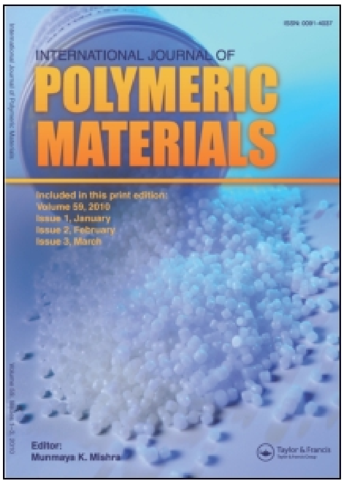

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Strength of Elastomeric Adhesive Films in the Triaxial Stress State†

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In model experiments, the triaxial stress state is realized in thin polymer films placed between two solid surfaces and subjected to extension under the action of a force oriented perpendicular to the interface. In this case, the ultimate (fracture) stresses in adhesive joints of uncured flexible-chain polymers of narrow and wide molecular-mass distributions with solids of various nature have been studied as a function of the rate of loading. The results are in good agreement with the data obtained by investigating the durability of the same materials under the conditions of the triaxial stress state. In the region of cohesive fracture the strength of adhesives of narrow MMD is substantially dependent on molecular mass and temperature. In adhesive tear-off, the strength is noticeably affected by the nature of the support, but it is not practically influenced by the molecular mass of the adhesive. The results of the investigation of the strength properties of thin polymer films in the triaxial stress state have been compared with the data obtained for the same polymers subjected to uniaxial extension and shear flow.

INTRODUCTION

The study of the behaviour of polymers under the conditions of the triaxial stress state is one of the most important and interesting trends in the investigation of viscoelastic materials. The majority of investigations of the strength of polymers are, however, conducted under the conditions of uniaxial extension or shear. In this connection, the following questions arise: Could the data obtained under the simplest conditions be unambiguously

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extended to the case of a complex stress state? Are there simple relationships between the strength of a viscoelastic material and the type of the stress state developing in it?

New possibilities in the search for answers to these questions are offered by uncured linear flexible-chain polymers of narrow molecular-mass distribution (MMD), whose behaviour under the conditions of uniaxial extension and shear have been thoroughly studied.[1-5]

The triaxial stress state in model experiments[6, 7] is realized in thin polymer films placed between two solid surfaces and subjected to extension with the operating force directed perpendicular to the interface. In this case, according to literature data,[8] a state is developed in the film, which is similar to hydrostatic extension.

Our earlier work[9] was concerned with study of the durability of thin films of uncured polybutadienes of narrow MMD as adhesives in contact with various solids. The results of the investigation have shown that under the conditions of the triaxial stress state the durability of elastomers is 1.0–1.5 decimal orders higher and the fracture stresses are about 3 times greater than those obtained in the case of uniaxial extension.[1-3] The last result correlates with the literature data[8] obtained by studying the behaviour of polyurethane under the conditions of triaxial extension.

The present work is devoted to the study of the ultimate (fracture) characteristics of adhesive joints formed by uncured polybutadienes (PB) and polyisoprenes (PI) of narrow MMD and various solids.

EXPERIMENTAL

The adhesives used in this work are uncured polybutadienes (PB) and polyisoprenes (PI) of narrow MMD ($M_w/M_n < 1.1$). The molecular masses of the materials used are as follows: 8×10^4, 4×10^5, 6.4×10^5, 7.9×10^5 for polybutadienes and 1.6×10^5, 3.75×10^5, 5.75×10^5, 1.8×10^6 for polyisoprenes. Polymers of narrow MMD were synthesized by anionic polymerization, using butyllithium as the catalyst. They contain about 45% of 1,4-cis and 1,4-trans groups and about 10% of 1,2 groups. Polymers of wide MMD were also used. Polybutadienes of wide MMD were prepared by mixing equal weight parts of PB of narrow MMD having various molecular masses. For this sample, calculations gave the value of $M_v = 2.2 \times 10^5$ and $M_w/M_n = 2.1$. Polyisoprene of wide MMD is a commercial polymer with $M_v = 4.25 \times 10^5$ and $M_w/M_n = 2.2$.

We investigated adhesive joints made up of these materials and steel, copper, platinum, quartz, PMMA, glass, and PTFE with loading rates ranging from about 10^{-1} to 2×10^3 N/sec.

The fracture stresses at constant rates of loading were investigated by using an adhesiometer which is schematically shown in Figure 1.

Films of the polymeric adhesive A of circular shape with an outer diameter of 9 mm, an inner diameter of 3 mm and a thickness of 80–100 μm were applied to the butt-end of a steel cylinder B according to the procedure described in the literature.[9] The cylinder B can move reciprocatingly with a low friction in the duct C of the guiding block D. The support E was placed on a thermal unit F, through which a thermostatted liquid was passed. The specified temperature was maintained by means of thermostats. The accuracy of temperature control was ± 0.5°C. The temperature was controlled by means of thermocouples.

The investigations were conducted as follows. The contact between the polymer and the solid surface was formed under a pressure p_0 during time t_0 at a temperature T_0. The following test conditions were used: $p_0 = 0.5$ MPa, $t_0 = 30$ min, $T_0 = 60$°C for PB, and $p_0 = 0.6$ MPa, $t_0 = 45$ min, and $T_0 = 70$°C for PI.

