The Main Peculiarities of Viscoelastic Behaviour of Elastomers with Different Polymerhomologues Series in Wide Range Temperature, Frequencies and Rules of Determination.

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The present report sums up the certain principal results of investigation in the field of viscoelastic behaviour and rupture of elastomers at elavated temperatures, rate and frequencies of deformation and different conditions of deformation.

Introduction

As one knows the deformability of polymers depends on their physical states, the relaxation transitions from one state to another are of importance. This problem has been widely elucidated in literature. The transitions are determined by typical temperatures or moduli. What is most convenient means of detecting the relaxation transitions ? This is our first topic.

The results below were obtained for simple shear and uniaxial extension in continuous deformation, and periodic deformation (dynamic measurements). What is an influence of such relaxation transitions on the flow features of elastomers by different way of deformation ? This is our second topic.

The present work demonstrates that there exists a range of elastomer deformation regimes in which elastomer fracture is determined by the initial value of the elastomer viscosity. This is important, since it allows prediction of the limiting conditions tests. What is universal parameters one can describe of elastomers fracture by deformation ? This is our third topic.

Thermomechanical Estimation of Relaxations Transitions and a Dual Approach to their Determination

At present, studies of the rheological properties of polymer systems based on experiments with periodic low-amplitude deformation, are widely used in practice. Such studies have been successfully used to analyze the behaviour of polymer system in transition from one physical state to another and to evaluate the conditions under which these states are attained at varying strain rates or frequencies or temperatures.

In this connection let us consider two approaches : variable frequency and constant temperature, or variable temperature and constant frequency. In the former case one can to study the properties of the polymer and the relaxation transition from fluid to forced rubbery, leathery and glassy states achieved under the effect of mechanical factors. The literature contains many descriptions of experiments based on both approaches. A dual approach to determination of relaxation transition is illustrated for 1,2-polybutadiene (PB) of narrow MWD in *figure 1*. It can be seen that the method of varying temperature is more effective for determining relaxation transitions than that of varying frequence, since it is much more difficult to perform measurements of over several frequency decades than to increase the temperature by several tens of degrees.

The Transition of Polymers from the fluid to Rubbery State in Simple Shear. The Spurt Effect

The relaxation transition from the fluid to rubbery state can be studied in simple experiments with constant-pressure capillary viscometers. This can be seen from *figure 2*, which shows the

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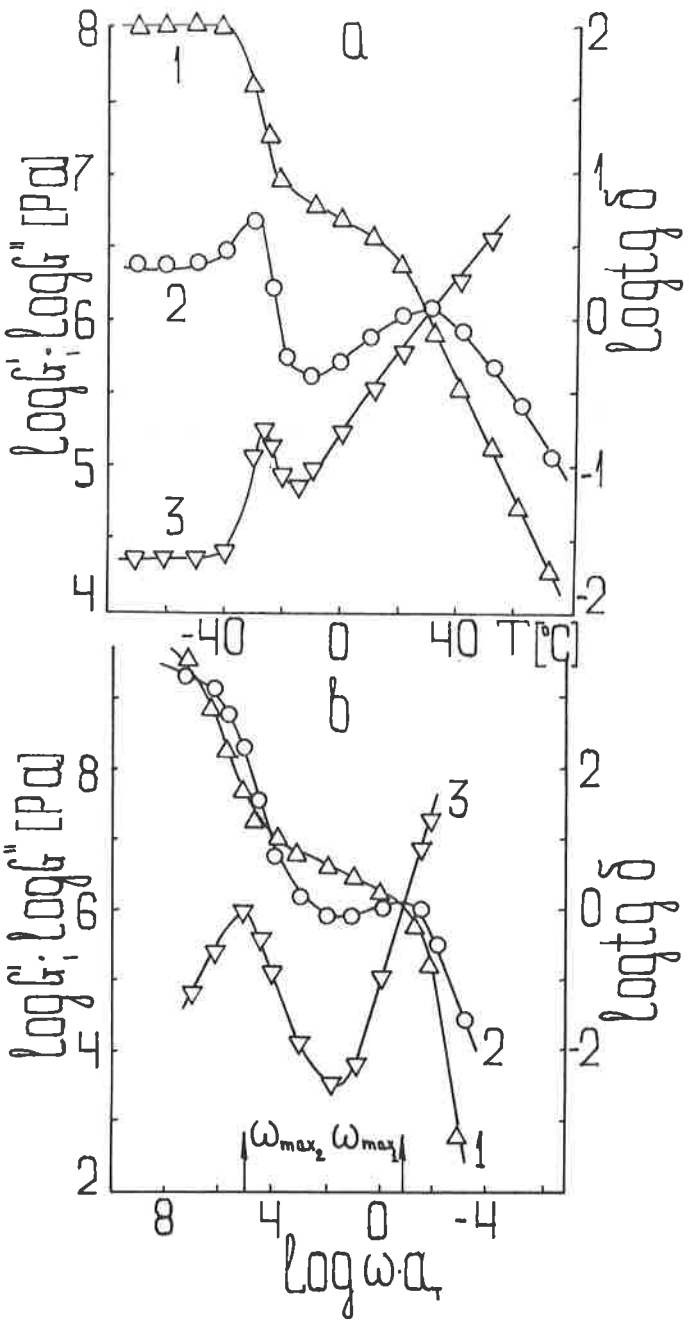

