

Fracture of uncured linear flexible-chain polymers of narrow molecular mass distribution in triaxial stress (behaviour of elastomers as adhesives)

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Possibly the simplest method of studying polymers under conditions of triaxial stress is the investigation of the behaviour of thin films of adhesive between two rigid surfaces. The adhesives used were uncured linear flexible chain polymers—polybutadienes. These polymers were of narrow molecular mass distribution (*MMD*). The use of high molecular polymers of narrow *MMD* allows the evaluation of the behaviour of elastomers as adhesive joints to be simplified. It has been shown recently that, depending on the rate of deformation, the behaviour of polymers of this kind may be similar to that of viscoelastic liquids or systems in the high-elastic state, which behave as quasi-cured systems. The transition from the fluid to the high-elastic state is a pure relaxation process. It would be expected that the behaviour of the adhesive would vary substantially, depending on its physical state. The fracture behaviour of the adhesive and the rupture of its contact with the solid surface must be dependent on this factor. Cohesive, cohesive—adhesive and adhesive fractures may be observed in such cases. Cohesive fracture is typical for regimes of polymer deformation upon transition from the fluid to the high-elastic state. The further the transition of the polymer to the high-elastic state, the more sharply pronounced is the adhesive fracture of the polymer in triaxial stress. The present work is concerned with the investigation of the temperature—time dependence of the parameters characterizing the fracture of the adhesive and its contact with the solid surface. The results of experiments carried out under conditions of triaxial stress are compared with the data obtained for the same polybutadienes by experiments involving simple shear and uniaxial extension.

INTRODUCTION

The viscoelastic properties of uncured polybutadienes (PB) of narrow *MMD* under conditions of simple shear and uniaxial extension have already been studied^{1–3}. The most important result of these investigations is extensive information on the properties governing the forced transition of polymers from the fluid to the high-elastic state at temperatures above the glass transition temperature, which may be accompanied by fracture. It is precisely in this case of linear polymers with a narrow distribution of high molecular masses (*MM*) that a distinct dependence of behaviour on the rate of deformation or stress acting is observed.

According to the data reported in the literature^{4–6}, thin films of polymers placed between two solid surfaces, with the operating force normal to these surfaces, are characterized by the triaxial stress state. Therefore, in studying the behaviour of thin films of elastomers in contact with solid surfaces we might hope to obtain the fundamental characteristics specific to the triaxial stress state, including adhesion strength and long-term durability.

In considering the adhesion characteristics of elastomers we have to deal with a number of fundamental problems. First of all, we aim to elucidate the nature of the rupture of contact between thin films of polymers and a solid body, to

determine conditions under which the observation of cohesive fracture is possible and to find out how distinct is the transition to cohesive—adhesive fracture and then to adhesive fracture.

EXPERIMENTAL

We have investigated two samples of PB of narrow *MMD* ($M_w/M_n < 1.1$) and *MM* 6.4×10^5 and 1.5×10^5 in contact with steel and Teflon at various temperatures over a range of stresses from 5×10^{-2} to 1 MN/m^2 . The polymers were synthesized by anionic polymerization with *sec*-butyllithium as the catalyst. They contained about 45% *cis*-1,4- and *trans*-1,4- groups and about 10% 1,2- groups. Thin circular films were obtained by evaporation from a solution in toluene applied to the butt-end of a cylindrical steel ring. It has been found that the residual content of toluene in the films may amount to 7–10%. The thickness of the films was 80–100 μm , the outer diameter 9 mm and the inner diameter 3 mm.

The polymers under investigation were subjected to extension under the action of a constant force oriented perpendicular to the interface, on an instrument shown diagrammatically in *Figure 1*.

A support B (Swedish precision block) was placed on thermal unit A. A thermostatted liquid was passed through the thermal unit, which permitted the experiments to be conducted at temperatures of 3° to 100°C. The accuracy of temperature control was $\pm 0.5^\circ\text{C}$. The temperature was controlled by means of thermocouples.

The films of polymeric adhesive C were applied to the working edge of a cylindrical ring D in the manner described above. The ring D was arranged inside the duct E of the guiding block F. It was loaded in the direction of the axis. The cylindrical ring near the working edge is coned so that the portion of the polymer film squeezed during the formation of a contact beyond the perimeter of the working edge does not get into the vertical gap between ring D and duct wall E. The duct E is made of PTFE. Therefore, the force of friction upon movement of the cylindrical ring D with duct walls E was insignificant.

The duct E and the guiding block F were made in assembly. The axis of the cylindrical ring is perpendicular to the surface of the Swedish precision block so that fracture of the adhesive joint occurs uniformly over the entire surface area.

