Effect of liquid media on the ultimate strength characteristics of viscofluid polymers in uniaxial extension

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The fracture properties and deformation behaviour of a linear amorphous polymer (1,2-polybutadiene) above the glass-transition temperature (−18°C) in liquid media have been studied. In accordance with data published earlier it is found that when fractured above T_g polymers behave like cured elastomers. Experiments conducted in low-molecular alcohols at 10°C show that the ultimate strength, durability (time-to-fracture) and development of irrecoverable deformation of viscous flow depend very strongly on the nature of the liquid medium, whereas the development of the elastic component of deformation is independent of the nature of the alcohols. It has been established that the dependence of durability on true fracture stress for the polymer studied is described by a power function. A simple correlation has been found between the surface tension at the polymer–liquid interface and the durability and ultimate strength of the polymers.

Keywords Polymers; fracture; deformation; 1,2-polybutadiene; glass transition; stress; surface tension

INTRODUCTION

Interest in a study of the effect of liquid media on the mechanical behaviour of polymers is accounted for, in the first place, by the fact that polymers are materials which are often exposed to various kinds of liquid media, some of which change markedly the physico-mechanical properties. Extreme cases are possible:liquid media can either exert a substantial effect, as a result of which the swollen polymer is plasticized[1–3], or the action of the liquid medium is associated with change of surface properties of a polymer due to the adsorption which decreases the surface energy at the polymer–liquid medium interface[4–6].

The question of the effect of adsorption-active media on the mechanical properties of polymers has been examined in the literature for solid (glassy and crystalline) substances[6–11] and also for vulcanized rubbers[12]. But the question of the effect of liquid media on the deformation-strength properties of uncrosslinked amorphous polymers above their glass-transition temperatures has not been studied. No general theoretical treatment of the interaction between the sruface of polymers at $T > T_g$ and liquid media has been carried out; nor have the practical aspects been studied. During extrusion and moulding the products are often exposed to various liquid media.

The general setting-up of the problem of the deformation of fluid polymers in liquid media must be based on fundamental investigation of the uniaxial extension of linear polymers at temperatures above their glass-transition temperatures[13,14].

The importance of uniaxial extension depends on the fact that upon deformation of this kind an especially broad range of stresses and deformation rates can be realized[15].

In this connection, it is important to inquire into the effect of liquid media on the general regularities of the behaviour of fluid polymers in uniaxial extension and, in particular, on the ratio of recoverable and irrecoverable deformations and the conditions of fracture of polymers at $T > T_g$.

Special attention will be paid to the conditions of the transition of liquid polymers to the forced rubbery-quasicrosslinked and leathery states. The latter is intermediate with respect to the ability to display recoverable deformation and brittleness. Such transitions occur as the rate of deformation increases, when the relaxation characteristics of the polymer are shifted, respectively, from the fluid to the rubbery and leathery states (or, using the terminology currently employed for the description of the dynamic properties of polymers, from the terminal zone to the rubbery plateau and the transition zone). The problem of forced transitions from one state to another has been intensively studied by Vinogradov and his associates since 1975[14,16]. A summary paper was published in *Polymer* in 1977[15]. The above-mentioned forced transition has recently been discussed by Vinogradov[17] and in a paper written by a group of authors[18].

EXPERIMENTAL

The investigations were carried out on amorphous linear 1,2-polybutadiene (PB), which had the following

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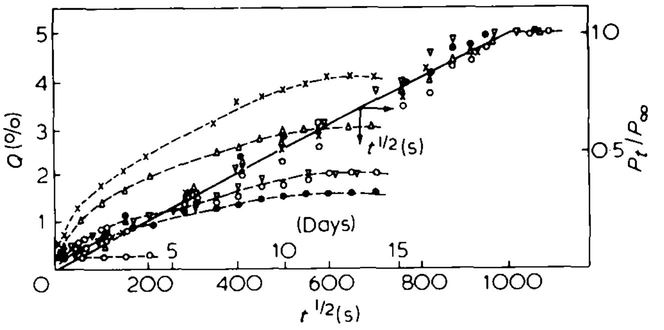

