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Plastics, Resins, Rubbers, Fibers

VOLUME 8

Keratin
to
Modacrylic Fibers

independent of any other functions of t and ω. The latter condition is tantamount to the requirement that the results of action of the stress be invariant if the moment of the beginning of the deformation process is changed. The elasticity constants $b_{rs.ik}$ can be expressed through constants $a_{ik.rs}$ (see eq. 14).

$$\epsilon_{rs}(t) = \sum_{i=1}^{3} \sum_{k=1}^{3} b_{rs.ik}\sigma_{ik}(t) + \sum_{i=1}^{3} \sum_{k=1}^{3} \int_0^t b^*_{rs.ik}(t - \omega)\sigma(\omega)d\omega \qquad (51)$$

If the higher terms of the expansion into a series of the functionals in equation 50 are taken into account, nonlinear integral equations can be obtained relating the deformation and stress tensors to any degree of accuracy. Another method of introducing nonlinear relationships is to consider nonlinear functionals directly, as is done in the general theory of functionals developed by Volterra.

There is no doubt that in precisely this way (using operator methods, which facilitates all calculations considerably) a general nonlinear phenomenological theory of elastoviscous and viscoelastic polymeric bodies can be developed and attempts can be made to relate the parameters contained in the equations to the molecular and supermolecular structure of polymers.

Mechanical Properties and Structure of Polymeric Bodies

A phenomenological description of the mechanical properties of polymers appeared long before the first conceptions of the molecular nature of these bodies were formed. The discovery that polymer molecules are very large and are flexible if their structure is linear led to a new stage in the development of the theory of the mechanical properties of polymeric bodies (61,62,78,79). This stage no longer confined itself to a mere description of the mechanical properties peculiar to polymeric bodies, but went on to establish the relationships between their mechanical properties and the basic characteristics of macromolecules.

These characteristics are: size of macromolecules (ie, their degree of polymerization or molecular weight), flexibility (ie, segment size), and the characteristics of intermolecular interaction. Establishment of the relationships between these characteristics and the mechanical properties gave an insight into the reasons for the appearance of any particular properties, and thus made it possible to find ways of synthesizing new polymers of desired properties.

The theory of the mechanical properties of polymeric bodies was based on two main premises:

1. Deformations of the polymer depend wholly on the behavior of its macromolecules, reversible deformations being due to changes in conformations of the macromolecules, and irreversible deformations, to their displacement.

2. Isotropic amorphous polymeric bodies are homogeneous bodies consisting of randomly arranged macromolecules, isotropic crystalline polymeric bodies being regarded as the result of ordering of small regions of these bodies into microcrystals.

It was considered that the macromolecules pass through several such crystalline regions and unordered (amorphous) regions separating them (see also CRYSTALLINITY). The anisotropy of polymeric bodies was attributed to straightening and orientation of their macromolecules. The homogeneity of polymeric bodies was taken for granted.

The first polymeric bodies whose mechanical properties rapidly became an object of study were amorphous synthetic rubbers, the structures of which corresponded more than those of other polymers to the basic premises mentioned above. However, as the sphere of polymeric objects expanded, various complications began to arise. It was especially difficult to reconcile such simplified ideas of the structure of a polymeric body with the mechanical properties observed in crystalline polymers. The discovery of supermolecular structures (see also MORPHOLOGY) in amorphous and crystalline polymers (25–31,80,81) showed that the basic premises concerning the structure of polymeric bodies, which had previously seemed self-evident, were no more than a first approximation which could serve only in the simplest cases. This marks the beginning of the second stage of development in the theory of the relationships between the mechanical properties of polymeric bodies and their structure. At this stage the theory was based on the following premises:

1. All polymeric bodies, whether isotropic or anisotropic, liquid or solid, amorphous or crystalline, contain supermolecular formations of different degrees of complexity and of different sizes. Their existence makes it impossible to consider polymeric bodies homogeneous or even continuous in some cases.
2. The deformations of a body and its mechanical properties are governed by the specific forms of its supermolecular formations and their properties, which in their turn depend both on their own characteristics (structure and size of the supermolecular formation, ties between these formations, etc) and on macromolecular characteristics (size of the macromolecules, their flexibility, and their chemical composition, the latter determining their intermolecular interactions).

Thus, at this stage, polymeric bodies were in some cases regarded as continuous and homogeneous, and in others, as heterogeneous and rather even as microconstructions. Closest to the first group were polymer solutions and melts, and to the second group, crystalline polymers.

The second, modern stage in the theory of the mechanical properties of polymeric bodies features very rapid progress in both experimental and theoretical investigations, and in separation of the structural mechanics of polymers into an independent division of polymer mechanics.

History of Concepts. The rise of the ideas of ordering in the arrangements of macromolecules and of the supermolecular structure of polymeric bodies has a rather instructive history, knowledge of which is indispensable to an understanding of the highly contradictory views encountered at present in the literature.

It has long been known that the molecules of any condensed system (liquid or solid) are never arranged entirely at random. Owing to intermolecular interaction some order always appears in the mutual arrangement of the molecules, resulting in a correspondingly more compact packing. In the case of liquids this very imperfect order covers a distance of only a few molecular layers (so-called near order), ie, the mutual arrangements of the molecules are correlated only over small distances. But in crystalline bodies the order covers indefinitely long distances (so-called long-range order) and manifests itself in the existence of relatively perfect three-dimensional crystal lattices. It is quite obvious that these ideas, developed for low-molecular-weight bodies, had to be reviewed critically before they could be applied to polymers.

The first ideas of the structure of polymeric bodies arose as a result of the discovery of the chain structure and large size of their molecules. These specific features of macromolecules, an inevitable consequence of which is the greater or lesser flexibility of the macromolecules, as well as the circumstance that all polymers (except for a few natural ones) are always polydisperse, ie, constitute a mixture of macromolecules of different length, resulted in rejection of the ideas attributing any substantial order to polymeric bodies.

It seemed quite self-evident that no structures anywhere near perfect could form from immense filament-like macromolecules of varying shapes and sizes. On the contrary, it was natural to assume that such macromolecules would get entangled at random with one another and form a sort of molecular matting. It would seem that an amorphous polymeric body of such a structure should possess mechanical properties governed by deformations of the entangled interacting flexible macromolecules.

The discovery of crystallization in polymers and of the fact that crystallization (eg, of natural rubber) is a first-order phase transition had no substantial effect on the development of the ideas of the relationships between the mechanical properties of polymeric bodies and their structure. Since x-ray investigations of crystallizing polymers revealed that the size of the crystal in polymeric bodies was very small, much smaller even than the length of individual macromolecules, it was assumed that crystallization occurs only in the regions of local ordering of the chain macromolecules, ie, only where they were arranged approximately parallel to one another. See also CRYSTALLINITY; KINETICS OF CRYSTALLIZATION.

