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by recrystallization. For this reason the yield stress of crystalline polymers is also known as the recrystallization stress. At sufficiently high stresses, recrystallization of the polymer occurs, during which the elements of its crystal structure recrystallize under the action of the applied external stresses.

In a polymer on which no external forces are acting crystallization results in the formation of variously arranged elements of crystal structure, and the body becomes isotropic as a whole (see also CRYSTALLINITY; ORIENTATION). Under uniaxial tensile stresses the melting points of these structural elements change, depending on how they are arranged with respect to the direction of the forces acting on them. The melting points of some of these structural elements rise and they become more stable, whereas those of others, arranged in other directions, drop, and these elements may melt at sufficiently high stresses.

Since the melt is unstable at any given temperature at which extension takes place (since the polymer is crystalline it is at a temperature below its melting point), it does not become a liquid, but elements of its crystal structure change their form of spatial arrangement, i.e. elements so oriented with respect to the external stresses that they become unstable recrystallize into elements so arranged that the external stress raises their melting point.

It must, however, be pointed out that in a real polymer this picture is greatly complicated by the presence of many different forms of the crystal structure elements, i.e. by the coexistence of various forms of supermolecular structure, capable of passing into one another (25-31), as well as by the low rate of crystallization often observed in polymers (see MORPHOLOGY; KINETICS OF CRYSTALLIZATION). In the latter case, complete conversion of the crystalline specimen into the amorphous state may occur as a result of extension, because the specimen is incapable of crystallizing in the course of the time available during the test (32,33).

Comparison of Glassy and Crystalline Polymers. A few words of explanation can be offered concerning the resemblance between the behavior of glassy and crystalline polymers.

The reason is that both glassy and crystalline polymers are solids in which the mobility of macromolecules or their segments is greatly limited by forces of interaction. The macromolecules in both kinds of bodies are more or less ordered, although in degree of ordering and in diversity of forms of ordering crystalline bodies surpass glassy ones by far. Nevertheless, these common traits are sufficient for the stress-strain diagrams of these two types of solid polymeric bodies to resemble each other in their main features. The difference in their phase states is manifested in the location of the various temperature regions on the temperature scale, in their strength values, and in other properties.

A vivid example is isotactic polystyrene which crystallizes slowly and can therefore be obtained both in the crystalline and in the glassy states. With respect to composition and structure, one and the same polymer, when in the solid physical state but in different phase states, displays different sets of mechanical properties, but the temperature dependencies of these properties are similar in general features. Indeed, although they are both brittle at low temperatures and capable of developing forced rubbery deformations at higher temperatures, glassy polystyrene becomes a rubbery body (which may subsequently crystallize) at as low a temperature as about 80°C, whereas crystalline polystyrene only loses its brittleness at such temperatures and begins to display a capacity for forced rubbery deformation which remains,

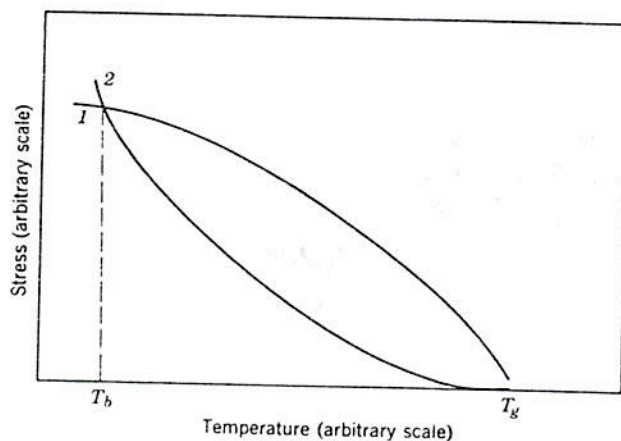


Fig. 18. Schematic diagram of temperature dependence of strength (1) and yield stress (2) for a glassy polymer.

though decreasing gradually due to amorphization, right up to its melting point at 230°C.

Brittleness. Now let us consider the causes of the appearance of brittleness in a solid polymer.

At a given deformation rate, the lower the temperature, the higher the strength of a polymeric body. The yield point also rises at a constant deformation rate with decreasing temperature.