FIGURE 1. - *Dependence of storage G' and loss G" moduli and loss tangent tan δ of 1,2-PB on temperature at ω = 10⁻² s⁻¹ (a) and on frequency ω at 23 °C (b).*

behaviour of 1,4-PB with narrow MWD. Up to certain critical values of the shear stress, the polymers behave as newtonian liquids. This is typical for the elastomers with narrow MWD for temperature much more heigher then glass-transition temperature. It should be noted, however, that with decreasing temperature the non-newtonian nature of the flow becomes stronger and stronger. These qualitative considerations are confirmed by experiments over a range of temperatures.

The critical shear stress τ_{sp} is an important characteristic for all high molecular weight polymer compositions. As the viscosity remains about constant untill τ_{sp} is reached, the critical values of shear rate are inversely proportional to the initial viscosity and therefore are correspondingly dependent on temperature and molecular weight. After the transition to the rubbery state an

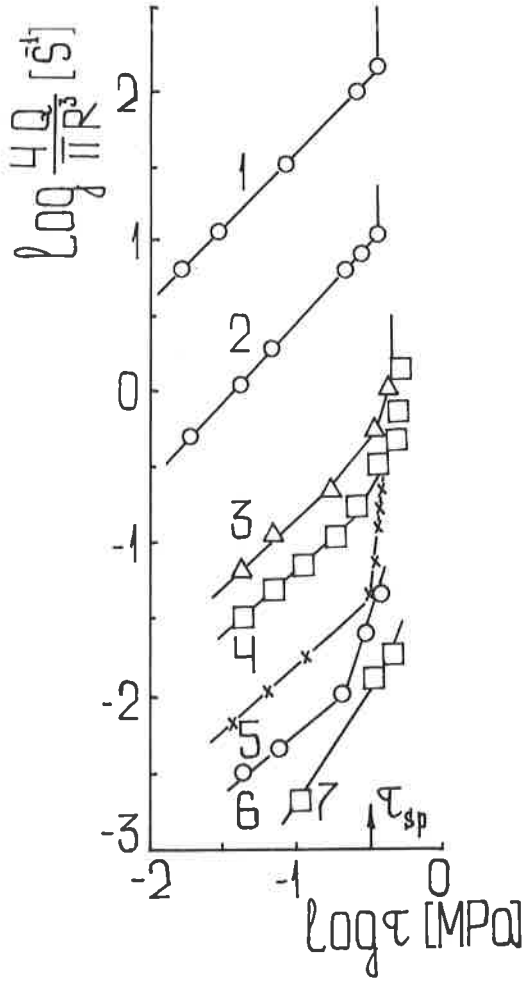

FIGURE 2. - *Shear rate versus shear stress τ for 1,4-PB. Curves 1-7 temperatures respectively, °C ; 100 ; 23 ; - 17 ; - 27 ; - 47 ; - 49 ; - 51.*

elastomer behaves in a quasi-crosslinked manner with its fluidity being suppressed. As large recoverable (high-elastic) deformation is accumulated, the elastomer fractures like cured rubber. A sharp jump in the flow rate, corresponding to the spurt effect, appears as a result of detachment of elastomer in the rubbery state from capillary walls.

Since in steady-state flow the stress uniquely determines the unrecoverably lost energy, there exists a quantitative correspondence between the shear stress and the loss mudulus.