The cylindrical ring D is hinged, via a rigid tie G, to the right arm of the balanced lever H, which is free to move on ball bearings. Weights, I, are suspended from the left arm of the lever H. To suppress the elastic vibrations of the polymer adhesive, which arise from the rapid loading of the samples, use is made of a hydraulic damper J.

The contact between the adhesive and the solid surface was formed at a temperature of 60°C for 30 min under a pressure of 0.5 MN/m². The stress indicated was set up in

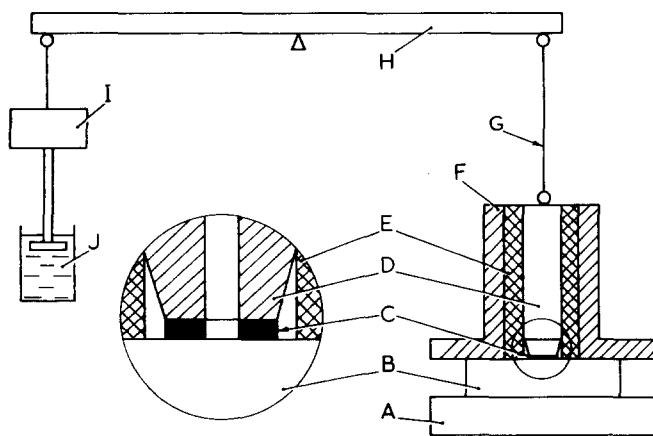


Figure 1 Schematic diagram of an adhesiometer

the contact zone for less than 1 sec. Then the contact temperature was brought to the required value, the specimen was loaded and the time to fracture was measured. The long-time durability of the polymeric film and of its contact with the solid surface was measured over a period of 0.1 sec to several days. The scatter of the data obtained was 25–30% with a reliability of 0.96.

The fracture behaviour of the adhesive joint was determined with the aid of optical and scanning electron microscopy, and also visually.

RESULTS

The dependence of the time to fracture t^* on the stress σ^* for PB of two MM in contact with steel and PTFE at a temperature of 20°C is presented in Figure 2. The results were treated by the least squares method. Assuming that the relations are approximated by power equations:

$$t^* = B(\sigma^*)^{-m} \quad (1)$$

where B and $-m$ are constants; their values are given in Table 1.

From Figure 2 it is seen that on the t^* versus σ^* curves for PB in contact with steel there are two regions of stress and time to fracture with different values of the indicated constants. These regions represent the different modes of fracture of PB films. In the region of lower values of B and $-m$ (indicated by filled symbols in Figure 2) cohesive fracture was observed. For cohesive fracture, just as in uniaxial extension, the long time durability falls off with decreasing MM of the adhesive.

At higher stresses (symbols Δ, \diamond in Figure 2) cohesive–adhesive fracture was recorded. In this case only some of the portions of the Swedish block surface were covered with the polymer

At stresses above 0.9 MN/m² the fracture becomes adhesive for two specimens of PB in contact with steel, but the tear-off occurs so quickly that it is impossible to measure the time to fracture (< 0.1 sec).

The effect of MM on long-term durability in the case of adhesive fracture has been studied for PB of the same molecular masses in contact with PTFE at a temperature of 20°C. The results of these studies are presented in Figure 2 (open symbols). The equations with the calculated constants are given in Table 1; fracture was adhesive and the long-term durability in this case is practically independent of the MM of the adhesive.

The adhesive joints of PB ($MM = 6.4 \times 10^5$) with steel

Table 1 Equations for the experimental relation between time to fracture, t , and fracture stress, σ , at various temperatures. PB of two MM in contact with steel and PTFE (in a range of stresses from 5×10^{-2} to 1 MN/m²)

Molecular mass	Temperature	Fracture		
		Cohesive	Cohesive–adhesive	Adhesive
6.4×10^5	5			$t = 1.6 \times 10^{-2} \sigma^{-3.96}$
	6		$t = 3.2 \times 10^{-1} \sigma^{-5.9}$	
	20	$t = 4.0 \times 10^2 \sigma^{-4.3}$	$t = 7.9 \times 10^{-3} \sigma^{-15.5}$	$t = 7.2 \times 10^{-11} \sigma^{-11.7}$
	35	$t = 1.6 \times 10^2 \sigma^{-4.3}$	$t = 6.3 \times 10^{-4} \sigma^{-25.1}$	
	50	$t = 1.0 \times 10^2 \sigma^{-4.1}$		
	60		$t = 4.4 \times 10^{-8} \sigma^{-10.0}$	
80	$t = 4.0 \times 10 \sigma^{-4.1}$			
1.5×10^5	20	$t = 5.0 \times 10 \sigma^{-4.0}$	$t = 5.0 \times 10^{-5} \sigma^{-14.7}$	$t = 2.0 \times 10^{-9} \sigma^{-10.2}$