The ultimate strength of both glassy and crystalline polymers at higher temperatures is above the yield stress. Therefore, as the stress is increased during extension the value σ_y is reached first and a high forced rubbery deformation develops. Failure occurs only after this. However, on cooling to a sufficiently low temperature the yield stress becomes higher than the breaking stress and the body fails before it becomes capable of large deformations. In this case, when the body fails with small deformations it is said to have undergone brittle failure. Hence, at temperatures where $\sigma_s > \sigma_y$, polymeric solids are considerably deformable and not brittle. But when $\sigma_s < \sigma_y$, the solid polymer undergoes brittle failure. Figures 18 and 19 are schematic representations of the temperature dependencies of the breaking stress and yield stress for a glassy and a crystalline polymer. It can be seen from these figures that the intersection of the curves of these dependencies determines the position of the brittleness temperature, T_b . Attention should be drawn to the fact that for glassy bodies σ_y becomes zero at the glass-transition temperature, because above this temperature the body is rubbery in itself. Therefore, the region of the nonbrittle state of such solid polymeric bodies is situated below the glass-transition temperature.

In the case of crystalline polymeric bodies, however, σ_y , although decreasing, retains a finite value up to the melting point of the polymer. Therefore, the region of the nonbrittle state in a crystalline polymer extends from the melting point to temperatures close to the glass-transition point observed more or less in crystalline polymers. When a crystalline polymer is cooled to the glass-transition temperature its yield stress increases sharply with a relatively small increase in strength, as a result of which the temperature-dependence curves of σ_y and σ_s intersect at that temperature (or close to it), i.e., the polymer passes into the brittle state. Comparison of Figures 18 and

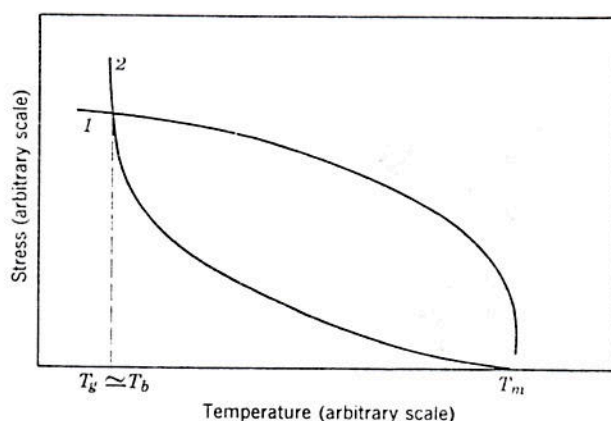


Fig. 19. Schematic diagram of temperature dependence of strength (1) and yield stress (2) for a crystalline polymer.

19 shows clearly that, although there are common features in the temperature dependencies of their mechanical properties, glassy and crystalline polymers differ substantially in properties.

The Time Factor. When discussing the principal mechanical properties of polymers at different temperatures it was mentioned that the mechanical properties of polymers depend considerably on the time factor, i.e., on the duration of constant stresses, on the rate of deformation, on the rate of loading, etc. It was especially stressed that such characteristics as glass-transition temperature, modulus of elasticity, and ultimate strength should always be related to the conditions under which they are determined. The same refers to the brittleness temperature. The greater the rate of extension or other type of strain at which the brittleness temperature is determined, the higher the yield stress and ultimate strength. The yield stress rises faster than the ultimate strength and therefore the point of intersection of the curves shown in Figures 18 and 19 shifts to higher temperatures. Hence, as the rate of deformation increases, the brittleness temperature rises, always remaining, of course, below the glass-transition temperature of the glassy polymer (provided both these temperatures are determined under the same time conditions of deformation) or the melting point of the crystalline polymer.

Relaxation Phenomena

The dependence of mechanical properties on the time factor is generally very important. Disregard of this fact has more than once resulted in polymeric materials, which displayed satisfactory performance during laboratory investigations, being found to be of poor quality or even quite useless when manufactured into finished goods. This discrepancy between the data of laboratory tests and actual usage was due to the difference between the conditions of the tests and the conditions of deformation during usage. It seems interesting, therefore, to discuss in greater detail the complex of so-called relaxation phenomena, i.e., the set of phenomena resulting from the dependence of the mechanical properties of polymers on the time factor.

The dependence of the mechanical properties of a polymer on the duration of force action was first discovered in 1835 by Weber (34), who studied the creep of

natural silk filaments. Subsequently, a large number of investigations of silk, rubber, and other substances appeared devoted to ascertainment of the basic phenomenological dependencies (35-48) among stresses, strains, and time, as well as the molecular mechanism of these phenomena (36,37).

At the end of the 19th century these investigations were almost all discontinued without having elucidated substantially the nature of the phenomena; these studies did, however, result in the formulation of the basic phenomenological equations giving a general description of the characteristic features observed.