The critical shear stress τ_{sp} is numerically equal to the maximum loss modulus. Furthermore, the correlation between these parameters is emphasized by the fact that the two quantities are practically independent of temperature and molecular weight. The parameter under consideration are important characteristics of elastomer compositions. It has been found that for various elastomer compositions the values of the critical fracture stress, the maximum loss modulus and dynamic storage modulus on the viscoelastic plateau differ by less than a factor of 20. The absolute value of the critical stresses lie between 0.1 and 1 MPa. These values also characterize the limiting stresses for steady-state flow of elastomers. The spurt process does not depend on temperature.

In overspurt regimes an elastomer loses its continuity at channel entrance, after which elastomer fragments densely compressed by the pressure drop in the channel move like a solid body.

It should be noted that in overspurt regimes the nature of the

dependence of the volume output on the shear stress is practically independent of the chemical nature of the elastomers. The difference in stresses required to obtain the same flow rate is small ; in the limiting cases, these stresses may differ by a factor of two.

When considering the complex of phenomena observed in deformation of elastomers in the spurt region the question arises : how does the strain effect the elastomer transition to the rubber-like state ? The answer to this question can be obtained from the results of dynamic tests with increasing amplitudes of deformation. It was found that with increasing amplitude, the transition from the fluid state to the rubber-like state shifts towards lower frequencies. A comparison of frequencies corresponding to critical amplitudes of deformation at which the spurt effect takes place with the frequencies corresponding to the maximum on the loss modulus vs frequency curves in experiments with low amplitudes, shows that although large deformations affect to a certain extent the transition of the system from the fluid state to the rubber-like state, the spurt occurs as a result of limited fluidity of an elastomer in the rubbery state.

Since the transition under consideration is of the relaxation type, its deformation rate characteristic, i.e. the amplitude of the rate of deformation, is most important. Experiments show that for large deformations, the transition from the fluid state to the rubber-like state occurs at a critical value of the amplitude of the deformation rate, which is constant for a given temperature. Moreover, the spurt observed in these experiments can be characterized by the same value (figure 3). One can show that the magnitude of the critical amplitude of the deformation rate coincides with the magnitudes of the critical shear rate obtained in experiments with a capillary viscometer and depends in a similar way on the molecular weight and temperature.

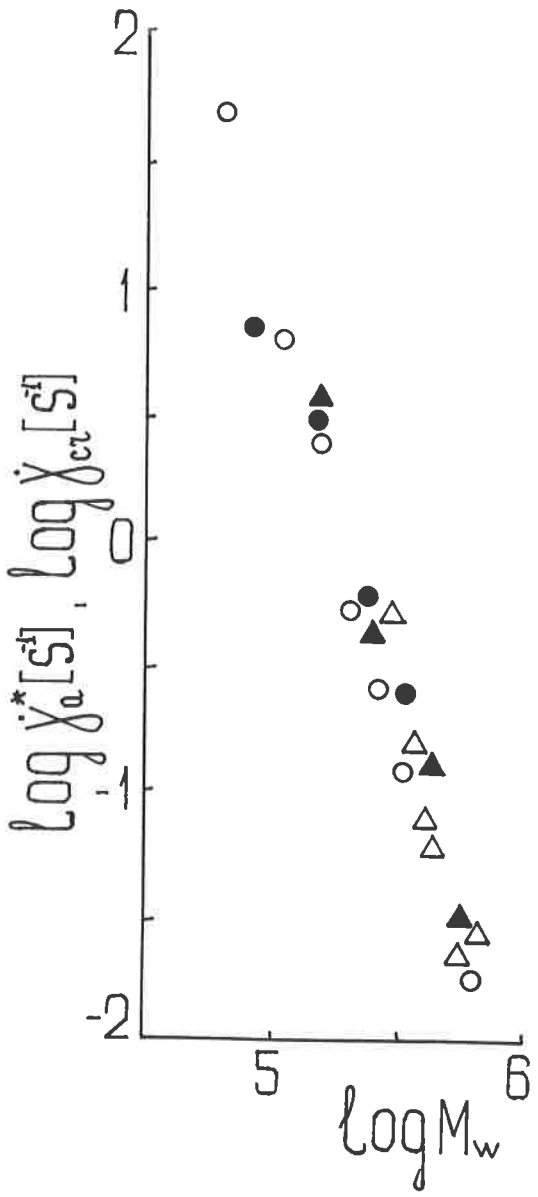

FIGURE 3. - *Dependence of the critical amplitude of the deformation rate $\dot{\gamma}^*_a$ (Δ) and critical shear rate $\dot{\gamma}_{sp}$ (O) on the molecular weight M_w of 1,4-PB at 23 °C.*