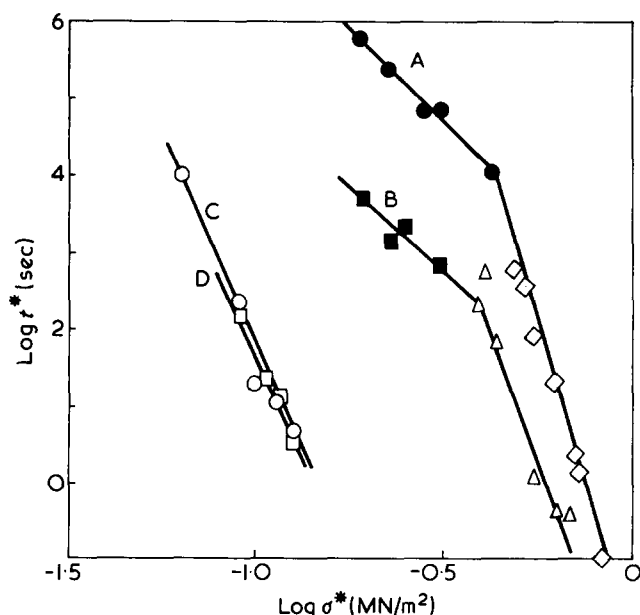


Figure 2 Durability t^* versus stress σ^* for PB of various MM in contact with steel (curves A and B) and PTFE (curves C and D) at 20°C . \bullet, \blacksquare , Cohesive fracture; \triangle, \diamond , cohesive-adhesive fracture the unfilled signs represent Adhesive tear-off: $\circ, MM = 6.4 \times 10^5$; $\square, MM = 1.5 \times 10^5$

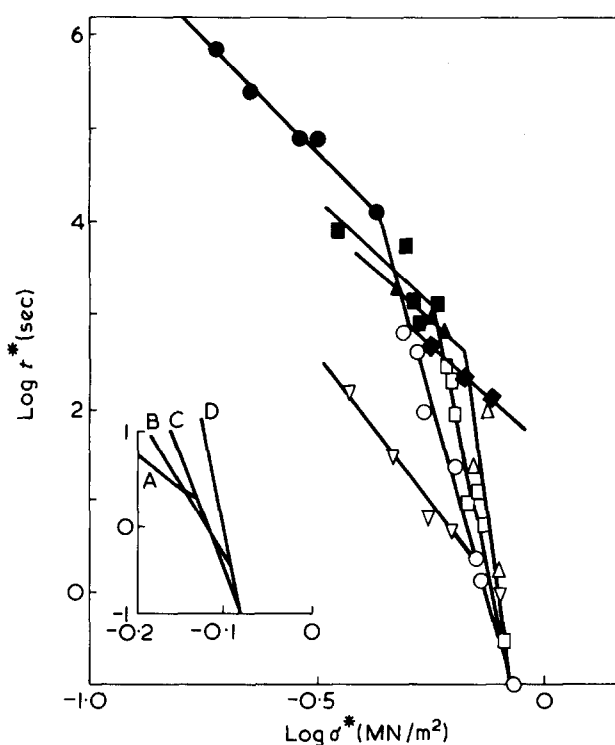


Figure 3 Ultimate strength versus time for PB ($MM = 6.4 \times 10^5$) in contact with steel at different temperatures. Cohesive fracture: $\bullet, \blacksquare, \blacktriangle, \blacklozenge$. Cohesive-adhesive fracture: $\triangle, \diamond, \circ, \square$. In the left-hand lower corner is the region of intersection of the t^* versus σ^* curves for the cohesive-adhesive fracture on an enlarged scale: A, 6°C ; B, 20°C ; C, 35°C ; D, 50°C

have been studied over the range of temperatures from 6° to 80°C . The results obtained are presented in Figure 3. The relevant equations which describe the long-term durability are given in Table 1.

From Figure 3 it is seen that in the case of cohesive fracture (filled symbols), just as in uniaxial extension, the time to fracture decreases with increasing temperature. At the same time for cohesive-adhesive fracture (open symbols)

the effect of temperature is ambiguous. The time to fracture increases with rising temperature at stresses below $0.7\text{--}0.8\text{ MN/m}^2$ and decreases at higher stresses. The latter case is presented schematically in the left-hand lower portion of Figure 3.

The temperature dependence of long-term durability has been studied at temperatures of $5^\circ, 20^\circ$ and 60°C for the joint of PB ($MM = 6.4 \times 10^5$) with PTFE. The results are given in Figure 4 and the relevant equations are presented in Table 1.