During the second quarter of this century interest in these questions revived in connection with the development of the production of artificial fibers, plastics, and synthetic rubber. The new solid and liquid materials obtained displayed mechanical properties which could not be explained on the basis of the familiar laws of elasticity theory and hydrodynamics. Meanwhile, the growing usage of these materials demanded elucidation of the nature of relaxation phenomena and establishment of the relationships between the structure of polymers and their properties.

The totality of these efforts resulted in the general theories of relaxation phenomena known to us today.

Description of Relaxation Phenomena. Relaxation phenomena are the phenomena which arise upon reestablishment of equilibrium in a system brought out of equilibrium by the action of external forces. Hence, relaxation phenomena are nothing but the entire complex of processes of reestablishment of equilibrium, developing in nonequilibrium systems. Naturally, depending on the conditions under which the equilibrium state is restored, various kinds of relaxation processes are observed. Therefore it is impossible to describe the entire diversity of processes of this kind and only the most important and simplest cases need be discussed.

Duration of External Force. Mechanical relaxation processes always arise in polymers when the duration of the external influence is comparable with the duration of the processes of regrouping of macromolecules or their aggregates. Indeed, if some force begins to act on a polymeric body, a certain length of time is required for the deformation corresponding to that force to develop, during which the structural elements of the body can be displaced sufficiently to change its shape. The weaker the interaction between the elements and the higher their thermal energy, ie, the higher their temperature, the more rapidly can these displacements be brought about. In addition, the rate of displacement may depend on the magnitude of the external mechanical stress applied.

The result of all this is that after the mechanical forces have started acting, a certain length of time passes during which the structural elements, which were until then in equilibrium, pass into new positions corresponding to equilibrium with the acting forces. If the action of the external forces is now stopped, the equilibrium thus established is lost and displacement of the structural elements will begin to positions corresponding to the equilibrium of an unstressed body, ie, in the reverse direction. Hence, relaxation processes may occur in either direction, depending on the initial state of the body and the state corresponding to equilibrium, with allowance for the external influences in question. If the external influences depend on time, the establishment of equilibrium may not go to completion owing to changes in the conditions of equilibrium. The polymeric body will then be continuously rearranging its structure, and hence its mechanical properties as well. In the particular case of action of a periodic external force, the structure of the body and its mechanical properties will

gradually pass into a steady state of periodic change, but the changes in structure and, hence, the deformations will lag behind the changes in mechanical influences. In the case of sinusoidal influences this lag results in a phase shift between stress and strain (see Fig. 13).

Relaxation processes are practically imperceptible on very short-time observation. In such cases, the bodies stressed by the external forces have not yet had time to change the position of their structural elements. (The times in question are much smaller than relaxation times, i.e. the times required for rearrangement of the mobile elements of the body.) Nor are relaxation processes perceptible upon very prolonged observations, when there has been ample time for an equilibrium state to be established. (The relaxation time is much smaller than the time of action of a constant stress or much smaller than the time it takes in practice for an alternating mechanical influence to change.)

Therefore the most vivid manifestations of relaxation processes are observed during intermediate times of action, not too small and not too large compared to the duration of the structural rearrangement processes.

Temperature Effects. At a given duration of an influence the possibility of relaxation phenomena manifesting themselves depends considerably on the temperature. At very low temperatures when rearrangement of the structural elements is practically fully suppressed, relaxation phenomena will be almost or completely absent, because any duration of the influence under such conditions is small compared to the infinite time of relaxation. This is why relaxation phenomena are very weakly exhibited by glassy and crystalline polymers, becoming perceptible only (a) under the action of sufficiently high mechanical stresses, which facilitate displacement of the structural elements, (b) on approaching the glass-transition temperature, when mobility begins gradually to appear in glassy polymers, or (c) on approaching the melting point, when the influence of the unordered regions of the structure possessing high mobility becomes perceptible in crystalline polymers. The development in polymer solids of forced rubbery deformations is a vivid example of relaxation processes appearing as a result of the increase in mobility of the structural elements when mechanical stresses appear in the body.

At very high temperatures when rearrangement of the structural elements occurs so rapidly that any given duration of action is always much larger than the relaxation time, relaxation phenomena are again not observed, because there is always time for equilibrium to be established. This is why no relaxation phenomena are, in practice, observed in the rubbery state of a polymer at temperatures considerably exceeding the glass-transition temperature. However, when the region of appearance of fluidity is reached and still larger structural elements (macromolecules as a whole and their aggregates) begin to be displaced perceptibly, relaxation phenomena again appear.