Figure 1 Time dependence of the degree of swelling (broken line) and of the relative weight change (solid line) of the samples; ⊙ – water; ● – ethanol; △ – isopropanol; ○ – propanol; △ – butanol; X – amyl alcohol

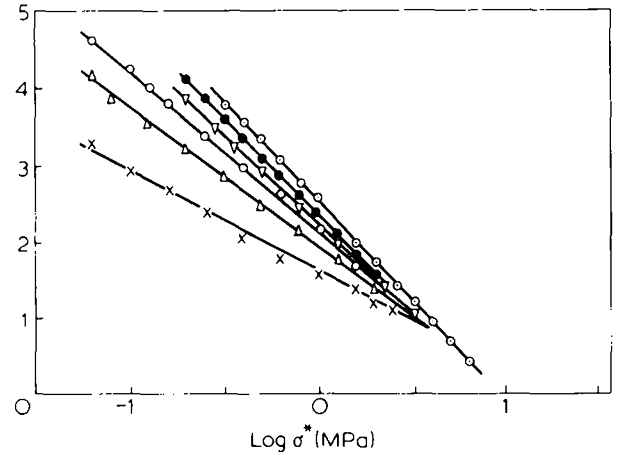

Figure 2 Dependence of durability on the true fracture stress in short-time experiments. The designations are the same as in *Figure 1*

characteristics: average-viscosity molecular mass 135 000, degree of polydispersity $M_w/M_n = 1.75$, the content of units in 1,2-position 84%, and $T_g = -18°C$. The test samples of cylindrical form, produced by compression moulding, were 30 mm long and 5 mm in diameter. All measurements were made at a temperature of 10°C on samples of the same size in order to eliminate the effect of the relative surface dimensions on the experimental results when going from one liquid medium to another[19]. The liquid media used were normal alcohols: ethanol, propanol, butanol, amyl alcohol, and also *iso*propyl alcohol and water. To evaluate the degree of swelling of PB in these liquid media, the kinetics of swelling were studied (*Figure 1*). From the data obtained it follows that the degree of swelling of the polymer is relatively low in these liquids. The maximum degree of swelling for 14 days is 4% in amyl alcohol. It has been found that the diffusion coefficient is practically the same for all alcohols and is equal to 1×10^{-12} m^2 s^{-1}. The given value of the diffusion coefficient is consistent with literature data[20].

Two sets of experiments were conducted. In short-time experiments adsorption played a dominant role and the quantity of absorbed alcohols did not exceed tenths of a percent. In long-term experiments equilibrium swelling of the polymer was attained.

The measurements of the rheological properties in uniaxial extension were made under creep conditions at different values of true stresses in an apparatus analogous to the one described in the literature[21]. The Hencky relative strain was used as a quantitative measure of strain[22].

The total, recoverable and irrecoverable deformations are as follows:

$$\varepsilon = \ln(L/L_0) \qquad (1)$$

$$\varepsilon_e = \ln(L/L_f) \qquad (2)$$

$$\varepsilon_f = \ln(L_f/L_0) \qquad (3)$$

where L_0 is the initial length of the sample; L_f is the residual (relaxed) length; and L is the total length of the sample.

RESULTS AND DISCUSSION

Firstly, considering the results of measurements of the time-to-fracture (t^*, durability) of the polymer in various liquid media (short-time experiments), these are presented in *Figure 2* and correspond to the power law typical for crosslinked rubber[23].

As the points in *Figure 2* correspond to different states of polymer swelling, the values of the parameters which describe the power function have only a qualitative meaning.

The regularity known for the vulcanized rubber indicates that the exponent of the function under consideration diminishes when going from a rigid to a soft rubber, namely from 12 to 3[23]. In our case the exponent diminishes from 3 for polybutadiene in air and water to 1.4 in amyl alcohol. This demonstrates the fact that under the action of alcohols the ultimate strength of the elastomer decreases and the deformability increases.

