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THE DEFORMATION OF POLYMERS (CHAPTERS 14 AND 15)

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RUSSIAN AND ENGLISH TRIGONOMETRIC FUNCTIONS

Russian	English
sin	sin
cos	cos
tg	tan
ctg	cot
sec	sec
cosec	csc
sh	sinh
ch	cosh
th	tanh
cth	coth
sch	sech
csch	csch
arc sin	$\sin^{-1}$
arc cos	$\cos^{-1}$
arc tg	$\tan^{-1}$
arc ctg	$\cot^{-1}$
arc sec	$\sec^{-1}$
arc cosec	$\csc^{-1}$
arc sh	$\sinh^{-1}$
arc ch	$\cosh^{-1}$
arc th	$\tanh^{-1}$
arc cth	$\coth^{-1}$
arc sch	sech^{-1}
arc csch	csch^{-1}

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rot	curl
lg	log

GRAPHICS DISCLAIMER

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Block	Italic	Transliteration	Block	Italic	Transliteration
А а	*А а*	A, a	Р р	*Р р*	R, r
Б б	*Б б*	B, b	С с	*С с*	S, s
В в	*В в*	V, v	Т т	*Т т*	T, t
Г г	*Г г*	G, g	У у	*У у*	U, u
Д д	*Д д*	D, d	Ф ф	*Ф ф*	F, f
Е е	*Е е*	Ye, ye; E, e*	Х х	*Х х*	Kh, kh
Ж ж	*Ж ж*	Zh, zh	Ц ц	*Ц ц*	Ts, ts
З з	*З з*	Z, z	Ч ч	*Ч ч*	Ch, ch
И и	*И и*	I, i	Ш ш	*Ш ш*	Sh, sh
Й й	*Й й*	Y, y	Щ щ	*Щ щ*	Shch, shch
К к	*К к*	K, k	Ъ ъ	*Ъ ъ*	"
Л л	*Л л*	L, l	Ы ы	*Ы ы*	Y, y
М м	*М м*	M, m	Ь ь	*Ь ь*	'
Н н	*Н н*	N, n	Э э	*Э э*	E, e
О о	*О о*	O, o	Ю ю	*Ю ю*	Yu, yu
П п	*П п*	P, p	Я я	*Я я*	Ya, ya

*ye initially, after vowels, and after ъ, ь; e elsewhere. When written as ё in Russian, transliterate as yё or ё. The use of diacritical marks is preferred, but such marks may be omitted when expediency dictates.

GREEK ALPHABET

Alpha	Α	α	α		Nu	Ν	ν	
Beta	Β	β			Xi	Ξ	ξ	
Gamma	Γ	γ			Omicron	Ο	ο	
Delta	Δ	δ			Pi	Π	π	
Epsilon	Ε	ε	ϵ		Rho	Ρ	ρ	ϱ
Zeta	Ζ	ζ			Sigma	Σ	σ	ς
Eta	Η	η			Tau	Τ	τ	
Theta	Θ	θ	ϑ		Upsilon	Υ	υ	
Iota	Ι	ι			Phi	Φ	φ	ϕ
Kappa	Κ	ϰ	κ	×	Chi	Χ	χ	
Lambda	Λ	λ			Psi	Ψ	ψ	
Mu	Μ	μ			Omega	Ω	ω	

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The Deformation of Polymers

Part V - Modern Conceptions of the Mechanical Work Capacity of Polymers

By the term "mechanical work capacity," we mean the ability of the polymers to avoid fracture and softening under given conditions of mechanical and thermal action. Having thus defined the work capacity of polymers, one may immediately point to two reasons for loss work capacity (or "load-carrying capacity," applicable to structures). The first reason is the fracture of a polymeric material with very small deformations. The second reason is the softening of a polymeric material, causing the development of large strains without loss of integrity.

In each mode of mechanical action, during constant or variable temperature, one of these two reasons will be principal, and precisely this reason will cause the loss in the work capacity of the polymeric material. With rare exception, every polymeric material may exist under conditions where fracture will occur first, and under conditions where softening will occur first, within a given range of temperatures and rates of mechanical action, fracture will be preceded by large deformations. The material will be softened before it breaks.

When we indicate the fracture of hard solids, it is understood that fracture is always associated with a loss in the integrity of the material, e.g. its breaking into pieces. When we speak of softening, various connotations may be intended. Characterizing the softening of polymeric solids, one often has in mind a particular temperature (or narrow temperature range) corresponding to the glass point. Above this temperature, it is found in a solid (glasslike or crystalline) state. This point of view reflects only one special case - the softening of polymers in the absence of mechanical stresses and in a fixed temperature mode.

During mechanical actions, as well as in different modes of heating or cooling, the softening point may assume different values. It was shown above that any temperature, theoretically, may be the softening point, with the appropriate choice of the magnitude and duration of stress. However, even this well-known fact is not the point. The softening of polymeric substance cannot be characterized by temperature alone, nor even by the dependence of the softening point on stress. Although such a dependence gives a more complete picture of the softening of polymers, it does not completely account for the time factor. Meanwhile, time, or the life of the polymeric materials form, may be physically substantiated as a characteristic of its softening.

In any mode of mechanical and thermal action, the polymer loses its shape, e.g. is softened, over a given period of time. Softening, permitted during the rapid development of deformations occurs spasmodically. In the simplest case, when a uniaxial stress (for example, stretching) and temperature are constant, softening is manifest in the initiation and rapid growth of a neck. Under these conditions, the process of the neck's initiation has the same spasmodic character as is manifest during ordinary continuous stretching. The time elapsed between the moment the load is applied and the rapid loss of a sample's original form (e.g. its softening) depends on the magnitude of the stress. The larger the stress, the shorter the life of a polymeric material's form. Temperature exerts a similar effect. An increase in temperature with stress remaining constant reduces the time necessary for the beginning of rapid deformation, and vice versa.

Thus, characterizing the softening of polymers, one should indicate not the softening point, but of the period of time before the beginning of softening, when the form of the polymeric material is still essentially unchanged. In turn, the life of the material's form depends on temperature and stress. Below, we will examine such dependences for a number of polymers, and describe how they were experimentally determined.

In practice, the load-carrying capacity of structures is in many instances calculated according to the limit of tolerable strain. This means that the deformation of material developed as a result of creep should not exceed a certain magnitude.

During this, no "neck" has yet formed, but the structure's shape has changed to the extent th-t it may already be non-functional. However, since creep in hard polymer materials is nothing more than the development of forced-elastic strain, this process may also be defined as the softening of material over time.

The strength of polymers has been characterized for a relatively long time as the life of a polymeric material, or its durability. Such a characteristic is usually connected with fracture in the presence of very small deformations, and may therefore indicate insubstantial changes in the structure of the material. However, although maximum deformation is small under conditions of brittle (or close to brittle) fracture, it always accompanies fracture processes, and is generated continously during the period of load action. Thus, questions of strength and fracture should be given more attention in books devoted to polymer deformation.

In this part of the book, we will discuss the interaction between the processes of fracture and softening. Having taken the time elapsed between the application of the load and fracture or softening as a characteristic of these processes, it immediately becomes necessary to evaluate the ratio of the ratio of the rates of these processes. If, under given conditions of mechanical and thermal action, the life of the material is greater than the durability of its form, then softening will occur over a certain time interval. If the life of the form exceeds that of the material, then fracture will begin first. Obviously, it is also possible to set up conditions where by both characteristics will be identical. Then fracture and softening will occur simultaneously.

One important question yet remains concerning the interdependence between the processes of fracture and deformation. Deformation is generated in the durability testing of polymers under constant pressure (σ = constant). And, although strain may be small (several percentages) before fracture, the rate of its development proves to exert a substantial effect on the final characteristic - durability. A number of studies undertaken in recent years have attempted to connect the rate of deformation with the life of the polymeric material. The results of these studies will be reviewed below.

Finally, studies of local deformations at a site of fracture in the polymeric material are accorded special significance. These very unique strains may be fairly large, even though total deformation of the sample as a whole before fracture is insubstantial.

Let us begin our exposition of modern conceptions of the mechanical work capacity of polymers with a look at the phenomenon of mechanical fracture.

Chapter 14

The Mechanical Fracture of Polymers

Physical Concepts

The fracture of solid materials is usually considered as the most dangerous form of loss of work capacity. This assertion may be agreed to if brittle or near-brittle fracture is indicated. It is vitally important in this instance to learn to increase the strength of the material, so that it may withstand prolonged periods of heavy loading. When fracture has a non-brittle (ductile or tough) character, increasing the material's strength may not give the desired result. As follows from our examination of tests conducted by Yu. S. Lazurkin, during continuous loading, the elastic limit corresponds to lower stresses than does ultimate strength. The potential strength of the material may not be used on account of the "premature" development inelastic strains. Let us first of all discuss fracture occurring at low strain.

The first physical theory of strength is usually associated with the name Griffith[1 - 2]. According to his concept, the fracture of hard solids has a critical character, e.g. it occurs instantaneously after the attainment of a certain critical (ultimate) stress. According to Griffith, real solids, in contrast to ideal solids, do not possess a perfect structure, but instead contain a great number of defects, weakening the material. Any imperfections in the crystalline lattice, microcracks, etc. may be defects.

During the loading of a hard solid in the apices of microcracks, large local overstresses develop; such overstresses exceed the mean stress in the sample ten or even a hundred times. When these overstresses are capable of overcoming reactive forces between adjacent structural elements (beginning with individual atoms, and ending with large structural formations) a crack begins to develop rapidly, and the solid is fractured. If the load is such that the overstresses are still in no condition to overcome reactive forces between structural elements, the fracture does not occur, and the solid may survive indefinitely.

Griffith's theory explained well two experimental facts, characteristic for practically all types of hard solids.

The first fact is the enormous difference between theoretical and technical strength. If the structure of a hard solid is known, it theoretical strength may be calculated. Knowing the dependence of the potential energy of the atoms' interaction on the distance between them, and considering the number of interatomic bonds per unit of cross-sectional area, one may determine the magnitude of the force required to overcome the total interaction. Computing theoretical strength in this manner almost always yields a value several decimal orders (as a rule, from one to three) less than the experimental value. According to Griffith, overstresses in the apices of various defects are greater than the mean stress in the sample by just that factor. Thus, on the whole, theoretical strength is not attained, although it is reached in the apices of microcracks.

The second fact is the constancy of pressure at which fracture occurs under usual strength-testing conditions for materials (determination of tension and compression diagrams). If test conditions (for example, the rate of stretching) are kept fairly stable, each solid will display a roughly constant amount of tensile strength (within the limits of the variability of results, of course). At first glance, it seems that the stability of the strength values obtained confirm the critical character of fracture.

Griffith's theory enjoyed much success, and Griffith himself had many followers who further elaborated his theory. The basic mathematical relationship in Griffith's theory is based on the law of the conservation of energy, and its application to concrete aspects of tests explains many experimental facts. Griffith's theory, in its original form, is now substantially dated, and even his followers have been forces to consider new experimental data conflicting with the theory.

The critical mechanism governing the fracture of hard solids, and consequences of this mechanism, are being subjected to review. However, other aspects of Griffith's theory have kept their value. The substantial role of microdefects, which weaken the material, the effect of large overstresses, initiating in the apices of microcracks, ets, were asserted by his theory. These positive features of the theory are used with success to describe the macroscopic fracture of hard polymeric solids.

One of the principal assumptions of Griffith's theory - the critical mechanism of fracture - does not withstand experimental verification. At first singly [3 - 8], and then systematically [9 - 23], tests demonstrated that a hard solid may be fractured not only under stresses corresponding to critical stresses, but also under substantially lesser stresses. It is quite unnecessary to increase stress up to the so-called "ultimate strength" in order to cause the fracture of polymeric materials. Applying a much lesser stress, one may always wait for the fracture of the material. The smaller the load being applied to a hard solid, the greater the durability, or life of the solid.

The inability of polymers to infinitely withstand mechanical action which is less than the ultimate strength disproves the critical mechanism of the fracture of solids. Even this fact alone indicates that fracture is not an instantaneous, but a gradual process, occurring over time. As a result, the fundamental characteristic of the fracture process proves to be time - mechanical durability -, not ultimate stress.

Before discussing the nature of the mechanical fracture of polymers, let us examine some experimental data. The first studies[3] of the durability (τ) of polymeric materials showed that the dependence of log τ on stress at a constant temperature has a linear character. Later, the systematic investigations [9 - 19] of S. N. Zhurkov and others led to the discovery of general laws: they are manifest in the unique change in the durability of polymers within a wide range of temperatures and mechnical stresses.

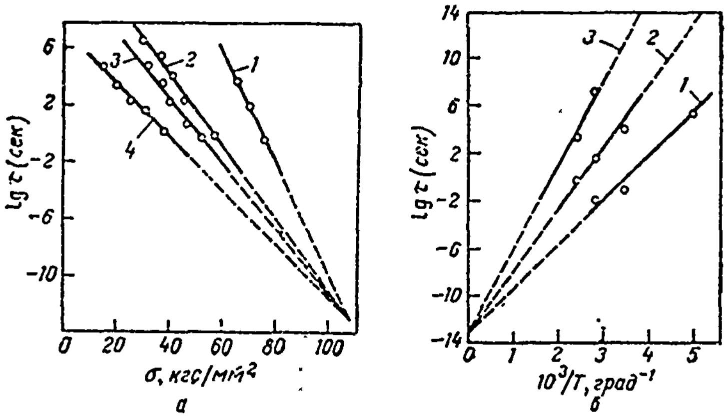

Figure 1.

The dependence of the logarithm of durability on stress ( ) and on inverse absolute temperature (b) for viscose fiber.

In Figure V.1, a: 1 - minus 75 °C; 2 - 20; 3 - 80; 4 - 150 °C. In V.1, b: 1 - 60 kgf/mm^2; 2 - 40; 3 - 20 kgf/mm^2.

In order to obtain the dependence of durability of temperature and stress, the following procedure is usually employed: with temperature constant, a load is applied to a sample, inducing a rigidly constant stress σ which is maintained by a special device. Changing the load, one then records the moment of time τ from the moment the load is applied until the moment of the sample's fracture. The same experiments are then conducted at other temperatures.

After completing a series of experiments in the range of temperature and stress appropriate to each polymer, one may then construct a graph of the dependence of log τ on σ and 1/T. As Zhurkov showed, these dependences are linear for many hard polymers, appearing as shown in Figure V.1, a, b. It is interesting to note that they converge at a single point - the pole. The pole's ordinate is always log $\tau_0 = -(12 - 13)$ (sec).

The character of the experimental dependence shown in Figure V.1 a, b allow one to write an equation for the durability of polymers in the form

$$\tau = \tau_0 e^{\frac{U_0 - \gamma\sigma}{RT}} \qquad \text{(V.1)}$$

where τ is the durability of the polymer; α_0 is the pre-exponential multiplier; U_0 and γ are parameters of the material; σ is α constant stress.

If we are interested in the dependence of durability on stress at a single temperature, Eq. (V.1) is simplified:

$$\tau = Ae^{-\alpha\sigma} \qquad (V.2)$$

The dependence of log τ on σ
at different temperatures
$(T_1 > T_2 > T_3 > T_4)$.

where A and α are parameters of the material.

Pre-exponential multiplier τ_0 is roughly the same for all polymers, and is equal to 10^{-12} - 10^{-13} sec. This value corresponds with the period of oscillation of atoms in solids. Parameter U_0 corresponds to the energy of activation of polymers' thermal degradation and if such occurs with a breaking of the chemical bonds in the main chain, the value of U_0 corresponds in turn with the energy of these bonds.

An analysis of experimental data on the durability of polymers, expressed by means of parameters τ_0, U_0 and γ and very characteristic values for these parameters, allowed Zhurkov to formulate a concept of the nature of the process of polymer fracture. This concept can be more easily explained and understood with the aforesaid analysis of relazation phenomena in polymers, having much in common with the process of fracture. The concept of the kinetic character of the processes is found at the base of both phenomena.

During relaxation, the structure is rearranged as a result of the overcoming of energy barriers $U_{\gamma,\ o}$, opposing such α rearrangement. In the event of fracture, the breaking up of the solid into parts occurs with the overcoming of energy barriers U_o, opposing the breaking of the chemical bonds in the polymer's main chain. In both cases, mechanical stress reduces the total energy barrier and facilitates the completion of the process. As a result of the energy barrier's lowering $(U_o - \gamma^{\sigma})$, less heat energy is needed to attain the same durability. Thus, in the presence of substantial loads, fracture occurs in the same amount of time at a lower temperature.

Mechanical stress, therefore, is not the origin of the fracture of polymeric materials. It only lowers the activation barrier, facilitating the breaking up of macromolecules. As a whole, fracture may be pictured in the following manner. Atoms in the solid oscillate relative to their equilibrium positions with a frequency of $10^{12} - 10^{-13}$ $\sec^{-1}$. The interatomic bonds are broken by heat fluctuations. Having determined the probability of the bonds' breakage in the usual way as $W = W_o e^{-U/RT}$, let us assume that $U = U_o - \gamma^{\sigma}$. This means that the probability of the bonds' breakage depends not only on temperature, but also on mechanical stress. Th bonds between the atoms are gradually broken, while mechanical stress increases the rate of this process. The accumulation of elementary fracture events (the breaking of more and more bonds) leads over time to the complete fracture of the solid.

If mechanical action is reduced, the rate of the bonds' breakage decreases, and at $\sigma = 0$ appraches the rate of polymers' thermal degradation. Thus, the value of U_0 is approximately equal to the activation energy of the thermal degradation process. Furthermore, it may be stated that the durability of the material as a whole is inversely proportional to the probability of the breakage of chemical (or other) bonds, and then we immediately arrive at Eq. (V.1).

Postponing discussion of other aspects of the problem of strength for the moment, let us examine the relationship between two characteristics of the fracture mechanism - time (durability) and stress (ultimate strength). For this purpose, we turn to Figure. V.2, which shows the dependence of log τ on σ at different temperatures.

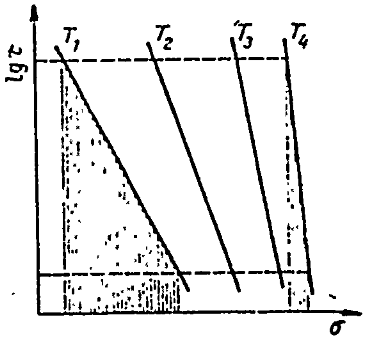

Figure V.2 Caption
on page 16.

The dependence of log τ on σ
at different temperatures

$(T_1 > T_2 > T_3 > T_4)$.

Increasing the temperature, the straight line log $\tau = f(\sigma)$ becomes more and more vertical, and then within a very small range of stress, durability $\tau_{\rho\gamma}$, assuming then that if the applied stress is less than $\sigma_{\rho\gamma}$, the material as a whole may survive indefinitely; if the applied stress is greater than $\sigma_{\rho\gamma}$, the material will undergo almost instantaneous fracture.

At higher temperatures, the temperature-time dependence of strength is such that a broad range of stresses will be required for substantial changes in the durability of the material. All of this demonstrates the conditional nature of the concept "ultimate strength." Although such a concept may be useful in comparing different materials, it loses its value when the issue is the physical nature of fracture.

Eq. (V.1) reflects the experimental fact testifying to the gradual occurrence of the fracture process. This process, proceeding over time is caused by the formation of free macroradicals[24 - 26, 117]. Their concentration is increased in time, similar to the manner of deformation growth in a polymer during creep. It may be stated that, since the polymer sample is still far from fracture, creep is accompanied by the formation and accumulation of free radicals. The dependence of the logarithm of the rate of radical formation on mechanical stress (Figure. V. 3) has the same linear character as the dependence of log τ on σ. The above phenomenon was studied for hard linear polymers.

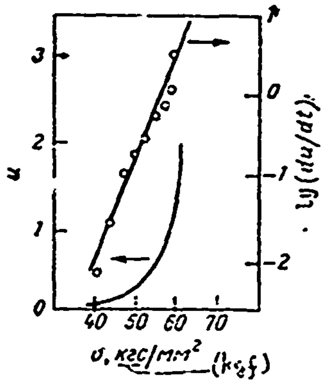

Figure V.3.