The Relaxation Transitions in Uniaxial Extension

The spurt phenomenon and the failure of adhesive contact of elastomer with the wall with respect to which it moves limit investigation of elastomers in the simple shear regime. However, experiments with uniaxial extension are free of these limitations. It turns out that there exists a relation between the spurt regime and fracture conditions for uniaxial extension, and, furthermore, that the appearance of spurt can be used to predict fracture conditions for a polymer undergoing extension. In uniaxial extension polymer fracture can be studied over many decades of extension rates and stresses, and the strength characteristics can be determined over a very wide range of deformation rates, in particular, for the transition from the rubbery to leathery states.

In uniaxial extension two limiting modes of elastomer behaviour can be seen especially clearly : steady-state flow and elastomer fracture *(figure 4)*. In the fluid state, which is to the left of the vertical dashed line, theoretically unlimited strain can be accumulated and steady-state flow can be attained. With increasing rate of deformation, a transition from the fluid to the rubbery occurs, where elastomer deformation is limited and as a result the sample breaks. This is a criterion of the transition to the rubbery state. An increase in rates and stresses above their critical values rapidly reduces the ability of polymer to accumulate unrecoverable deformation. Consequently, in longitudinal deformation the critical parameters must be determined by the regime of transition from unlimited deformation, or by extrapolation of the rates and stresses to the values corresponding to steady-state flow conditions.

The critical deformation rate $\dot{\varepsilon}^{**}$, which corresponds to the vertical dashed line, correlates with the critical fracture stress σ^{**}, which is simply related with the critical shear stress at which the spurt occurs, namely $\sigma^{**} = 3\,\tau_{sp}$.

The critical deformation rate in extension, $\dot{\varepsilon}^{**}$, is inversely proportional to the initial viscosity and, as a function of molecular weight, varies by many orders of magnitude. In this case, the effect of temperature can be accounted for by the temperature reduction coefficient, determined by the temperature variation of the initial viscosity.

In supercritical regimes non-recoverable deformation rapidly decreases while recoverable (high-elastic) deformation continuously increases. The results is that the total deformation passes through a minimum. To the right of the minimum the deformation is recoverable and the curve has a maximum corresponding to the transition of a polymer first to the leathery and then to the glassy state.

It is essential that near the maximum of the dependence of strain on the deformation rate ε^* ($\dot{\varepsilon}$) the degree of deformation of

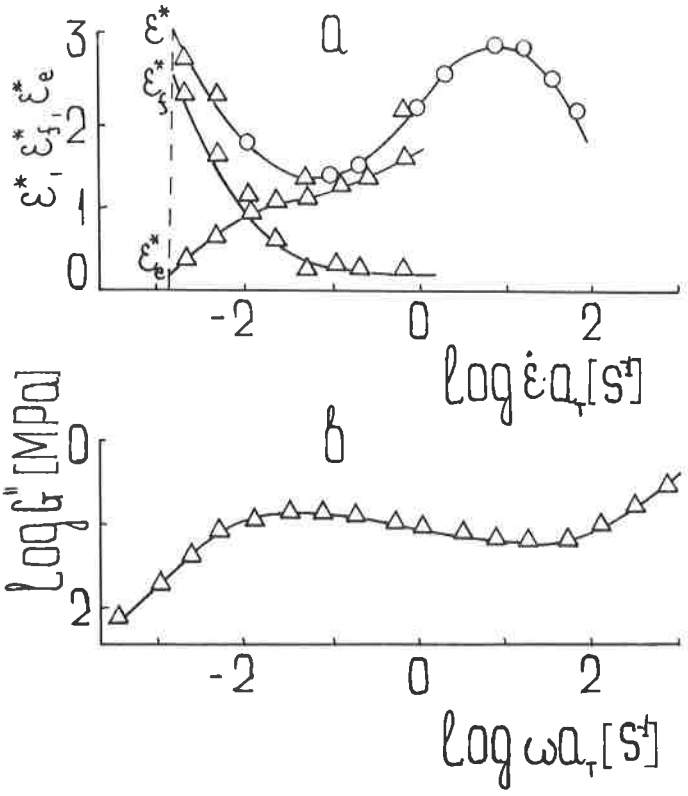

FIGURE 4. - *Total fracture strain (ε*) and its recoverable (ε_e^*) and irrecoverable (ε_f^*) components versus strain rate $\dot{\varepsilon}$ (a) and loss modulus vs frequency (b) for 1,2-PB. Reduction temperature 25°C (experimental temperatures, °C : ○- 0 ; □- + 10 ; Δ - + 25 ; ▽ - + 50.*