On examining *Figure 2*, one can see that there exists a 'pole' at which all the dependences $t^*(\sigma^*)$ plotted for deformation in different media intersect. This point at $t^*_{cr} \sim 10$–20 s and $\sigma^*_{cr} \approx 3$–4 MPa may probably be treated as certain 'instantaneous' strength. At $t \leq t^*_{cr}$ the surrounding medium does not affect the conditions under which the specimens being stretched are fractured because it has no time to be adsorbed on the polymer surface.

Figures 3a and *b* present data obtained for polybutadiene under the conditions of equilibrium swelling. Comparison of *Figures 2* and *3a* reveals the fact that, as can be expected, at a given value of t^* the ultimate strengths for the swollen samples are noticeably reduced.

In the region of low stresses, when noticeable flow deformations are developing in the material, the effect of the medium is stronger the higher the durability of the sample. Of interest in this connection is the consideration of the effect of liquid media on the limiting values of the ultimate total deformation ε^* at the moment of fracture and its components: the elastic component ε^*_e and the viscous component ε^*_f.

Figure 4 is a plot of the total fracture deformation ε^* against the fracture stress σ^* in various liquid media. As can be seen, the dependences $\varepsilon^*(\sigma^*)$ are extremal, i.e. they are described by the curves with a minimum. The cause of this course of the dependence $\varepsilon^*(\sigma^*)$ has been elucidated in a series of publications by G. V. Vinogradov and colleagues[13-16,24-27]. It is associated with the ratio of the irrecoverable deformation ε^*_f, which decreases with increasing σ, to the increasing elastic (recoverable) deformation ε^*_e, and is most characteristic of high-molecular polymers with a narrow molecular-mass distribution. As regards the minimum on the extreme left $\varepsilon^*(\sigma^*)$ curve plotted for extension in amyl alcohol (short-time experiments), its appearance can be expected at even

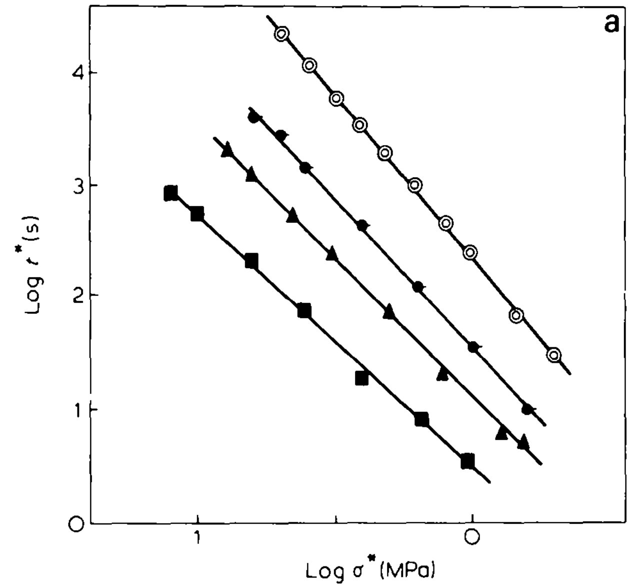

Figure 3a Dependence of durability on the true fracture stress in long-term experiments; ◎ – air; ● – propanol; ▲ – butanol; ■ – amyl alcohol