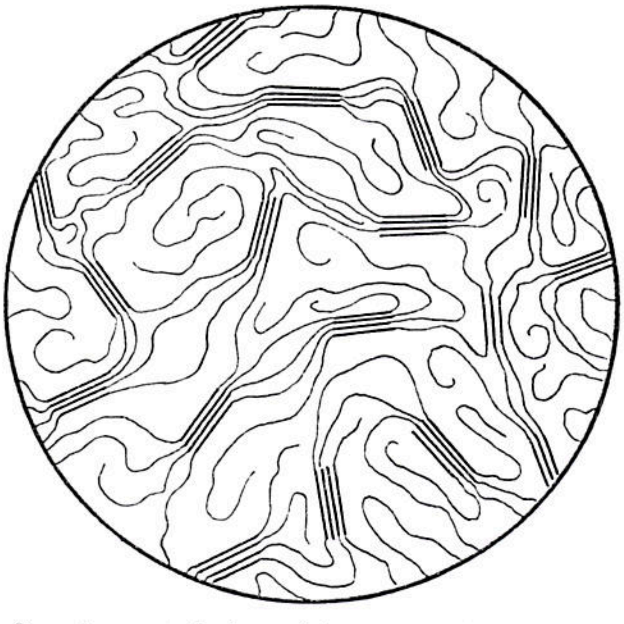


Fig. 36. Generally accepted scheme of the structure of a crystalline polymer.

It seemed natural that individual macromolecules should pass through a number of such crystalline regions, separated by unordered, ie, amorphous regions. Schematic representations of crystalline polymeric bodies (Fig. 36) often encountered in the literature correspond to this conception. Here the crystalline polymeric body is inevitably regarded as a two-phase system; the solid phase (microcrystals) is essentially not deformed by mechanical influences, since it consists of particles, as it were, of an active filler of the amorphous phase, particles which link the separate macromolecules very strongly to each other. It is clear that with such an approach the mechanical properties, for instance, the modulus of elasticity, should be governed by the content of the crystalline phase, ie, by what is known as the degree of crystallinity.

It seemed that it would be enough to determine only the degree of crystallinity to assess the extent to which the properties of a partly crystallized polymer differ from the properties of the same polymer in the fully amorphous state. In all the papers of this period the degree of crystallinity was the only structural characteristic of such polymers. This characteristic, determined by various methods (from density, optical data, x-ray scattering data, spectral data), despite its conventionality, which will be discussed below, was still found sufficient for weakly crystallizing polymers, eg, for rubbers, and for crystalline polymers at temperatures close to their melting points.

Subsequently, it gradually became clear that the actual structure of polymeric bodies is considerably more complex than initially supposed.

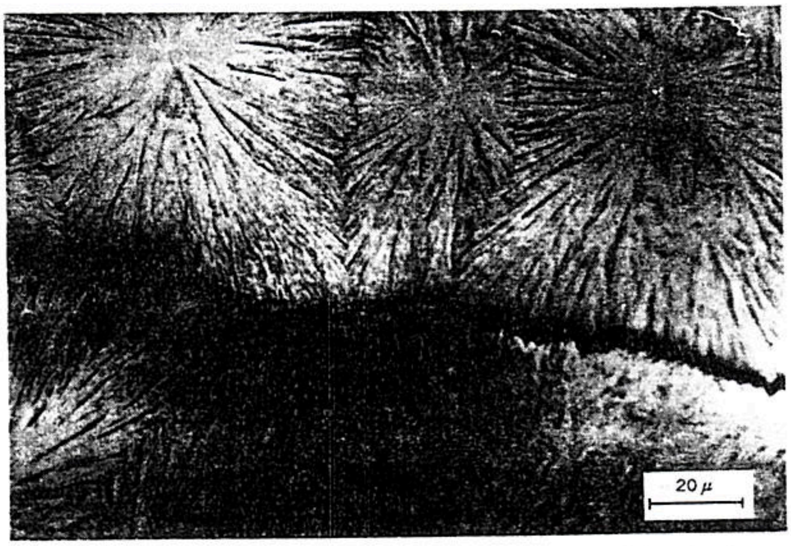
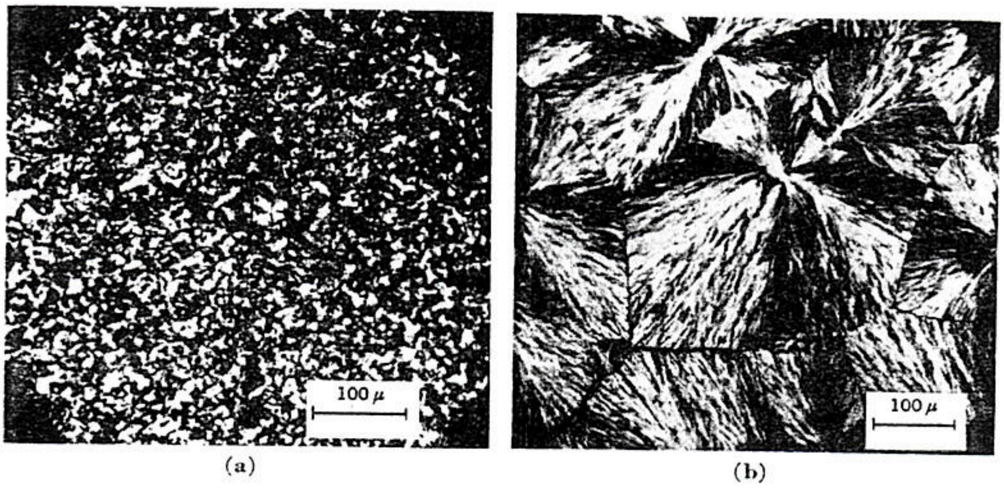


Fig. 37. Development of a crack along spherulite boundaries (119).

It was discovered (25–31) that crystallizing polymers are capable of forming very perfect structures, even unit crystals with regular external faces, as well as less perfect structural forms, ie, spherulites, which are aggregates of crystalline fibrils grown from a common center or nucleus. The size of these formations may be fairly large (single crystals may measure tenths of a millimeter, and spherulites, up to several millimeters). The most common structures (eg, those of polyolefins, polyamides, and polyesters) are spherulite structures consisting of individual spherulites and their aggregates (80,82) in the form of ribbons or sheets. In most cases, spherulites are from tenths of a micron to several dozen microns in size, and possess distinct boundaries along which cracks often form (Fig. 37). Spherulites and their aggregates, in most cases, become readily visible under an optical microscope (the surface of the polymeric body being prepared in the same way as the surface of metals, ie, it is obtained by fracturing in the brittle state or by cutting and etching with a poor solvent). (Theories of crystal formation, including chain folding, the fringed-micelle model, reentry folding, order distribution, etc, are discussed in CRYSTALLINITY. See also MORPHOLOGY.)