elastomers with linear structure can amount to 2000-3000 and more percent. These values considerably exceed recoverable fracture strains for crosslinked rubbers.

Prediction of Polymer Fracture on the Basis of Non-Destructive Test

Of importance is the prediction of elastomer fracture on the basis of non-destructive tests. As has already been shown above, the transition of elastomers from one physical state to another can take place in isothermal conditions. There exists a close relationship between the dependence of the total deformation on the deformation rate and the frequency dependence of the dynamic loss modulus G" (ω). The maximum in the total fracture strain corresponds to the minimum in the loss modulus *(figure 4)*. This correlation has far-reaching consequences since it becomes possible to predict the change in the ultimate fracture strains for an elastomers using the data on non-fracture low-amplitude deformation for this polymer.

Fracture Envelope and its Generalization for Uncured Elastomers

It is well known that polymer fracture is time dependent and assumes a certain relation existing between the breaking strain σ* and breaking stress. For cured rubbers, this relation is established by the well-known Smith fracture envelope. *Figure 5* shows the fracture envelope for 1,2-PB in the true breaking stress vs total fracture strain coordinates (dark circles). In the same figure, there are deformation curves obtained under conditions of a constant deformation rate (light symbols). It can be seen that an increase in the deformation rate or a decrease in temperature result in the displacement of breaking points along the envelope towards higher stresses. Experiments show that the upper part of the curve, convex with respect to the coordinate axis, is invariant relative to deformation conditions. As in the case of cured-rubbers, its extremal nature is explained by the polymer transition to the leathery and then to the glassy state associated with increasing stress or decreasing temperature. The lower part of the envelope, concave with respect to the coordinate axis, is determined by the transition of an elastomer from the fluid to the high-elastic state, which is typical only of uncured polymers. Hence, this is generalization of the results obtained by Smith for uncured elastomers.

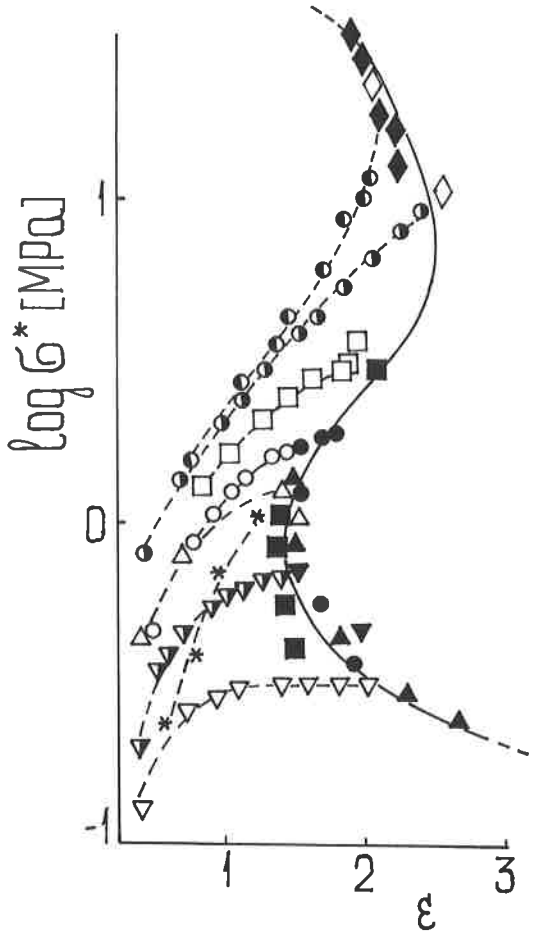

FIGURE 5. - *Fracture envelope to 1,2-PB, measured at σ = const. (temperature, °C : ▼ - 50 ; ▲ - 25 ; ■ - 10 ; ● - 0 ; ◆ - - 10). Dashed lines σ - ε prior to rupture at constant strain rates (s^{-1}) and various temperatures :*

▽ - 5.10^{-2} ; ▼ - 2.10^{-1} (50 °C); Δ - 1.10^{-1} (25 °C) ;
○ - 1.10^{-2} ; ◑ - 2.10^{-1} ; ◐ - 4.10^{-1} (0 °C) ;
□ - 5.10^{-2} (10 °C).