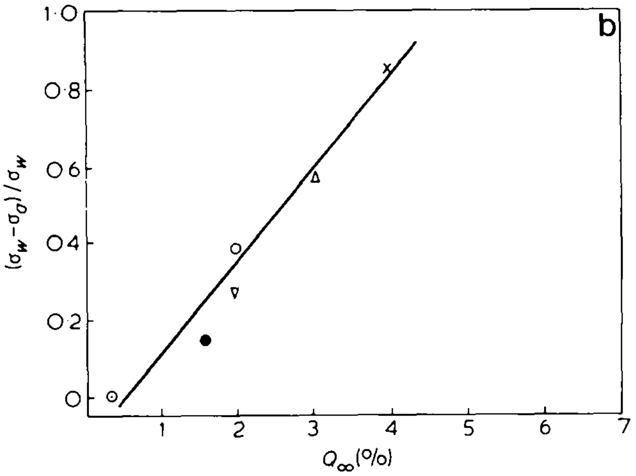

Figure 3b Dependence of relative change in ultimate strength (here σ_W and σ_a correspond to the ultimate strength of polymer in water and alcohols) on the limiting equilibrium quantity of alcohols) on the limiting equilibrium quantity of alcohols adsorbed by the polymer (long-term experiments). The designations are the same as in *Figure 1*

lower stresses which fall within the sensitivity limits of the experimental method. From the analysis of *Figure 4* one can conclude that as the activity of the liquid medium increases the position of the minimum of the dependence $\varepsilon^*(\sigma^*)$ shifts toward lower stresses. This also gives rise to a sharp difference between the values of ε^* in the region of low stresses, depending on the nature of the medium (in short-time experiments, for example, at $\sigma = 0.3$. MPa in water the sample can be stretched 800% and in amyl alcohol 200%). In the region of high stresses (at $\sigma > \sigma^*_{cr}$; where the value of σ^*_{cr} is regarded as the 'pole' in *Figure 2*) the liquid medium has practically no effect on the course of the ascending branch of the $\varepsilon^*(\sigma^*)$ curve. This means that in the region of $\sigma > \sigma^*_{cr}$ where there is practically no viscous flow, the development of elastic deformation must be insensitive to the medium surrounding the sample. This is well illustrated for the short-time experiments by *Figure 5*, from which it is seen that the limiting fracture elastic strain is independent of the nature of the liquid medium over the entire range of stresses. It has been found[24] that ε_e^{cr} is invariant to the nature of the polymer, temperature and deformation regimes. Where $\varepsilon_e^{cr} = 0.5$. This conclusion is generalized for the data obtained, which indicate that the amount of recoverable deformation is independent of the nature of low-molecular alcohols; with the alcohols (in short-time experiments) ε_e^{cr} is close to the above indicated value.

It is also important to note that when linear PB is stretched in air and water at sufficiently high stresses ($\sigma \geqslant 0.1$–0.15 MPa) there begins an inhomogeneous deformation; a neck is formed. As the activity of the liquid medium increases there takes place a monotonous shift of stresses (at which a neck is formed) toward higher values.

The behaviour of the samples at $\sigma < \sigma^*_{cr}$ is associated with the effect of liquid media on the mode of development of irrecoverable flow deformations. This is illustrated by *Figure 6*. The right branches of the curves presented in the figure correspond asymptotically to the critical value σ^*_{cr} which describes the transition of the system from the fluid to the rubbery state. It is seen that as the activity of the alcohols increases the value of σ^*_{cr} diminishes greatly.

Now consider the interelationship of the durability and compliance of the samples in short-time and long-term experiments. The relevant data are presented in *Figure 7*.

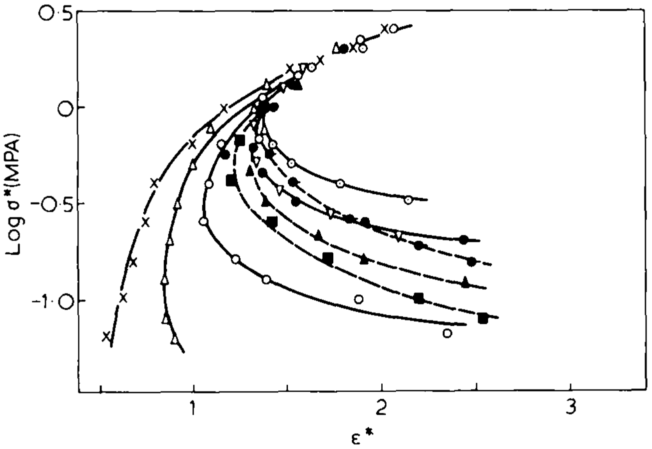

Figure 4 Dependence of true fracture stress on the total fracture deformation (short-time and long-time experiments). The designations are the same as in *Figures 1* and *3a*