After the contact was formed the load was increased up to fracture. This was provided by the translational motion of the cylinder B in the duct C. The translational movement of the cylinder with a specified velocity was provided by means of a micrometer screw H, which is brought to rotational motion through a magnetic coupling I by an electric motor J with a reducer K. Set up between the nut of the micrometer screw L and the cylinder B is an elastic dynamometer M with tensometric wire pickups, the signal from which is automatically recorded by an electronic potentiometer or photographed from the screen of an electronic oscillograph. The potentiometer is preliminarily calibrated in strength units. The measurement errors were 3–5%

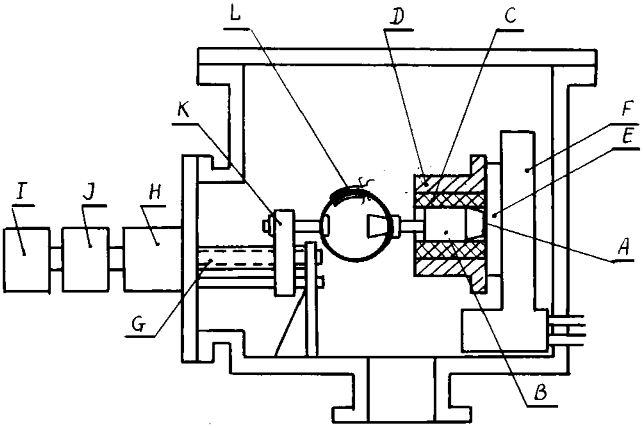

FIGURE 1 Schematic diagram of an adhesiometer.

in the investigation of polymers of narrow MMD and 15–20 % for polymers of wide MMD at a 0.95 confidence interval.

The mode of fracture of the joints was determined with the aid of optical and scanning electron microscopes and also visually.

RESULTS

Figures 2 and 3 are plots of the fracture stresses σ_B versus the rate of loading $\dot{P}$ for PB of narrow MMD and four molecular masses and for PI of narrow MMD and four molecular masses with steel (the Swedish precision block).

The relationships between σ_B and $\dot{P}$ in the given range of loading rates are curves consisting of two branches. Portions can be distinguished on the curves, which correspond to the various types of fracture of the joints. At relatively low rates of loading (from 0.13 to about 3 N/sec) there is observed a cohesive fracture and then a cohesive-adhesive fracture sets in with the cohesive fracture predominating. This is represented by the left ascending branch of the curve of σ_B vs. $\dot{P}$.

In the case of cohesive fracture and the predominantly cohesive fracture, the strength of the material is significantly influenced by the molecular mass of the elastomer and the fracture stresses increase with increasing M_v. This correlates with the data obtained for the same materials on uniaxial extension,[1–5] and by the investigation of the durability of thin films of uncured PB of narrow MMD under the conditions of the triaxial stress state.[9]

As the rate of loading increases the fraction of cohesion in the cohesive-

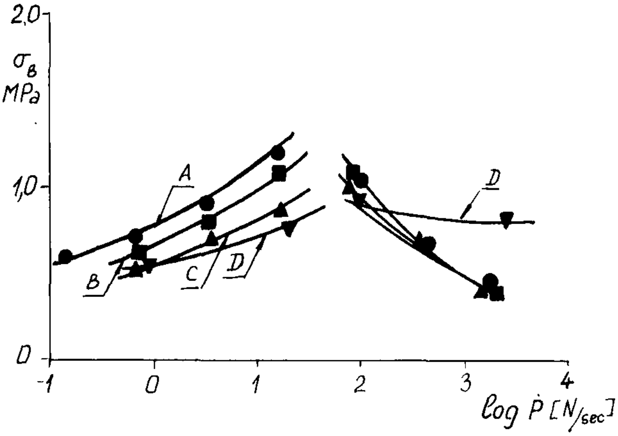

FIGURE 2 Fracture stress σ_B versus the rate of loading $\dot{P}$. Polybutadienes of narrow MMD and four MM in contact with steel: ● = M_v = 7.9 × 10^5; ■ = M_v = 6.4 × 10^5; ▲ = M_v = 4 × 10^5; ▼ = M_v = 8 × 10^5.

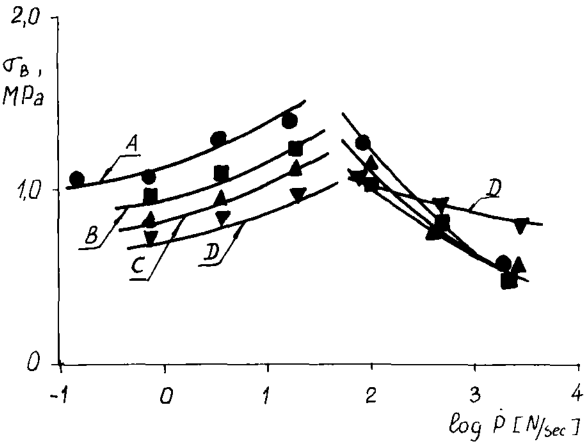

FIGURE 3 The relationship between σ_B and $\dot{P}$. Polyisoprenes of narrow MMD, having the following four molecular masses, in contact with steel: ● = $M_v = 1.8 \times 10^5$; ■ = $M_v = 5.75 \times 10^5$; ▲ = $M_v = 3.75 \times 10^5$; ▼ = $M_v = 1.6 \times 10^5$.

adhesive fracture decreases and at a loading rate of about 400 N/sec there takes place the changeover to the adhesive tear-off. This is represented by the descending branch of the curve of σ_B vs. $\dot{P}$. As seen from Figures 2 and 3, in the adhesive tear-off the molecular mass has practically no effect on the strength, just as we observed during the investigation of the durability of adhesive joints of uncured PB of narrow MMD and PTFE.[9]

The relationships between σ_B and $\dot{P}$ for PB with $M_v = 8 \times 10^4$ and for PI with $M_v = 1.6 \times 10^5$ are specific (Figures 2 and 3, curves D). Here the fracture is practically cohesive over the entire range of loading rates, except for the values of $\dot{P} \geqslant 400$ N/sec when the changeover to the cohesive-adhesive fracture was observed. Special emphasis will be placed on this fact below.

