on shear in the fracture of the polymer usually on the duct wall and, generally, in the boundary layers, which is accompanied by an enormous increase of the flow rates or by a sharp pressure drop in the flow of the polymer in ducts (the spurt effect). On uniaxial extension in the corresponding range of deformation rates there is observed a sharp decrease in irrecoverable deformation, this being accompanied by fracture of the specimens and being responsible for the minimum of total deformation. To the regions of decrease in loss modulus there corresponds the instability of the regime of uniaxial extension, neck formation in the polymer being deformed.

To the minimum of the loss modulus there corresponds the midpoint of the high-elasticity plateau and the beginning of the transition of the polymer from FHES to FLS (this must be followed by the transition to the forced glassy state, which was not attained in the present work). This interval of deformation rates corresponds to the maximum of total deformation on extension (which is actually equal to the recoverable deformation). Close to this point, neck formation ceases and the fracture of the polymer becomes brittle.

Under all the regimes for the fracture of the uncured polymer that have been studied, the long-term durability of the polymer as a function of true stress is described by the power function typical for cured elastomers.

Fracture of the polymer is uniquely determined by the recoverable (high elastic) deformation accumulated in it. There exists a critical value of recoverable deformation, above which the specimen is always fractured or necking starts.

For uncured elastomers, the dependence of the fracture stress on recoverable deformation (on total deformation at high stresses and rates of deformation) is described by the failure envelope typical of cured elastomers.

The forced transition of polymers from one physical state to another, the fracture of polymers and neck formation are relaxational in nature.