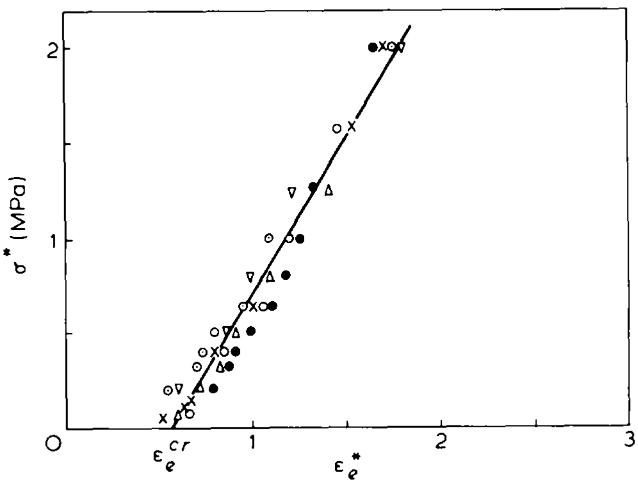

Figure 5 Dependence of ultimate strength on the recoverable strain in short-time experiments. The designations are the same as in *Figure 1*

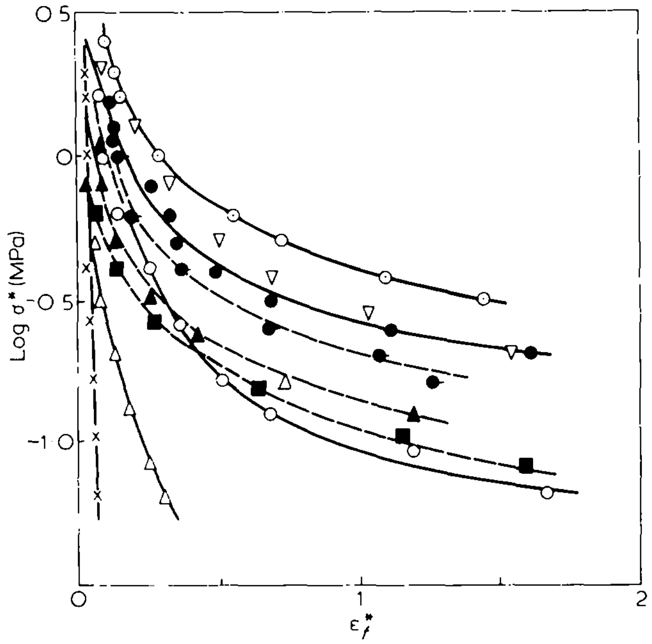

Figure 6 Dependence of ultimate strength of polybutadiene on the irrecoverable deformation. The designations are the same as in *Figures 1* and *3a*