The effect of the nature of the support on the strength properties of adhesive joints has been studied for PB of narrow MMD with $M_v = 7.9 \times 10^5$ in contact with copper, platinum, steel, glass, quartz and PTFE. The corresponding data are presented in Figure 4. The form of the curves is the same as before. In the cohesive fracture, the nature of the support has an insignificant effect on the fracture stresses. It begins to play an appreciable part only when the predominantly adhesive fracture and adhesive tear-off occurs (the right branches of the curves of σ_B vs. $\dot{P}$). Similar data on the effect of the nature of the support on the strength of adhesive joints of elastomers with solids have been obtained by other authors as well.[10]

A special case is the relationship between σ_B and $\dot{P}$ for joints of PB with PTFE (Figure 4, curve F). Here was observed an adhesive tear-off over the entire range of loading rates and a monotonous decrease of fracture stresses with increasing rate of loading.

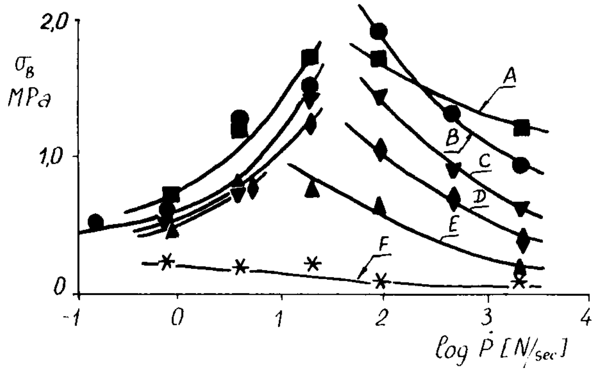

FIGURE 4 The relationship between σ_B and $\dot{P}$. Polybutadienes of narrow MMD ($M_v = 7.9 \times 10^5$) in contact with various supports: ■ = glass; ● = copper; ▼ = platinum; ◆ = steel; ▲ = quartz; ✳ = PTFE.

We have also studied the relationships between fracture stresses and the rate of loading for joints of PB and PI of wide MMD with steel. The corresponding data are given in Figure 5. Here the curves A and B show the relationships between σ_B and $\dot{P}$ for PB and PI, respectively. In the entire range of loading rates there was observed the cohesive mechanism of fracture, and the fracture stresses remained constant within the experimental accuracy. For comparison, the dashed line in Figure 5 shows the relationship between σ_B and $\dot{P}$ for PB of narrow MMD ($M_v = 7.9 \times 10^5$) in contact with steel.

DISCUSSION

As follows from the experimental data, in a general case the dependences of fracture stresses on the rate of loading for adhesives of narrow MMD consists of two branches—as the rates of loading increase the fracture stresses first increase and then decrease. Portions can be distinguished on the curves, which correspond to the various mechanisms of rupture of adhesive joints. At low loading rates there was observed a cohesive fracture. Then the fracture becomes cohesive-adhesive, and at high loading rates it becomes adhesive.

Cohesive and cohesive–adhesive fracture

The analysis of the results for the cohesive and the predominantly cohesive fracture shows that the character of the relationships between σ_B and $\dot{P}$ for thin films of uncured PB and PI of narrow MMD is qualitatively similar to the earlier obtained relationships between true stresses σ^* and the rate of

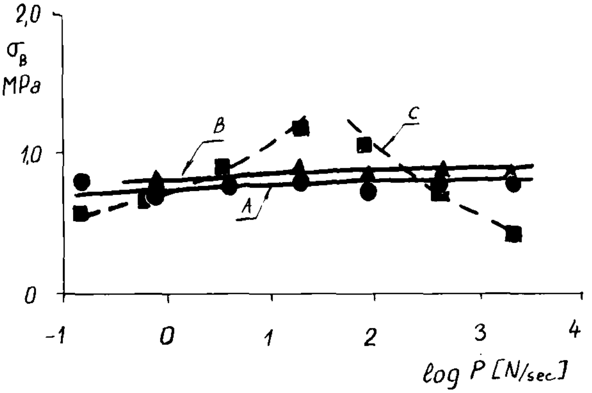

FIGURE 5 The relationships between σ_B and $\dot{P}$. Polymers of wide MMD in contact with steel: A = PB; B = PI. The dashed line represents the dependence of σ_B on $\dot{P}$ for PB of narrow MMD (M_v = 7.9 × 10^5) in contact with steel.

deformation $\dot{\varepsilon}$ for the same materials under the conditions of uniaxial extension.[1–3] This is illustrated by the data given in Figure 6. This figure shows the dependences of true stresses σ^*, the total deformation ε and its recoverable, ε_e, and irrecoverable, ε_f, components on the rate of deformation $\dot{\varepsilon}$. The curves were obtained for PB of narrow MMD with M_v = 2.9 × 10^5 at various temperatures and were reduced to the temperature 25°C by shifting the curves along the abscissa axis.