At 5° and 20°C the fracture was adhesive over the entire range of stresses used; at 60°C a transition from the cohesive-adhesive to the adhesive tear-off was observed (in Figure 4 the portion of the cohesive-adhesive tear-off is indicated by filled symbols). The indicated transition influenced with t^* versus σ^* curve, and altered its slope.

DISCUSSION

As follows from the experimental data, three characteristic portions may be distinguished on the t^* versus σ^* curve, which correspond to the cohesive, cohesive-adhesive, and adhesive fractures. Upon transition from the cohesive to the cohesive-adhesive fracture a sharp change in the stress dependence of long-term durability is observed, so that in the case of adhesive fracture the long-term durability falls off dramatically with increasing stress which is usually typical of brittle fracture.

Cohesive fracture

The long-term durability of the joints in the case of cohesive rupture is related to the stress, temperature and molecular mass, M_v , by the following equation:

$$t^* = B_1(\sigma^*)^{-m} \exp \frac{U}{kT} M_v^\alpha \quad (2)$$

where U is the activation energy of the rupture process; B_1 , $-m$ and α are constants.

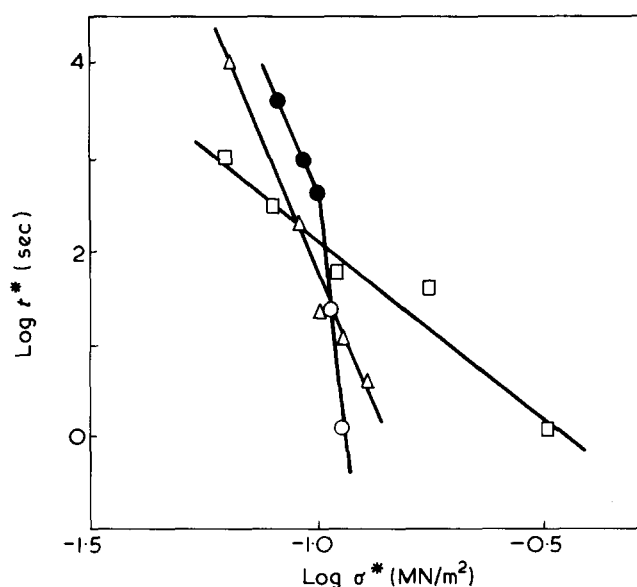


Figure 4 Ultimate strength versus time for PB ($MM = 6.4 \times 10^5$) in contact with PTFE at different temperatures. The unfilled signs denote adhesive tear-off; the filled signs represent cohesive-adhesive fracture. $\square = 5^\circ\text{C}$; $\triangle = 20^\circ\text{C}$; $\circ = 60^\circ\text{C}$

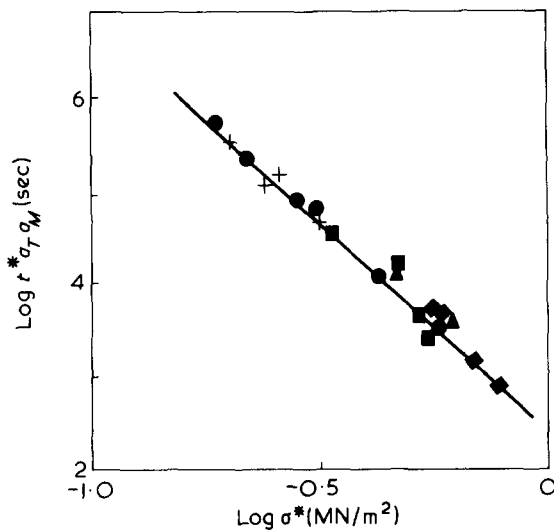


Figure 5 Master curve showing the dependence of the time-to-fracture on the fracture stress (reduced to 20°C). PB ($MM = 6.4 \times 10^5$). The signs are same as in Figure 5; + - PB ($MM = 1.5 \times 10^5$)

The dependence of long-term durability on stress and temperature is analogous to that reported in the literature for cured rubbers⁷⁻⁹. This may be regarded as indirect evidence that over the range of stress investigated, non-cured polymers are in the forced high-elastic state and behave as cured elastomers. According to a recently developed hypothesis⁴, the transition to the high elastic state results from the manifestation of a spatial fluctuating entanglement network in non-cured polymers, which at high deformation rates is like a network formed by chemical bonds.

Special investigations have shown that, just as in the case of uniaxial extension, the long-term durability of thin films on cohesive fracture is related to molecular mass by the following equation:

$$t^* = f(M_v^\alpha) \quad (3)$$

where $\alpha = 3.2$ to 3.3.