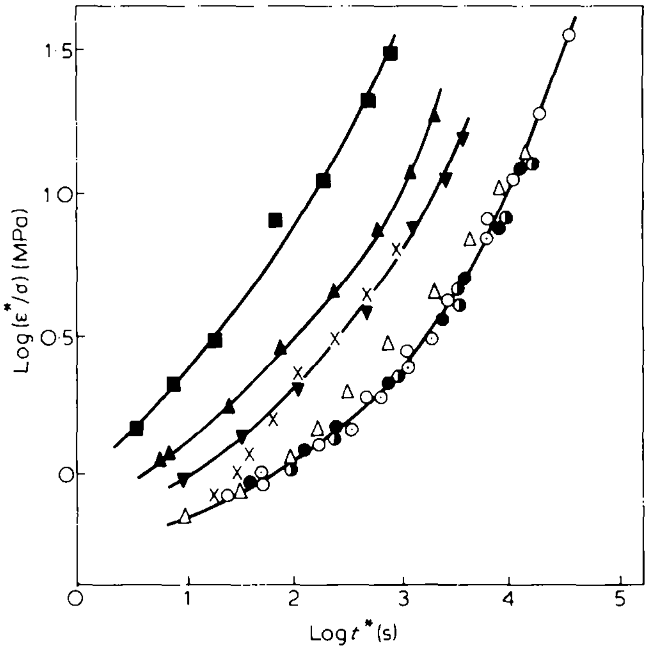

Figure 7 Dependence of the compliance on durability in short-time and long-term experiments. The designations are the same as in *Figures 1* and *3a*

The polymer used in the present work undergoes a slight equilibrium swelling in the alcohols (1–2%; only in amyl alcohol does it reach 4%). The absorption of the liquid does not exceed tenths of a percent during the time interval used in short-time experiments. Therefore, in this special case we cannot speak of bulk plasticization of the samples. This is also evidenced by the constancy of the values of the elastic modulus (see *Figure 5*) and of the extensional viscosity (*Figure 8*). Thus, in short-time experiments the liquid medium surrounding the polymer sample has no effect on the bulk resistance to deformation. All these experimental data allow one to conclude that the change of the durability and limiting (fracture) deformations of PB in short-time experiments are due mainly to the adsorption decrease in the interfacial tension energy and local plasticization of the surface layers of the polymer by physically active liquid media.

In order to determine if there exists a correlation between the durability of the polymer in various liquid media (short-time experiments) and the nature of the surface interaction, the surface tensions $\gamma_{p,l}$ at the polymer-liquid medium interface were determined for the liquids studied. The values of $\gamma_{p,l}$ were calculated from the results of measurements of the contact angle θ with the aid of Young's equation[28]:

$$\gamma_{p,l} = \gamma_p - \gamma_l \cos\theta \tag{4}$$

where γ_p and γ_l are the surface tensions of the polymer and alcohols at the interface with air. The angle θ was determined from the projection of a liquid drop applied onto the surface of the plate of PB pressed between mirror surfaces made of stainless steel. It has been found that the magnitude of θ is practically independent of the degree of swelling of PB in the media studied. The reproducibility of measurements of $\cos\theta$ was ±10%. The value of γ_p was determined from the dependence $\cos\theta = f(\gamma_l)$ upon extrapolation of $\cos\theta$ to unity[29]. The value of γ_p obtained was close to the published value of the surface tension of polybutadiene (3.1×10^{-2} N m^{-1})[28].

Figure 9 gives the dependence of durability and ultimate strength on $\gamma_{p,l}$. It is seen that the durability at a constant stress (in this particular case the stress was equal to 0.1 MPa) depends exponentially on $\gamma_{p,l}$. Accordingly, this dependence is expressed by the following empirical formula, which is valid for all the media studied:

$$t^* = C e^{k\gamma_{p,l}} \sigma^{-(\alpha_0 + b\gamma_{p,l})} \tag{5}$$

where the empirical constants have the following values: $C = 0.25$; $k = 0.2$; $\alpha_0 = 0.9$ and $b = 0.146$.

Calculations by this formula have shown that within the limits of experimental error (±0.1 of decimal order) it describes rather well the properties of PB samples stretched in the liquids studied. The inaccuracy given above does not exceed the error of measurement of the durability.