It has been established that the strength of the uncured elastomer increases

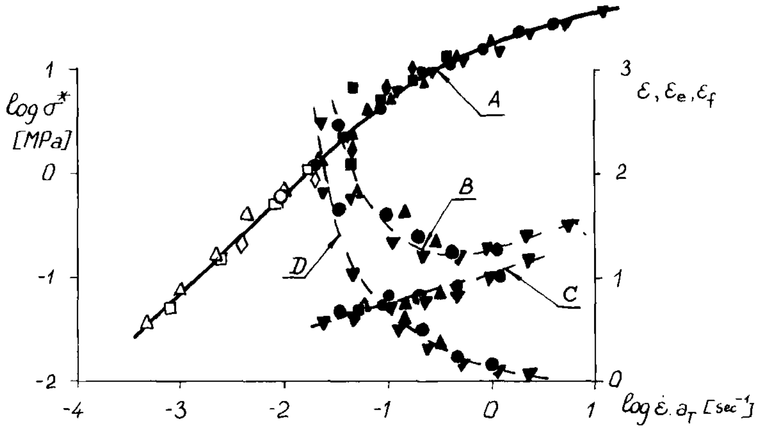

FIGURE 6 Master curves of true stress σ^* (A), total deformation ε (B), recoverable deformation ε_e (C), and irrecoverable deformation ε_f (D) on the rate of deformation $\dot{\varepsilon}$. Uniaxial extension. PB of narrow MMD (M_v = 2.9 × 10^5). Uniaxial extension. PB of narrow MMD (M_v = 2.9 × 10^5) at various temperatures (reduced to 25°C). ▼ = −25°C; ● = 0°C; ▲ = 25°C; ■ = 50°C; ◆ = 75°C.

with increasing rate of deformation, but the increase of the strength is retarded in the region of high rates of deformation. The extension that takes place here leads either to the attainment of steady flow conditions (the unfilled signs on curve A), or to the fracture of the specimens (the filled signs on curve A) at certain critical stress values σ^*_{cr} and rates of deformation $\dot{\varepsilon}_{\mathrm{cr}}$. The latter circumstance is an indication of the transition of the uncured polymer to the forced high-elastic state. In this case the value of critical stresses for PB and PI is equal to 0.1–0.5 MPA and is independent of molecular mass and temperature. At the same time, molecular mass and temperature have a strong effect on the critical rate of deformation.

The curves of σ^* vs. $\dot{\varepsilon}$ obtained at various temperatures and with samples of various molecular masses can be made to converge by shifting along the abscissa axis. It has been shown that the relation between the rate of deformation and molecular mass is expressed as follows:

$$\dot{\varepsilon} \sim -M_v^{(3.4-3.6)} \tag{1}$$

and the relation between the rate of deformation and temperature is given by

$$\dot{\varepsilon} \sim e^{-U/kT} \tag{2}$$

where U is the activation energy of the fracture process, which is close to the activation energy of the viscous flow of the corresponding polymer.

The strength properties of thin films of uncured polymers of narrow MMD depend on molecular mass in a similar manner. The relationships between σ_B and $\dot{P}$ for PB and PI of various molecular masses can also be reduced to a certain molecular mass by shifting the corresponding curves along the rate axis. The master curves of σ_B vs. $\dot{P} \cdot a_M$ for PB of three molecular masses and PI of three MM are presented in Figures 7 and 8, respectively. Here the shift factors for MM, a_M, are satisfactorily described by expressions similar to the WLF equation:

$$\log a_M = -\frac{C_1(M-M_0)}{C_2+(M-M_0)} \tag{3}$$

where M_0 is the molecular mass to which the reduction is made. The constants C_1 and C_2 are calculated by the method of least squares in accordance with the procedure proposed in the literature.[11] Their values for PB are as follows: $C_1 = 4.08$ and $C_2 = 21 \times 10^5$ (at $M_0 = 6.4 \times 10^5$) for PB; $C_1 = 1.09$ and $C_2 = 22 \times 10^5$ (at $M_0 = 1.8 \times 10^5$) for PI.

Calculations show that the rate of deformation is related to MM in the following way:

$$\dot{P} \sim -M_v^{(3.0-3.3)} \tag{4}$$

Special investigations carried out over the temperature range from 3 to 40°C have allowed us to establish that the effect of the test temperature on

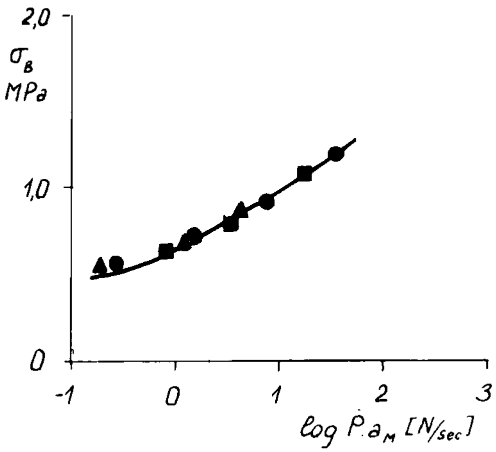

FIGURE 7 Master curves of σ_B versus $\dot{P} \cdot a_M$. Cohesive and predominantly cohesive fracture. PB of narrow MMD having the following three molecular masses. The designations are the same as in Figure 2. $M_0 = 6.4 \times 10^5$.

the rate of loading is similar to that considered earlier [see Eq. (2)]; here the activation energy calculated for PB has been found to be equal to 6–7 kcal/mole, which is close to the activation energy of the viscous flow of PB.