(a) (b)

Fig. 38. Dependence of supermolecular structure of isotactic crystalline polypropylene on the conditions of crystallization; heating time of the melt at 180°C is 5 sec for (**a**) and 60 sec for (**b**) (92).

Investigation of the structure of polymeric bodies under the electron microscope has revealed many simpler or underdeveloped forms of ordering of macromolecules existing alongside and simultaneously with the structural forms just described. (See also ELECTRON MICROSCOPY.)

Crystal Structures. Naturally, the coexistence in the same body of supermolecular structural elements of different types and sizes substantially affects its mechanical properties. Since the development of particular forms of supermolecular structure and the sizes of the individual elements depend on the conditions of crystallization (the temperature prehistory of the melt before crystallization and the conditions of crystallization proper), the mechanical properties of the crystallized polymeric body also depend essentially on the conditions of crystallization (Figs. 38–41).

All this indicates clearly that the crystalline state of a polymeric body cannot be characterized fully enough by the degree of crystallinity as the only parameter. Not only the relative quantity of ordered and unordered polymeric substance is important,

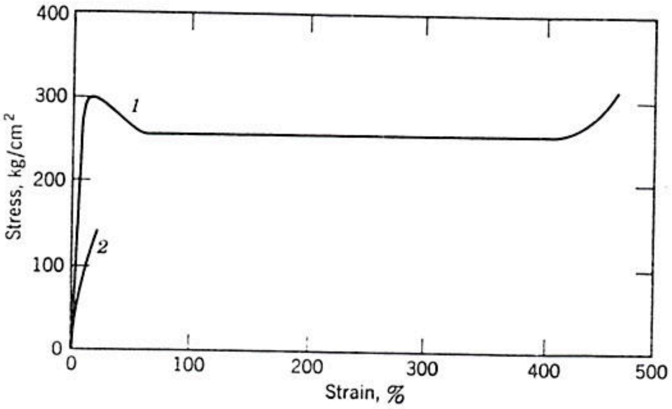
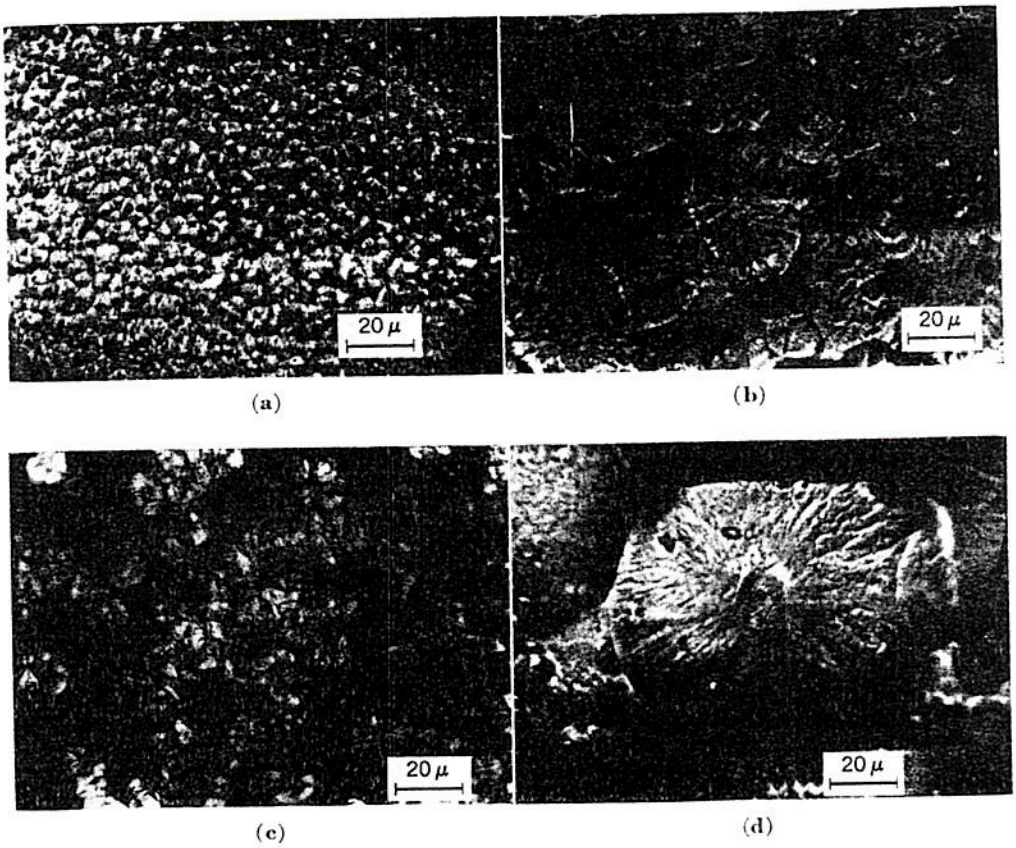


Fig. 39. Stress–strain diagrams of the specimens from Figures 38**a** and 38**b** (curves *1* and *2*, respectively) (92).



(a) (b)

(c) (d)

Fig. 40. Dependence of supermolecular structure of gutta percha on conditions of crystallization: (**a**) crystallized from melts (compression temperature 150°C); (**b**) crystallized from CCl_4 solution (solvent evaporated during 48 hr at 20°C, then during 4 hr at 70°C); (**c**) crystallized from benzene solution (solvent evaporated during 30 hr at 20°C); (**d**) crystallized from benzene solution (solvent evaporated during 330 hr at 20°C) (92).

but also the types and the relative quantities of the forms of the structures in which it is ordered.

An essential distinguishing feature of polymeric crystalline bodies is that they possess a complex structure, the separate elements of which are not macromolecules but larger intermediate formations.

During the crystallization of low-molecular-weight substances the microcrystal formed grows as a result of the addition to it of individual molecules, ions, or atoms (depending on the nature of the crystal), but the crystallization of high-molecular-weight substances involves the appearance of structural elements, aggregation of which results consecutively in the formation of more and more complex forms. The macromolecules combine into the simplest structural formations, packets, usually containing several tens or hundreds of macromolecules arranged approximately parallel; packets aggregate into larger structural elements, fibrils, or, by bending, into sheets; fibrils or sheets form spherulites and single crystals; the aggregation of spherulites into ribbons or sheets results in the largest structural formations in polymeric bodies.