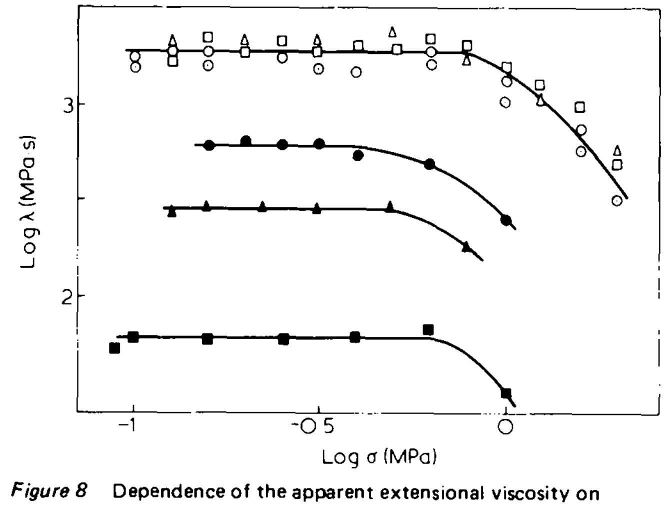

Figure 8 Dependence of the apparent extensional viscosity on stress under the conditions of sample fracture. The designations are the same as in *Figures 1* and *3a*

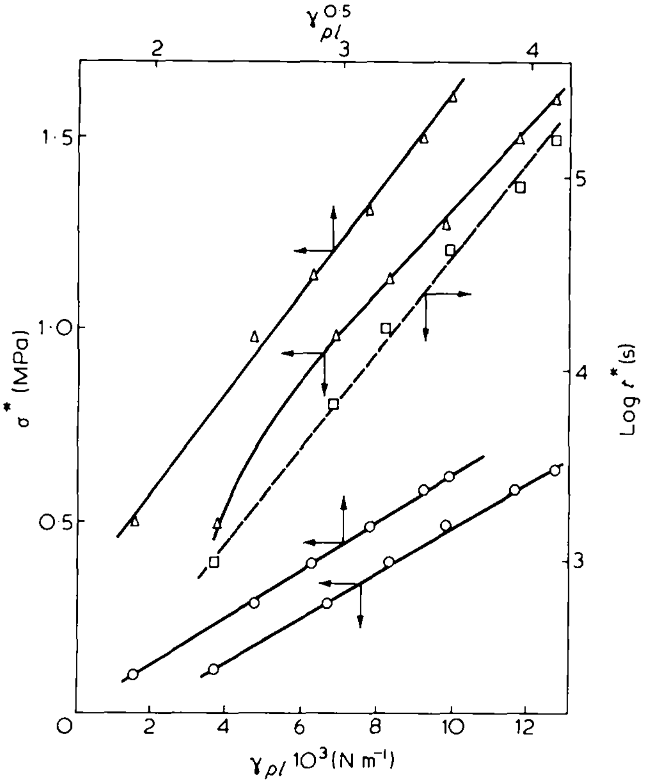

Figure 9 Dependence of durability at $\sigma = 0, 1$ MPa (broken line) and ultimate strength (solid line) on interfacial tension between polymer and alcohols: △ – *at* $t^* = 10^2$ s; ○ – *at* $t^* = 10^3$ s

The data presented in *Figures 9* and *2* allow one to conclude that in short-time experiments the fracture process is not a process that takes place in the bulk; its velocity as estimated by the durability is goverened by the state of the surface layers. The more greatly changed is the surface of the polymer by liquid media, the lower are the values of $\gamma_{p,l}$ and the lower is the durability of the material.

Figure 9 also shows a typical relationship between the ultimate strength and interfacial tension (for the time-to-fracture $t^* = 10^2$ and 10^3s in this particular case). Considering that $\gamma_{p,l}$ changes by more than three times, apart from the linear dependence of σ^* on $\gamma_{p,l}$, an attempt has been made to describe the strength in short-time experiments as a function of $\gamma_{p,l}^{0.5}$, which must correspond to the Griffith theory[30].

However, taking into account that the Griffith theory is not always applicable in experiments with solid polymers and rubbers and also the fact that we used a limited number of liquid media, it follows that it is important only for a purely qualitative treatment of the problem. It should also be taken into account that even in short-time experiments a certain influence can be exerted by the swelling of the surface layer of the polymer, which is the subject of a later paper.

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