The analysis made has shown that a number of properties of uncured polymers of narrow MMD are of the same type upon changeover from uniaxial extension to the triaxial stress state. In the first place, this refers to the mechanism of fracture of uncured polymers. The relations (1), (2) and (4)

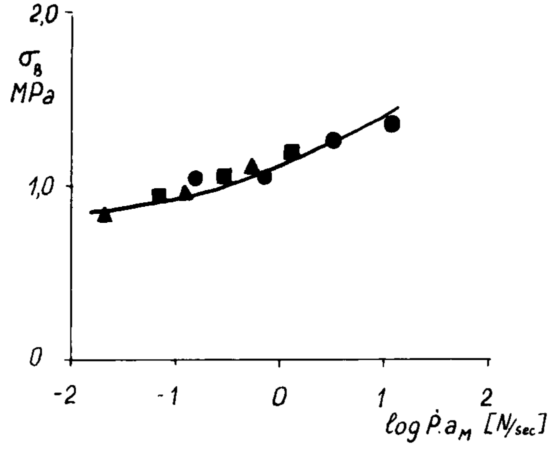

FIGURE 8 Master curves of σ_B versus $\dot{P} \cdot a_M$. Cohesive and predominantly cohesive fracture. PI of narrow MMD with and three MM's molecular masses. The designations are the same as in Figure 3. $M_0 = 1.8 \times 10^6$.

show that in both cases the fracture of uncured elastomers is relaxational in character, i.e., is not associated with the rupture of the macromolecules, which is characteristic of the glassy state and highly crystalline polymers.

The state of stress has a noticeable effect on the strength properties of uncured elastomers. A precise quantitative estimation of this phenomenon was obtained by measuring the rates of deformation corresponding to the rates of loading used in the present work. It has been shown that at minimum loading rates (~0.2–0.5 N/sec), rates of deformation of about 10^{-3} to 10^{-2} sec^{-1} are attained, which is close to the critical rates of deformation for high MM. This has made it possible to establish that the limiting stresses in films being in the triaxial stress state are about 2.5 times greater than in uniaxial extension. The result correlates well with our data[9] and with the data obtained by other authors.[8]

Additional interesting possibilities for the analysis are provided by the dependences of the time to fracture for thin films, t^*, on the limiting stress σ_B. The pertinent data for PB of narrow MMD and three molecular masses are given in Figure 9. The treatment of these data by means of the method of least squares has shown that the relationship between the time to fracture t^* and the limiting stress σ_B, temperature T and molecular mass M_v can be satisfactorily approximated with the aid of the following expression:

$$t^* = B(\sigma_B)^{-m} e^{U/kT} M_v^{\alpha} \tag{5}$$

where B, m and α are constants; U is the activation energy of the fracture process, which is close to the activation energy of the viscous flow of the corresponding polymer. The numerical values of the constants for PB are as follows: $m = 4.5$–5.5; $\alpha = 3.0$–3.3.

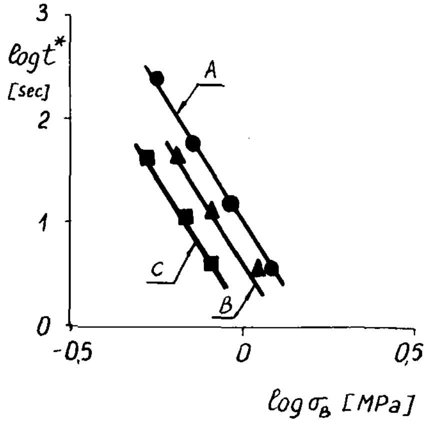

FIGURE 9 The dependence of the time to fracture on the fracture stresses. PB of narrow MMD and three molecular masses: ● = $M = 7.9 \times 10^5$; ▲ = $M = 6.4 \times 10^5$; ■ = $M = 4 \times 10^5$.

It has been shown earlier[1–3, 9] that the relationships between the durability and the applied stress, the temperature and MM on uniaxial extension and in the triaxial stress state are described by expressions analogous to expression (5). The activation energy in both cases is close to the activation energy of viscous flow: $\alpha = 3.0–3.6$; the value of m is 2–3 for uniaxial extension and 4.0–4.4 for the triaxial stress state.

Thus, the analysis has confirmed the conclusion made above, that the mechanism of the fracture of uncured polymers is independent of the type of the stress state. The principal part in resisting the fracture in all cases is played by the intermolecular forces, which is reflected in the constancy of the last two cofactors in expression (5) for the case of the stress state under consideration.

In expression (5) the factor $(\sigma_B)^{-m}$ (the exponent varies from 2 to 5.5) depends on the type of the state of stress. The outcome of this is that the durability of the uncured polymer which is in the forced high-elastic state (i.e., at stresses greater than 0.1–0.5 MPa) is by 1.0–2.0 decimal orders and the fracture stresses by 2.5–3 times greater than in the case of uniaxial extension.

The relationships given evidently point to a characteristic relation between the durability of the elastomer and the state of stress arising in the bulk of the material.

Adhesive fracture

In the adhesive tear-off the relationships between σ_B and $\dot{P}$ over the given rates of loading are decreasing functions. Here the fracture stresses are practically independent of MM (for sufficiently high MM), but the strength is considerably influenced by the nature of the support.

To explain these results, use may be made of the conception advanced earlier[9] to account for the temperature dependences of the durability t^* for adhesive joints of uncured PB of narrow MMD with solids. By studying the joints indicated it has been found that the relationship between t^* and T^{-1} is external in character, as shown in Figure 10.

The concept is based on the following propositions. Suppose that for the adhesive fracture there is required a certain critical energy w^*. Then the fracture process is started if the energy accumulated during the deformation of the elastomer attains the value of w^*.