The nature of the dependence of long-term durability on stress, temperature, and MM shows that the cohesive strength of elastomers in the triaxial state of stress is determined by their relaxation characteristics and, in particular, by the initial viscosity. Considering that the cohesive fracture in question is relaxation in character, it is legitimate to make use of the reduction of the temperature-time relationships for the strength, with the shift factors calculated by the WLF equation

$$\log a_T = \frac{C_1(T - T_0)}{C_2 + T - T_0} \quad (4)$$

The values of the constants, $C_1 = 1.26$ and $C_2 = 31$, were calculated by the least squares method, assuming that the relationship $\log a_T$ versus $(T - T_0)$ approximates to a straight line. The procedure used here has been suggested in the literature¹⁰. Reduction was made to $t = 20^\circ\text{C}$.

Figure 5 shows the master curve representing the relation between $\log t^* a_T a_M$ and $\log \sigma^*$ for PB with $MM = 6.4 \times 10^5$ and 1.5×10^5 , reduced to 20°C and to $MM = 6.4 \times 10^5$ (a_M is assumed to be equal to α in equation 3). The corresponding equation calculated by the least squares method is $t^* = 2.5 \times 10^2 (\sigma^*)^{-4.4}$.

A comparison of the results under consideration with the

data reported in the literature^{1,3} shows that the long-time durability of thin films in the triaxial stressed state is 1.0–1.5 decimal orders higher and the fracture stresses 2–3 times greater than the corresponding values obtained under conditions of uniaxial extension. The comparison of the fracture stresses and long-term durabilities for the triaxial and uniaxial stressed states was made at equal durabilities and fracture stresses, respectively. It should be pointed out that the 2.5-fold increase of the fracture stress in the triaxial stressed state as compared with uniaxial extension has been reported in the literature⁶. This is indirect evidence that the specimens assume the triaxial stressed state under the conditions used in this work.

Investigation of the kinetics of fracture of the adhesive by means of the full internal reflection method has shown that it coincides with that described in the literature⁶ for the case of the triaxial stressed state. Fracture begins with the formation of microbubbles in the bulk of the adhesive. There is a delay from the moment of loading to the formation of the first bubbles. The fracture process progresses as follows: the size of the bubbles increases and the bubbles multiply until multilobe figures are formed. This stage of the fracture process also takes a certain period of time. The final stage, which proceeds at considerable speed, consists of the formation of crack-forking. Also, an important fact is established; at all stages in the fracture process removal of the load does not lead to recovery of the continuity (for several hours). This is accounted for by the fact that over the investigated range of temperatures and stresses plastic deformation predominates.

A comparison of the topology of the fracture surfaces of the adhesive with that reported in the literature⁶ for triaxial stress shows their undoubted similarity.

Cohesive-adhesive and adhesive fracture

In the case of cohesive-adhesive and adhesive fractures, the t^* versus σ^* curves at various temperatures have a more complicated character than those obtained for cohesive fracture.

The fracture of the polymeric layer between two solid surfaces and its tear-off from the solid surface depends largely, according to the literature data¹¹, on the state of the adhesive, namely, whether it behaves as an elastic, viscoelastic, or a plastic body.

Let us now discuss the dependence of the long-term durability on the inverse absolute temperature under conditions of cohesive-adhesive fracture and adhesive fracture. The relevant data are presented in Figures 6 and 7. They were obtained by substitution of the different values of $\log \sigma^*$ in the corresponding equations calculated from the experimental data (see Table I). The values of stress are indicated in the captions to the Figures.

The relationship between $\log t^*$ and T^{-1} can be reduced to the specific stress along the abscissa and the ordinate. The possibility of reduction to stress has been indicated in the literature¹².

The master curve of $\log t^* a_\sigma$ versus $(T^{-1} + a_\sigma)$ for adhesive tear-off is represented by a broken line in Figure 7. Reduction was made to stress $\sigma_0 = 0.106 \text{ MN/m}^2$. In contrast to the temperature shift factor for cohesive fracture, which was calculated from equation (4), in the case of adhesive tear-off the value of the shift factor for stresses, a_σ , was found by shifting the corresponding curves along the axes of inverse absolute temperature and time to achieve a superposition.