The dependence of concentration U and rate of radical formation du/dt on stress for caprone (polycaprolactam resin).

During the loading of three-dimensional polymers, free radicals are formed mainly as a result of the breakage of cross-links. This phenomenon, accompanied by the process of chemical flow, is observed not only under heavy mechanical action[27 - 33], but under milder conditions as well.

Relating the process of polymers' fracture with mechanochemical phenomena, one may pose an interesting question for investigation. In studying the mechanism of the thermal degradation of a polymer, one usually tries to find the weakest bonds, which break first and limit the polymer's resistance to heat. Naturally, the substitution of these bonds by stronger bonds (e.g. a directed change in the chemical structure of the polymer) will increase the polymer's thermal stability. If the concept of the heat-fluctuating nature of fracture is valid, then such a substitution may increase not only the thermal stability, but also the strength of the polymer. Thus, it is very important to detect the weak bonds in the polymer[26], which will also be responsible for the strength (more precisely, for the "weakness") of α plymeric material.

The search for the weaker bonds in α polymer may best be conducted not only on the molecular level (by determining which chemical bonds are the first to break); it is also vital to know the weak places in the polymer's super-molecular structure, because t the fracture mechanism will also be generated at these sites.

In an oriented crystalline polymer (for example, a fiber) crystalline and amorphous regions alternate along the orientation axis. Such analternation is characteristic for many (but not all) polymeric fibers. The fibrils in the amorphous region are the first to be deformed upon the application of a mechanical load to this unique "structure."[34]

It is highly probable that the rate of occurrence of elementary fracture events (the breaking of chemical bonds) will be greatest in precisely these areas, so that the amorphous regions "shape" the strength properties of the fiber as a whole. In connection with this, it is necessary to know the structure of the amorphous regions in a cyrstalline polymer. It is worth noting that the degree of orientation in precisely these regions, and not in the crystalline regions, is closely allied with the strength properties of several fibers.[35]

The presence of amorphous regions in any crystalline polymer may be practically regarded as the presen ce of unique defects in a hard solid. Elimination of the amorphous regions, as with all other structural defects, leads to a sharp increase in strength. By applying unique methods of obtaining perfect crystalline solids without fefects, one may demonstrate conclusively the adverse effect of amorphous regions on strength properties.

One of these methods is the formulation of polymers via polymerization of monomer crystals in the solid phase. For example,[36, 118], the polymerization of trioxane, taken in the form of crystals, leads to the formulation of spicular crystalline formations of polyoxymethylene, devoid of any would-be defects in the crystalline lattic. Strength increases as a result, and ultimate tensile strength may reach 300 kgf/mm^2.

It should be kept in mind that amorphous regions in a crystalline polymer play not only a negative, but a positive role. By weakening a polymeric solid and facilitating a decrease in its strength, these regions help reveal the elastic properties of the polymer. Without them, the polymeric material proves strong, but very brittle - this would be extremely undesirable. Thus, control of the structure of a crystalline polymer should be exercised with reason, in accordance with the demands being made of a given material.

If great strength is required of a material, and its brittleness is not specially stipulated, the presence of amorphous regions should be avoided. If the material should be elastic, and withstand repeated flexure and other forms of periodically variable strain, the presence of amorphous regions is advantageous (and sometimes necessary) even in a strongly oriented polymer.*

Returning to the molecular mechanism of fracture, let us note that the process of thermal degradation is not limited to the breaking of macromolecules into large fragments. Monomers may be

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*Recall that oriented polymers are the least brittle of all polymeric systems.

set free during the breaking of chemical bonds in the main chain. Volatile products are also liberated in the thermal degradation process as a result of the detachment of side groups. When a polymer is loaded with a mechanical force, degradation begins with the breaking of chemical bonds in the main chain[37 - 39], so that the volatile products are monomers.

For several polymers (polymethy methacrylate, polystyrene, polypropylene) the products of pure thermal and mechanical degradation coincide[39]. For other polymers (polyvinyl chloride, polyacrylonitrile), these products are different, since thermal degradation occurs intially with the detachment of side groups, and mechanical degradation is accompanied by the rupture of bonds in the main chain.

These experimental facts confirm the validity of S. N. Zhurkov's conception of the kinetic character of the fracture of polymers, closely allied with degradation processes.

The complexity of the processes of thermal and mechanical degradation causes several deviations from the temperature-time function of xx strength, expressed by means of Eq. (V.1). This equation is valid at stable values for parameters U_o and y and is indeed satisfied for a large number of polymers. It should be kept in mind, however, that it may be used only within a range of temperatures and stresses defined for each polymer; to extend its use further would be risky. Thus, in the region of small stresses, experimental durability is always greater than that predicted by E. (V.1).

The main reason for deviations from Eq. (V.1) is the possible change in parameters during the experiment. This applies especially to structure-sensitive parameter y. If orientation, crystallization and other changes in structure occur during the experiment, parameter y is changed, and the conditions necessary for satisfying Eq. (V.1) are violated.[40 - 43]

The character of thermal degradation proves to have a singular effect on the temperature-time function of strength. If the formation of secondary radicals initiates the degradation process, function (V.1) is complicated, and takes the form

$$\tau = \tau_0 e^{\frac{U_0-\gamma\sigma}{R}\left(\frac{1}{T}-\frac{1}{T_{\Pi(\gamma)}}\right)} \qquad (V.3)$$

The dependence of concentration U and rate of radical formation du/dt on stress for caprone (polycaprolactam resin).

where T_p is the temperature of the pole; the remaining parameters have the same meaning as in Eq. (V.1).

Relation (V.3), as (V.), describes the set of straight lines in coordinates log τ - $1/T$ coming out of a pole located not on the ordinate axis, but somewhat to its right (Fig. V.4). The point of the pole corresponds to temperature T_p. The introduction of an inhibitor into the polymer, supressing secondary radical reaction, shifts the pole leftward to its normal position.[44] These facts leave no doubt as to the close connection between the processes of fracture and thermal degradation.

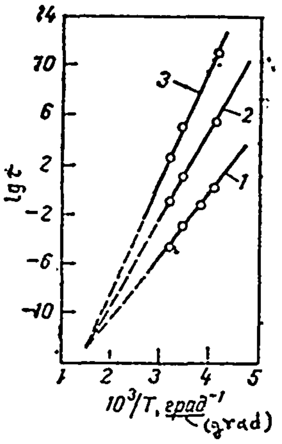

Figure V.4

The dependence of the logarith of durability on inverse absolute temperature for polystyrene at a stress σ:

1 - 11 kgf/mm^2; 2 - 8; 3
3 - 5 kgf/mm^2.

Thermal, and in particular thermal-oxidative degradation, may exert a substantial effect on durability characteristics. In the absence of mechanical stress, both forms of degradation ultimately cause the fracture of the material. Thus, Eqs. (V.1) and (V.3) do not lose their physical meaning at $\sigma = 0$, as it may seem at first glance. These equations predict the ultimate durability of polymeric materials in the absence of mechanical loading.

Thermal-oxidative degradation also proves to have an effect on character of the temperature-time dependence of strength.[45, 46] The dependence of log τ on σ deviates from the linear and has a very complex S-shaped character (Fig. V.5). In the simpler cases, under the influence of a single external factor (ultraviolet radiation, gamma radiation, etc.), the character of the temperature-time dependence of strength remains unchanged[47 - 50], with only the parameters of the Zhurkov equation being altered. Under heavy loading, radiation has little effect on durability; under small loads, it has a very substantial effect, while the coincident effect of mechanical stress and radiation proves to be greater than the effect produced by their alternating action. An aggressive medium also exerts a unique effect on the durability of polymers.

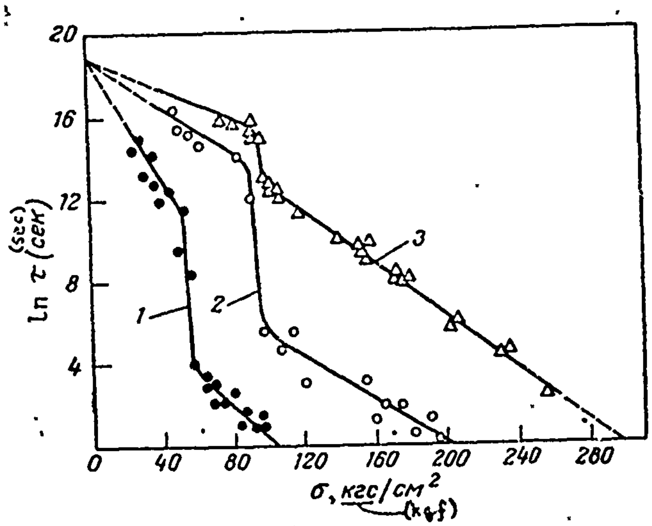

Figure V.5. Caption on page 26

The dependence of log τ
on σ for polyethylene
at temperature:
1 - 11 kgf/mm2; 2 - 8;
3 - 5 kgf/mm2.

Up until now, we have examined the temperature-time dependence of strength for hard (amorphous and crystalline) solids. A temperature-time dependence of strength is also characteristic of polymers in a high-elastic rubberlike state. The life of these polymers is determined by the magnitude of the applied stress and temperature. The fracture of elastomers may occur under loads substantially smaller than "ultimate strength." However, the temperature-time dependence of strength for elastomers, as a rule, is somewhat different from the similar dependence (V.1) for hard polymeric solids. The durability function for (cured) rubber, according to the work of G. M. Barteneu[53 - 57], is described by the following relation:

$$\tau = A\sigma^{-m}e^{U/RT} \qquad (V.4)$$

where τ is the durability; A and m are parameters of the material. The remaining symbols have the same meanding as in Eq. (V.1).

If test are conducted at a single temperature, Eq. (V.4) is simplified, and takes the form

$$\tau = B\sigma^{-n}$$

where B and n are parameters of the material.

The experiment shows that experimental data for pure rubber are described well by Eq. (V.4), although they are satisfied with the same approximation by Eq. (V.2). The dependence for pure rubbers[57] is described better by Eq. (V.2). Transitions to other temperature regions also changes the character of the temperature-time dependence of strength. Even within the limits of the high-elastic state, one may distinguish temperature ranges in which durability is described by relation (V.1) or relation (V.4).

It follows from Eq. (V.4) that the activation energy for the fracture process is independent of stress. On the other hand, Eq. (V.1) shows that such a dependence exists, while for hard polymers the activation energy decreases with increasing stress. For elastomers[57], one observes the reverse: the activation energy increases with an increase in the load. This phenomenon is easily observed with thermosetting polymers[58], which may be changed from the solid state into the high-elastic state for the convenient study of temperature ranges. In a glasslike condition, the durability of these polymers is described well by Zhurkov's equation with a "normal" (positive) coefficient γ. This equation is also valid for the high-elastic state, although here the value of γ is negative. Thus, activation energy increases with increasing load, and durability increases along with it.

This experimental fact, interesting by itself (durability being greater for loaded material than for unstressed), is explained by the fact that in the high-elastic state, intermolecular bonds play a large role. They take on part of the load, releasing the chemical bonds from work. Under small loads, the rate of the fracture process is slow, and the intermolecular bonds, assuming the load, facilitate a more uniform distribution of the stress. Hence the characteristic form of graphs of the temperature-time dependence of strength for thermosetting polymers (Fig. V.6).

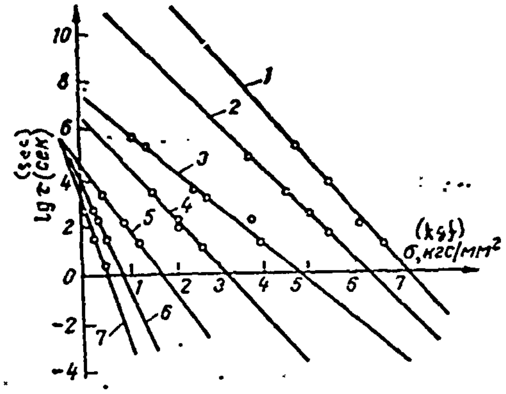

Figure V.6.

The dependence of log τ on σ for melamine-formaldehyde films within a wide range of temperatures:

1 - minus 23 °C; 2 - 0; 2 - 20;

4 - 30; 5 - 50;

6 - 60; 7 - 70 °C.

In the low-temperature region (glasslike condition) the graphs have the normal form, following Eq. (V.1). In the region of high temperatures (high-elastic state), the slope of the graphs testifies to the increase in the value of U with increasing stress. In the intermediate (transition) region, activation energy is independent of stress. In general, the durability of elastomers may be described with more complex relations[59] than Eqs. (V.1) and (V.4).

The dependence of durability on stress and temperature invariably appears in the form of exponential functions when the activation process of the rupture of interatomic bonds is assumed to be the basis of the fracture mechanism. Here, concrete instances of the appearance of such a mechanism may be approached in several ways. For example, in the 1940's, Tabolsky and Eyring[60] explained the dependence of durability on stress and temperature starting from the mechanism activating the breaking of interatomic bonds. Assuming that the life of the material is determined by the rate of the bonds' rupture, they proceeded to the relation

$$\tau = A\frac{N_0}{\sigma}e^{\frac{\Delta F-\sigma\lambda}{kT}} \qquad \text{(V.6)}$$

where A is a parameter; N_0 - the original number of bonds; ΔF - the activation barrier which must be overcome to break a single bond; Λ - the deformation of the bonds during rupture; k - Boltzmann's constant.

The fracture mechanism is treated somewhat differently in the works of Bueche[61] and his followers[62, 63]. They also hold that chemical bonds are broken under load, with the load lowering the activation barrier. Since the number of unbroken bonds decreases with time, Bueche introduced a second assumption on the uninterrupted increase in the load discernable with these bonds. Describing the probability of the bonds' rupture in the usual manner, Bueche derived the following equation for durability:

$$\tau = \frac{1}{\omega} e^{\frac{U_0 - 2.7\delta s\sigma}{RT}} \qquad \text{(V.7)}$$

where w is the natural frequency of the bond's oscillations; δ - the deformation of the bonds during rupture; S - the cross-sectional area per bond.

Bueche's theory was later refined, and although it does not always agree with experimental data, it may be used, for example, to describe the fracture of pure and impure (filled) rubbers.[62, 63]

Up until now we have looked at the fracture mechanism only as it is related to the heat-fluctuating rupture of chemical bonds. But a large role is played in polymers by intermolecular interaction caused by the presence of bonds of a physical nature (van der Waals forces, bonds between polar groups, hydrogen bonds). According to V. E. Gul[64 - 66], the inclusion of these bonds in the work has a substantial effect on the whole process of fracture. The basic premise elaborated in Gul's work is that the loading of a polymeric solid first causes the rupture of intermolecular bonds. The load on the chemical bonds is increased according to the accumulation of these initial ruptures.

By introducing the probability of the rupture of intermolecular bonds and their proportional load on the chemical bonds, and by examining the rate of crack propagation in a polymeric solid, Gul derives the following relation for durability:

$$\tau = \frac{B}{(\sigma - \sigma_x)^{\alpha}} e^{\frac{U_0 - \gamma\sigma}{RT} \beta} \tag{V.8}$$

where B, σ_x, $\alpha, \gamma' \beta$ are material constants.

Somewhat earlier, Gul[64] found a relation connecting load at rupture σ_γ with the rate of deformation v:

$$\sigma_{p_{(r)}} = Av^n \exp^{(U/RT)} \tag{V.9}$$

where A, n and U are material constants.

Relation (V.9) was later the basis for calculating the strength of composite materials. All of these studies are generalized on a survey[65] and monograph[66].

Original approaches to the description of the fracture process have been suggested by A. A. Ulyushin and P. M. Ogibalov[68], as well as A. I. Gubanov and A. D. Chevychelov[69 - 71]. Thus, in a series of works[69 - 71], Gubanov and A. D. Chevychelov examined a theoretical dependence of durability on stress and temperature for several polymers which has the form of Zhurkov's formula. Their theory allows one to compute the coefficients in the durability equation beforehand, and to predict the path of creep curves.

The Kinetics of Crack Propagation in a Hard Solid

The systematic investigations of S. N. Zhurokov and his collaborators, as well as the work of a number of other authors, leaves no doubt as to the heat-fluctuating nature of the fracture of polymeric solids. The fracture process consists of the gradual rupture of interatomic bonds as a result of heat fluctuations, while mechanical stress reduces the activation barrier and hastens the completion of the process.

Elementary fracture events in an actual polymeric solid take place more rapidly at the sites of greatest stress. These sites are essentially the same as any imperfection in the structure of a hard solid. For example, stress concentration occurring in the peaks of microcracks exceeds the mean stress in the samply by 10, and sometimes 100 times. It is clear that the interatomic bonds at these sites will be ruptured most rapidly. And although the fracture process has not progressed too far in the rest of the sample, it has been completed at the site of the most dangerous defect. As a result, the sample's durability is exhausted and it is broken into two sections.

If the whole sections of the sample remaining after fracture are tested again to fracture, the ultimate stress at fracture may sometimes differ little from the original value. This expimental fact seems to conclusively disprove the statement that the fracture process has a heat-fluctuating character and is generated throughout the entire sample. However, it is easily demonstrated that a defective hard solid should behave in precisely this manner.

The fact is that the dependence of durability on stress has an exponential character [see Eq. (V.2)]. Therefore, if the apices of the microcracks are under a load which is substantially larger than that acting on the rest of the sample, the rate of the rupture of bonds in the apices will increase catastrophically. Conversely, with relatively light loading of the parts of the sample free of defects, the rate of the bonds' rupture will be negligible. In these parts, the number of bonds having broken between the moment of the load's application and the moment of fracture will be insignificant.

The exponential dependence of durability on stress also points out the fact that even in other, less dangerous defects, stress will not cause any notable rupture of interatomic bonds. Only maximum stresses play a decisive role in determining durability, all other stresses being negligible. All of this leads to the concurrence of the results of initial and repeat tests.

It is interesting that if one takes material free of defects (more exactly, almost free of defects), specially prepared fiber glass for example[72], then it will be converted to powder upon fracture. Here, elementary fracture events are indeed generated throughout the entire sample. Thus, the macroscopic fracture of the sample occurs at all of its points simultaneously.

The concentration of stress in the peaks of microcracks and the abrupt acceleration of the rupture of bonds at these sites demands that attention be given the study of the fracture mechanism generated by the initiation and propgation of cracks.

In Griffith's works[73, 74], there was an attempt to establish a mathematical dependence between the strength of a hard solid and the character of cracks. In particular, for a sample with a rim crack of length l_o, critical stress σ_K is calculated according to the formula

$$\sigma_K = \sqrt{\frac{2\alpha_0 E}{\pi l_0}} \qquad (V.10)$$

where E is the modulus of elasticity; α_o is the potential surface energy.

Griffith's followers repeatedly proved relation (V.10) experimentally. For many polymers[75 - 78], ultimate tensile strength is actually proportional to $1/\sqrt{l_o}$. In other cases[79], deviations are observed, especially in the temperature dependence of the proportionality coefficient between σ_K and $1/\sqrt{l_o}$.

The deviations compel consideration of the different losses arising during the initiation and propagation of cracks[72, 80 - 82]. At least three forms of mechanical loss may be indicated[72]: strain losses arising from irreversible deformations in the apices of microcracks; dynamic losses accompanying the conversion of elastic strain energy into kinetic energh during the separation of the walls of a microcrack; losses during the degradation of elastic strain energy at the moment of the rupture of interatomic bonds in the microcracks' apices.

In describing the fracture process, one should consider all three forms of loss; only strain losses may be ignored, in the case of an ideally brittle solid.

The presence of microcracks in an actual hard solid does not alter the basis of the conception of the fluctuating rupture of interatomic bonds' and the gradual accumulation of elementary fracture events. However, the peculiar pattern of the initiation and propagation of cracks in polymers obliges us to look for different ways of describing the process.

"Silvering" of a material or, as is sometimes said, the appearance of "milk" is often observed during the fracture of polymers. These phenomena are connected with the initiation and propagation "silver cracks," differing structually from ordinary fatigue cracks.[83- 88] The walls of silver cracks are connected to very fine strands of oriented polymeric material. These strands facilitate a more uniform distribution of stress in the material.