According to the literature data,[12] the total energy of deformation of the elastomer per unit volume is expressed as the following sum:

$$w = w_e + w_e(t) + w_d \tag{6}$$

where w_e is the accumulated elastic energy which is independent of time; $w_e(t)$ is the time-dependent component of the accumulated energy; and w_d is the dissipated energy.

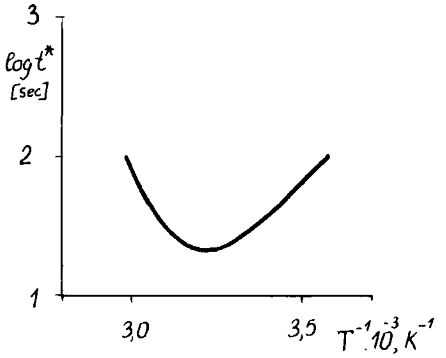

FIGURE 10 The temperature dependence of the durability t^*. Adhesive tear-off. PB of narrow MMD ($M_v = 6.4 \times 10^5$) in contact with PTFE.

In accordance with the present-day conceptions[12,13] the dissipation losses retard the progress of the fracture process, which leads to an increase of the durability.

The components of the total energy are associated with the deformation characteristics of the elastomer. Thus, the accumulated energy is due to the recoverable component of total deformation and the dissipated energy is due to the irrecoverable component. The treatment of the results presented in Figure 6 has enabled us to obtain the temperature dependences of the deformation characteristics of uncured polymers of narrow MMD. The relevant data are given in Figure 11. This figure shows the master curves of σ^*, ε, ε_e and ε_f versus the inverse absolute temperature, obtained at various rates of deformation and reduced to $\dot{\varepsilon} = 0.01\ \text{sec}^{-1}$.

The analysis of these curves has shown the following. Just as in the tests carried out under the conditions of $\dot{\varepsilon}$ = constant, the durability of an uncured polymer of narrow MMD increases with decreasing temperature, but the growth of the strength is retarded in the region of low temperatures. The extension leads either to the steady flow conditions (the unfilled signs on curve A) or to the fracture of the specimens (the filled signs on curve A) at critical values of the stress σ^*_{cr} and temperature T_{cr}^{-1}. The latter circumstance is evidence of the transition of the polymer from the fluid to the forced high-elastic state. However, even after the transition indicated, there may develop considerable irrecoverable deformations in the polymer. The fluidity of the polymer is found to have been practically suppressed only in the far post-critical region of stresses and temperatures. In this connection, we may introduce the concept of the region of stresses and temperatures, in which there is observed the transition of the uncured polymer from the fluid to the well-established high-elastic state, when the irrecoverable deformation becomes negligibly small as compared with the recoverable deformation.

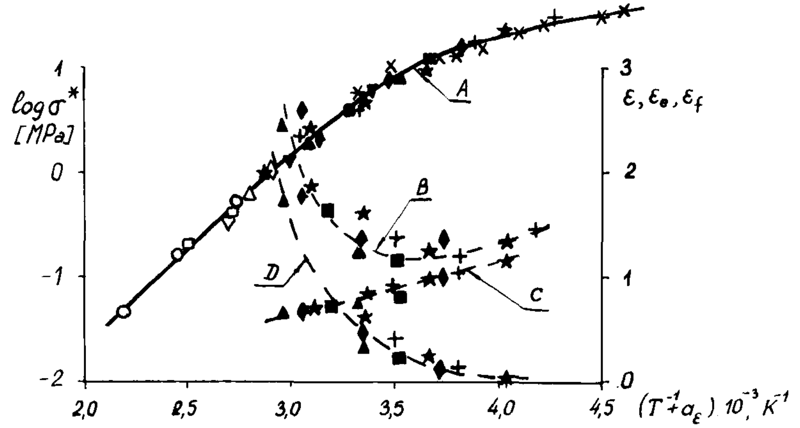

FIGURE 11 Master curves showing the temperature dependence of true stresses σ^* (A), total deformation ε (B), recoverable deformation ε_e (C), and irrecoverable deformation ε_f (D). Uniaxial extension. PB of narrow MMD ($M_v = 2.9 \times 10^5$) at various rates of deformation (reduced to the deformation rate 0.01 $\sec^{-1}$). ● = 0.002; ▼ = 0.005; ▲ = 0.01; ■ = 0.02; ◆ = 0.05; ★ = 0.01; + = 0.2; ∗ = 0.5; × = 1.0 $\sec^{-1}$.

From Figure 11 it is seen that in the transition region the irrecoverable deformation decreases rapidly (curve D) and the recoverable deformation increases (curve C) with decreasing temperature, so that the total deformation passes through a minimum (curve B) similar to the minimum on the curve of t^* vs. T^{-1} (Figure 10). The transition region has limits with respect to stresses (0.1 to 1.0 MPa) and to temperatures, [(3.0 to 3.7) × 10^{-3} K^{-1}] for PB with $M_v = 2.9 \times 10^5$ at a deformation rate of 0.01 $\sec^{-1}$. In the left part of the transition region there predominate irrecoverable deformations. The dissipated energy is accordingly high. This leads to the retardation of energy accumulation up to the required critical value w^* and to the increase of the time required for the process of adhesive fracture to begin. As the temperature decreases the irrecoverable deformation and, hence, w_d, fall of rapidly. The time for energy accumulation up to w^* decreases correspondingly. In the right-hand part of the transition region the dissipation of the energy becomes low. The time of energy accumulation up to w^* is but slightly dependent on temperature, and the major part is played by the temperature dependence of the energy w^*, which increases with decreasing temperature.[14] Thus, the extremum observed on the curve of t^* vs. T^{-1} is determined by the different character of the temperature dependences of the two processes—the energy accumulation up to the value leading to the beginning of the fracture of the polymer-solid contact and the fracture proper, in which the decisive role is played by the temperature dependence of the critical energy w^*.