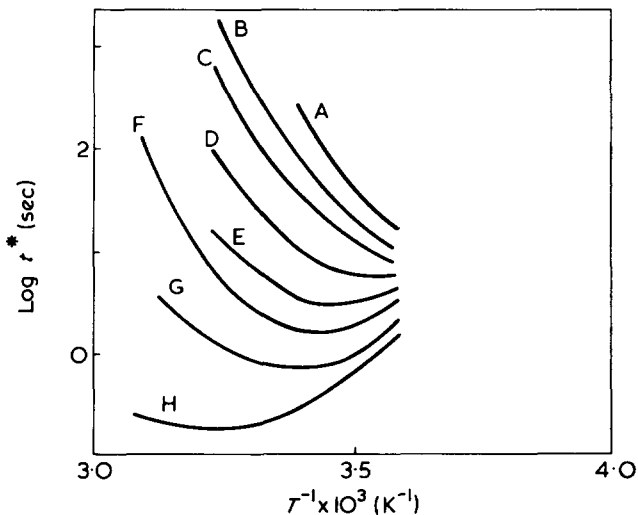


Figure 6 Cohesive-adhesive fracture. The long-term durability t^* versus the inverse absolute temperature T^{-1} at various stresses σ^* : A = 0.53; B = 0.56; C = 0.595; D = 0.63; E = 0.67; F = 0.71; G = 0.75; H = 0.8 MN/m²

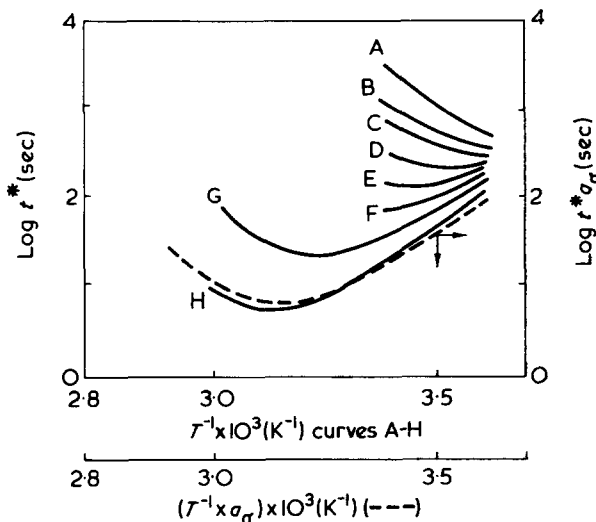


Figure 7 Adhesive tear-off. The long-term durability t^* against the inverse absolute temperature at various stresses (solid lines) σ^* : 1 = 0.071; 2 = 0.075; 3 = 0.08; 4 = 0.084; 5 = 0.089; 6 = 0.094; 7 = 0.1; 8 = 0.106 MN/m². The dashed line is the master curve of $\log t^* a_{\sigma}$ versus $(T^{-1} + a_{\sigma})$, $\sigma_0 = 0.106$ MN/m². PB (MM = 6.4×10^5) in contact with PTFE

The master curve of $(\log t^*) a_{\sigma}$ against $(T^{-1} + a_{\sigma})$ for the cohesive-adhesive fracture is given in Figure 8 (curve A). Reduction was made to stress $\sigma_0 = 0.8$ MN/m². The shift factor, a , was found by the method described above. The sign in Figure 7 indicates the values of long-time durability obtained experimentally at stress $\sigma^* = \sigma_0$. The experimental values are found to agree satisfactorily with the points lying on the master curve.

For the interpretation of Figures 7 and 8 we use the reported results of investigations on non-cured PB of narrow MMD¹ and those obtained by Velosevitch under conditions of uniaxial extension. These data allow us to obtain the master curves showing the dependence of true tensile stresses, σ , total deformation, ϵ^* , and its recoverable, ϵ_e , and irrecoverable, ϵ_f components on the inverse absolute temperature, these curves being reduced to a certain rate of deformation. The corresponding curves are shown in Figure 9.

The results given show that, just as in the case of investigations carried out at constant deformation rate, the process of extension at various temperatures may end up either with the attainment of steady-state flow conditions (open symbols on the curve of σ versus T^{-1}) or with rupture of the specimen at a certain critical stress σ_{cr} (filled symbols on the curve of σ versus T^{-1}). According to the data reported in the literature¹, the transition of non-cured polymers from the fluid to the forced high-elastic state occurs in this way. However, as follows from the character of the temperature-dependence of irrecoverable deformation, the value of ϵ_f remains considerable in the initial region of the high-elastic state. The fluidity is found to be almost suppressed only in the far post-critical stress region.