Silver cracks grow at an almost constant rate from the surface to the center of the material[89, 90]. As a result of the successive rupture of strands, silver cracks are transformed into ordinary cracks, the walls of which are not connected to the strands. The growth of these cracks also leads eventually to the complete fracture of the solid.

In evaluating the strength of glassy polymers, it should be kept in mind that the glasslike state itself is in the first approximation subdivided into brittle and non-brittle substates. (see Chap. 15). At low temperatures, fracture has a brittle character and is almost completely determined by the propagation of ordinary stress cracks. In the non-brittle forced-elastic region, silver cracks predominate.

The durab ility of the polymeric material will be exhausted only after silver cracks have spread over a large portion of the sample (this will be adequate for the beginning of the rapid propagation of macroscopic fatigue cracks). This leads to the characteristic configuration of the fracture surface; it consists of two areas, rough and shiny.[91, 92] It should be noted that ordinary cracks are propagated much faster than silver cracks.

The development of two types of cracks in the material leads to the division of the fracture process into at least two (sometimes into three) stages. In oriented polymeric fibers, the application of a load is followed by a "drawing" of the fiber, e.g. a change in structure. This process is later slowed, and cracks appear in the second stage. In the final stage, the cracks are rapidly propagated throughout the entire sample. Naturally, the largest role in determining the durability of material belongs to the second, and longest stage of the fracture process.

The heat-fluctuating mechanism of the rupture of structural units in the apices of microcracks, as a rule, is the basis of the theory of polymer strength. This phenomenon is discussed differently by a number of authors. In one set of cases[93 - 95], brittle destruction is regarded as the result of the propagation of cracks to the so-called critical dimension, while others[22, 23, 96] consider the slippage of polymer chains relative to each other.

The theory of the temperature-time dependence of strength elaborated by G. M. Bartenev and his collaborators[97, 98] offers a detailed relation for the durability of polymeric materials. This theory, based on the heat-fluctuating mechanism of the rupture of interatomic bonds in the apices of microcracks, is founded on the following premises. The bonds between atoms may be ruptured and restored, but if at a given stress there is equal likelihood of rupture and restoration of the bonds, then the crack will not grow. The theory also introduces the concpet of a safe stress σ_0 below which this condition is observed, and above which the probability of the bonds' rupture exceeds the probability of their reestablishment.

By determining the probability of the above process in the usual manner and by considering that the rate of crack propagation is proportional to the probability of the bonds' rupture, one may derive a relation for durability in which material parameters accounting for the scale factor are included.* (*Accounting for the scale factor means that one takes into consideration the form of the sample, its dimensions, the dimensions of initial cracks, etc.)

For circular rods in the case of brittle fracture, Bartenev's equation for durability takes the form

$$\tau = \frac{\pi r R T}{\lambda \nu_0 \omega \beta \sigma \chi^2} e^{-\frac{a}{R}} e^{\frac{U_0 - \omega \beta \sigma}{RT}} \quad \text{(V.11)}$$

where r is the radius of the rod; σ and T are constant stress and temperature; λ is the average distance between adjacent broken polymer chains in the path of the crack's propagation; v_0 is the frequency of thermal oscillations of the atoms in the polymer chain; w is the fluctuating volumne in which the elementary fracture event (the rupture of bonds or bond groups) occurs; β is the coefficient of stress concentration at the tip of the propagating crack; χ s the scale factor $(1 - s_0/s)^{-1}$, where s_0 is the initial sectional area of the most dangerious microcrack; "α" is a constant accounting for the dependence of activation energy on temperature.

Constants U_0 and $w\beta = \gamma$ are similar to the corresponding constants in Eq. (V.1). The structure-sensitive parameter γ is the volumne in which the elementary fracture event occurs, multiplied by the coefficient of stress concentration.

If fracture occurs as a result of the propagation of silver cracks, e.g. in a non-brittle manner, the life of the polymer is determined by the durability of the strands and is described by the simpler relation

$$\tau = \frac{r}{\lambda'\nu_0} e^{-\frac{\varepsilon}{R}} e^{\frac{U_0 - \omega'\beta'\sigma}{RT}} . \qquad (V.12)$$

Parameters λ' w' and β have the same meaning as in Eq. (V.11) but have different values.

In the region of non-brittle fracture, relaxation processes become quite important; their calculation allos a more precise description of the durability of polymers in this temperature region. The transition from the temperature region where nearly ideal brittle fracture occurs to the region in which fracture is non-brittle changes[100 - 102] the character of the dependence of log τ on σ. Two clusters of straight lines, each having a different slope, are formed instead of one such cluster[102], and the correlation of these experimental data leads to two different values for the activation energy and parameter $\gamma = w\beta$.

In a theory developed by Barenblatt and associates[103] for the kinetics of crack propagation in a hard solid, the adhesive force acting in the annular region of the surface of cracks is assumed to be time-dependent, even under constant load. The adhesive forces are transmitted by structural elements (s-rands) connected to the walls of the propagating crack. If it is assumed that the rate of the change in the density of these load-carrying elements is described by an equation similar to a first-order reaction equation.

$$\frac{dn}{dt} = -kn \qquad \text{(V.13)}$$

where n is the density of the load-carrying elements, equal to the ratio of the number of these elements in an infinitely small area to the total area; t is the time; k is the transfer rate then one may derive all of the basic relations for long-term strength.

Equation (V.13) is the basis for describing the kinetics of crack propagation and the fracture of a polymeric solid as a whole. Such an apporach[103] permits the formulation of the conditions of brittle fracture, the examination of several questions concerning long-term strength, and the substantiation of criteria of fracture under variable load.

Fracture occurs in an actual polymeric material as a result of the propagation of cracks, with considerable stress concentrated at the tips of such cracks. The material is fractured first at these most dangerous sites. However, a check of the stress concentration again leads to the usual temperature-time dependence of strength. THis is not surprising, since kinetic conceptions of the gradual heat-fluctuating rupture of bonds between atoms or larger structural particles are the basis of both the purely molecular mechanism and the mechanism connected with crack initiation and propagation in an actual hard solid.

The equation given by Barenblatt and his collaborators for th durability of polymeric materials appears thus:

$$\tau = \tau_0' e^{\frac{U_0 - \gamma' \sigma}{RT}} \qquad \text{(V.14)}$$

where

$$\tau_0' = \frac{3 l_0 e^{-C} B \tau_0}{\delta (B + D)}; \quad \gamma' = \pi \gamma_0 \sqrt{\frac{2 l_0}{\delta} \frac{D + B}{4D + B}}; \quad \gamma_0 = \frac{\Gamma}{G_0 n_0} \qquad \text{(V.15)} \qquad \text{(V.15)}$$

Here l_0 is the initial dimension of the crack at t - 0; C is Euler's constant (C = 0.577 . . .); B is the coefficient characterizing the bond's tensile growth rate with its elongation v; τ_0 is the oscillation period of atoms in a hard solid; σ is the length of the end region; D is a constant; Γ is a meterial constant; G_0 is a material constant equal to the characteristic tension of an individual bond; n_0 is the number of bonds per unit surface area of cracks outside the end region.

Comparing relations (V.14) and (V.15) with Zhurkov's equation, it may be stated that quanity γ_0 has the meaning of parameter γ in Zhurkov's equation in cases where the hard solid is free of defects and the load is distributed evenly over all bonds (a purely molecular fracture mechanism). The factor

$$\pi \sqrt{\frac{2l_0}{\delta} \frac{D + B}{4D + B}}$$

has the meanding of the particular coefficient of stress concentration.

An experimental investigation of the propagation rate of main cracks in a number of polymers showed [119] that most of the (durability of a sample τ under load is consumed by the propagation of precisely these visible cracks, not by the τ initiation of nucleated cracks. In any mode of loading, their propagation increases exponentially with increasing stress, which is in complete accord with the basic equation of the temperature-time dependence of strength.

The above-examined theoretical and experimental studies pertain, as a rule, to uniaxial tension. Efforts have been made to consider a complex stress condition.[120 - 123]

The Durability of Polymers under Variable Load and Temperature

In examining the physical nature of polymers' strength to find the parameters of the temperature-time dependence of strength, experiments are conducted under static conditions, holding stress and temperature rigidly constant. Constant temperature and stress are more the exception than the rule, however, under the conditions of the polymers' practical use. Any material is almost always subjected to variable temperature and load during its work in constructions. It is vital that one determine the durability of polymers under complex conditions of mechanical and thermal action. It may be sssumed that if a sample's durability is gradually exhausted by a constant load, cyclic loading (with rests) will have the same effect. It is very important to know if the rest periods affect the ultimate durability of the sample, and if so, how.

Many observations show that imperfections in the material are not mended in the relaxation period. This is easily confirmed. Let us place side by side two identical samples of polymeric material and load them with an uninterrupted constant load P. This load should not be so great as to cause the material's immediate fracture. Over a certain period of time $\nabla\tau_n$, let us take the load from the second sample and allow it to rest for a period of time $\nabla\tau_0$, with $\nabla\tau_0$ not differing substantially from $\nabla\tau_n$. We will then again load this sample with the same force and await the fracture of both samples.

If all of the experimental conditions and the structures of the samples are exactly identical, the first sample will fracture before the second one, and the difference in their durability wil amount to $\nabla\tau_0$. The total time that the two samples will have been under load before fracture will be the same. This means that the second sample "remembered" the period of time it was under load, and that none of the imperfections were mended in the rest period.*

This simplest of tests testifies to the observance of the principle of "the summing of imperfections." The principle says that imperfections occurring in a sample as the result of loads are irreversible, e.g. they do not dissappear during a rest period. This also confirms the heat-fluctuating nature of the fracture process, in the course of which elementary events of interatomic bond rupture gradually occur. The number of broken bonds accumulates over time, leading as a result to the macroscopic fracture of a polymeric solid.

The congruence of the durability of samples under uninterrupted or cyclic loading implies the following mathematically. Let the durability of a sample under a certain constant stress be equal to τ. Let us assume that this stress acted for a period of time $\nabla\tau_1$, while $\nabla\tau_1 < \tau$. Having removed the load, we allow the sample to rest. It is quite obvious that the relative "aging" of the sample will be $\nabla\tau_1/\tau$. Let us again load the sample with the same force and maintain that load for period of time $\nabla\tau_2$. After the repeated mechanical action, the sample's relative "aging" will amount to

$\nabla\tau_1/\tau + \nabla\tau_2/\tau$. Let us continue the complete fracture of the sample after its loading for period $\nabla\tau_n$. At the moment of fracture, th relative "aging" will be

since
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$$\frac{\Delta t_1}{\tau} + \frac{\Delta t_2}{\tau} + \cdots + \frac{\Delta t_n}{\tau} = 1 \qquad \text{(V.16)}$$

$$\sum_{i=1}^{n} \Delta t_n = \tau$$

We can now look at a load changing constantly over time. We begin in this instance as usual. Let us distinguish an infinitely small time inteval $d\tau$ and consider that within this time interval stress is constant and equal to an instantaneous value $\sigma(\tau)$. Then we substitute $\nabla\tau_i$ for $d\tau$, and the summation changes to integration. Relation (V.16) takes the form

$$\int_0^{t_p^{(r)}} \frac{dt}{\tau[\sigma(t)]} = 1 \qquad \text{(V.17)}$$

where τ_γ is the time from the moment the load is applied to the fracture of a polymeric solid; $\tau\,[\bar{\sigma}(\tau)]$ is durability during constant stress, equal to instantaneous value $\sigma(\tau)$.

In order to determine the durability of a polymeric material under variable load, it is necessary to first substitute the dependence of stress on time $\sigma(\tau)$ in any of the relations (V.1), (V.8), (V.11), etc. and then determine the fixed interval (V.17). The upper limit of this interval will also give the sought-after value for durability under variable load. Relation (V.17) was first introduced by Bailey[104] and was named Bailey's criterion.

Bailey's criterion is based on two assumptions. The first is the irreversibility of the fracture process, already mentioned above. The second is the independence of the rate of fracture on the previous mechanical history of a material. Both of these assumptions are not always valid. If the rate of the change in stress is insubstantial, the stress period is approximately equal to the rest period, and the structure of the polymer is unchanged under load, Bailey's criterion is completely satisfied.[105 - 109]

When these conditions are not observed, the calculated values for durability τ_γ deviate from experimental values. For example, during cyclic loading with a large number of cycles, intensive initial heating of the material occurs, and the temperature increases and differs substantially from the initial temperature. Naturally, by substituting the initial temperature in (V.17), we will obtain an overstated value for durability.[109, 110]

There may be other reasons for the discrepancies (a change in the structure of the material by mechanical action, local heating). These deviations do not by any means signify the basic principle - the irreversibility of the fracture process, leading to the gradual accumulation of imperfections in the material - is not observed. The divergence between calculated and experimental values of durability means only that there are other parameters of Eqs. (V.1), (V.8), (V.11) etc. apart from stress. As a result, the actual experimental conditions as well as the structure of the material (e.g.) temperature, structure-sensitive parameter γ) differ from the initial conditions according to which calculations by means of Bailey's criterion were performed.

In order to account for these changes, Bailey's criterion must be written as follows:

$$\int_{0}^{t_p(\tau)} \frac{dt}{\tau[\sigma(t), T(t), \gamma(t)]} = 1 \qquad \text{(V.18)}$$

where $\tau[\sigma(\tau), T(\tau)\ \ \gamma(\tau)]$ is the durability at constant stress, temperature and structure-sensitive parameter γ, respectively equal to instantaneous value $\sigma(\tau)$, $T(\tau)$ and $\gamma(\tau)$.

Calculation of the changes in all of these quantities over time is complicated in itself, not to mention the fact that solving Eq. (V.18) also becomes more complex. Generally, the "life" of a material is less with variable values for σ, T and γ than for equivalent constant values. Thus, imperfections in the material are not mended, but are accumulated, e.g. the principle of the irreversibility of the fracture process is completely satisfied.

Having eliminated local overheating or changes in the structure of a material, one may approach complete agreement between experimental and rated durability^{110}, calculated by means of Eq. (V.18). It follows from this equation that under any conditions of mechanical and thermal action, durability is a function of the parameters of stress, temperature and structure of a hard solid.

One may arrive at the same durability by different paths. For example, one may at first assign a small load which, even acting over a prolonged period, does not consume much of the material's durability. The load may then be increased, and durability will be expended much more rapidly. Sometimes the converse is necessary: the material is subjected to active loading, and subsequently to weaker loading. Here, most of the durability will be expended early, but the result will be the same: fracture will occur at the moment when the relative exhaustion of durability (relative "aging") equals unity.

It should always be remembered that the dependence of durability on stress and temperature has an exponential character, so that the existence of the material a very short time under a heavy load will lead to the same depletion of durability as the material's maintenance under a small load for a long time.

The reliability of the operation of various devices is often tested in practice by the creation of large loads. If overloads are endured, it is obvious that the device will function under small loads. But it is also clear that by assigning large loads, we are substantially reducing total durability.

Adherence to Bailey's criterion makes possible yet one more conclusion, important from a practical viewpoint. Testing a given part under periodic loads, we think that the unit should be shut off from time to time, thus giving it a "rest." It seems to us that this procedure prolongs the life of the part's operation. However, the total durability of a material under periodic load remains the same, regardless of whether it is rested or not. Moreover, if the rest period substantially exceeds the period of loading, total durab ility will be less, not greater, than under uninterrupted load.

This conclusion, paradoxical at first glance, is confirmed by numerous experiments[43, 111], while the difference in durability is expressed in several decimal orders. How does one explain this astonishing phenomena? The authors[43, 111] who first observed it explained the sharp reduction in durability by the change over time in structure-sensitive parameter γ in Zhurkov's equation, as well as by relaxation processes.

It may be assumed that under load, the sample's structure changes somewhat (owing to drawing and orientation), as if it were adapting to new conditions. These changes are such that they facilitate the survival of the material in a loaded condition (redistribution of stresses in the most dangerous places, orientation in amorphous regions of semi-crystalline polymers, etc.). By adapting to the load, the material accepts it more easily.

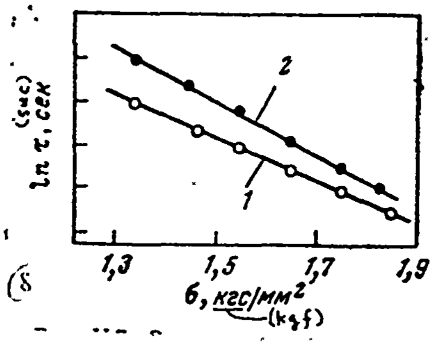

Figure 7.

The dependence of durability on stress for high-density polyethylene under constant load (1) and cyclic loading (2). Time under load is 20 min, period of rest is 10 min.

If the load is removed and the material is rested, the material's structure will return to its original condition (typical relaxation process). With short rests, the rebuilding of the structure does not proceed too far, and after repeated loading it will correspond in a very short time to the structure at the moment of the load's removal. During long rests, the rearrangement will cause additional irreversible changes in material. Total durability is reduced as a result.

These questions, interesting and important from all viewpoints are found in the beginning stage of study, while the results often prove contradictory. High-density polyethylene is characterized[124] by an increase in durability under continuous loading under conditions where $\sigma =$ constant). It is understood that during such a comparison only the time under load is considered. Thus the question of the effect of rest on the durability of polymers is still open, and only further systematic compilation of experimenta data will allow us to make any final conclusions. It is possible that the "mending" of cracks in the polymeric material occurs during the relaxation process, the more so as studies[125] of recent years have made it possible to sub stantiate such an assertion.

I. V. Pazumovskaya[112] has made a thorough analysis of the conditions under which Bailey's criterion is or is not satisfied.

W

With variable loading, Bailey's criterion generally exceeds unity and is written in the form

$$\int_0^{\overset{\text{ВПДе}}{t_p}(\text{r})} \frac{dt}{\tau[\sigma(t)]} = 1 + I, \qquad (\text{V.19})$$

where I is an extremely complex function, dependent on the dimensions of the sample, the length of the initial crack and the rate of changes in stress with time $d\sigma/dt$.

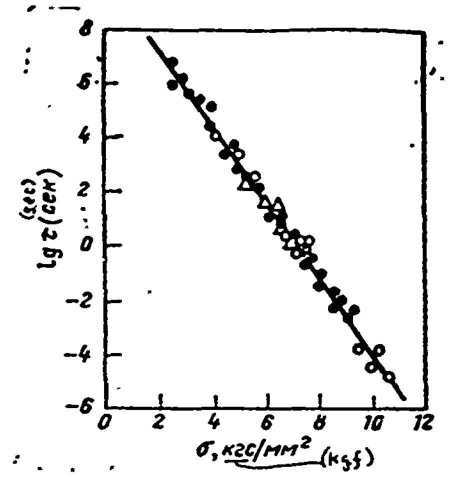

Figure 8.

The dependence of durability o on stress for polymethyl methacrylate: o - durability at σ = constant; Δ - durability under cyclic loading; o - durability computed by means of Bailey's criterion.

Under static loads ($d\sigma/dt = 0$), Bailey's criterion is strictly observed. If $d\sigma/dt \neq 0$, Bailey's criterion may exceed unity. With small rates of load changes, these deviations may be completely ignored, since they lie within the accuracy limits of durability experiments. Under ehe usual conditions of dunamometric tests, as well as during cyclic loading with a small frequency ^{105}, the values for durability computed by means of (V.17). agree with experimental results (Fig. V.8).

Thus, the durability of a polymeric material under variable load may in many instances be computed by means of Bailey's criterion. This is a straightforward problem. The opposite problem may also be solved: determine parameters U_0 and γ in Zhurkov's equation from data from dynamometric tests conducted at several temperatures. The tension curves obtained as a result of such tests must be reconstructed into coordinates of true stress - time. Generally, these curves are of variegated form, and cannot be described by some kind of simple equation. Then the problem can only be solved graphically.^{113}

Let us write Bailey's criterion with regard to Eq. (V.1), in which stress changes with time by the arbitrary law (t):

$$\int_0^{t_p^{(r)}} \frac{dt}{\tau_0 e^{\frac{U_0-\gamma\sigma(t)}{RT}}} = 1 \qquad (V.20)$$

After conversion of relation (V.20), we find for a certain temperature i:

$$\ln \int_0^{t_{p,i}^{(r)}} e^{\gamma\sigma_i(t)/RT_i} = \ln \tau_0 + \frac{U_0}{RT_i} \qquad (V.21)$$

where t_r, i is the time to fracture of the sample at temperature T_i; $\sigma_i(t)$ is the dependence of true stress on time at the same temperature.