The decrease of the fracture stresses with increasing rate of loading (or the rate of deformation) in the case of adhesive tear-off can be explained in an analogous manner. For this purpose, we should determine the character of the rate dependences of the recoverable and irrecoverable deformations. They are presented in Figure 6 (curves C and D, respectively).† Here it is also possible to establish the existence of the region of transition of an uncured polymer from the fluid to the forced high-elastic state. Its boundaries with respect to rates of deformations are 0.03 and 1 $\sec^{-1}$ (for PB with $M_v = 2.9 \times 10^5$ at 25°C). In the transient region, the irrecoverable deformation decreases rapidly, and the recoverable deformation increases with increasing rate of deformation, so that the total deformation (curve B in Figure 6) passes through a minimum.

It has been shown above that in our experiments at a minimum rate of loading there was attained a deformation rate of the order of 10^{-3} to 10^{-2} $\sec^{-1}$. This means that the investigations of the fracture stresses were mainly carried out within the limits of the transition region. In this connection, the processes of energy accumulation and dissipation must have a substantial effect on the strength properties of adhesive joints.

Indeed, on the left of the transition region the energy dissipation is great and considerable loads must be applied for the deformation of the polymer film to attain the required value, at which the accumulated energy will become close to the critical value w^*. As the rate of loading (or the rate of deformation) increases the energy dissipation falls off (in accordance with the course of the curve of ε_f vs. $\dot{\varepsilon}$, the curve D in Figure 6). This leads to the decrease of the load required for the corresponding amount of deformation to be attained.

In the given range of the rates of loading the complete transition of the polymeric adhesive to the well-developed high-elastic state could not however be effected, and therefore the curve of σ_B vs. $\dot{P}$ contains only a descending branch for adhesive tear-off.

The effect of the nature of the support on the strength in the case of adhesive tear-off is due to the fact that the critical energy w^* depends on this factor.

Finally, the absence of the effect of the molecular mass of the adhesive on its strength can be accounted for in the following way. On the one hand, the strength of the contact (and, hence, the energy w^*), other conditions being identical (the nature of the support, temperature, etc.), depends primarily on the number of molecular contacts between the adhesive and the support. This quantity is determined by the mobility of the polymer chain, i.e., its ability to come into contact with the solid surface to distances sufficient for a strong joint to be formed. The mobility of the macromolecule of an uncured polymer is in its turn determined by the chain length between the adjacent

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†The comparison of Figure 11 with Figure 6 illustrates spectacularly the validity of the well-known principle of the temperature-rate equivalence for the case of fracture processes.

nodes of the physical (fluctuating) entanglement network. This entanglement network has been shown[15,16] to be independent of the molecular mass of of the polymer.

On the other hand, the ratio of the recoverable to the irrecoverable deformation of a polymer of narrow MMD under the conditions of its transition to the high-elastic state at a given stress does not depend on molecular mass. Summing up what has been said above, it may be stated that the course of the two processes—the energy accumulation and the fracture—is independent of MM (for sufficiently high MM).

Let us now compare the results of the investigation of adhesive joints of thin films of uncured polymers of narrow MMD with solids and the flow of these materials through capillaries.

It has been found[3,9] that the dependence of the durability of an adhesive joint of a polymer of narrow MMD with a solid on the stress in double logarithmic coordinates contains three portions which differ in the slope to the abscissa axis (Figure 12). These portions correspond to the various types of fracture of the joints. On the portion A there is observed a cohesive fracture, and on the portions B and C the cohesive-adhesive fracture and adhesive tear-off take place.

As has been established[3,9] in the case of the cohesive fracture the dependence of the durability on the stress, temperature, and the molecular mass of the adhesive is expressed by an equation of the type (5). In the case of cohesive-adhesive fracture the durability increases with decreasing MM and depends on temperature in a complicated way. On adhesive tear-off the durability is independent of MM.

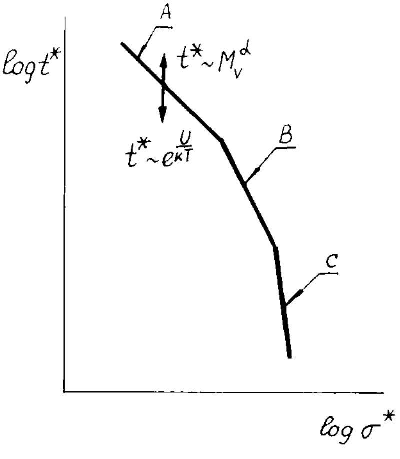

FIGURE 12 Schematic representation of the dependence of the durability t^* on stress σ^*. Adhesive joints of polymers of narrow MMD with solid surfaces. A = cohesive fracture; B = cohesive-adhesive fracture; C = adhesive tear-off.

The investigations of the flow of uncured PB and PI of narrow MMD[4, 5] have shown that two flow regimes are realized: the steady and non-steady flow conditions. In the latter case, two effects are observed. The first is the appearance on the extrudate surface of periodic distortions, which are increased as the pressure increases, so that the extrudate surface becomes screw-like. The second effect reveals itself at a certain critical value of the pressure drop (or shear stress), when a slight increase in the pressure (stress) leads to a sharp increase of the flow rate of the polymer. This phenomenon, which is the extreme form of nonsteady flow, is known as the spurt.