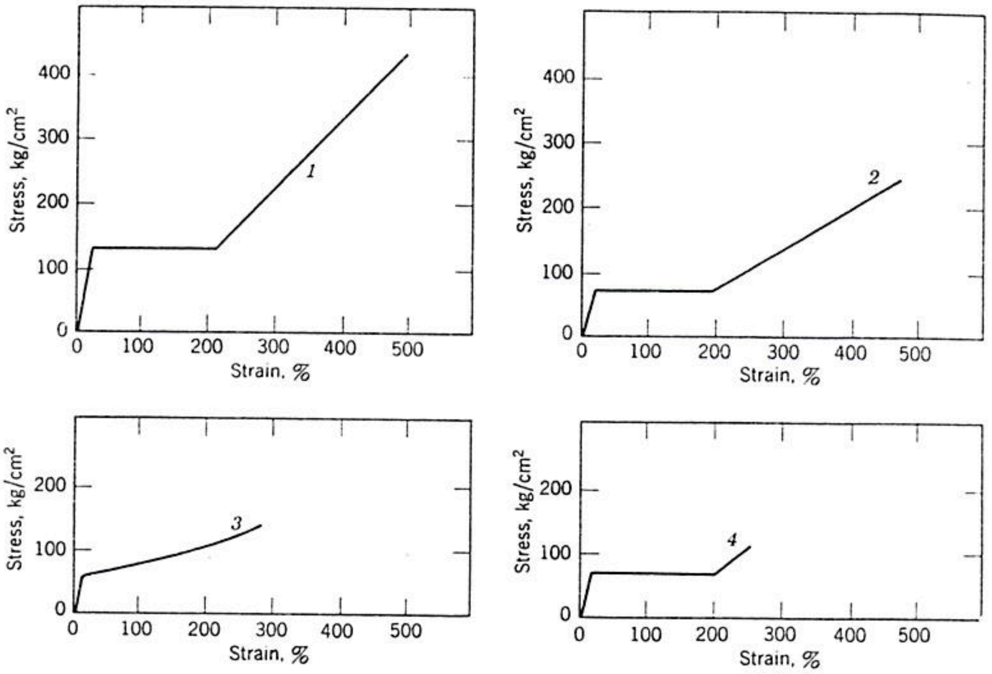


Fig. 41. Stress-strain diagrams of the specimens from Figures 40a–40d (curves *1–4*, respectively) (92).

Thus, the highest structural forms in polymers are a result of a multistep process of ordering.

Effects of Deformation. Stepwise crystallization is characteristic only of polymers and plays a very important part in forming the mechanical properties of polymeric bodies. Each of the structural forms described has its own inherent features of deformation. Therefore they deform differently under mechanical influences and, moreover, are capable of changing into one another. Breakage of the body as a result of deformation also occurs stepwise, various complex forms of the supermolecular structure breaking up first, while the body remains outwardly intact. This process of decay will be more or less profound depending on the conditions of deformation. Eventually, it will result in complete amorphization of the formerly crystalline body, that is, in destruction of the highest forms of ordering, which are not characteristic of amorphous polymeric bodies. This will occur only after drastic breakup of the supermolecular structure.

Breakup of the supermolecular structure as a result of deformation is accompanied by the simultaneous formation of new supermolecular structural elements compatible with the conditions of deformation. Therefore a crystalline polymeric body may become amorphous during deformation if crystallization is too slow (32,33), but may remain crystalline, although with structural elements of other types or other arrangements, if crystallization occurs rapidly.

The presence of the simplest forms of supermolecular structure in amorphous polymers is responsible for the fact that similar, although simpler, stepwise changes are observed in them during deformations. The principal types of structure in this connection are globules containing one or several coiled macromolecules, and fibrils.

On aggregating, the globules form complex clusters (eg, in silicon and fluorinated rubbers (83–85), as well as in different glassy polymers (86)), whereas fibrils give various dendritic forms, sometimes of surprising size and regularity (87).

The presence in polymeric bodies of a complex supermolecular structure consisting of particles of different sizes and structures and capable of developing and decaying stepwise, and the ability of its component particles to change into one another, make it necessary to regard polymeric bodies as extremely heterogeneous; their mechanical properties are governed not only by the chemical composition and length of the macromolecules, but by the macroscopic characteristics of the supermolecular structure of the body as well. Naturally, such characteristics as the particle size of the different types of elements of the supermolecular structure, their quantitative ratio, the deformability and strength of these structural elements, their cohesion with one another, etc, become very important.

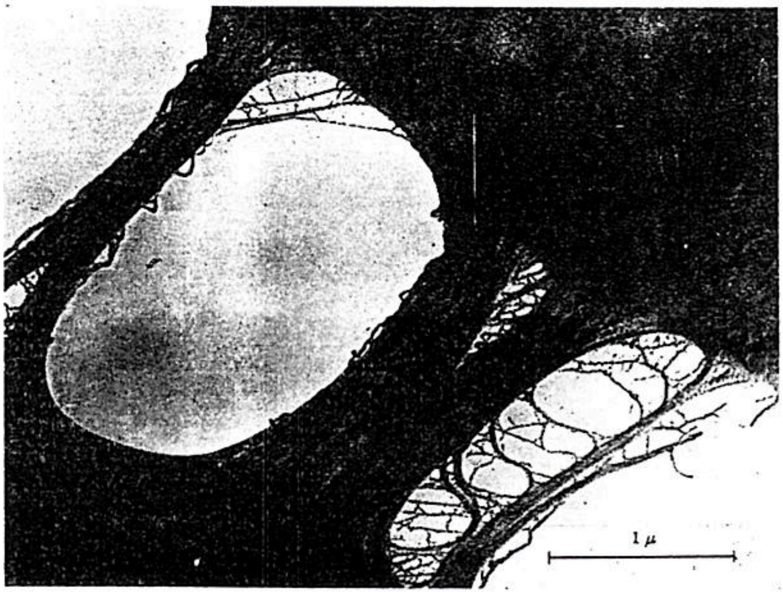


Fig. 42. Neck in polyethylene (120).

Unfortunately, so far, there are no more or less distinct quantitative data in this important and very young branch of the structural mechanics of polymers. Data are being accumulated concerning the forms of supermolecular structures, the dependence of the appearance and disintegration of their various forms on external conditions, the influence of the size and structural type on the elasticity and strength of polymeric bodies, etc.

Neck Formation. A phenomenon of special interest is neck formation on extension of crystalline polymeric bodies. Discovered in the 1930s (88), this phenomenon clearly could not be explained on the basis of the early simple concepts of the structure of polymeric bodies. Only the advent of the concept of supermolecular structure made it possible to discover the nature of the neck and to elucidate a number of features of the relations between structure and mechanical properties, which are peculiar to polymers only.