By conducting dynamometric tests at several constant temperature T_i, we derive a set of equations based on (V.21). A solution to this set may be found with any trial-and-error method. It is desirable that the number of equations in the set exceed the number of unknowns (U_0, γ, and τ_0), since in this case the results obtained may be correlated and checked. The problem is greatly simplified if the interval in Eq. (V.21) is determined in finite form, for example with a linear increase in stress with time $\sigma = vt$ Then the parameters of Zhurkov's equation are easily determined by a special nomogram.[114, 115]

The parameters in Zhurkov's equation are determined from data from thermomechanical tests in similar fashion. By keeping stress constant and assigning a fixed mode of increase of temperature with T (t), let us write Bailey's criterion with regard to (V.1) in the following manner:

$$\int_0^{t_{p(r)}} \frac{dt}{\tau_0 e^{\frac{U_0 - \gamma\sigma}{RT(t)}}} = 1$$

where t_r is the time to fracture under the conditions of a thermomechanical test.

To determine the integral in (V.22) in finite form, it is convenient to make use of modes of heating conveyed by Eqs. (1.88) or (1.89). By conducting thermomechanical tests at several constant stresses σ_i and having determined the durabilities t_r, i corresponding to them, one can easily find the values of parameters U_0 and γ by a special nomogram.[115, 116]

Chapter 15

The Mechanical Softening of Polymers

As has already been mentioned above, the softening of polymers together with fracture is the most dangerous form of loss of work capacity. Mechanical softening is manifest in the development of large deformations of a polymeric solid under load. For amorphous glassy polymers, this effect is called forced elasticity[1, 2], and for crystalline solids - recrystallization.[3, 4] In all cases, the deformation process process entails the rearrangement of the original structure, affecting all levels of the polymer's super-molecular and molecular organization - from the mutual displacement of large structural elements to changes in the form of individual macromolecules, even to the point of their fragmentation.

Depending on temperature and load conditions, these different deformation mechanisms are uniquely superimposed on one another, while one may predominate. Independently of the mechanism, the development of significant strains in a polymeric solid leads to a loss of its capacity for work, even though it remains intact. Naturally, we are speaking of hard plastics, which must preserve their form under load. Yet still another, equally important demand may be made of such polymeric materials: to "collect" the required stress and store it for the entire period of the material's work.

In the first case, products fabricated in a given mode of strain should, according to their working conditions, ensure the creation of the necessary stress (inpparticular, the transmission of force through a shaft made of a polymer). In the second case, we may designate all devices (in particular, the rubber seals for piston devices) which ard made hermetic by a certain compressive force.

Thus, examining the possible reasons for the loss of work capacity in a solid, one may indicate two general instances:

1) deformation exceeding tolerable levels develop

1) deformation exceeding tolerable levels develops under given load-conditions;

2) stress is reduced below required levels due to relaxation under given load and temperature conditions.

Naturally, in the first instance we may examine the process of creep in polymeric materials, and in the second - the general process of stress relaxation. Both are determined by the modes of mechanical and thermal action, and special cases where σ = constant and T = constant or ε = constant and T = constant give, respectively, the simplest processes of creep and stress relaxation usually studied.

Before proceeding to a detailed examination of these fundamental instances of work-capacity loss, let us turn to the important concept of the thermal stability of polymers. In connnecting thermal stability with the loss of strength or softening of polymeric materials[5] , this property is usually characterized by the glass point (for amprphous hard plastics) or the temperature close to the melting poing (for crystalline polymers) at which the original structure of a solid cannot be maintained.

In practice, thermal stability is characterized by several temperatures (for example, thermal stability according to Vika or Martens) at which deformation may develop to a strictly defined degree under given test conditions, It is not always considered that with such a characteristic the actual sofetning of the polymeric material may occur not only at the glass point, determined under certain load and temperature conditions, but at any point in the temperature range for the glassy state, if other stresses are applied or if the duration of their action is changed.

The latter is most important, because the time factor plays an important role in the mechanical behavior of polymers. Thus, whether we are speaking of the work capacity of polymeric materials in general or of thermal stability in particular, we need to relate temperature, stress and period of time for which work capacity is preserved to one another.

The work capacity (thermal stability) demands on polymeric materials formulated above lead to a physically expedient characteristic of work capacity having a sense of the time interval over which work capacity is maintained. In the first case, this time is $t_{\emptyset}$,,over which strain reaches a certain tolerable level. In the second case, it is time t_{γ}, over which stress, increasing or decreasing, reaches a certain tolerable level. Let us examine these cases in greater detail.

The Work Capacity of Polymers In Creep (1st Case)

The conditions according to which deformation ε (t) should not exceed a fixed tolerable magnitude $\varepsilon_{\rho r}$ may be formulated in the form of an inequality.

$$\varepsilon(t) \leqslant \underset{(\rho r)}{\underline{\varepsilon_{\text{пр}}}} \qquad \text{(V.23)}$$

The time interval for which this inequality holds determines the work capacity of hard solids, since they should not change their form above certain limits during any mode of mechanical and thermal action. It should be noted that the inverse inequality

$$\varepsilon(t) \geqslant \overline{\varepsilon_{\text{пр}}}^{(\rho r)} \qquad \text{(V.24)}$$

requires the development of deformation at least up to the fixed magnitude. Such requirements must always conflict during the fabrication of finished products from polymeric materials (for example, cold forming, stamping, etc.). Consequently, inequality (V.24) determines the feasibility of the material's fabrication, since it must be satisfied in the time allowed by a given fabrication method.

Let us examine the region of tolerable magnitudes of deformation in which the value $\varepsilon_{\rho r}$ should be found. For this purpose, we turn to ordinary creep curves. Tests show that the rapid development of deformation begins only after a certain period of its slow development, and is accompanied by a spasmodic change in the conditon of the solid. The study of creep curves as well as data[6 - 16] recently obtained show that generally the creep curve may be subdivided into three sections (see Fig. II.30). The last section reflects the rapid growth of deformation, e.g. the softening of the material. This third section of the creep curve, formed over a definite period of time under load, corresponds to a certain magnitude of deformation designated by $\varepsilon_{\kappa r}$ (see Fig. II.30). The spasmodic change in deformation during its passage through ε_{kr} is observed not only in the special case of isothermal creep when σ = constant, but in any mode of mechanical and thermal action.

Naturally, the first - but not always adequate - requirement of the material with respect to its efficiency will be

$$\varepsilon_{\text{пр}} \leqslant \varepsilon_{\text{кр}} \tag{V.25}$$

since the form of the material changes raiidly after deformation equal to   has been attained. The condition required for workability (ability to be fabricated), of course, is written in the form

$$\varepsilon_{\text{пр}} \geqslant \varepsilon_{\text{кр}} \qquad \text{(V.26)}.$$

Since deformation greater than ε_{kr} has a forced-elastic character (see Chap. 5), the product holds the form given it during fabrication long after removal of the load.

Both of these conditions [(V.25) and (V.26)] may prove to be inadequate. For example, many workpieces may prove incapable of work even at magnitudes of deformation below ε_{kr}. In these cases, the tolerable level of deformation, and hence the durability of the form, is determined by the particular demands made of a given product. Requirement (V. 26) may also be unsatisfactory if deformation much greater than ε_{kr} is required for the fabrication of a specific product.

In order to determine the period of time over which the disturbance of the material's forms does not exceed tolerable limits, it is necessary to know the dependence of deformation on time. Let us examine general cases of such, and proceed later to specific problems of mechanical action.

As is know [17, 18], when one is speaking of isothermal conditions, deformation is generally a function of stress history Under non-isothermal conditions, deformation is a function of both mechanical and thermal T (t) history over a period of time from 0 to t:

$$\varepsilon(t) = \Phi\left[\overset{t}{\underset{0}{\sigma(t)}};\ \overset{t}{\underset{0}{T(t)}}\right] \qquad \text{(V.27)}$$

It is assumed ere that the temperature was constant up to t = 0, and that mechanical stress was absent.

In the case given, we are interested in the time which elapses from the moment of the beginning of mechanical and thermal action until the development of a deformation equal to ε_{pr}. In other words, we need to determine the durability (longetivity) of the form t_{ϕ} of a polymeric material, since the material loses its capacity for work at the moment ultimate deformation ε_{pr} is attained, owing to an intolerable change in its form. Obviously, the durability of the form is determined from (V.23), providing conditions exist whereby $\varepsilon(t_{\phi}) = \varepsilon_{pr}$, and in accordance with Eq. (V.27):

$$\varepsilon_{\underset{(pr)}{\text{пр}}} = \Phi\left[\overset{t_{\Phi}}{\underset{0}{\sigma(t)}};\ \overset{t_{\Phi}}{\underset{0}{T(t)}}\right]. \qquad \text{(V.28)}$$

It follows from Eq. (V.28) that the form's durability t_{ϕ} is also a function of functions $\sigma(t)$ and T (t). Let us illustrate this with a special example.

Let us examine an isothermal ($T = T_O$) deformation and assume that the function in Eq. (V.28) is linear according to stress.* Then in place of Eq. (V.28) we may use Boltzmann's equation (see page 110) which is our symbolization takes the form

$$\varepsilon_{\underset{(pr)}{np}} = \frac{\sigma(t_{\phi})}{E(T_0)} + \int_0^{t_{\phi}} \varphi(t_{\phi} - \tau;\ T_0)\,\sigma(\tau)\,d\tau \tag{V.29}$$

where $E(T_O)$ and $(\ ;T_O)$ are respectively, the instantaneous modulus of elasticity and a memory function (dependent on $\omega = t_{\phi} - \tau$) accounting for stress history - taken for temperature T_O.

It is obvious from Eq. (V.29) that for a specific material, e.g. for knowns $E(T_O)$ and $\varphi(\omega;T_O)$, and for a specific magnitude ε_{pr}, the form's durability t_{ϕ} is completely determined by stress history σ (t), so that it is a function of stress. If the process were isothermal, t_{ϕ} would depend not on the value of T_O, but on the entire thermal history.

Now is is expedient to find the conditions under which the material attains the specific magnitude of deformation most rapidly. Consequently, we need to determine the value of t_{ϕ}, which corresponds to the minimum amount of time required for the development of the tolerable deformation magnitude ε_{pr}. This may be accomplished with an examination of any possible stress histories, under conditions limiting their absolute value, e.g. $|\sigma(\tau)| \leq \sigma_m$.

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* Linear according to stress means that function $(t_{\phi} - T;\ T_O)$ in Eq. (V.29) is independent of stress.

Considering that $(t_\phi - t;\ T_\phi)$ is a positive function, monotonically decreasing with an increase of $(t_\phi - t)$, and replacing $\sigma(t)$ with its maximum value σ_m (e.g. examining creep at constant stress σ_m), we obtain

$$\varepsilon_{\substack{\text{пр}\\(\text{pr})}} = \frac{\sigma_m}{E(T_0)} + \int_0^{t_\Phi} \varphi(t_\Phi - \tau;\ T_0)\,\sigma_m\,d\tau \qquad \text{(V.30)}$$

or, designating $t_\phi - t = w$

$$\varepsilon_{\substack{\text{пр}\\(\text{pr})}} = \frac{\sigma_m}{E(T_0)} + \sigma_m \int_0^{t_\Phi} \varphi(\omega;\ T_0)\,d\tau \qquad \text{(V.31)}$$

It can easily be seen that with the substitution of σ_m for $\sigma(t)$, the value of t_ϕ can only decrease. Therefore t_ϕ, determined from Eq. (V.31), is the least of all time periods for attaining deformation ε_{pr}. This is valid for any isothermal modes of change in stresses, not exceeding the magnitude σ_m. Thus, Eq. (V.31) gives the value of time period t_ϕ over which work capacity is guaranteed, e.g. deformation in the material will not exceed the specific value ε_{pr} in this period of time if stress is not raised above σ_m.

In similar fashion, an arbitrary thermal history of creep may be examined and the non-linearity of the dependence of deformation on stress may be confirmed. For this purpose, it is necessary to introduce the dependence of the parameters of memory function $(\omega; T_0)$ on stress and temperature.

Returning to a material's fabrication ability, we note that relation (V.28) determines the time required to obtain the necessary deformation $\varepsilon_{\rho r}$. If the modes of mechanical and thermal action are fixed, then the duration of the fabrication process is determined, for example, the duration of isothermal molding at a certain temperature and fixed pressure.

If the duration of the fabrication process is fixed, e.g. t_{ϕ}, as well as the value of ε_{pr} then one must find from relation (V.28) the thermal-mechanical modes that are satisfactory, and select the most convenient mode. This generally difficult problem may be solved in individual special cases, for example, corresponding to Eq. (V.29). The examination of these questions is interesting to itself, but lies outside the scope of the present work.

According to relation (V.25), the most dangerious instance of loss of work capacity arises when deformation exceeds ε_{kr}. At this moment, a neck is formed and deformation begins to increase very rapidly. The material is softened. The formation of a neck and the softening of polymers is best studies under uniaxial tension at a certain velocity. The tension diagrams obtained for amorphous and crystalline polymers under such conditions are described in detail in Chapters 5 and 11.

Neck formation is also possible under a constant load. Systematic investigations[6 - 16] have shown that when σ = constant, a fixed amount of time passes between the application of a load and the formation of the neck, with the time interval called the induction period. The greater the stress and the higher the temperature, the less the induction period.

In accordance with the terminology used above, this period will be called the durability of the form of the material under constant stress and temperature, and will be designated t_{ϕ}. It was shown[6] that for crystalline polypropylene, original and modified with artificial nucleators, the dependence of t_{ϕ} on temperature T and stress σ is described by the equation

$$\tau_{\Phi} = A\sigma^{-b} e^{U'/RT} \qquad \text{(V.32)}$$

where A, b and U' are parameters of the material.

The processes of fracture and creep were studied from these same viewpoints in polypropylene, and in other polyolefins.[12]

Under constant load, various forms of work-capacity loss may be observed. Depending on the load and temperature, these polymers may display brittle fracture (without neck formation) or softening (with neck formation).

During tests conducted at the same temperature, both brittle and non-brittle fracture may be observed in polymer samples. Large constant loads cause fracture of the sample earlier, but small stresses lead to softening (neck formation) first. Authors[12] have found that the life of a polymeric solid t and the durability of its form t_{ϕ} lie on the same stress function curve and, consequently, are subject to the same equation, (V.1).

Under constant load and temperature, glassy polymers are also capable of neck formation after a certain period of time has elapsed from the moment of the load's application.[8 - 10] for polymethyl methacrylate and polystyrene, the dependence of the form's durability t_{ϕ} on temperature T and stress σ is described[10] by the relation

$$\tau_{\Phi} = \tau_{\Phi,0} e^{\frac{U'_0 - \gamma'\sigma}{R}\left(\frac{1}{T} - \frac{1}{T'_{\text{п}(p)}}\right)} \qquad (V.33)$$

where $t_{\phi,o}$ is the pre-exponential multiplier; U'_o, y' and T'_p are material constants, while T'_p corresponds to the temperature of the pole (a fan of straight lines of the dependence of lg t_{ϕ} on 1/T come out of this point).

Thus, if a polymeric material is capable of displaying large deformations, it may neck not only during tension at a certain rate, but also under constant load. This means that necking (softening of the material) is a kinetic process, and in this connection is quite similar to the fracture process.

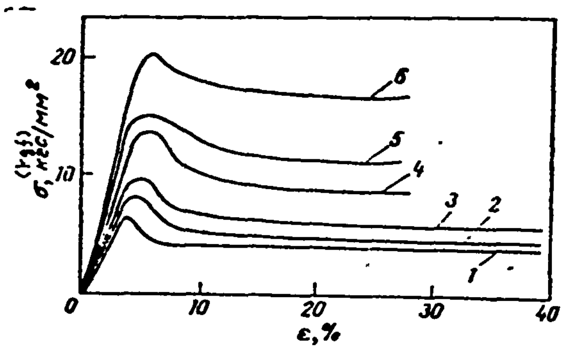

Figure V.9.

Compression diagram for polystyrene (deformation rate d /dt = 0.02 min^{-1}) at temperature: 1 - 60°C; 2 - 40; 3 - 20; 4 - minus 20; 5 - minus 50; 6 - minus 140°C.

Under uniaxial compression, the creep curve also consists of several sections.[11] Curiously, if small humps are observed on a polymer's compression diagram (Fig. V.9), then an abrupt acceleration of deformation will be observed on the creep curve after a period of slow deformation increase (Fig. V.10). Consequently, the durability of a polymeric material's forms is also depleted during compression at constant stress. The larger the applied load, the less the time elapsed from the moment of its application ot the abrupt increase of deformation.

Independently of the amount of stress, and even of test conditions (creep at σ = constant or compression with a constant velocity), the accelerated growth of deformation begins at practically the same value.[11] Evidently, after the attainment of this "critical" deformation, there occurs abrupt overall disturbance of the material's structure, preceded by the accumulation over time of elementary softening events.

The formation of a neck has been studied in amorphous films of lavsan.[13] The durability of the form t_{ϕ} of this material under constant stress and temperature is described by relation (V.32).

Let us compare the results of dynamometric tests[13, 19] on this polymer with the dependences of t_{ϕ} on stress and temperature. Let us assume that, as during fracture, the abrupt nucleation of a neck occurs after the durability of the polymeric material's form has been fully exhausted. Then, under increasing stress, the form's durability t_{ϕ} should be determined from a relation similar to Bailey's criterion:

$$\int_{0}^{t_{\Phi}} \frac{dt}{\tau_{\Phi}[\sigma(t)]} = 1 \qquad \text{(V.34)}$$

where $t_{\phi}[\sigma(t)]$ is the durability of a form under a constant stress, equal to the instantaneous value $\sigma(t)$.

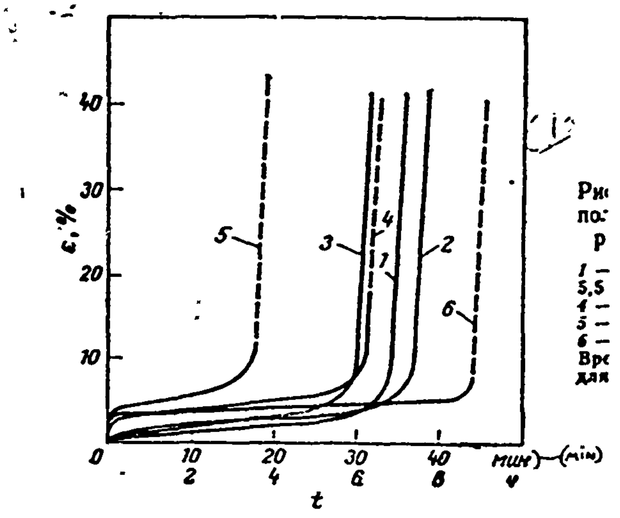

Figure V.10.

Creep curves for polystyrene under compression. Temperature and stress are equal to:
1 - 60 °C, 4.5 kgf/mm^2;
2 - 40 °C, 5.5 kgf/mm^2;
3 - 20 °C, 7.5 kgf/mm^2;
4 - minus 20 °C, 12.5 kgf/mm^2;
5 - minus 50 °C, 14.5 kgf/mm^2;
6 - 15 °C, 21.5 kgf/mm^2. Times on the abscissa for curves 1, 4 and 6 are in minutes; for curves 2, 3 and 5, in hours.

Substituting relation (V.32) in Eq. (V.34), we obtain

$$\int_0^{t_\Phi} \frac{dt}{A\,[\sigma(t)]^{-b} e^{U'/RT}} = 1 \qquad (V.35)$$

Considering that under dynamometric test conditions the true stress, as a rule, changes according to the law $\sigma \doteq vt$[*] (v is the rate of stress increase over time, t is the time), after integrating

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[*] The relation $\sigma = vt$ is valid only up to the amount of a neck's formation. This dependence is violated with further tension.