In this case, the duration of the influence is comparable with the duration of the relaxation processes of rearrangement of these large structural elements, whereas at the temperatures in the glass-transition region it is comparable with the duration of regrouping of the small structural elements (eg, macromolecular segments). Naturally, on further rise of the temperature (provided no chemical changes occur in the polymer) the relaxation phenomena again become hardly perceptible, because their duration becomes too small.

Thus, relaxation processes are always the most pronounced in temperature regions of transition from one physical state into another (ie, in the regions of the transitions

from the glassy to the rubbery state, from the rubbery to the viscofluid state, and from the crystalline to the amorphous state).

Relaxation Mechanisms. Attention should be drawn to the very important fact that if the relaxation process in the system had only one mechanism, i.e., if there were only one type of rearrangement of the structural elements, there would be only one time characteristic of that process, i.e., a single relaxation time. But in the case of polymeric bodies in the amorphous state two characteristic time values are observed, or, accordingly, two temperatures at which relaxation phenomena are especially pronounced. This points to the complexity of relaxation phenomena in polymers, and to the existence of at least two mechanisms of relaxation phenomena. Indeed, one of them is related to rearrangements of small structural elements and is exhibited in the region of glass transition, whereas the other is connected with rearrangements of large structural elements and is applicable in the region of the appearance of the fluidity in the polymeric body.

However, the actual situation is much more complex than the simple concept of two types of movements in polymeric bodies caused by the movement of segments and of macromolecules. Even the movement of segments in a system of randomly entangled macromolecules results in many relaxation times, because various types of rearrangements are possible in this case, involving different numbers of segments under various chance conditions of interaction. The same situation also pertains to rearrangements of macromolecules. Therefore, instead of two relaxation times it is necessary to consider two sets of relaxation times which may overlap or be distinctly separate. (The glass-transition and fluidity regions may overlap if the molecular weights of the polymers are not very large, but may be distinctly separate if the molecular weights are high enough.)

However, in polymeric bodies the macromolecules are not arranged at random but are ordered to some extent into various elements of supermolecular structure (see MORPHOLOGY, and also pp. 492-506 of this article). This enhances the diversity of durations of rearrangements in the structure of the body still more owing both to the diversity of structural elements and to the fact that some of the structural elements may change into others on deformation of the body. The latter especially complicates relaxation processes in crystalline polymers that contain a great variety of coexisting forms of supermolecular structure (25-31).

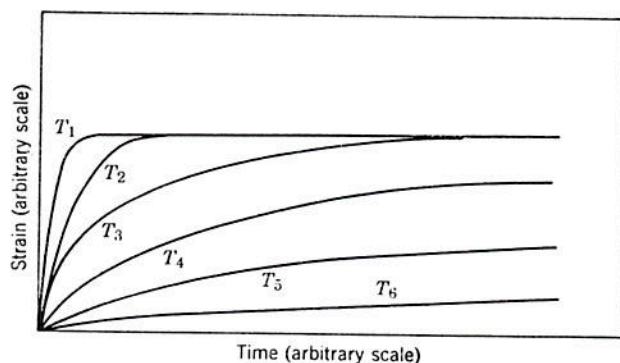


Fig. 20. Time dependence of deformation at various temperatures for an amorphous viscoelastic polymeric body. (Temperature decreases with increasing order of subscript.)

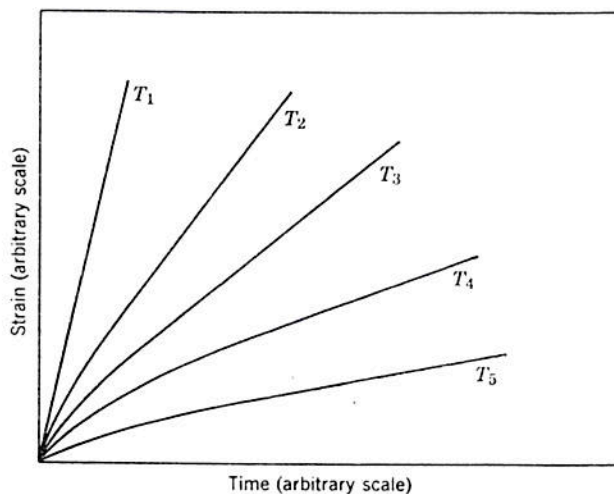


Fig. 21. Time dependence of deformation at various temperatures for an amorphous elastoviscous polymeric body. (Temperature decreases with increasing order of subscript.)