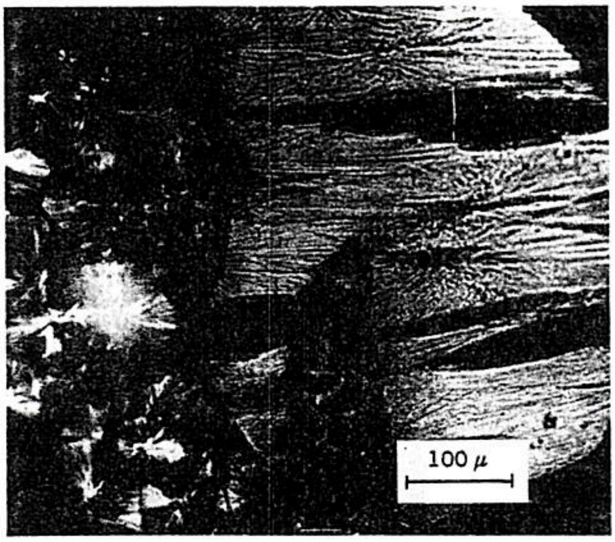


Fig. 43. Neck in polypropylene (92).

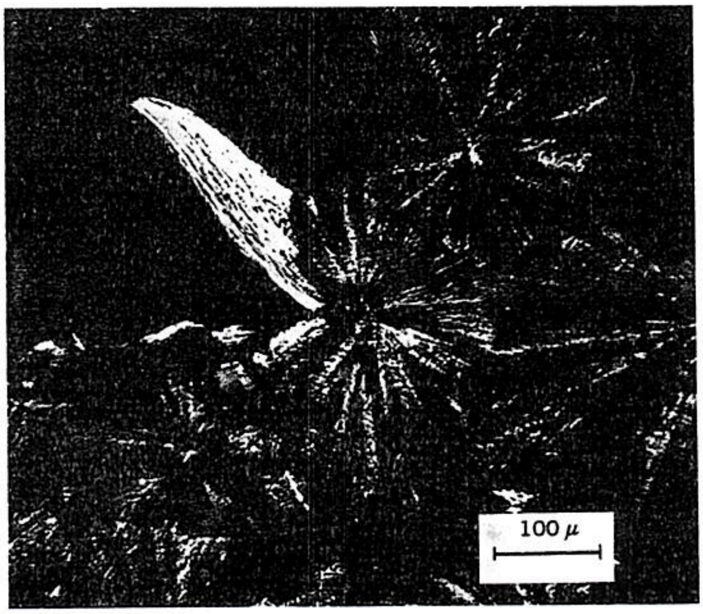


Fig. 44. Microneck in polypropylene (119).

The formation and development of the neck was described briefly in discussing the general mechanical properties of crystalline and glassy polymers (see p. 463). The structural changes occurring in the neck and their influence on the mechanical properties of polymeric bodies can now be examined in greater detail in the light of the above review of supermolecular structure.

Figures 42 and 43 illustrate neck appearance in polyethylene and in polypropylene. The abrupt change in structure and the transition from the nonoriented to the oriented state can be seen readily. It should be pointed out that cases have been observed where crystalline specimens undergo considerable deformation with no visible neck formation. However, even in these cases, microscopic investigations reveal micronecks (Fig. 44), indicating that the transition to the oriented state is always discontinuous in nature even though it may be imperceptible macroscopically.

That orientation occurs abruptly during neck formation is supported by x-ray diffraction data. Figure 45 is the stress–strain diagram of a crystalline polymer specimen, showing a general view of the specimen at various stages of extension and the corresponding schematic x-ray powder patterns. It can distinctly be seen that the specimen passes suddenly from the isotropic to the anisotropic (oriented) state at the moment of neck formation.

This sharp transition is typical of highly crystalline polymers which alter their mechanical properties as a result of a transition. At the initial stage of deformation the polymer behaves like an elastic solid (high values of elastic moduli; reversible and small deformations). At stresses below recrystallization stresses such polymeric bodies are suitable materials for use in rigid constructions. Their properties are characterized by their recrystallization stress values and elasticity moduli (at definite loading rates and temperatures).

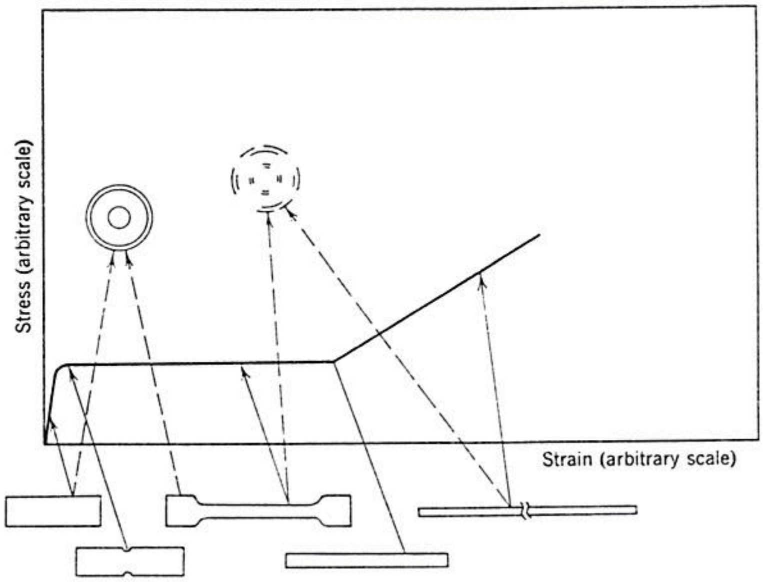


Fig. 45. Stress–strain diagram of a crystalline polymer, showing appearance of specimen and corresponding Debye powder patterns.

When the recrystallization stress is reached the polymeric body does not fail, but forms a neck. The ensuing very large deformations, irreversible at temperatures below the melting region of the polymer, and the appearance of anisotropy in the extended part of the polymeric body substantially alter the possibilities of usage of such materials.

During the transition to the oriented state strength anisotropy appears: the material is found to be much stronger in the direction of extension. This increases the resistance to crack development and brittle failure, owing to the appearance of a neck, ie, a strengthened section, at the points of stress concentration, eg, at the apex of the notch or crack, which stops the development of the defect. This is the reason for the high resistance of many crystalline polymeric films to tearing, and of massive articles, to impact.

The characteristic set of properties related to neck formation is naturally displayed within a definite temperature interval (see Fig. 17) bounded below by the appearance of brittleness and above by melting of the polymer.

Thus, neck formation is of great practical importance and has therefore drawn the attention of investigators for some time. Characteristic features of neck development greatly resemble those of a phase transition: (a) the appearance of two regions with sharply differing properties (one isotropic, the other anisotropic) and a distinct boundary line; (b) the discontinuous nature of the change; (c) preservation of the properties of each of the regions throughout the entire transition, which occurs at a constant stress value and alters the quantitative ratio between the isotropic and anisotropic regions. For these reasons it was assumed that the mechanical stress caused the isotropic crystalline polymer to melt, and the melt to become oriented and crystallize in the orientated state. This reflected amorphization of crystalline polymers on extension in cases where crystallization took place very slowly. The formation of a second neck on extension of an already formed neck at right angles to the first extension was understood similarly. (The oriented crystalline polymer melts on extension at right angles to the direction of orientation; the melt reorients and then recrystallizes in the direction of action of the forces.)