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REFERENCES

- 1 Kargin, V. A. and Sogolova, T. I. *Zhurnal Fiz. Khim.* 1949, **23**, 530
- 2 Tobolsky, A. V. and McLaughlin, J. R. *J. Polym. Sci.* 1952, **8**, 543
- 3 Vinogradov, G. V. *Polymer* 1977, **18**, 1275
- 4 Hutton, J. F. *Nature* 1963, **200**, 646; *Proc. Roy. Soc., A* **287**, 222; *Rheol. Acta* 1969, **8**, 54
- 5 Cruver, J. T. and Kraus, G. J. *J. Polym. Sci. A-2* 1964, **2**, 797
- 6 Vinogradov, G. V. *Pure Appl. Chem.* 1971, **26**, 423
- 7 Vinogradov, G. V., Malkin, A. Ya., Yanovsky, Yu. G., Borisenkova, E. K., Yarlykov, B. V. and Berezhnaya, G. V. *J. Polym. Sci. A-2* 1972, **10**, 1061
- 8 Vinogradov, G. V. *Rheol. Acta* 1973, **12**, 357
- 9 Vinogradov, G. V., Insarova, N. I., Boiko, F. B. and Borisenkova, E. K. *Polym. Eng. Sci.* 1972, **12**, 323
- 10 Vinogradov, G. V., Isayev, A. I. and Katsyutsevich, E. V. *J. Appl. Polym. Sci.* 1978, **22**, 1011
- 11 Brizitsky, V. I., Vinogradov, G. V., Isayev, A. I. and Podolsky, Yu. Ya. *J. Appl. Polym. Sci.* 1978, **22**, 751
- 12 Vinogradov, G. V., Malkin, A. Ya., Blinova, N. K., Sergeenkov, S. I., Zabugina, M. P., Titkova, L. V., Yanovsky, Yu. G. and Shalганova, V. G. *Eur. Polym. J.* 1973, **9**, 1231
- 13 Malkin, A. Ya., Blinova, N. K., Vinogradov, G. V., Zabugina, M. P., Sabsai, O. Yu., Shalганova, V. G., Kirchevskaya, I. Yu. and Shatalov, V. P. *Eur. Polym. J.* 1974, **10**, 445
- 14 Vinogradov, G. V. *Pure Appl. Chem.* 1974, **39**, 115
- 15 Vinogradov, G. V. *Pure Appl. Chem.* 1975, **42**, 527
- 16 Vinogradov, G. V., Malkin, A. Ya., Volosevitch, V. V., Shatalov, V. P. and Yudin, V. P. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1721
- 17 Vinogradov, G. V., Malkin, A. Ya. and Volosevitch, V. V. *Appl. Polym. Symp.* 1975, **27**, 47
- 18 Smith, T. L. in *Rheology* (Ed. F. R. Eirich), Vol 5, p 143, Acad. Press, N.Y., 1969
- 19 Kamei, E. and Onogi, S. *Appl. Polym. Symp.* 1975, **27**, 19
- 20 Chen, I. J., Nagler, G. E., Abbot, L. E., Bogue, D. C. and White, J. L. *Trans. Soc. Rheol.* 1972, **3**, 473
- 21 Cogswell, F. N. and Moore, D. R. *Polym. Eng. Sci.* 1974, **14**, 573
- 22 Cogswell, F. N. *Appl. Polym. Symp.* 1975, **27**, 1
- 23 Bartenev, G. M. and Zuev, Yu. S. 'Strength and Fracture of Highelastic Materials' (in Russian), Khimiya, Moscow, 1964, Ch. XII, XIII
- 24 Anderson, J. N., Barzan, M. L. and Adams, H. E. *Rubber Chem. Technol.* 1972, **45**, 1273
- 25 Vinogradov, G. V., Radushkevich, B. V. and Fikhman, V. D. *J. Polym. Sci., A-2*, 1970, **8**, 1
- 26 Vinogradov, G. V., Fikhman, V. D. and Radushkevich, B. V. *Rheol. Acta* 1972, **11**, 296
- 27 Vinogradov, G. V., Leonov, A. I. and Prokunin, A. N. *Rheol. Acta* 1969, **8**, 482
- 28 Ulyanov, L. P., Yanovsky, Yu. G. and Neimark, N. M. *Zarodskaya Laboratoriya* 1978, **44**, 222
- 29 Vinogradov, G. V. and Prozorovskaya, N. V. *Plastmas*, 1964, **5**, 50
- 30 Ferry, J. 'Viscoelastic Properties of Polymers', p 77 and Chap 11, J. Wiley, N.Y., 1970
- 31 Ninomiya, K. and Ferry, J. *J. Colloid Sci.* 1959, **14**, 36
- 32 Landel, R. F. and Fedors, R. F. in 'Fracture Processes in Polymeric Solids', (Ed. B. R. Rosen), Chap 3, Interscience, N. Y., 1964
- 33 Leonov, A. I. and Vinogradov, G. V. *Dok. Akad. Nauk USSR* 1965, **162**, 869
- 34 Lodge, A. S. C. 'Elastic Liquids', Chap 3, Academic Press, 1964
- 35 Dealy, J. M. *Polym. Eng. Sci.* 1971, **11**, 433
- 36 Regel, V. R., Slutsker, A. I. and Tomashevsky, E. E. 'Kinetic Nature of the Strength of Solid Bodies', Nauka, Moscow, 1974 (in Russian)
- 37 Gul, V. E. 'Structure and Strength of Polymers' (in Russian), 3rd edition, Khimiya, Moscow, 1978, Chap IV
- 38 Bartenev, G. M. and Zuev, Yu. S., loc. cit., Chap II
- 39 Eirich, R. F. and Smith, T. L. in 'Fracture, An Advanced Treatise', (Ed. H. Libowitz), Vol 7, Acad. Press, N.Y. and London, 1972
- 40 Krigbaum, W. R., Kurz, J. K. and Smith, P. J. *Phys. Chem.* 1961, **65**, 1981
- 41 Tsvetkov, V. N., Eskin, V. E., Frenkel, S. Ya. 'Structure of Macromolecules in Solutions', Nauka, Moscow, 1964, Chap IV (in Russian)