(V.35) we obtain

$$\frac{v^{b} t_{\Phi}^{b+1}}{A e^{U'/RT} (b+1)} = 1 \qquad \text{(V.36)}$$

Considering that $vt_{\phi} = \dot{\sigma}_{ve}$ (σ is the limit of forced elasticity), after calculating the logarithm of (V.36), we have

$$\lg \sigma_{\underset{(ve)}{\text{вэ}}} = \frac{\lg (b+1) A v}{b+1} + \frac{U'}{2{,}3RT(b+1)} \qquad \text{(V.37)}$$

Eq. (V.37) describes the dependence of forced elastic limit on temperature T and loading velovity v (under conditions whereby $\sigma = vt$). Substituting numerical values for A, U', b and v in Eq. (V.37) obtained by direct measurement at σ = constant and T = constant, we may construct the dependence of log σ_{ve} on 1/T (Fig. V.11).

The values of σ_{ve} computed by means of relation (V.37) are always higher than experimental values. This, in turn, indicates the nonequivalance of structural changes occuring under constant stress and increasing stress. No direct structural studies have yet been conducted, however, that allow us to pass unambiguous judgment on both of these changes.

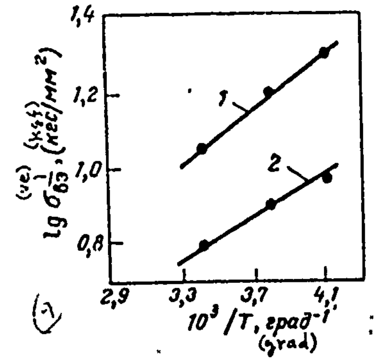

Figure 11.
Caption on next page.

The dependence of the forced elastic limit σ_{ve} on inverse absolute temperature $1/_T$ for amorphous lavsan films:
1 - calculated values of σ_{ve}.
2 - experimental values of σ_{ve}.

The efficiency of Polymers in Stress Relaxation (2nd Case)

What is often require of a polymeric material is not that it keep its form, but that is support a certain stress - often, both are required. In connection with this, it is necessary to examine the second case of a polymer's work capacity when stress relaxes further than that amount tolerable under working conditions.

The condition according to which stress, relaxing in a certain mode of deformation and thermal action should not be reduced below a required value σ_{pr}, can be written in the form

$$\sigma(t) \geqslant \underset{(pr)}{\sigma_{np}} \qquad (V.38)$$

Here, two types of problems are possible:

1) The magnitude of stress satisfying condition (V.38) should be attained after the passage of time under load t_n:

2) after time of retention t_r, the relaxing stress, exceeding σ_{pr}, should remain greater than it.

The inverse inequality

$$\sigma(t) \leqslant \sigma_{\underset{(\mathrm{pr})}{\text{пр}}}, \qquad \text{(V.39)}$$

may be required in evaluating the feasibility of a polymer's fabrication (for example, in evaluating the possibility of stamping polymeric products without creating overly strong breaking forces in the working apparatus).

Let us look again at condition (V.38), and determine the region of tolerable stresses in which σ_{pr} should be found. For this purpose, let us turn to ordinary stress relaxation curves. A test shows that if stress created at the beginning of the relaxation process approximates the value of the forced elastic limit σ_{ve}, then the relaxation processes will undergo abrupt acceleration. This phenomena often has a spasmodic character, for example, owing to the growth of a neck during tensile deformation. Thus, there exists a value σ_{kr} above which σ_{pr} cannot exist. In particular, during tensile deformation at a constant rate, the role of σ_{kr} is filled by the corresponding forced-elastic limit σ_{ve}.

In order to determine the period of time over which the required stress is achieved and then maintained, it is necessary to know the dependence of stress on time under the given conditions of deformation and thermal action. However, let us first examine general relations.

To obtain general functions, we use the relation following from Eq. (V.27)

$$\sigma(t) = F\left[\varepsilon\overset{t}{\underset{0}{(t)}};\ T\overset{t}{\underset{0}{(t)}}\right] \tag{V.40}$$

It may be used to solve the first and second problems (see above). It follows from Eq. (V.40) that the value of σ_{pr} is connected with period t_n (e.g. with the period of time necessary to create the stress $\sigma(t) = \sigma_{pr}$ in a solid) by the relation

$$\underset{(pr)}{\sigma_{\text{пр}}} = F\left[\varepsilon\overset{t_{\text{н}}\ (n)}{\underset{0}{(t)}};\ T\overset{t_{\text{н}}\ (n)}{\underset{0}{(t)}}\right] \tag{V.41}$$

It is quite obvious that <u>time under load</u> is a function of functions $\varepsilon(t)$ and $T(t)$. Limiting isothermal deformations ($T = T_o$) and assuming that the function in Eq. (V.41) is linear according to deformation, we obtain a relation similar to Eq. (V.29)

$$\underset{(pr)}{\sigma_{\text{пр}}} = E(T_0)\,\varepsilon(\underset{(n)}{t_{\text{н}}}) - \int_0^{t_{\text{н}}\ (n)} f(\underset{(n)}{t_{\text{н}}} - \tau;\ T_0)\,\varepsilon(\tau)\,d\tau, \tag{V.42}$$

Here $E(T_o)$ and $f(\omega\ ;\ T_o)$ are, respectively, the instantaneous modules of elasticity and a memory function (accounting for the deformation history) taken for temperatures T_o; $\omega = t_n - t$.

For a specifically chosen material, e.g. for fixed $E\ (T_o)$ and $f\ (\omega\ ;\ T_o)$, and for a fixed value of σ_{pr}, the value of t_n is determined completely by the deformation history $\varepsilon(t)$. It is apparent from Eq. (V.42) that t_n, as might be expected, is a function of deformation. It is useful to calculate the value of period t_n required for the development of minimum stress σ_{pr} necessary for the product's work.

If one examines a set of arbitrary deformation processes characterized only by their uninterrupted increase, then the values for deformation to moment of time t_n may be different. If, however, the set is such that there exists the least deformation attainable to moment of time t_n, equal to $[\varepsilon\ (t_n)]_{\min}$, it may be asserted that the stress, in the process of its relaxation of constant deformation ε_o, will be the least of all stresses attainable in this time period for any increasing modes of deformation.

It may easily be demonstrated that stress relaxing at a constant deformation equal to any of the attainable values of $\varepsilon(t_n)$ will be less than in any other mode leading to the same deformation $\varepsilon(t_n)$.

Let us prove this assertion.

From Boltzmann's equation

$$\sigma(t) = E\varepsilon(t) - \int_0^t f(t-\tau)\,\varepsilon(\tau)\,d\tau \qquad \text{(V.43)}$$

when (t) = $_o$ = constant, we have

$$\sigma(t) = \varepsilon_0 \left[E - \int_0^t f(t-\tau)\, d\tau \right] \tag{V.44}$$

It can be seen from Eq. (V.44) that during the increase of deformation $_o$, stress is always higher at any moment, since the expression in the brackets is independent of ε_o, but $\sigma(t)$ increases with increasing ε_o. For the sets of any undiminishing deformations $\varepsilon(t)$ attaining to fixed moment $t = t_n$ a certain value ε_o, minimum stress $\sigma(t_n)$ will be obtained in the mode of deformation $\varepsilon(t) = \varepsilon_o$ = constant. Actually, it follows from Eq. (V.43) that for $t = t_n$:

$$\sigma(\underset{(n)}{t_H}) = E\varepsilon(\underset{(n)}{t_H}) - \int_0^t f(\underset{(n)}{t_H} - \tau)\,\varepsilon(\tau)\, d\tau \tag{V.45}$$

The first term in Eq. (V.45) does not depend on the deformation mode $\varepsilon(t)$, so that it has (conditionally) a constant value $\varepsilon(t_n) = \varepsilon_o$. Obviously, the largest value for the integral in this equation will be attained when $\varepsilon(t) = \varepsilon_o$, since all of the deformations observe under this condition will be undiminishing. Consequently, in the mode $\varepsilon(t) = \varepsilon_o$, stress over time interval t_n from the beginning of deformation will be the least of the whole set of undiminishing modes of deformation, attaining to moment t_n the value $\varepsilon(t_n) = \varepsilon_o$. According to Eq. (V.44), this assertion is also valid for modes of undiminishing deformation attaining to moment of time t_n values exceeding ε_o.

A+ deformation equal to $[\varepsilon(t_n)]_{min}$, stress will be minimal since a decrease in the magnitude of deformation at which relaxation occurs always signifies a reduction in stress.

Thus, if one is required to create over time t_n a stress treater than or equal to some fixed value$\sigma\sigma_{pr}$, then this will be accomplished in any case where $\varepsilon(t_n)$ is no less than ε_o. Thus *

Таким образом *

$$\sigma(t_{\underset{(n)}{\text{н}}}) \geqslant \sigma_{\underset{(pr)}{\text{пр}}} = E\varepsilon_0 - \int_0^{t_{\text{н}}^{(n)}} f(t_{\underset{(n)}{\text{н}}} - \tau)\varepsilon_0\, d\tau = \varepsilon_0 \left[E - \int_0^{t_{\text{н}}^{(n)}} f(\omega)\, d\omega\right]. \qquad \text{(V.46)}$$

and for ε_o we have

$$\varepsilon(t_{\underset{(n)}{\text{н}}}) \geqslant \varepsilon_0 = \frac{\sigma_{\text{пр}}^{(pr)}}{E - \int_0^{t_{\text{н}}^{(n)}} f(\omega)\, d\omega}. \qquad \text{(V.47)}$$

The value of ε_o may be determined from Eq. (V.47) if time under load t_n is given, or time under load t_n may be determined if ε_o is given. Here, of course, the temperature T_o and the value of σ_{pr} should be known.

Let us proceed now to the solution of the second problem. This problem consists of the determination of the time interval of retention relaxing stress t_r, in the course of which a stress is created in the

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*For the sake of abbreviation, $f(\omega; T_o)$ will from here on be written simply as $f(\omega)$, since we are speaking only of isothermal deformation.)

solid and, decreasing, remains higher than a certain tolerable limit $_{pr}$. Let us examine one of several possible, sufficiently general cases. Let initial stress σ_n, greater than σ_{pr}, be fixed practically instantaneously, e.g. assume that time under load $t_n = 0$. Then in accordance with Eq. (V.47), the following will be required to create this minimum deformation

$$\varepsilon_0 = \frac{\overset{(N)}{\sigma_{\text{н}}}}{E} \tag{V.48}$$

The value $_{pr}$ will be attained only after the lapse of time t_r, determined in accordance with Eq. (V.43)

$$\underset{(pr)}{\sigma_{\text{пр}}} = E\varepsilon_0 - \int_0^{\overset{(r)}{t_{\text{р}}}} f(\underset{(r)}{t_{\text{р}}} - \tau)\,\varepsilon_0\,d\tau = \underset{(N)}{\sigma_{\text{н}}} - \varepsilon_0 \int_0^{\overset{(r)}{t_{\text{р}}}} f(\omega)\,d\omega \tag{V.49}$$

or

$$\frac{1}{E}\int_0^{\overset{(r)}{t_{\text{р}}}} f(\omega)\,d\omega = \frac{\sigma_{\text{т}} - \overset{(pr)}{\sigma_{\text{пр}}}}{\underset{(N)}{\sigma_{\text{н}}}} \tag{V.50}$$

Let us show how Eqs. (V.49) and (V.50) are used to find the stress retention time t_r for a number of polymers. If stress is a polymeric solid relaxes according to Kohlrausch[20], then in accordance with the work[21]

$$f(\omega) = E_1 \frac{k}{\underset{(r)}{\tau_{\text{р}}}} \left(\frac{\omega}{\underset{(r)}{\tau_{\text{р}}}}\right)^{k-1} e^{-(\omega/\underset{(r)}{\tau_{\text{р}}})^k} \tag{V.50a}$$

where t_r,k,E_1 and E are constants, while $E_1 \leq E$.
Then it follows from Eqs. (V.49) and (V.50) that:

$$E_1\left[1 - e^{-\left(\underset{(r)}{t_{\text{р}}}/\underset{(r)}{\tau_{\text{р}}}\right)^k}\right] = \frac{\overset{(N)}{\sigma_{\text{н}}} - \overset{(pr)}{\sigma_{\text{пр}}}}{\underset{(N)}{\sigma_{\text{н}}}} \tag{V.51}$$

or

$$\underset{(r)}{t_{\text{р}}} = \underset{(r)}{\tau_{\text{р}}} \ln^{1/k} \frac{\overset{(N)}{\sigma_{\text{н}}} E_1}{\underset{(N)}{\sigma_{\text{н}}} E_1 - E\,(\underset{(N)}{\sigma_{\text{н}}} - \underset{(pr)}{\sigma_{\text{пр}}})} \tag{V.52}$$

Knowing the constants of a relaxing material t_r, K, E_1 and E, as well as the fixed values σ_n and σ_{pr}, it is easy to determine the time of retention of relaxation stress, t_r, in the course of which stress will be greater than σ_{pr} if stress σ_n was fixed at t = 0. Let us note as well that at $E_1 = E$, Eq. (V.52) describes a visco-elastic solid according to Kohlrausch, for which

$$\underset{(r)}{t_{\text{р}}} = \underset{(r)}{\tau_{\text{р}}} \ln^{1/k} \left(\frac{\overset{(N)}{\sigma_{\text{н}}}}{\underset{(pr)}{\sigma_{\text{пр}}}}\right) \tag{V.53}$$

For a visco-elastic Maxwell body.

$$\underset{(r)}{t_{\text{р}}} = \underset{(r)}{\tau_{\text{р}}} \ln \left(\frac{\overset{(N)}{\sigma_{\text{н}}}}{\underset{(pr)}{\sigma_{\text{пр}}}}\right) \tag{V.54}$$

In practice, deformation is not fixed instantaneously, but after the lapse of a certain time interval. If time under load

$t_n \neq 0$, then it is important to determine the interval of time t_r over which the relaxing stress remains greater than σ_{pr}, beginning from the moment the original stress value $\sigma_n = \sigma(t_n)$ is attained.

In this case, it is sufficient to examine the relaxation of stress $\sigma(t)$ at t t_n and at a constant deformation value ε_o equal to its value attained to the moment of time t_n. Here, it is not yet possible to hypothesize how deformation increases during the time under load. By making use of Boltzmann's equation (V.43), we have

$$\sigma_{\underset{(n)}{\text{н}}} = \sigma(t_{\underset{(n)}{\text{н}}}) = E\varepsilon_0 = \int_0^{t_{\text{н}}\,(n)} f(t_{\underset{(n)}{\text{н}}} - \tau)\,\varepsilon(\tau)\,d\tau \qquad \text{(V.55)}$$

$$\sigma_{\underset{(pr)}{\text{пр}}} = \sigma(t_{\underset{(n)}{\text{н}}} + t_{\underset{(r)}{\text{р}}}) = E\varepsilon_0 - \int_0^{t_{\text{н}}\,(n)} f(t_{\underset{(n)}{\text{н}}} + t_{\underset{(r)}{\text{р}}} - \tau)\,\varepsilon(\tau)\,d\tau - \qquad \text{(V.56)}$$
$$- \int_{t_{\underset{(n)}{\text{н}}}}^{t_{\underset{(n)}{\text{н}}} + t_{\underset{(r)}{\text{р}}}} f(t_{\underset{(n)}{\text{н}}} + t_{\underset{(r)}{\text{р}}} - \tau)\,\varepsilon_0\,d\tau$$

By computing the second equation from the first, we find

$$\sigma_{\text{н}} - \sigma_{\text{пр}} = -\int_0^{t_{\text{н}}} [f(t_{\text{н}} - \tau) - f(t_{\text{н}} + t_{\text{р}} - \tau)]\,\varepsilon(\tau)\,d\tau + \qquad \text{(V.57)}$$
$$+ \varepsilon_0 \int_{t_{\text{н}}}^{t_{\text{н}} + t_{\text{р}}} f(t_{\text{н}} + t_{\text{р}} - \tau)\,d\tau$$

hence, considering that

$$\int_{\underset{(n)}{t_{\text{н}}}}^{\overset{(n)\,(r)}{t_{\text{н}}+t_{\text{р}}}} f(\underset{(n)}{t_{\text{н}}} + \underset{(r)}{t_{\text{р}}} - \tau)\,d\tau = \int_0^{t_{\text{р}}^{(r)}} f(\omega)\,d\omega \qquad \text{(V.57a)}$$

we have

$$\int_0^{t_{\text{р}}^{(r)}} f(\omega)\,d\omega = \frac{\sigma_{\text{н}}^{(n)} - \sigma_{\text{пр}}^{(r)}}{\varepsilon_0} + \frac{1}{\varepsilon_0}\int_0^{t_{\text{н}}^{(n)}} [f(\underset{(n)}{t_{\text{н}}} - \tau) - f(\underset{(n)}{t_{\text{н}}} + \underset{(r)}{t_{\text{р}}} - \tau)]\,\varepsilon(\tau)\,d\tau \ \text{(V.58)} \qquad \text{(V.58)}$$

In the special case where $t_n = 0$ (instantaneous loading), $\sigma_n = E\varepsilon_0$, and Eq. (V.58) is converted to Eq. (V.50). The integral in the right member of Eq. (V.58) is always positive, as if there were no mode of increase in undiminishing deformation $\varepsilon(t)$ during the period under load /it should be noted that $f(t_n - t_r - t) > f(t_n - t)$, since the memory function always decreases with an increase in its argument/. Thus, the less the upper limit t_r of the integral standing in the left member of Eq. (V.58) the less the right member of this equation. Consequently, it may be asserted that the time of stress retention, determined from the condition

$$\int_0^{t_{\text{р}}^{(r)}} f(\omega)\,d\omega = \frac{\sigma_{\text{н}}^{(n)} - \sigma_{\text{пр}}^{(r)}}{\varepsilon_0} \qquad \text{(V.59)}$$

will be minimal.

Thus, finding the value t_r from this guarantees a period of retention of a stress, greater than σ_{pr}, created with any magnitude of deformation attaining the value ε_o in the course of t_n and thereafter remaining constant, with the loading of undiminishing deformations, for which $\varepsilon(t_n)>\varepsilon_o$, and with deformations continuing to increase in any manner after stress σ_n is attained.

All of the avove-mentioned, of course, amy be distributed over a non-isothermal mode /see Eqs. (V.40) - (V.42/ and non-linear deformation. The relaxation properties of polymers under non-isothermal conditions will be discussed below.

Returning to the general problem of the work capacity of a polymeric solid in different modes of mechanical and thermal action, the value of creep experiments conducted at σ = constant and relaxation experiments conducted at ε = constant should again be emphasized. The systematic investigation of these basic types of relaxation processes in polymers is vital, especially in connection with their structure. More attention should be given the non-linearity of deformation and relaxation processes.

In many important practical situations, stress and deformatio are such that the linearity of laws governing relaxation are observed, so that the above relations can be used. However, a non-linear effect (in particular, necking during tension) connected with a change in the structure of a stressed solid is displayed at sufficiently high deformations and stresses. This circumstance, which cannot exceed a certain stress value (σ_{kr}) at any deformation, is also an example of the non-linear behavior of relaxing polymeric solids.

In principle, the above relations may be generalized for the region of non-linearity (by using non-linear functions introduced by Volterra[17, 18] to describe mechanical relaxation phenomena). However, at present this problem is still far from a solution, so that it is important here that systematic experimental data be introduced.

Let us examine these data[23] for characteristic representations of three classes of glassy polymers: polymethyl methacrylate, polycarbonate with a base of bisphenol-A and aromatic polyimide anilineflourene, and tetracarboxydiphenyloxide.

In order to determine the stress retention time, including the critical σ_{kr}, it is necessary to conduct a series of stress relaxation tests within a potentially large range of deformations.