However, neck formation can be observed in glassy polymers, in which such recrystallization was considered impossible, as well as in crystalline polymers.

This shows that neck formation should embrace a wider sphere of structural transformations than the transformations due to recrystallization in the usual sense of the word, ie, destruction and restoration of the crystal lattice in microcrystals. The discovery of supermolecular structures in crystalline and amorphous polymeric bodies made it possible to disclose the nature of these structural transformations; besides ordinary recrystallization, they also included various steplike discontinuous transformations of different supermolecular structures into one another.

Special attention should be drawn to the fact that owing to the extreme structural heterogeneity of polymeric bodies due to their supermolecular structure, and to the multiplicity of structural transformations occurring in them, thermodynamic concepts must be applied to such systems with great care (89,90). If the main features of a first-order phase transition can be noticed at the level of crystallization of macromolecular packets possessing a crystal lattice, on passing over to larger and more complex crystal formations the distinct nature of the phase transition gradually disappears in the polymeric body and transitions appear which are characteristic of colloidal systems, in which surface phenomena play the predominant role. Therefore, such notions as phase, phase transition, and, in particular, crystallization, melting, and recrystallization, require certain modifications when applied to polymers. In passing, it may be noted in connection with the existence of supermolecular structures in amorphous polymers that the concept "amorphous" also loses its initial meaning.

Thus, neck formation is a vivid illustration of the exceedingly diverse ability of polymeric bodies to change their structure and properties under external mechanical influences. It is remarkable that the processes of structure formation in polymers are so developed that in some cases extension results not only in breakup of the structural elements into smaller ones, but simultaneously in growth of some of the structural elements, for instance, the spherulites (91,92). It is quite evident that when deformation is accompanied by profound structural transformations the polymeric body possesses a different structure at the moment of its failure than it had in its initial state. Since the entire complex of mechanical properties is related to the structure of the body, no direct relationship can exist between the properties of the polymer at large deformations and its initial structure. This is one of the characteristics distinguishing polymeric bodies from other solids.

Range of Structural Changes. Naturally, the above discussion refers to temperatures at which mobility of the structure is possible owing to molecular motion. At very low temperatures, when such mobility is out of the question, mobility of another type may appear. An example is the slow deformation of polypropylene with well-formed large spherulites at temperatures down to that of liquid nitrogen (93) (see also CRYOGENIC PROPERTIES). The large deformations occurring in this case may be due simply to displacement of comparatively large supermolecular formations, fibrils in this case, without any change in internal structure. (Evidence of this is the fact that x-ray powder patterns of such specimens remain unchanged even though the latter are extended to an extent of 100–120%.) The deformation of the material is connected with the displacement of large unchanging structural blocks which remain isotropic during the deformation.

Thus, during the deformation of polymeric bodies two extreme types of phenomena can be distinguished. One is the rubbery deformation of elastomers whose supermolecular structure is the least pronounced, and whose mechanical properties therefore depend most heavily on the properties of the flexible macromolecules themselves. The other extreme case is the deformation of crystalline polymers at very low temperatures when the mechanical properties depend only on the displacements of the large elements of the supermolecular structure. In the latter case, the polymeric body approaches metallic bodies in behavior, though it preserves a number of specific features (for example, its characteristic fibrillar structure due to the chain structure of its macromolecules).

All other manifestations of mechanical properties related to changes in macromolecular conformation, reconstitution of all types of supermolecular structure, and deformation of the structural elements themselves, lie between these two extremes (92,94,95).

Basic Structural Forms. The great diversity and mobility of structural forms in polymeric bodies makes it necessary to develop the taxonomy of these forms and the corresponding terminology (nonexistent as yet) and to establish the relationships between the main types of structures and the corresponding mechanical properties.

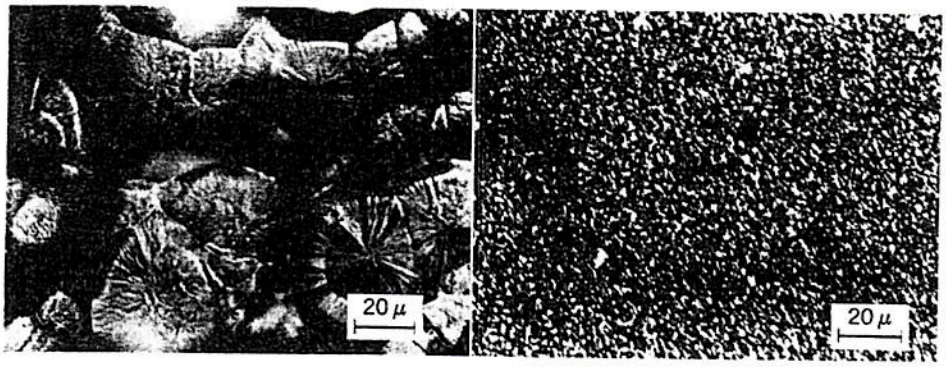
Although very little has been done so far in this field, some basic structural types can already be outlined and the most important mechanical properties of polymeric bodies can be related to them.

The simplest type of supermolecular structure is the *globular* type. Any polymer whose macromolecules are sufficiently flexible can be obtained in a globular structure which will be stable or unstable depending on the temperature. Polymeric amorphous bodies possessing globular structure lose all characteristic features that can be traced to the flexibility of their macromolecules (provided, of course, their globules do not straighten during deformation); they prove to be brittle, solid materials (eg, phenol-formaldehyde resins) or very weak rubbers (in this case, however, the globules may uncoil partly). But if deformation involves a structure transformation, the globular structure changing, for example, to a fibrillar one, the complex of mechanical properties also improves substantially.

Thus, when considering the influence of the structure of polymeric bodies on their mechanical properties two cases should always be distinguished: either the structure is preserved until the body fails completely, or structural transformations occur during the deformation.

Another characteristic type of supermolecular structure is the *fibrillar* type. Polymeric bodies with fibrillar structure are always more deformable and stronger than polymeric bodies of the same composition and molecular build, but of globular structure (86). In the case of crystallizing polymers of fibrillar structure a large number of more complex structural forms appear with corresponding complexes of properties (see also FIBERS).

The next type of supermolecular formations is the *lamellar* type. As in the case of the fibrillar type sheets aggregate into a diversity of more complex structural forms. Polymers of sheet structure also possess a better complex of properties than do polymers of globular structure.