In uniaxial extension, fracture of PB of narrow MMD was observed at critical stresses of the order of 0.1 MN/m². The irrecoverable deformation accumulated in the specimen was of the order 0.2 ϵ_e at stresses ~ 1.0 MN/m². The stress region from 0.1 to 1.0 MN/m² coincides to a considerable extent, with that used in the present work, i.e. investi-

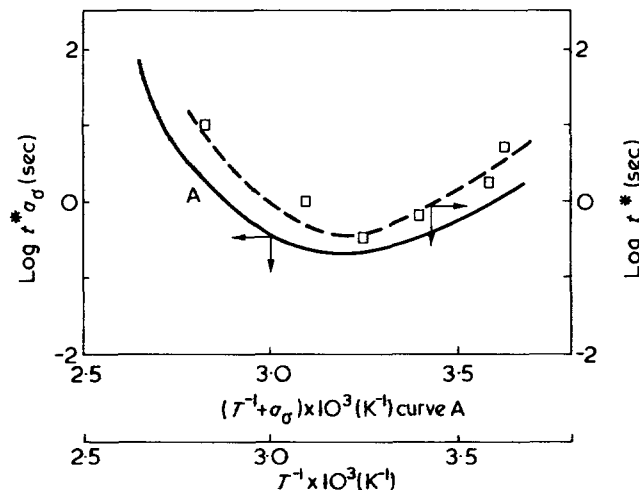


Figure 8 Cohesive-adhesive fracture. The master curve of $\log t^* a_{\sigma}$ versus $(T^{-1} + a_{\sigma})$ reduced to the stress $\sigma_0 = 0.8$ MN/m²; \square = experimental values of durability at the stress $\sigma^* = \sigma_0$. PB (MM = 6.4×10^5) in contact with steel

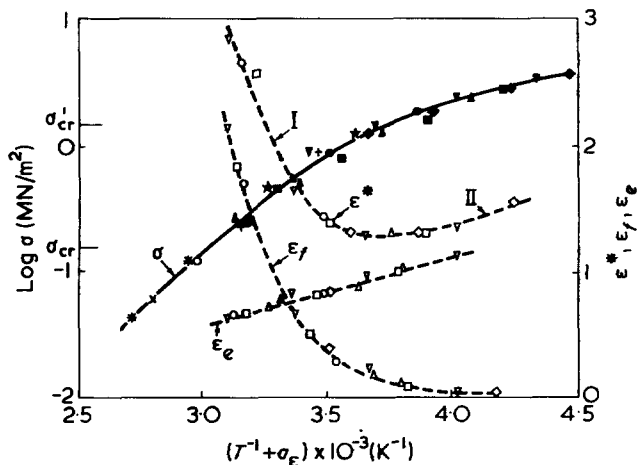


Figure 9 Master curve for the temperature dependence of true extension stress σ , total (ϵ^*) recoverable (ϵ_e) irrecoverable (ϵ_f) deformations which correspond to the rupture of PB (MM = 2.9×10^5) in uniaxial extension at various deformation rates (reduced to the rate equal to 0.56 sec⁻¹; $\diamond = 1.0$; $\triangle = 0.56$; $\square = 0.18$; $\triangle = 0.1$; $\circ = 0.056$; $*$ = 0.018; $\times = 0.01$ sec⁻¹

gations of adhesive strength were carried out in the transition region of the non-cured polymer from the fluid to the developed high-elastic state.

Let us now consider the temperature dependence of ϵ^* , ϵ_e and ϵ_f . The steeply descending curve of irrecoverable deformation shows the manner in which the ability of the polymers to accumulate irrecoverable deformation in the post-critical region decreases. The recoverable deformation in the post-critical region increases, and the total deformation passes through a well defined minimum. The shape of the resulting master curve of total deformation *versus* reduced absolute temperature is the same as that of the master curves presented in *Figures 7* and *8*.

According to the concept developed earlier¹², the total strain energy/unit volume may be expressed as the following sum:

$$W = W_e + W_e(t) + W_d \quad (5)$$

where W_e is the time-independent stored elastic energy, $W_e(t)$ is the time-dependent component of stored energy, and W_d is the dissipated energy.

For the tear-off of an adhesive from the solid surface or a cohesive–adhesive fracture to be realized, an energy W^* is required. These processes begin when W^* is greater than W_d , the thermodynamic work required for the formation of an interface (these quantities may become equal in the limiting case of very low rates or high temperatures when the viscoelastic energy dissipation around the microcracks, bubbles and macrocracks tends to zero).

The kinetics of the tear-off of the polymer from the steel has been studied. On the whole, it is qualitatively similar to that described above for the cohesive fracture. It has been established that the process starts with the formation of bubbles. A certain period of time elapses from the moment of loading to the moment of appearance of the first bubbles; this period of time depends on the magnitude of the applied stress. It is probably during this period of time that the stored energy increases up to the critical value. The visible fracture process then proceeds due to the increase of the number of bubbles and of their size. The final stage of this fracture process is the development of crack forking.

The duration of the two processes – the energy accumulation and the propagation of fracture – is temperature-sensitive. A decrease of temperature suppresses the mobility of molecules and increases the duration of the visible fracture process.