At a chosen temperature, a series of ordinary stress relaxation curves are determined, with each curve corresponding to a

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The chemical composition and synthesis of this polymer is described in the work.[24]

certain constant deformation. Figure V. 12 shows such a series for polymethyl methacrylate at 50° C. In the region of small deformations, the relaxation curves are regularly shifted upward with an increase in ε. In the region of large deformations, relaxation stresses pass deeper, and the curves begin to move downward. This is also a manifestation of the non-linearity of relaxation processes.

In each series of experiments, depending on the fixed temperature, the deformation ranges should be chosen so that the dependences of stress on deformation, taken for the same moment of time, pass through the maximu. To observe the maximums, the relaxation curves are reconstructed on the coordinates stress-deformation. Thus, if the curves shown in Figure V.12 are reconstructed on these coordinates, a new set of curves is formed (Figure V.13). Each curve corresponds to a strictly defined duration of the stress relaxation process, and the maximum on each characterizes the greatest stress that can be maintained by a polymeric material in the course of the indicated interval of time at the given temperature, e.g. it characterizes σ_{kr} (see page 412).

This characteristic of a polymeric solid is very important since when time t_r has expired, stress theoretically cannot be greater than σ_{kr}. A higher stress simply cannot be retained in the course of t_r. Henceforth, we will use only these maximum stresses, since we are most interested in evaluating the duration of the retention of the highest possible stress and in characterizing the role of the process' nonlinearity.

Of particular interest is the dependence of equilibrium stresses σ_{oo} on deformation, which correspond to the duration of relaxation $t_r = oo$ The maximum value σ_{oo} has the meaning of σ_{kr} for indefinitely large time intervals. In order to determine the value of σ_{oo} , we may use Kohlrausch's equation:

$$\sigma(t)=\sigma_0 e^{-\{(t/\tau_{\underset{(r)}{p}})^k} + \sigma_\infty \qquad \text{(V.60)}$$

where $\sigma(t)$ is the relaxing stress; σ_o, k and t_r are parameters of the curve; σ_{oo} is the equilibrium stress.*

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* In accordance with Eq. (V.60), the value of σ_{oo} characterizes that stress which is established during time of construction t→oo. In actuality, as experiments conducted[25] earlier have shown, new drops in stress with subsequent new retardations of relaxation caused by structural changes may be observed on the relaxation curve over fixed periods of time. a consequence, the value of $_{oo}$ may be regarded as a conditional characteristic of equilibrium stress; it is determined by the extrapolation of σ to t = oo in accordance with Eq. (V.60). However, having determined the value of σoo and all other parameters of Eq. (V.60), one may calculate the tresswhich will be attained over a very long period of relaxation[25], of course barring further structural changes.)

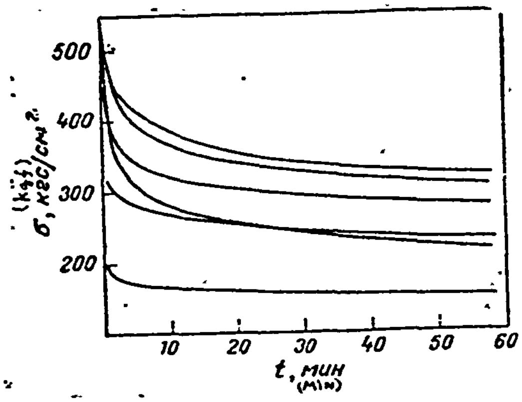


Figure V.12.

Series of stress relaxation curves for polymethyl methacrylate at 50 °C. Each curve corresponds to a specific strain.

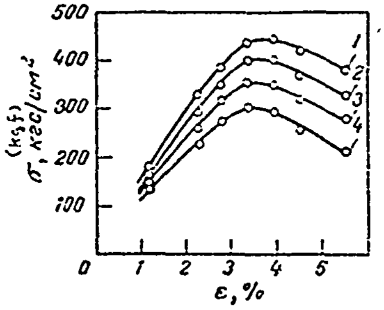


Figure V.13

The dependence of stress on strain for polymethyl methacrylate at 50 °C. Duration of the relation process:
1 - 1 min; 2 - 3;
3 - 10; 4 - 60 min.

Having determined maximum stresses σ_{kr} (t_r, T) corresponding to a specific duration of relaxation t_r at each temperature T, and having completed measurements in all accessible temperature range up to the glass point, one should construct the temperature functions of these critical stresses atcconstant values of time t_r. Such functions are shown in Figure V. 14 for polymethyl methacrylate, polycarbonate and polymide.

It is obvious that the greater the required time under load and the higher the temperature, the less the stress that will be retained by a polymeric material. Moving along line A - B in Figure V. 14, a, e.g. examining the constant stress condition, one may see how the duration of the retention of a chosen stress changes with temperature. Furthermore, looking at isothermal conditions (line C - D), it is easy to determine how the duration of the retention of critical (e.g. maximum) stress changes with increasing values of this stress. If a fixed value is assigned the stress retention period, one can always determine the maximum temperature at which this requirement will be met.

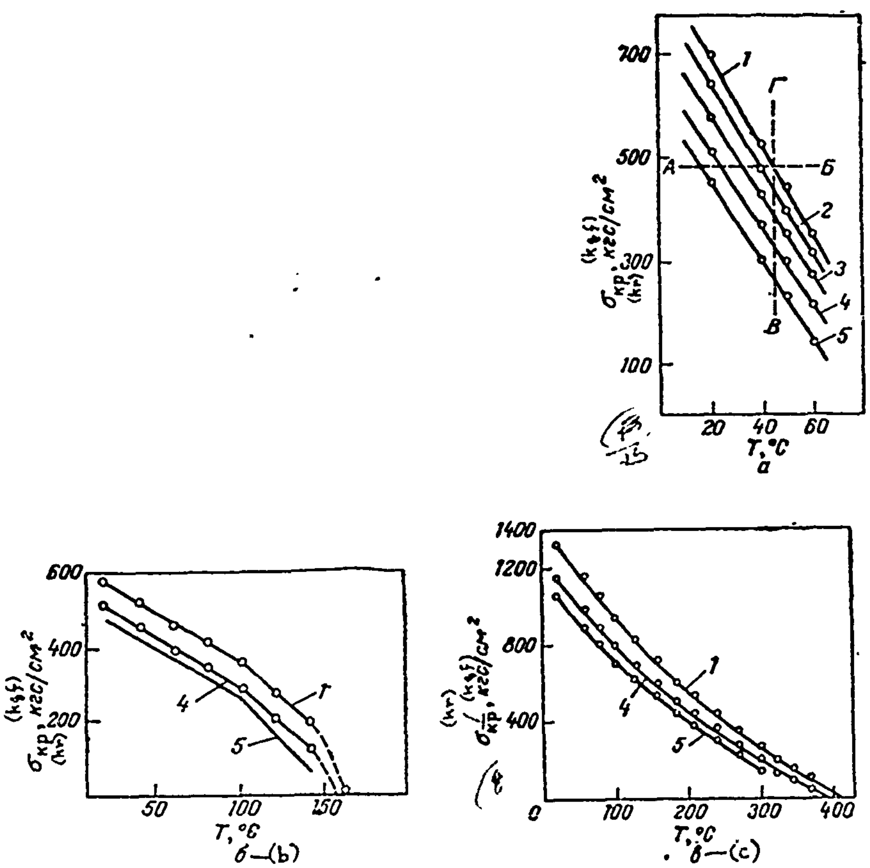


Figure V.14

The dependence of critical stresses on temperature for polymethyl methacrylate (a), polycarbonate (b) and polyimide (c). Duration of the relaxation process:
1 - 1 min; 2 - 3; 3 - 10; 4 - 60 min; 5 - oo.

Let us go on now to quantitative relations. It should be noted beforehand that in logarithmic coordinates, the dependence between t_r and σ_{kr} is rectified in the range of values of t_r from minutes to 10^4 sec (Fig. V.15). The slope of the lines depends on temperature. Having designated the absolute value of the tangent of the line's angle of slope as α and having constructed a graph of the dependence of on temperature, one may observe a very interesting pattern (Fig. V.16).

These graphs have the form of broken lines. In the presence of a broad glass-transition region, the broken line consists of three sections, e.g. there exist three temperature ranges in which the dependence of α on T is different (see Fig. V.16). The value of α decrease with an increase in T in the first section, are independent of temperature in the second section and again decrease in the third section (the one closest to the glass point). Two such sections exist for polycarbonate, and only one - the last section - exists for polymethyl methacrylate.

Thus, the characteristic form of the dependence of α on T testifies to the fact that before the transition to brittleness, the glassy-state region may be subdivided into substates in which the mechanisms relaxation processes are different. Between these substates, of course, transitional regions are observed. For polyimide, these regions correspond to temperatures 100 and 200 °C. For polycarbonate, one can distinguish two substates with a single intervening transition region (100 °C); for polymethyl methacrylate - only one substate.

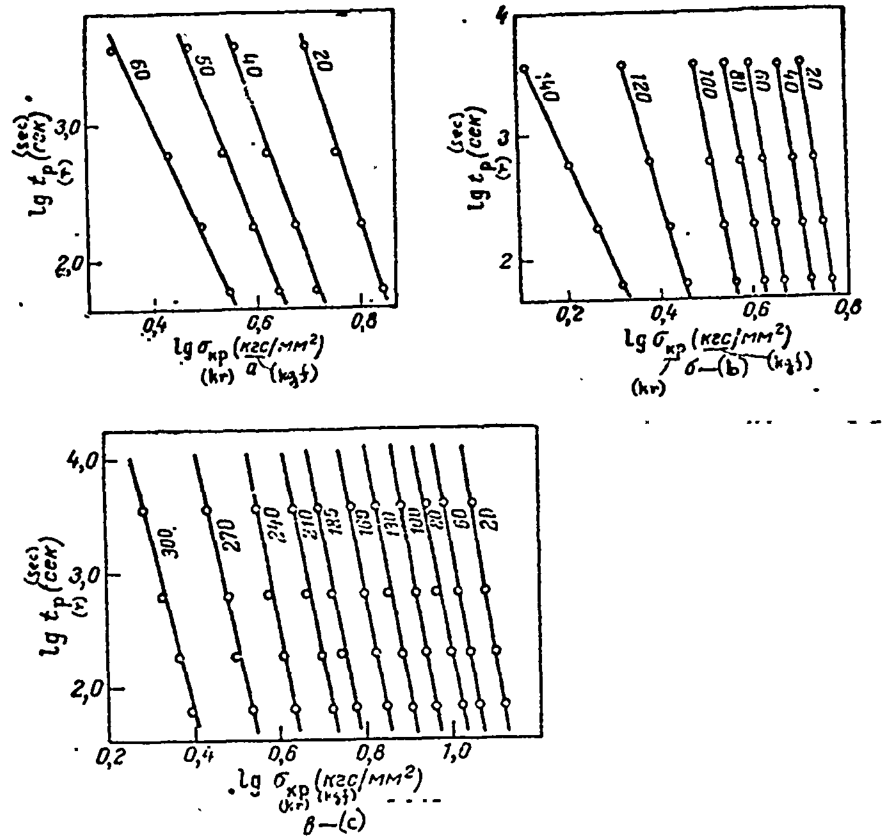


Figure V.15

The dependence of log t_r on log σ_{kr} for polymethyl methacrylate (a), polycarbonate (b) and polyimide (c). at different temperatures. The number on the curves are the temperatures in °C.

Since the graphs of the dependence of log t_r on log σ_{kr} are straight lines (see Fig. V.15), it may be written that at T = constant

$$\underset{(r)}{t_{\text{p}}} = B\underset{(kr)}{\sigma_{\text{кр}}^{-\alpha}} \qquad \text{(V.61)}$$

where t_r is the time over which the required stress is retained, e.g.

the work capacity of a solid compressed to a specific magnitude of deformation; σ_{kr} is the constant stress; B and α are parameters, generally temperature-dependent.

The dependence of α on temperature examined above (see Fig. V.16) may be described with sufficient accuracy in each of the substates by the relation

$$\alpha = \alpha_0 - xT \qquad (V.62)$$

while in the second section x = 0.

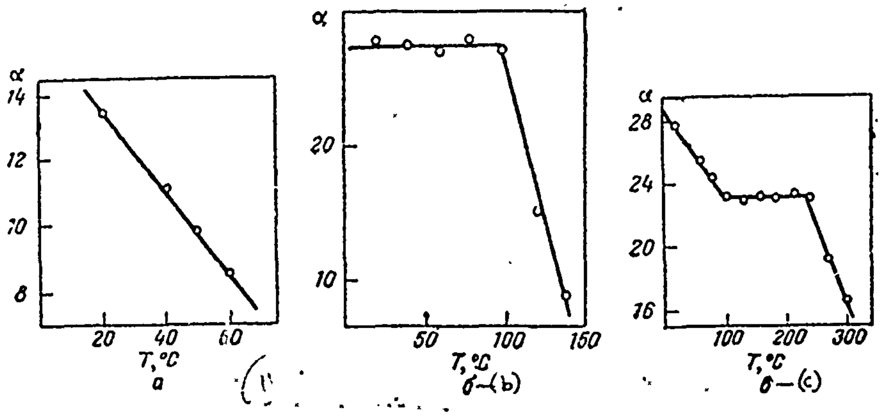


Figure V.16.

The dependence of α on temperature for polymethyl methacrylate (a), polycarbonate (b) and polyimide (c).

Experimental data [23] show that the dependence of log B on $1/_T$ also has a linear character, so that

$$B = Ae^{U/RT} \qquad (V.63)$$

where A and U are material parameters.

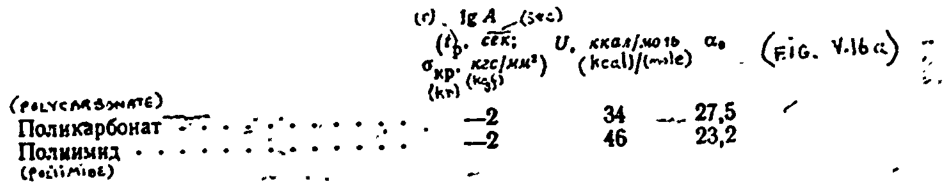
Then Eq. (V.61), with respect to (V.62) and (V.63) is written thus*

$$\underset{(r)}{t_\text{р}} = A\underset{(kr)}{\sigma_\text{кр}}^{-(\alpha_0-xT)}e^{U/RT} \qquad \text{(V.64)}$$

In the case where x = 0, Eq. (V.64) takes the form

$$\underset{(r)}{t_\text{р}} = A\sigma^{-\alpha_0}e^{U/RT} \qquad \text{(V.65)}$$

Similar relations have been derived for calculating the durability (wear life) of rubber[26] and to describe the induction period of necking under a constant load[6] (see page 408). Shown below are the numerical values for parameters A, U and α_0 in Eq. (V.64) for the range of temperatures in which x = 0.



	lg A ($t_\text{р}$ (r), сек (sec); $\sigma_\text{кр}$ (kr), кгс/мм² (kgf))	U, ккал/моль (kcal)/(mole)	α_0
Поликарбонат (POLYCARBONATE)	—2	34	27,5
Полиимид (POLIIMIDE)	—2	46	23,2

(FIG. V.16a)

Figure V.16a.

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* In the case where x = 0, Eq. (V.64) takes the form

$$\frac{t_\text{р}^{(r)}}{t_0} = A\left(\frac{\sigma_\text{кр}^{(kr)}}{\sigma_0}\right)^{-(\alpha_0-xT)}e^{U/RT}$$

where t_0 and σ_0 are certain constants; parameters A and α_0 are dimensionless quantities; x has the dimension of the inverse absolute temperature.

If we choose t_0 = 1 sec and σ_0 = 1 kgf/mm^2, then we will obtain Eq. (V.64).

The quantity U, of course, connotes the activation energy, although there is a yet insufficient experimental data to explain the above process, assuming such an interpretation.

It was noted above that graphs of the dependence of log t_r on log σ_{kr} in a limited time interval t_r are straight lines. With large intervals of time, as tests have shown[23], they deviate from the linear toward the side of the increase* in stress retention time t_r. With large stress retention times t_r, the dependences between t_r and σ_{kr} (Fig. V.17), as ordinary stress relaxation curves, are described well by Kohlrausch's equation, which with variables σ_{kr} and t_r takes the form

$$\underset{(hr)}{\sigma_{\text{кр}}}\left(\underset{(r)}{t_{\text{p}}}\right)=\sigma_0^{\bullet}e^{-\left(\underset{(r)}{t_{\text{p}}}/\underset{(r)}{\tau_{\text{p}}^{\bullet}}\right)^{k^{\bullet}}}+\sigma_\infty^{\bullet} \qquad \text{(V.66)}$$

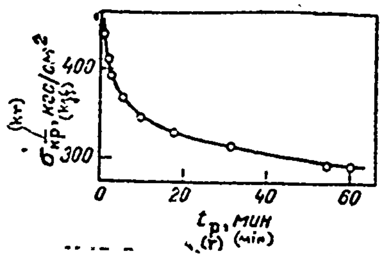

Figure V.17.

The dependence of critical stresses σ_{kr} on time t_r for polymethyl methacrylate at 50 °C.

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* The same deviation is also observed in studies of strength.[27]

The parameters of Eq. (V.66) are marked with an asterisk, since they are used not for describing classic stress relaxation curves, but for conveying the relationship between maximum stress σ_{kr} and the time t_r over which it is attained. Experiments and calculations show[23], that the dependences of $_{o}*$ k* and $*_{oo}$ on temperature are linear in each of the above-mentioned glassy substates, but that they may have different slopes. The temperature function of t_r^* are linear in the coordinates log t_r^* _ $1/_T$. Generally, the following relations, valid only within the boundaries of each substate, may be written

$$k^*(T) = k_0 - k_T T \qquad (V.67)$$

$$\sigma_0^*(T) = \sigma_{0,\,0} - \sigma_{0,\,T} T \qquad (V.68)$$

$$\sigma_\infty^*(T) = \sigma_{\infty,\,0} - \sigma_{\infty,\,T} T \qquad (V.69)$$

$$(r)\ \tau_p^* = A^* e^{U^*/RT} \qquad (V.70)$$

The values of parameters k_O, k_T, σ_O, o, σ_O T, σ_{OO}, c, σ_{OO}, T, A* and U* are shown in Table V.1.

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* The same deviation is also observed in studies of strength.[27]

Table V.1. Numerical Values of Parameters of Eqs. (V.67) - (V. 70)

1 Параметры	2 Полиметилметакрилат	3 Поликарбонат		4 Полиимид		
	20—60° C	20—100° C	100—140° C	20—100° C	100—210° C	210—300° C
k_0	0,69	0,47	0,47	0,487	0,487	0,487
$k_T \cdot 10^3$	1,67	0,787	0,787	0,683	0,683	0,683
$\sigma_{0,0}$, кгс/см²	—65	—93	—1780	450	450	450
$\sigma_{0,T}$, кгс/(см²·град)	2,75	1,0	5,25	0	0	0
$\sigma_{\infty,0}$, кгс/см²	2680	1295	2156	2320	1850	1543
$\sigma_{\infty,T}$, кгс/(см²·град)	7,62	2,75	4,8	4,32	3,06	2,43
lg A^* (сек)	—6,4	—1,05	—7,76	0,42	—2	—4,75
U^*, ккал/моль	10,8	4,6	14,3	3,6	7,8	13,8

1) Parameters
2) Polymethyl Methacrylate
3) Polycarbonate
4) Polyimide

By using these parameters, one may describe the work capacity, for thermal stability, of a polymer within the entire glassy state. For this purpose, we convert Eq. (V.66), having solved it relative to time:

$$\ln t_{\underset{(r)}{p}} = \frac{1}{k^*(T)} \ln \ln \frac{\sigma_0^*(T)}{\sigma_{\underset{(kr)}{\text{кр}}} - \sigma_\infty^*(T)} + \ln \tau^*_{\underset{(r)}{p}}(T). \qquad (V.71)$$

Equation (V.71) together with Eqs. (V.67) - (V.70) shows how the work capacity of a polymer, (e.g. the duration of the retention of a stress greater than σ_{kr}) changes in relation to temperature T. This relation is valid within the entire glassy state, although its parameters may be changed in the transition from one substate to another.