(a) (b)

Fig. 46. Effect of adding artificial nucleating agents to a polymer on its supermolecular structure: (**a**) polypropylene without nucleating agents; (**b**) polypropylene with 1% indigo (29,98).

Finally, it will be useful to discuss in greater detail the most common type of supermolecular structure in crystalline polymers, the *spherulite* type.

The smaller the spherulite, the more uniformly are the mechanical stresses distributed, and the more the behavior of the polymeric body approaches that of a homogeneous body. This is why such bodies can withstand fairly high stresses before they fail, and develop a neck, ie. change their spherulitic isotropic structure into an oriented anisotropic structure. For this reason, specimens of such bodies fail at larger ultimate elongations and under considerable stresses.

But if the spherulites are large, interfaces appear between them, which may be as large as cracks. Here, failure develops readily and the body suffers brittle rupture at small elongations and comparatively low stresses. (Of importance in the origin of mechanical properties are not only the size of the spherulites, but also their inner structure and the presence of coexisting structural formations. This accounts for the numerous exceptions to this rule.) Therefore, spherulite growth, which may occur during storage or usage of polymer articles, is very dangerous to the stability of property values.

There are a number of methods of preventing these phenomena, consisting of inhibiting the growth of large structural formations, both during the manufacture of the article and during its storage and use.

Among these methods are the introduction of small amounts of foreign particles which actively influence structure formation (29, 96–98), the introduction of surface-active substances (99), and chemical modifications of the macromolecules, in particular, grafting of other polymers (100,101).

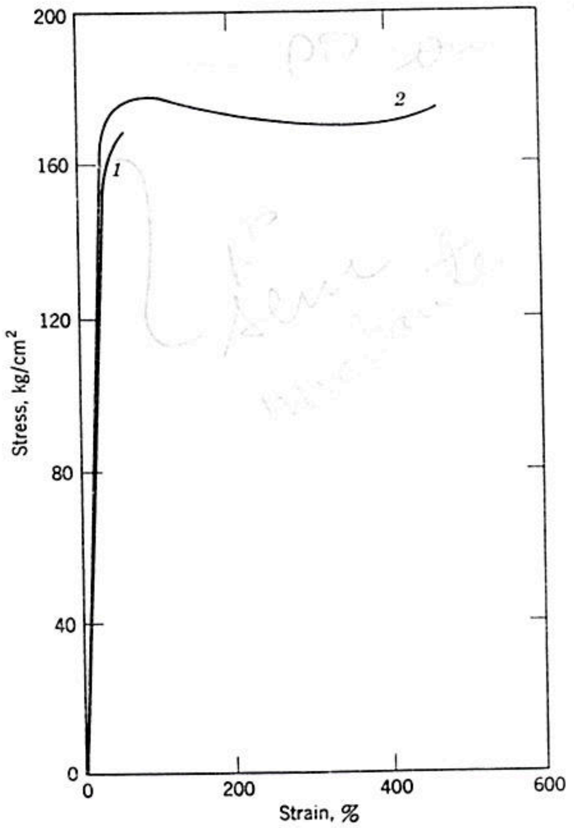


Fig. 47. Stress–strain diagram of the specimens from Figures 46a and 46b (curves *1* and *2*, respectively) (29,98).

To exemplify the influence of artificial nucleating agents on the crystallization of polymers, photomicrographs of various structures of a polymer obtained in the presence and in the absence of nucleating agents are given in Figure 46, and the corresponding stress–strain diagrams in Figure 47 (29,98). It can readily be seen that the introduction of nucleating agents substantially changes the supermolecular structure of the polymer, making it finer and accordingly improving the mechanical properties of the polymer. It should also be pointed out that the presence of nucleating agents has an important influence on the stability of the resulting supermolecular structures. Though remelted repeatedly, the type of supermolecular structure of such a polymer remains almost unchanged, whereas without nucleating agents remelting of the polymer coarsens its structure (Fig. 48) (98).

(a) (b) (c) (d)

Fig. 48. Effect of adding nucleating agents on the stability of the supermolecular structure in remelting crystalline polypropylene: (**a**) initial crystalline polypropylene; (**b**) the same polypropylene as in (**a**) but remelted three times at 210°C; (**c**) polypropylene crystallized in the presence of 1% of finely dispersed indigo particles; (**d**) the same polypropylene as in (**c**) but remelted three times at 210°C (98).

In concluding the discussion of the supermolecular structure of polymers and its influence on their mechanical properties it should be pointed out that during the past decade concepts of the structure of polymeric bodies have been extended considerably. It is now obvious that the entire diversity of mechanical properties of various classes of polymers cannot be described and predicted only on the basis of the crude ideas of polymers as amorphous (rubbery, glassy, and viscofluid) homogeneous bodies, or as two-phase amorphocrystalline bodies. The entire diversity of forms of supermolecular structure observed in polymeric bodies must be taken into account; polymers must be regarded as heterogeneous bodies whose properties are determined by the characteristics of their supermolecular structure and its transformations during deformation, rather than only by the flexibility and molecular weight of their macromolecules.

Mechanochemical Phenomena and Related Mechanical Properties

Besides structural transformations due to changes in mutual arrangement of flexible macromolecules there is an extensive range of structural changes which are due to chemical transformations of macromolecules. These changes in the structure of a polymeric body may naturally have a substantial effect on its mechanical properties. For example, as a result of various oxidative processes, the development of which may be accelerated perceptibly by the action of light, heat, ozone, etc, a polymer may lose its initial set of properties entirely and become quite useless. The occurrence of other chemical reactions resulting in degradation, in crosslinking, or in a change in chemical structure will have similar consequences. All the phenomena mentioned, known as aging of polymers, can be retarded by means of various small additions of substances which inhibit these processes, and more or less improve the efficiency of the polymeric articles (see also DEGRADATION).

It should be noted that such processes of chemical change of macromolecules may be sensitive to mechanical stresses. For example, stretched elastomers age at a rate different from that of unstretched elastomers. This is due to the fact that mechanically stressed valence bonds react more readily with oxygen or ozone than do unstressed bonds, ie, the mechanical stress lowers the energy of activation of these oxidative processes (102,103). Therefore chemical processes altering the structure of macromolecules, which do not occur in a polymer in the absence of mechanical influences, may become perceptible in stressed polymeric bodies.

It is natural to call chemical processes initiated by mechanical influences mechanochemical processes. They should not be confused with mechanochemical phenomena (110) that are changes in mechanical properties due to changes in the chemical properties of the environment of the polymeric body, eg, the reversible contraction and elongation of certain polymeric fibers due to changes in pH of the medium. It would be more correct to call the latter "chemomechanical" phenomena.