The temperature dependence of the duration of the accumulation of energy can be established by means of an analysis of the temperature dependence of the total deformation and its recoverable and plastic components. Here we assume that the character of the temperature dependences of the total, recoverable and irrecoverable, deformations in the cases of uniaxial extension and the triaxial stressed state are qualitatively the same. The components of the total energy, W , in expression (5) are related to the deformation characteristics of a non-cured adhesive. Thus, the stored energy, $W_e + W_e(t)$, is due to the amount of recoverable deformation and the dissipation of energy, W_d , to the amount of plastic deformation.

In the region of temperatures corresponding to branch I (of the ϵ *versus* T^{-1} curve *Figure 9*) the plastic deformation still plays an important part. Accordingly, the energy dissipation is extensive and the attainment of the value W_d takes a long time at the given stress. A fall of temperature leads to a decrease of the component W_d in expression (5) and of

the duration of the energy accumulation process. In the region of temperatures corresponding to the branch II (of the ϵ^* *versus* T^{-1} curve) the recoverable deformation prevails, while the dissipation of energy in the bulk of the adhesive is small. The time required for the energy equal to W^* to be accumulated will depend only slightly on temperature.

The transition to the region of temperatures corresponding to branch II implies the transition of the adhesive to the developed high-elastic state when the fluidity of the polymer is suppressed. The adhesive is an elastic body with a constant, practically temperature-independent modulus of high elasticity of the order of 1 MN/m² for PB. In this case the durability of the contact is largely governed by the duration of the visible fracture process. Here the decisive role is played by the temperature dependence of the energy required for the tear-off of an adhesive from the solid surface – the adhesive or cohesive–adhesive fracture – to take place. According to the data reported¹⁴, this energy increases with increasing rate of fracture. In accordance with the temperature–rate equivalence principle, the decrease of the contact temperature equivalence principle, the decrease of the contact temperature must also lead to an increase in the energy required for the tear-off to occur.

Thus, the extreme character of the temperature dependence of the durability of the contact of the adhesive with a solid surface (the broken line in *Figure 7*) is determined by the contributions of two processes – the accumulation of energy required for an interface to be formed and the kinetics of the fracture process. The course and duration of these processes depend substantially on temperature. The left branch of the t^* *versus* T^{-1} curve (the broken line in *Figure 7*) is found to be due to the temperature dependence of the energy accumulation and the right branch to temperature dependence of the energy W^* . It has been found that a rise of temperature leads to a considerable increase of the time of the accumulation of energy up to the formation of visible bubbles.

The concept proposed also accounts for the fact that the durability depends only slightly on MM in the case of adhesive fracture. As already stated, the strength of the coupling between the adhesive and steel (and, hence, the energy required for their separation) is determined by the number of molecular contacts, which is dependent on the ability of macromolecules to get into such a contact with the steel surface that a stable bond can be formed.

With high MM the effect of the ends of the macromolecules is immaterial. Therefore, for high-molecular adhesives the number of molecular contacts and hence the energy W_d , must not depend on the molecular mass of the adhesive.

On the other hand, it has been established^{1,3} that at the given stress and temperature the relation between the recoverable and irrecoverable components of total deformation determines the duration of the energy accumulation process. It is practically independent of the MM of a non-cured polymer of narrow MMD .

To sum up, we may state that the long-term durability of the contact between a non-cured polymer of narrow MMD and solid bodies in the case of adhesive fracture must not substantially depend on the MM of the adhesive.

CONCLUSIONS

The investigation of the strength properties of non-cured polymers of narrow MMD , using high-molecular polybutadienes as an example, in the triaxial stress state has shown

that the long-term durability is 1.0–1.5 decimal orders higher than that in the case of uniaxial extension, and the ultimate breaking stresses are 2–3 times greater than in uniaxial extension. On the whole, this is in agreement with the assumptions put forward in the literature concerning the effect of the state of stress on the strength properties of polymers.

At the same time, the dependence of the long-term durability of thin films of non-cured polymers of narrow *MMD* on temperature and stress are described by equations analogous to those derived earlier for cured rubbers. This points to the similarity between the effect of entanglement networks in non-cured elastomers and that of a network of chemical bonds in vulcanized rubbers. The decisive role in the fracture of thin films is played by the relation of high-elasticity and the viscosity of the polymer.

The study of the adhesion characteristics of non-cured polymers has demonstrated that in the case of adhesive and cohesive–adhesive fractures there is observed an extreme temperature dependence of long-term durability. Qualitatively, this is associated with the specific temperature dependence of total deformation and its components (recoverable and plastic) for non-cured polymers of narrow *MMD* in the

region of their transition from the fluid to the forced high-elastic state.

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