Thus, the region of the glassy state should be subdivided into several substates (not counting brittle), since one observes several transitions in the range $T_{xr} < T < T_g$, where T_{xr} and T_g are, respectively, the brittle and glass points. These transitions are particularly characteristic for strongly linked polymers, having on very broad glassy region. It is interesting that the brittle temperature T_{xr} in such systems is found far into the region of minus temperatures, while the glass point T_g is located in a high (for organic polymers) temperature region. Polymers of this type are aromatic polyamides, polyolefins and polyimides, as well as many other heterocyclic compounds.[5, 28, 29]

The large difference in the glass and brittle temperatures o a number of polymer systems allows one to distinguish a broader temperature range ($T_g - T_{xr}$) in which forced elasticity is displayed and various mechanisms are manifest for the development of relaxation processes[2, 29, 30] and fracture processes.[27, 31, 32]. The wider the interval $T_g - T_{xr}$, the more transitions within it. Thus, three substates and two intervening transition regions are manifest in aromatic polimide, two substates for polycarbonate, and one substate for polymethyl methacrylate, corresponding fully with the temperature range ($T_g - T_{xr}$).

Determination of the temperatures of these transitions with static methods is very important from both theoretical and practical points of view. The fact is that these transitions cannot always be observed with dynamic (mechanical and electrical) methods of study.

These transitions are of practical importance because a polymeric material begins to rapidly change its mechanical characteristics precisely at the temperatures of these transitions and may, for example, remain incapable of work long after the glass point has been reached. Each polymeric material works in a stable manner within each substate, especially within the second substate (see Fig. V.16), in which relative relaxation is insensitive to temperature.

The transitions of interest to us are made within the temperature range in which forced elasticity is manifest. It is no coincidence, therefore, that the graphs of the temperature dependences of the forced elastic limit display sharp breaks (see, for example, Fig. II.13). The point (more precisely, the interval) of the break also shows a temperature transition, dividing the glassy state into substates.

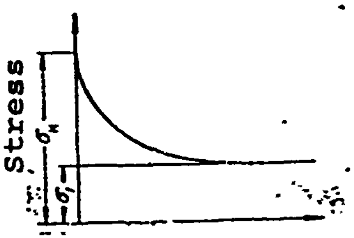

Figure V.18.

Relaxation curve
(layout).

In numerous experiments devoted to the study of forced elasticity, Yu. S. Lazurkin[2] observed two sections of the temperature dependence of σ_{ve} - sloping and steep, while the latter was in the immediate vicinity of T_g. It was thereby shown that the glassy state is expediently subdivided into different substates having different mechanisms of deformation. It should be noted that the temperature dependence of the activation energy must be introduced in order to describe the second, steep section (see page 142).

Nevertheless, it may be that the transitions can be more clearly observed with static relaxation methods, mentioned above. However, these methods are quite laborious, and we need a simpler and quicker method of determining all the substates of a glassy solid. It may prove advantageous to use a characteristic such as the reciprocal relative stress drop β after a strictly-defined period of isothermal relaxation, introduced in the works.[29, 30]

Figure V.18 shows an ordinary relaxation curve. One may distinghish several characteristic stresses on it: initial stress σ_n, which is developed after the fixing of strain, or over a very short, strictly-defined time interval subsequent to this; final stress σ_1, corresponding to a specific period of lapse of the relaxation process (for example, stress after one hour). We are interested in the characteristic of the relaxation process 1/ , the reciprocal of the relative stress drop:

$$\frac{1}{\beta}=\frac{\sigma_{K}^{(n)}}{\underset{(n)}{\sigma_{K}}-\sigma_{1}} \qquad (V.72)$$

If one conducts a series of stress relaxation tests under constant strain within the entire glassy state, and subsequently constructs the temperature dependence of $1/_\beta$, he may observe a pattern such as appears in Figure V.16. Let us introduce several diagrams as an example. The first (Fig. V.19) shows the temperature dependence of $1/_\beta$ for aromatic polyester (polyarylate) terephthalic acid and phenolphthalein.[29, 30, 33] Similar functions are shown in Fig. V.20 for polyimide aniline-flourine and tetracarboxydiphenyloxide, determined at three constant strains.

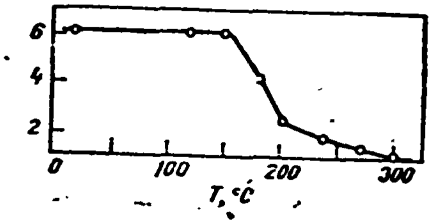

Figure V.19

The temperature dependence of $1/_{\beta}$ for polyarylate terephthalic acid and phenolphthalein.

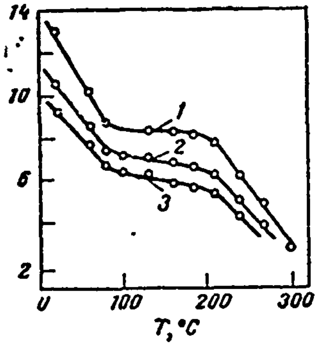

Figure V.20

The temperature dependence of $1/_{\beta}$ for polyimide at different strains:

1 - 4%; 2 - 6;
3 - 8%

It is easily demonstrated that the glassy state is divided into three substates in which the dependence of $1/_{\beta}$ on temperature is different. In the region of "subsidiary" transitions, the graphs have a break, defining the transition points. One of these transitions, the closest to the glass point, is observed for many polymers. Below the temperature of this first subisdiary transition, plastic is found in the area of stable work capacity. It is also easy to see that the dependences of $1/_{\beta}$ on T are quite similar to the dependences of α on T examined above (see Fig. V.16). They show that the relaxation process occurs differently in each of the substates. In one of the substates (sloped section), relative stress relaxation proves to be almost insensitive to temperature. With further increase in temperature, the relaxation process is accelerated, and at $T \to T_g$ has completely expired (the value of $1/_{\beta}$ approaches unity).

Thus a number of transitions within the glassy state may be detected with comparative ease by a simple series of stress relaxation tests (at the same strain) at different temperatures throughout the entire region of the glassy state. The construction of the temperature dependence of relative stress drop $1/_{\beta}$ allows one to immediately find the points of these transitions which, as can be seen from Fig. V.20, are practically independent of the chosen strain.

In conclusion, it should be emphasized once again that in evaluating the efficiency of polymers, it is necessary to take into account the different substates lying within the range of temperatures between the glass and brittle points.

Regions of the Work Capacity of Polymeric Materials

The methodology set forth in the preceding section may also be employed in the detailed study of the relaxation properties of polymeric solids, and in determining the period of retention t_r of the most dangerous (critical) and any other stress. In order to determine these characteristics, of course, a great deal of time must be spent and numerous series of experiments must be conducted at different strains and temperatures.

As always, the problem is very much simplified if the tests are conducted under non-isothermal conditions. By embracing the entire range of requisite temperatures in one experiment, one may quickly obtain information on the working capacity of polymers at any stresses and temperatures. Thus, often it is most expedient to conduct tests not under isothermal conditions, but with a continuously changing temperature.[29, 34]

It is especially convenient to conduct such tests under compression at increasing temperature. A specimen which displays a certain initial stress as a result of strain will expand upon heating. Under the conditions of relaxation tests, the "instantaneously" fixed strain is held constant, so that stress in the speciment will change very uniquely with increasing temperature. Let us discuss several possible variants.

Before the test is begun, a polymer specimen is placed between the working cylinders of a device suited for compression testing (Fig. V.21). The space between these cylinders is thermostated. In the simplest case, the polymer sample is situated so that initial strain (and thus tress as well) within it is zero (Fig. V.21, a); the working cylinders of a relaxometer are attached and the temperature in the thermostat is increased linearly. The rate of temperature increase may be chosen arbitrarily, but it should not be made too great, lest the specimen not be heated evenly throughout its thickness. For a specimen 3 mm in diameter, a convenient rate of temperature increase would be from 1.5 to 4 grad/min.

The attached relaxometer cylinders impede the free thermal expansion of the specimen during heating, so that a stress develops within it which may be recorded over different time periods or temperature ranges. The test results for any polymer may be used to construct a curve of the dependence of stress on temperature, shown graphically in Fig. 22.

In the first section of the graph, stress increases up to a certain temperature, until the polymeric material remains hard, and then begins to rapidly relax - this leads to the appearance of a maximum. At the point of the maximum, the rate of stress increase resulting from heat expansion is equal to the rate of its decrease resulting from relaxation. At a certain temperature, the stress relaxes completely, e.g. falls to zero. At this moment the curve intersects the temperature axis. The point of intersection characterizes the polymer's glass point.

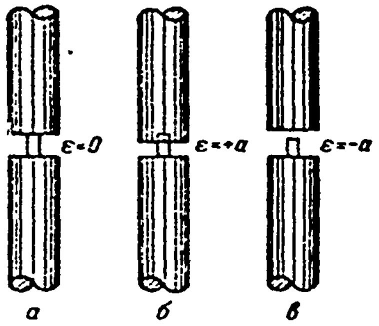

Figure V.21

Specimen and working relaxometer cylinders (layout).

The above test of non-isothermal stress relaxation is a special case. Generally, the initial strain may be a value other than zero (see Fig. V.21, b). It is fixed very quickly, causing the appearance of initial stresses in the specimen. By imparting different initial strains (and hence initial stresses) to the specimen, and assigning, as usual, a linear temperature increase in the thermostat, one may obtain a series of dependences of stress on temperature (see Fig. V.23). The value of the imparted initial strain should not be so great as to prevent a maximum from being obtained on the curve.

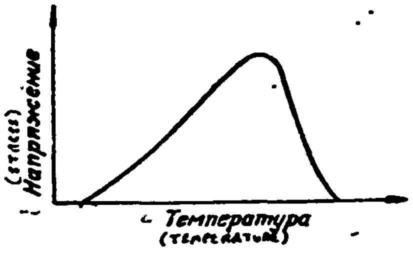

Figure V.22.

The dependence of stress on temperature in determining the region of work capacity. Initial strain and stress are equal to zero.

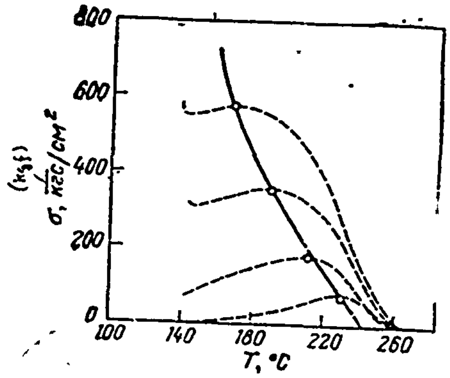

Figure V.23.

Curves of non-isothermal stress relaxation (dotted) and the work-capacity region of a polymeric material (polyarylate isophthalic acid and phenolphthalein).

Yet one more possible varient of positioning the specimen and the working cylinders of the relaxometer is shown in Fig. V.21, c. The specimen is placed so that there remains some possibility for free thermal expansion. When the specimen is stiffened against the upper working cylinder of the relaxometer, a stress appears in it. At first the stress will increase with increasing temperature, but will begin to decrease again at a certain stress value.

Thus, conducting the experiments at different strains (positive, zero, and formally speaking, even negative strains), one may obtain a set of curves each of which has one maximum. These curves are shown by the dotted lines in Fig. V.23. The geometrical site of the maximum's point (solid line in Fig. V.23) limits the region of temperatures and stresses in which the polymer specimen relaxes relatively slowly, and therefore displays a clearly expressed hardness. This region is called the <u>region of the work capacity of a polymeric material.</u>[29, 34] It should be noted that the set of subsidiary (dotted) curves converge at one point on the temperature axis, this point corresponding to the glass point.

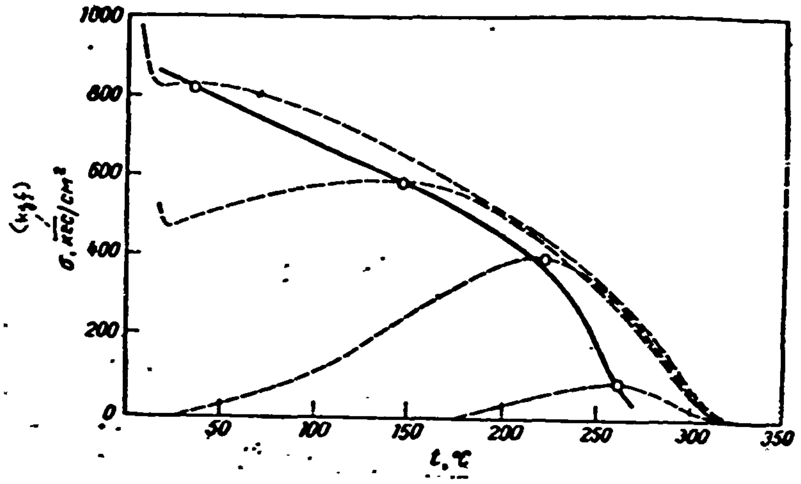

Figure V.24

Work capacity region of polyarylate terephthalic acid and phenolphthalein.

The curve limiting the region of work capacity, in a sense similar to the graphs, is shown in Fig. V.14. Tests show[35] that this curve corresponds roughly to the time of stress retention, equal to 1 min (the rate of temperature increase here is 4 grad/min). Of course, if non-isothermal stress relaxation tests were conducted at another heating rate, the position of the curve would be changed.

The shape of the curve limiting the region of a polymeric material' work capacity depends heavily on the temperature range in which the test is conducted. Approaching the work capacity region, it should be recalled that the glassy state is subdivided into a number of substates (see page 423). Each of these substates is characterized by its own relaxation mechanism, which is reflected in the shape of the curve.

If the test is conducted within a broad temperature range embracing several substates, the work capacity region will appear as shown in Fig. V.24. The curve limiting the region has an upward curvature and consists of two easily discernable sections. If the test is conducted in a comparatively narrow temperature range corresponding to the substate closest to the glass point, the work capacity region has a different appearance, and the curve limiting this region has a downward curvature and consists of only one section (Fig. V.25).

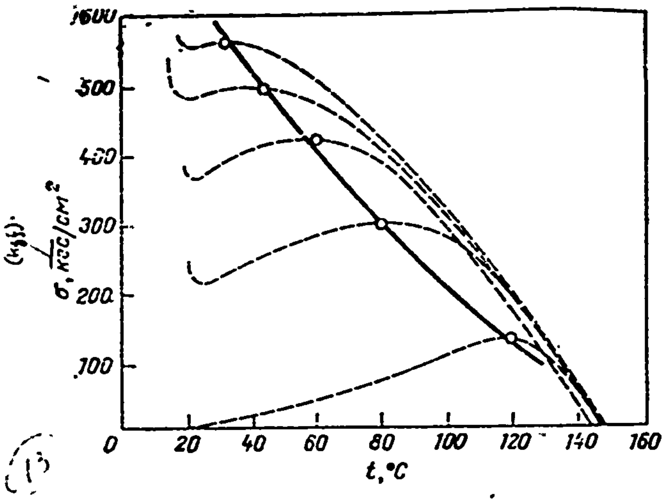

Figure V.25.
Work capacity region of polycarbonate.

It may be stated that in the latter case a single relaxation mechanism is at work, with the non-linearity of the relaxation process clearly evident. Of course, losses of work capacity due to softening are manifest in the abrupt acceleration of relaxation processes. Let us assume that a single Maxwell relaxation mechanism is acting, and let us consider the dependence of relaxation time t_r^* on stress σ and temperature T.** We may then write

$$\frac{d\sigma}{dt} = E\frac{d\varepsilon}{dt} - \frac{\sigma}{\underset{(r)}{\tau_{p.0}} \exp \dfrac{\underset{(r)}{U_{p.0}} - \gamma_p\sigma\text{—}(r)}{RT}} \qquad (V.73)$$

If the test is conducted with a linear increase in temperature T with time t, Eq. (V.73) does not have to be integrated. In fact

$$T = T_0 + \beta\tau \qquad (V.74)$$

where T_0 is the initial temperature; is the rate of temperature increase.

$$\varepsilon = \varepsilon_0 \pm \alpha\tau$$

where ε_0 is initial deformation; α is the rate of deformation increase owing to thermal expansion ($\alpha = \beta K$, where K is the coefficient of linear expansion).

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*See Eq. (I.40)

**See Eq. (I.43)

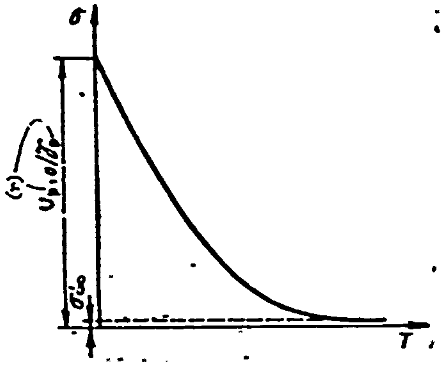

Figure V.26.

The curve limiting the work capacity region (layout).

Combining Eqs. (V.73), (V.74) and V.75), we obtain

$$dt = \frac{1}{\beta} dT; \qquad \text{(V.76)}$$

$$d\varepsilon = \alpha\, dt = \frac{\alpha}{\beta} dT = K\, dT$$

$$\beta \frac{d\sigma}{dT} = E\alpha - \frac{\sigma}{\underset{(r)}{\tau_{p,0}} \exp \dfrac{\underset{(r)}{U_{p,0}} - \underset{(r)}{\gamma_p}\sigma}{RT}} \qquad \text{(V.77)}$$

Eq. (V.77) describes the set of curves represented by the dotted line in Fig. V.23. However, we are interested in the curve limiting the work capacity region (solid curve in Fig. V.23). It pictures the geometrical location of the points of the maximums of the subsidiary relaxation curves. At these points, the rate of stress increase due to thermal expansion in the specimen is equal to the rate of stress decrease due to relaxation. In other words, at the points of the maximums on the subsidiary curves, d /dt = 0. Taking this condition into account, let us rewrite relation (V.77).

$$\sigma = E\alpha\tau_p \exp \frac{U_{p.0} - \gamma_p \sigma}{RT} \qquad (V.78)$$

Having designated

$$E\alpha\tau_{p.0} = \eta_0 \alpha = \sigma'_\infty \qquad (V.79)$$

we will finally write

$$\ln \frac{\sigma}{\sigma'_\infty} = \frac{U_{p.0} - \gamma_p \sigma}{RT} \qquad (V.80)$$

Eq. (V.80) describes the curve limiting the region of the work capacity of a polymeric material. This curve is shown graphically in Figure V. 26, with all conditional designations included. The accord of the shape of the theoretical curve (Figure V.26) with experimental curves (see Figs. V.23 and V.25) indicates the predominance of a single relaxation mechanism in a specific temperature range. This range is relatively narrow and is immediately adjacent to the glass point.

Thus, if a non-isothermal stress relaxation test is conducted only in one of the substates, directly adjacent to the point, the process may be described with a single temperature dependence of stress relaxation time. The correspondence of the shape of the theoretical and experimental curves limiting the work capacity region makes it possible to calculate, by means of the experimental curve, the parameters of the relaxation process - the energy of activation $U_{r,o}$ and the coefficient Y_r. The computational method is explained in detail in the works.[29, 34]

The Relationship between the Processes of Fracture and Softening

Fracture, regardless of its character, is almost always preceded by some deformation. Even in the case of brittle fracture, one may observe local deformations at separate points on the surface of the fracture. Under durability test condition where σ = constant, creep develops in the material. It turns out that the durability of a polymer is connected in a specific manner with the creep velocity. In the works[36, 37] the following function may be found

$$\frac{1}{\tau} = v^{mA} \qquad (V.81)$$

where τ is durability; $\bar{v}$ - the average rate of creep ($\bar{v} = (\varepsilon_r - \varepsilon_u)/\tau$, where ε_r and ε_u are, respectively, breaking and elastic deformation);

m and A are material parameters.