The Critical Value of Recoverable Strain as Universal Characteristic of Elastomer Fracture

In on the highly elastic state, the polymer fluidity is suppressed. In this connection, the question arise : to which extent is elastomer fracture above glass-transition and melting point determined by the storage of recoverable deformation ?

Figure 6 shows the dependence of the true breaking stress on the recoverable component of breaking strain for polyisoprene (PI) with different molecular weights and for 1,2-PB. The solid lines were obtained for different loading regimes and different temperatures, and the dashed lines correspond to the dependence of stress on highly elastic stain for a steady-state deformation regime. For elastomers there exists a universal critical value of recoverable strain determined by the intersection of the solid and the dashed lines. When the strain exceeds the critical value of recoverable component of deformation, ε^*e^*, the polymer-fractures. For elastomers series under study, this $\varepsilon^*e^* \approx 0{,}5$, which corresponds to the extension ratio of 1,65. Along with the critical values of fracture stress σ^{**}, and deformation rate ε^{**}, the critical value of recoverable strain is also a critical parameter determining the transition of an elastomer from the fluid to highly elastic state.

It is essential that breaking stresses linearly depend on respective recoverable strains. This dependence is invariant with respect to molecular weight, temperature, and deformation regimes. Hence, it follows that at stresses and strains exceeding the critical values the ratio of the rates of deformations and of relaxation processes alone cannot be considered to be a criterion of fracture of elastomers as continuous media.

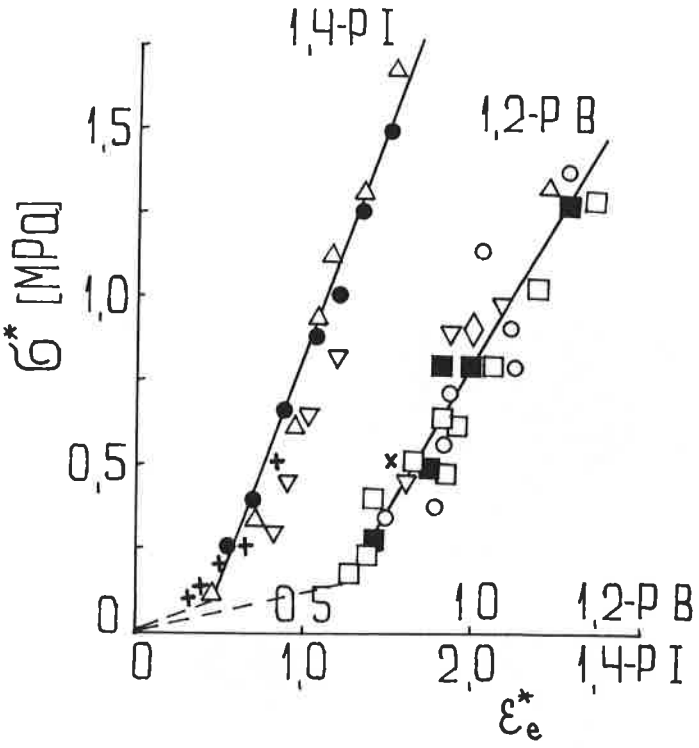

FIGURE 6. - *True breaking stress versus recoverable component of breaking strain at various deformation modes for 1,4-PI and 1,2-PB.*

Conclusion

Simple relation are found between the fracture strains and the initial values of parameters characterizing elastomers rheology at deformation rates and stresses approaching zero. Fracture regimes are determining by two groups of parameters. One includes critical values of stresses. They are invariant with respect to temperature and molecular weight of the elastomers. The values of critical stresses for different elastomer composition differ by a factor of 10 to 20. The second group of critical parameters includes the rates of deformation determined by the initial viscosity. The latter may vary by many orders of magnitude. There exists an universal critical value determining elastomer with linear structure fracture. It is invariant with respect to molecular weight, the temperature and the way of attaining a given state. This value is the recoverable critical strain and its equal to 0,5 according to Hencky.