In this connection, the flow curves, i.e., the curves of the flow rate of the polymer $4Q/\pi R^3$ versus the shear stress τ_s consists of three portions in a general case, which correspond to various flow conditions. Figure 13 presents a flow curve, but for the convenience of the subsequent comparison, it is plotted in the coordinates of the inverse flow rate $(4Q/\pi R^3)^{-1}$ versus the shear stress τ_s. Here the inverse flow rate has the dimensions of time and may be regarded as a certain generalized strength characteristic reflecting the resistance of the material to flow or to tear-off from the wall.

On the curve of $(4Q/\pi R^3)^{-1}$ versus τ_s there can be distinguished three portions corresponding to various flow conditions. The portion A corresponds to the steady flow of the polymer; the portion B corresponds to the nonsteady flow conditions, when the distortion of the extrudate surface is observed, and the portion C corresponds to the spurt.

Calculations have shown that the dependence of the inverse flow rate on the shear stress, temperature, and the molecular mass of the elastomer are

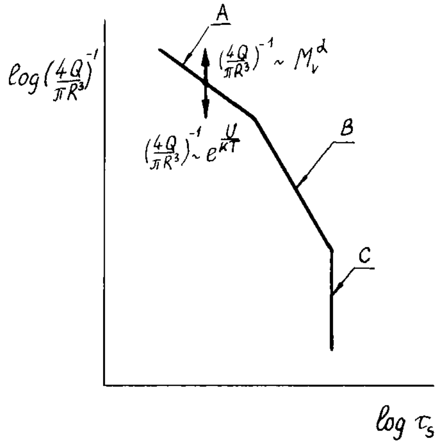

FIGURE 13 Schematic representation of the dependence of the inverse flow rate $(4Q/\pi R^3)^{-1}$ on the shear stress τ_s. The flow of polymers of narrow MMD through capillaries. A = true flow conditions; B = non-steady flow conditions accompanied by the appearance of distortions on the extrudate surface; C = flow spurt.

expressed by the following equation:

$$\left(\frac{4Q}{\pi R^3}\right)^{-1} = C(\tau^s)^{-m} e^{U/kT} M_v^{\alpha} \tag{7}$$

where C, m and α are constants; U is the activation energy of flow; the numerical values of the constants for PB are: $m = 0.7$ to 1.0; $\alpha = 3.2$ to 3.5.

The formal similarity between the relation (7) and the equation for the cohesive strength of uncured polymers (5) attracts attention. This allows us to interpret the flow as a form of the cohesive fracture of the polymer under shear conditions. The similarity between relations (5) and (7) reflects the fact that on cohesive fracture of uncured polymers and during their flow the resistance to fracture is mainly exerted by the intermolecular bonds. The main difference between the fracture and flow of polymers is that the flow does not involve macrofractures of the material due to the re-formation of intermolecular bonds; such macrofractures take place in cohesive fracture. However, on the level of microlinkages there is evidently no fundamental difference between the flow and fracture of uncured polymers.

If the latter supposition is valid, at least for uncured polymers of narrow MMD the dependence of the durability on stress, temperature and molecular mass in any state of stress is expressed in a general form by an equation of the type (5), and the effect of the stress state on the durability manifests itself in the change of the first factor in the equation, which expresses the power character of the relationship between the durability and the applied stress. The value of the exponent increases successively upon transition from a simple to a more complex stress state.

We shall now continue the comparison of flow curves with curves showing the dependence of the durability on the stress and examine the portions C on these curves (Figures 12 and 13). Here, too, a number of similar effects are observed. The durability of the joints on adhesive tear-off decreases very rapidly with increasing stress, just as the value of the inverse flow rate decreases in a jumpwise manner when a spurt takes place during the flow. It has been repeatedly pointed out above that the strength characteristics in the case of adhesive tear-off are independent of the molecular mass. An analogous picture is observed during the spurt.

What has been said above allows us to suppose that the spurt is caused by the transition from the flow (i.e., from the rupture of intermolecular bonds in the bulk of the material) to the tear-off of the uncured polymer from the capillary walls. This occurs as the result of the transition of the uncured polymer from the fluid to the forced high-elastic state. Here the durability of the polymer is greater than the strength of its contact with capillary walls. A number of experimental facts detected during the spurt (the electrization of the extrudate, the absence of its swelling, in which case the diameter of the stream may be even smaller than the capillary diameter) show that the tear-off of the extrudate from the walls does take place.

When the molecular mass decreases considerably, the sharpness of the spurt process is gradually degenerated; it is observed over a certain range of increasing pressure, just as in the case of the changeover from a narrow to a wider MMD. This is in good agreement with the facts considered in the present work, which shows that when MM decreases to $M_v = 8 \times 10^5$ for PB and to $M_v = 1.6 \times 10^5$ for PI the transition from the cohesive to the cohesive-adhesive fracture is smoothed out (see Figures 2 and 3, curves D).

CONCLUSION

The investigation of the process of fracture of adhesive joints of uncured elastomers of narrow and wide MMD with solids under the conditions of the triaxial stress state and the comparison of the data obtained with the known experimental facts for uniaxial extension and simple shear show that the changeover from simple shear and uniaxial extension to the triaxial stress state leads to an increase of the strength and durability of the joint. We have arrived at the conclusion that the strength is determined by the accumulation of elastic energy, while the durability depends on dissipation losses.

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