This dependence has been theoretically substantiated.[38]

Eq. (V.81) has a special character and is satisfied for hard polymers. To find the relationship between the breaking stress and deformations in elastomers, the visco-elastic properties of the material are examined[39] with consideration of the Muni-Rivlina equation [see Eq. (III.17)], along with the crack propagation process. Much of the material from studies of rubber fracture is set forth in a monograph by V. E. Gul.[40]

The initiation and growth of sub-microcracks plays a large role not only in the process of polymers' fracture[60, 61] but also in the acceleration of deformation processes.[62, 63]

Many authors connecting the deformation mechanish with the initiation and propagation of cracks in a specimen devote much of their attention to studying the character of the fracture's surface. This question has been repeatedly examined in many works (many of which are cited above). A number of these works include many microphotographs of the fracture surface, with very characteristic patterns imprinted on the photographs created by local deformations of the material in individual microregions.

Without going into these experiments in greater detail, let us note work done recently. Part of recent efforts have been devoted to methodological questions (determination of the mean coefficient of rupture within "silver cracks"[43] calculation of the work done in the formation of a new surface during cracking[44], etc.). Orientation effects in the peaks of microcracks have been conceded a large role in the strengthening of a material.

Systematic studies of the character of the fracture surface of glassy polymers have been conducted by Kambour.[45 - 48] The area embraced by modification of the material on this surface may be as much as several microns inthickness. As a result of these studies, the form and dimensions of "silver cracks" have been determined for a number of polymers; also accomplished was the determination of the magnitude of ultimate elastic strains within the cracks, an explanation of the role of heat effects in crack propagation, etc. Information on the modifications of material on the fracture surface, the topography of this surface and other corresponding phenomena may also be found in such works.[49 -54]

For some time now, the results of fractographic studies of the surface of polymers' fracture have been correlated with the temperature-time dependence of strength.[64 - 65]

A characteristic pattern in the shape of a parabola is formed on the fracture surface of glassy polymers during brittle fracture. However, the brittle fracture of such polymers is not always accompanied by the formation of a parabola. If a glassy polymeric solid is capable of forced-elastic deformation during a moderate rate of stress, and if the elements of the super-molecular structure in such a solid are bound to one another with sufficient strength, then under rapid mechanical action, brittle fracture may occur with the formation of a parabola on the fracture surface (Fig. V.27). If elements of the super-molecular structure in polymeric glasses are bound weakly to one another, then brittle fracture will be observed at both great and small rates of stress, and at both low and high temperatures. In this case, parabolas[55] are not formed on the fracture surface; there will be no regular pattern to the lines on the surface (Fig. V.28).

Thus, it is necessary to clearly distinguish two different concepts: "brittle fracture" and "brittle material." Brittle fracture may be displayed by practically any polymeric material, including, as it were, classic elastic materials such as raw rubber and cured rubbers with a raw rubber base. For this, one need only reduce the temperature or substantially increase the rate of mechanical action.

Brittle material, due to the poor coherence of elements of its super-molecular structure, is not capable of manifesting marked deformations under any temperature and time conditions of stress, so that it displays brittle fracture. In this case, everything depends on the type and dimensions of the super-molecular structure.

For example, in films of isotactic crystallized polypropylene, large well-formed spherulites may develop, and then in the great majority of cases such a film cannot be drawn even several percentages. Conversely, small spherulites may develop and under certain conditions[56] the film will, even at the temperature of liquid nitrogren, be capable of deformation by tens of percent.

Let us turn again to amorphous polymer glasses. These glasses may have various types o- super-molecular structure. The most common type is a globular structure, also characteristic for inorganic amorphous glasses.

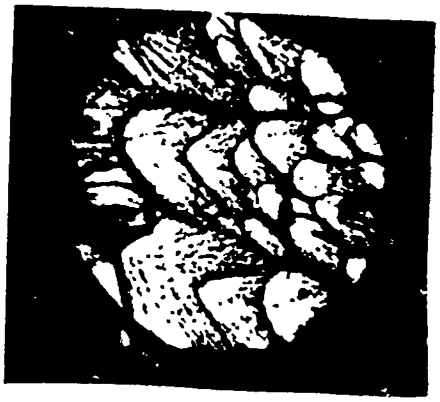

Figure V.27.

Parabola formation on the surface of fracture of polyarylate isophthalic acid and phenolphthalein (X200)

Figure V.28.

Fracture surface of polyarylate isophthalic acid and phenolphthalein with a globular supermolecular structure (X 100).

If the globules are compact, and their constituent macromolecules cannot be expanded under stress, brittle fracture will take place in the presence of very little strain. The ability of the macromolecules to resist uncoiling under stress may be due either to their rigidity or to the presence of a certain amount of physical or chemical bonds, "stitching coils."

As we already know, the super-molecular structure in glasses may, theoretically, be changed, altering it from globular form to a fibrillar or more complex form. Polymeric glasses of non-globular structure or "soft" globular structure display marked deformation, and in brittle fracture a notable change takes place in the polymer material on the fracture surface. This also leads, in particular, to the appearance of characteristic parabolas (see Fig. V.27).

Thus, from a polymer of a certain chemical composition, one may formulate different materials, both brittle and non-brittle; to indicate that a given polymer is brittle or is not brittle is incorrect.

Thus, the least change in the material on the fracture surface of polymeric glasses occurs in those cases where it is much easier to overcome the weak forces binding the globule-like elements of the super-molecular structure than it is to uncoil the macromolecules and cause the rupture of strong chemical bonds in the main chain. If this is done, one can observe a very interesting pattern.[40 - 42]

The ability of a polymeric material to display forced-elastic strain plays an important role in the fracture process. It was noted above that the fracture mechanism may be different in each of the substates of a glassy polymer.

In the substate in which forced elasticity is manifest, the fracture process is connected with relaxation (strain) phenomena in material, which is located in the peaks of microcracks. G. M. Bartenev believes[32] that the transition from brittle fracture to forced-elastic fracture occurs as soon as the relaxation time t_r becomes equal to the time t_s of the elementary event of crack propagation. Since the relaxation time and time t_s are stress-dependent, the brittle temperature is also a function of stress.

The correlation of temperature dependences of t_r and t_s for polymethyl methacrylate leads to a value for the brittle temperature conforming to experimental data.[2]

Another approach to the problem of the long-term strength of hard solids is based on phenomenological analysis and the use of methods of continuum mechanics.[66 - 69] In the work[66], brittle fracture is examined independently of he creep and is connected with the process of crack initiation evolving over time. It is assumed[66] that the process of crack propagation has basically no effect on creep deformation, but that if it does exert such an effect, then the creep curves from which the creep equation is set up will reflect the total effect.

The scalar χ, called continuity, i[illegible] introduced as a quantitative characteristic of damage to t[illegible] terial. At the initial moment when damage is absent, $\chi = 1$. Over time χ decreases, and at a certain small value $\chi_o > 0$, main cracks will appear in individual weak spots in the material, these cracks intensifying the fracture process. But since the value of χ_o cannot be experimentally determined and the time elapsing from the moment of major crack formation to the complete fracture of the specimen is insubstantial, then it is assumed that at the moment of brittle fracture, $\chi = 0$.

Thus, the time to brittle fracture will be know if one can determine the time over which the value of χ changes from 1 to 0. It is assumed that the rate of change in parameter χ depends on stress and the value of χ itself. In the work[67] structural parameter w is substituted for continuity χ, w being assumed a measure of "embrittlement." These parameters are related thus: $w - \chi$.

To simplify further calculations, let us assume an exponential dependence between the rate of continuity change and the ratio σ_0/χ which may be interpreted as the true mean stress at any moment of time.

Then

$$\dot{\psi} = -A\left(\frac{\sigma_0}{\psi}\right)^n \qquad (V.82)$$

where A and n are certain coefficients at constant temperature $(A > 0)$.

By integrating Eq. (V.82) for χ from $\chi = 1$ to $\chi = 0$ and for t from $t = 0$ to $t = t_{xr}$, we will find the time of brittle fracture

$$t_{xp} = \frac{1}{(n+1)A\sigma_0^n} \qquad (V.83)$$

Function V.83 corresponds to an idealized case, when creep in the material is completely absent.

Since in actuality creep does occur, it should be considered that stress will be increased owing to a decrease in cross-sectional area. The process of brittle fracture is thereby acclerated. As a consequence, mixed fracture occurs. L. M. Kachanov[66] derived the following expression for durability in creep t_k:

$$t_k = t_\text{в}\left[1-\left(1-\frac{m-n}{m}\,\frac{t_{\text{xp}}}{t_\text{в}}\right)^{\frac{m}{m-n}}\right] \qquad \text{(V.84)}$$

where t_v is the time of ductile fracture, determined by function (V.87); t_{xr} is the time of pure brittle fracture according to function (V.83); m and n are parameters in Eqs. (V.85) and (V.82).

It is obvious that Eq. (V.84) is valid when t_k t_v. An approximate model has been constructed to describe the process of crack propagation in the final stage under different stress condtions.

Yu. N. Rabotnov[67, 68, 70], using a hypothesis of the uniform flow of the crack propagation process, not only determined the time of brittle and mixed fracture, but also derived functions describing the part of creep preceding fracture.

The theories examined above, relating the processes of deformation and fracture, were not developed mainly for polymeric materials, so that their applicability to polymers is still unresolved.

Hoff[71] studied long-term strength under uniaxial tension, assuming that as a result of creep the cross-sectional area of the specimen was diminished over time, with this reduction having an effect on the magnitude of stress and, therefore, on the rate of creep in the specimen. For durability he took the time over which, as a result of creep, the cross-sectional area of a rod was reduced to zero. Such a form of fracture is accompanied by large linear strains and has a ductile character.

Hoff used a relation valid for small strains as a creep law

$$\frac{d\varepsilon}{dt} = a\sigma^m \qquad \text{(V.85)}$$

where "a" and m are experimentally determined constants.

We can assume that relation (V.85) is also valid in the region of large strains, if we substitute actual values for the stresses and strains determined with the relations

$$\sigma = \frac{P}{F}(1 + \varepsilon); \qquad \varepsilon = \ln\frac{l}{l_0}. \qquad \text{(V.86)}$$

where P is the applied external load; F is the cross-section of the specimen; l, l_o are the lengths of the specimen at any moment of time and at the moment of loading.

Hoff derives an equation making it possible to compute the cross-sectional area of a specimen for any moment of time, and consequently, the period of time t_v over which this area is reduced to zero:

$$t_v = \frac{1}{m a \sigma_0^m} \qquad \text{(V.87)}$$

where σ_o is stress at the moment of loading.

It should be noted that Hoff's approach does not have a wide application. The results hereby obtained pertain only to uniaxial tension, and cannot always be generalized for other forms of strain. Thus, according to this scheme, creep under torsion cannot lead to fracture, an assertion contradicted by experimental data.

Several questions pertaining to the relationship between deformation and fracture are posed in the works.[72 - 80]

Having detailed the different approaches to the processes of fracture and softening based on kinetic concepts, it would be helpful to proceed to the correlation of the temperature-time dependences of strength and deformability. Let us note once again beforehand that each mode of thermal and mechanical action corresponds to a specific value of a material's durability - the time elapsing from the moment of a load's application to the brittle fracture or softening of a material.

If stress σ and temperature T are constant, the durability of polymeric materials is described by one of the relations (V.1), (V.3), (V.8), (V.11) etc. Under these same conditions, the durability of the form t_{ϕ} is determined by either of the Eqs. (V.32) or (V.33). Depending on the numerical value of the parameters entering into these equations and on stress and temperature, the following inequalities will generally be satisfied.

$$\Phi_1 < 1 \qquad (V.88)$$

$$\Phi_1 > 1 \qquad (V.89)$$

Inequality (V.88) corresponds to the softening of a material, since the durability of the form t_{ϕ} is exhausted before fracture. Inequality (V.89) corresponds to the fracture of a material, since durability t is exhausted before the rapid development of deformation (softening). In the special case where $t = t_{\phi}$, fracture and softening take place simultaneously, and this condition corresponds with the advent of brittleness.

The above scheme for fracture and softening is a generalization of the well-known scheme for brittle and non-brittle (forced-elastic) fracture advanced by A. P. Alekcandrov and Yu. S. Lazurkin presented in detail on page 149.

Let us use in a geometric characterization of working capacity[57] to graphically illustrate the effect of the conditions of mechanical and thermal action, as well as the material parameters, on the working capacity of polymers. This volumetric characteristic represents a set of two (or more) areas, each of which is described by equations of the temperature-time dependence of strength and deformability. A generalized work capacity region is conveniently constructed in the coordinates σ, T, log t (log t_0).

Figure V.29 shows graphically the different variants of the reciprocal positions of areas of strength of deformability under the conditions σ = constant and T = constant. The coordinate planes correspond to certain constant values of , T and log t. It can easily be seen from these diagrams that, dependingoon the stress, temperature and material parameters, either fracture or softening will occur first. The line intersecting the areas represents the brittleness line, since it corresponds to the conditions under which one observes a transition from softening of the material to its brittle fracture. The region of the polymeric material's work capacity is determined by the set of the inner sections of both areas and the coordinate planes.

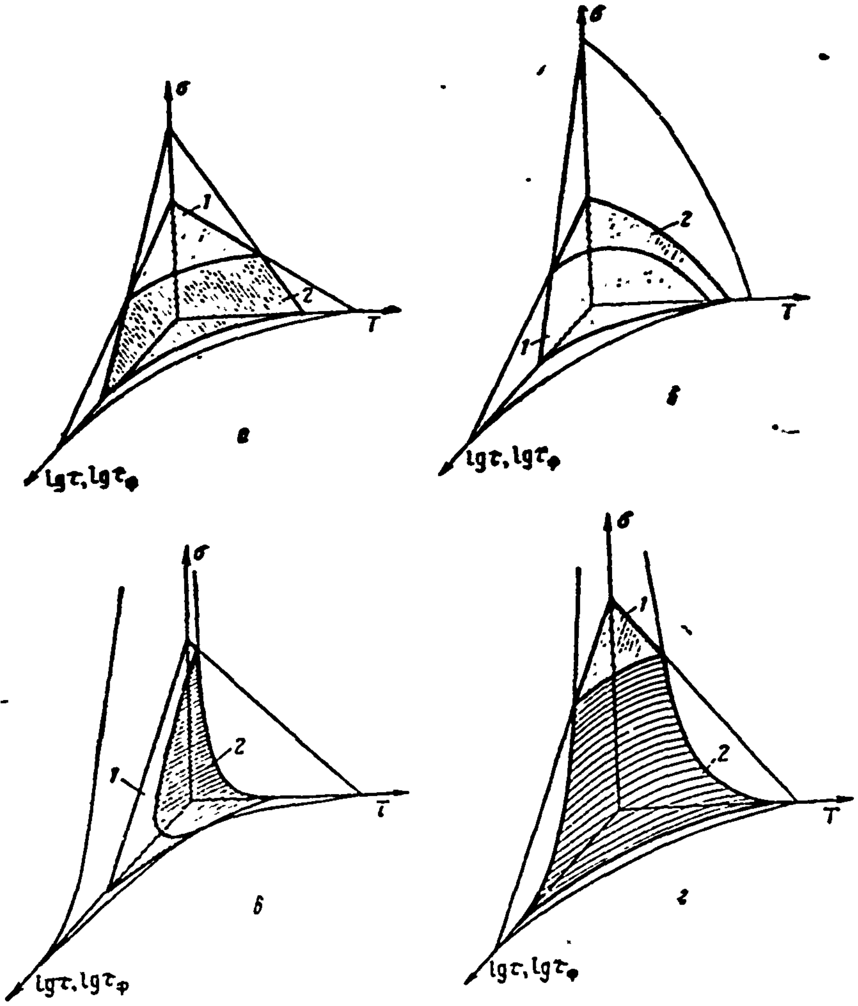

Figure V.29.

Volumetric characteristics of the work capacity of polymeric materials (layout):

a, b, c, d - different variants of the location of strength and deformability areas. 1 - strength area; 2 - deformability area.

The geometrical characteristic of efficiency for polycaprolactam fiber may be found in the work.[58] It should be noted that in individual cases, the surfaces may not intersect. In this case, if the area of deformability lies above the strength area, then brittle fracture will be observed at any stresses and temperatures. Such a phenomenon is very characteristic of polymers with a stable globular structure.[29, 59] The geometrical characteristics of polymers' mechanical work capacity shown in Figure V.29 are valid under constant stress and isothermal conditions. Generally, with arbitrary modes of thermal and mechanical action, the time to fracture or softening is a function of stress and temperature /see Eqs. (V.18) and (V.34)/.

In concluding, let us turn our attention once more to the several remarkable phenomena described above. One of these reflects the experimental fact according to which necking occurs in amorphous and crystalline polymers under conditions other than uniaxial tension with increasing load. A rigidly constant stress acting in a specimen also initiates the formation of a neck. The greater the stress, the less the time that elapses from the moment of loading until the spasmodic nucleation of a neck.

Thus, the nucleation of a neck is possible not only under stresses equal to the forced elastic limit σ_{ev} or recrystallization stress σ_{rekr}, but under other, substantially smaller stresses. However, fracture is more carefully studied from these viewpoints than is softening.

It may be assumed that softening, as fracture, is a kinetic process consisting of the gradual accumulation of elementary softening events and leading ultimately to the loss of the original form of a solid. The question of the nature of these elementary softening events remains open at present. They may possibly be connected with the rupture of intermolecular or interstructural bonds. The results of measurements of the activation energy[6, 8 - 10, 12, 13, 23, 35] of the process still have not made it possible to arrive at any firm conclusions on the process' mechanism. In any case, it may be asserted on the basis of numerous structural studies that softening is connected with the rearrangement of a polymeric solid's structure at all of its levels.

Let us now turn to another interesting phenomena. A specific interval of time elapses between loading and the beginning of necking. Under conditions where σ = constant, this period is determined by Eqs. (V.32) and (V.33). If stress is changed with time, the period over which the form of a solid will be retained is a function of stress and is determined by relation (V.34), quite similar to Bailey's criterion [see Eq. (V.17)]. This means that the form of a polymeric solid is lost gradually under a variable load, and at the moment when the loss of the form's durability equals unity, large deformations are spasmodically developed.

All of this allows us to approach the phenomenon of necking under uniaxial tension at a certain velocity in a new way. During tension, elementary acts of the softening process are occuring; over time, the durability of the form of a solid is lost. As soon as relative durability reaches unity, a neck is formed and conditions favoring the growth of large deformations are created (of course, during this, relative "aging" should not reach unity, or otherwise the specimen will be fractured).

This scheme allows us to explain all of the phenomena connected with the effect of temperature and loading rate on the forced-elastic limit σ_{ve} or on recrystallization stress σ_{rekr}. Thus, by increasing the rate of tension, we approach the moment of neck formation, and according to Eqs. (V.32) and (V.37), a spasm (nucleation of the neck) occurs at large values or σ_{ve} or σ_{rekr}. According to the same relations, an increase in temperature leads to a lowering of the values of σ_{ve} and σ_{rekr}.

Let us again try to connect the two processes of fracture and softening. Quite obviously, both of these processes occur simultaneously. It is well known that fracture occurs on the molecular level as a result of the rupture of the chemical bonds of macromolecules and, possibly, intermolecular bonds; on the super-molecular level, it occurs by means of the propagation of microcracks and the reordering of structural elements. All of these phenomena take place under the influence of a mechanical load.

The same load also influences the softening process, regardless of whether softening or fracture occurs first. Thus, it is clear that the rupture of chemical and intermolecular bonds, crack propagation and the rearrangement of structural elements occur during the softening process.

The question then arises - are not these processes identical, e.g. do they not occur by means of exactly the same mechanism? The identity of the mechanisms does not mean that both processes are fully equivalent.

Depending on its chemical composition and super-molecular structure, a polymeric solid will be dominated by that mechanism which encounters the least resistance. Thus, within the range of oriented systems, the rupture of chemical bonds in the main chain of macromolecules is more easily effected than the rupture of a large group of intermolecular bonds along the chains. As shown by S. N. Zhurkov (see Chap. 14), the fracture mechanism is such systems is dependent on the gradual accumulation of broken fragments of macromolecules. This is an extreme case.

In other instances, intermolecular bonds are broken, the structure is rearranged, cracks are developed, etc. As a result, a polymeric solid may remain whole, but it will undergo large deformations, e.g. soften. It should be noted once more that from kinetic points of view, the softening process has not yet been studied as thoroughly as has fracture, and we may expect the future to bring new and interesting results.

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