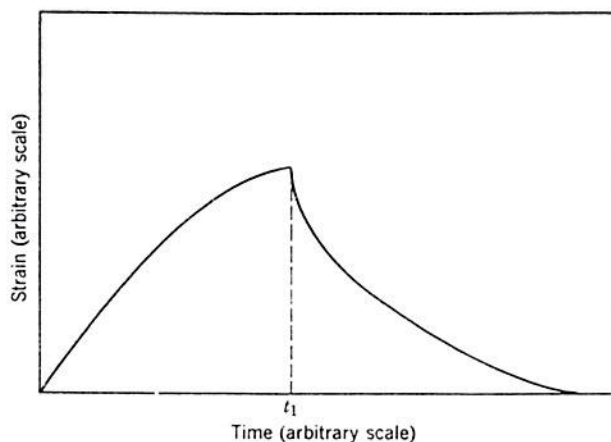


Fig. 22. Creep and restoration of the shape of a body in the absence of fluidity; t_1 is time of removal of deforming force.

Simple Types of Relaxation. The simplest types of relaxation phenomena will be considered in this section. If a constant stress is acting on a body, a deformation corresponding to that stress should develop. It should acquire a certain constant value in the case of an elastic body or should be proportional to time in the case of a viscous Newtonian body.

Creep and Elastic Aftereffect. The deformation of a polymeric body under the action of a constant stress either (a) develops gradually and finally reaches a constant value if the body is incapable of flowing (three-dimensional crosslinked polymers, or linear polymers at temperatures below T_f if they are amorphous and below T_m if they are crystalline) or (b) develops in a linear time dependence if the body is capable of flowing (linear amorphous polymers at temperatures above T_f or linear crystalline polymers at temperatures above T_m and T_f).

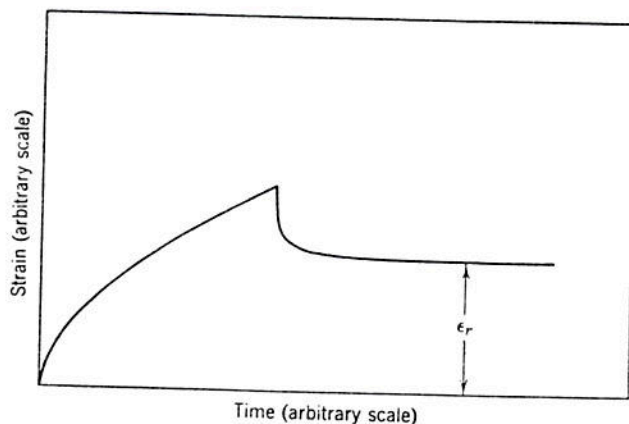


Fig. 23. Creep and partial restoration of the shape of a body possessing fluidity; ϵ_r is residual deformation.

Such deformation–time dependencies at various temperatures are shown schematically for an amorphous viscoelastic polymeric body in Figure 20, and for a linear elastoviscous polymeric body in Figure 21.

Owing to the gradual (very slow at low temperatures) and as it were, creeping, nature of the deformation, this particular case of relaxation processes has come to be called *creep*.

After the action of the stress has ceased, the released deformed polymeric body, by means of the new relaxation process, restores the equilibrium arrangement of its structural elements. In the case of a fully viscoelastic polymeric body (Fig. 22) this process results, after some time, in complete restoration of its initial shape (the deformation tends to zero), whereas the shape of a polymeric body capable of flowing (Fig. 23) is only partially restored (the deformation tends to a finite limit, ϵ_r , known as the true residual deformation). The value of ϵ_r , which depends on the nature of the body, is the higher, the greater the stress that acted on the body, the longer it acted, and the higher the temperature. This ability of polymeric bodies, on release of a deforming stress, spontaneously to return, either fully or partially, to their original shapes is called *elastic aftereffect*.

Special attention should be drawn to the fact that when polymers undergo any kind of treatment, such as calendaring, extrusion, or compression, the polymeric mass is subjected to the action of forces in the machine and then, after being put in the required shape, is relieved. This always results in elastic aftereffect, which may change the shape of the article substantially some time after its manufacture, especially if it is heated. These shrinkage phenomena are commonly known in technology but are not always taken into account. Very often the size of the article can be preserved by lowering the temperature sharply at the moment the external stresses are relieved. This “freezes” the relaxation processes and the article preserves the shape imparted to it. However, this also freezes high internal stresses into it, resulting sooner or later either in elastic aftereffect and loss of shape or in cracking of the article and deterioration of quality.

Analysis of elastic aftereffect and creep shows that to describe the phenomena observed the coexistence of many of the various relaxation mechanisms mentioned above must be taken into account; this is quite in agreement with the fact that any manifesta-