The effect of mechanical stresses on the chemical structure of a polymer has also proved very important in the case where no chemical changes of the macromolecules occur at all at first glance (104–109). It has been shown that rupture of macromolecules at a chemical bond, eg, at a C–C bond, may be due not only to the action of quanta of sufficiently powerful radiations, chemically active atoms, etc, but also to deformation.

As a result of such a purely mechanical rupture of a bond, free macroradicals appear possessing very high chemical activity and capable of initiating various chain processes, the nature of which depends naturally on the chemical structure and composition of the polymeric substance.

Thus, mechanical action causes chemical changes in the polymeric substances, notably degradation of macromolecules, appearance or enhancement of macromolecular branching, crosslinking, etc.

Fatigue. It is quite clear that such changes in structure should exert a perceptible influence on mechanical properties, this being displayed as a number of effects.

These include fatiguing of polymeric bodies due to repeated deformations, since a polymer is capable of withstanding a large number of deformation cycles without any perceptible change in mechanical properties, but fails suddenly at the end. It is quite obvious that each deformation cycle should cause certain practically imperceptible changes in structure, because if this were not so the condition of the polymeric body would not differ in any way from its initial state after any number of deformation cycles, and no failure would occur. It would seem that the accumulation of barely perceptible structural changes should result in a gradual change in the properties of the body, including its mechanical properties. However, it has been found that in many cases such changes hardly occur, and even the fragments of the broken body possess almost the same mechanical characteristics except for one, namely, the ability to resist repeated deformations. Such fragments can withstand fewer deformation cycles than the initial body, ie, their endurance is lower.

The explanation of the mechanism of fatiguing of polymeric bodies follows from an examination of mechanochemical phenomena (104–106,109). A certain number of macromolecules are ruptured during each deformation cycle; the macroradicals formed perish on interacting with the molecules of the inhibitors always present in any polymer, as well as on interacting with one another, or for other reasons. Therefore, the mechanical ruptures of macromolecules during the first cycles of deformation do not result in the development of chain processes and do not essentially change the structure of the polymer. However, as time passes, and the deformation cycles are repeated again and again, the inhibiting substances are gradually exhausted. Since the number of ruptures of macromolecules depends on the stress values, ie, on the amplitude of deformation, the inhibitors will be entirely exhausted sooner or later in some region which has been subject to greater mechanical action owing to the nonuniform distribution of stresses, or is impoverished in inhibiting substances owing to their nonuniform distribution: the newly formed free macroradicals then prove capable of initiating chemical chain processes. This results very quickly in an essentially local change of structure and a corresponding change in mechanical properties. The consequent heterogeneity of structure and properties of the polymeric body easily leads to the formation of a microcrack.

The microcrack grows rapidly (owing to the overstresses at its edges) and ends in breakage of the repeatedly deformed body. The structure and properties of the resulting fragments differ little from those of the initial body, but they contain fewer inhibiting substances, ie, their fatigue resistance is lower.

Thus, the mechanochemical nature of fatiguing of polymers should be taken into account when manufacturing articles intended for operation under prolonged cyclic mechanical influences. The polymer fashioned into such articles should contain as large quantities as possible of substances inhibiting chain processes, and the articles should be designed with allowance for maximum reduction of the stresses arising in them.

Chemical Flow. Another very important example of a mechanochemical process is chemical flow (111–113). At sufficiently high shear stresses and simultaneous volume compression, fluidity may develop in a polymer which is ordinarily incapable of flowing, eg, in a spatially crosslinked polymeric body. Chemical flow is due to mechanical breakup of the macromolecular spatial network into free macroradicals capable of being displaced. If the stresses are applied quickly, as by impact, the resulting macromolecular fragments can shift under the action of the same stresses and react with one another in their new positions, combining into a new spatially crosslinked system, not differing in structure, on the average, from the initial one, but resulting in a different external shape of the body (see also IMPACT RESISTANCE). Naturally, the more difficult is the ordinary flow due to displacement of the macromolecules, the more pronounced the chemical flow will be. It is thus the only possible kind of flow for spatially crosslinked polymers, although it may also occur in linear polymers, especially at low temperatures and under drastic conditions of treatment.

Polymer Processing. The mechanochemical processes occurring during the manufacturing of polymers into articles must be taken into account. On the one

hand, the consumption of inhibiting substances due to the formation of free ma
cals may be so considerable that their quantity is insufficient to protect the article properly from aging or to impart to it the necessary resistance to repe
formations. On the other hand, the formation of free macroradicals during processing makes the polymer chemically active and may result in a change in its chemical structure, and hence in its mechanical properties. In particular, the well-known method of obtaining block copolymers by mechanical action of a mixture of two polymers or a polymer and a monomer (114) is based precisely on the possibility of initiating chemical reactions by applying strong mechanical forces to the polymer (see also BLOCK AND GRAFT COPOLYMERS).

Strength and Life Time. The substantial influence of mechanochemical phenomena on mechanical properties of polymers shows that it is fundamentally necessary to take into account the chemical properties of the polymer when discussing the mechanical properties of polymeric bodies.

An especially important mechanical property is strength. It was thought formerly that there exists a definite critical stress value (eg, on uniaxial tension) at which the deformed body instantaneously breaks. Many handbooks give the strength values of different materials determined in one way or another (see TEST METHODS). However, it appears that failure of a body is not an instantaneous act, but a complex process which develops in time (115–118) (see also FRACTURE). It was found, moreover, that a definite rate of the failure process corresponds to each stress value, and therefore breakage of the body will occur after a definite time at any given constant stress value. Thus, no critical stress value can be indicated separating smaller stresses at which the body does not fail from larger ones at which the body fails instantaneously. Instead of the strength expressed as the value of such a nonexistent, as it turns out, critical stress, it is necessary to indicate the "life time," ie, the length of time during which a body kept at a constant stress will remain intact. Naturally, such a stressed body will exhibit creep, ie, will gradually become longer (see also p. 471). This involves complex processes of rearrangement of the various levels of the supermolecular structure of the body, and mechanochemical processes as well. In the end failure occurs.

As a result of detailed investigations of the life time, $\tau(\sigma,T)$, at various stresses, σ, and temperatures, it was established (115–117) that the following relationship exists, applicable to all polymeric solids

$$\tau(\sigma,T) = \tau_0 e^{(U_0-\gamma\sigma)/RT} \qquad (\sigma = \text{const}) \qquad (52)$$

where T is absolute temperature, R is the gas constant, and U_0, γ, and τ_0 are constants.

Table 1. Activation Energies of Degradation Processes

Polymer	U_0,[a] kcal/mole	E,[b] kcal/mole
poly(vinyl chloride)	35	32
polystyrene	54	55
poly(methyl methacrylate)	54	52–53
polypropylene	56	55–58
polytetrafluoroethylene	75	76–80
nylon-6	45	43

[a] From mechanical data.
[b] From thermal degradation data.