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Keratin
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MECHANICAL PROPERTIES

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This article deals with the mechanical properties of plastics, raw and cured elastomers, polymeric fibers and films, and other materials made of polymers. Mechanical properties are the totality of properties determining the response of bodies to external mechanical influences, manifested in the ability of the bodies to develop reversible and irreversible deformations and to resist failure.

The basic characteristics of the mechanical properties of solids are usually determined by tests resulting in various deformation-vs-stress dependencies, such as stress–strain diagrams. Examination of such dependencies readily brings out characteristics of elasticity, plasticity, and strength (expressed as elasticity modulus, limit of proportionality, elastic limit, ultimate strength, resistance to failure, etc). The mechanical properties of liquids are assessed by studying the dependence of the rate of strain on the stress applied. One of the most common mechanical characteristics determined in this way is viscosity.

However, all these characteristics are insufficient to describe polymeric bodies owing to the specific mechanical properties peculiar to these materials. The most important of these properties are: (a) highly pronounced mechanical relaxation processes (stress relaxation, creep, hysteresis, etc), owing to which the mechanical properties of polymers depend strongly on the temperature; (b) ability to develop enormous reversible deformations (that caused by axial tension, for instance, may be as high as several hundred percent), this ability being the most pronounced in elastomers; (c) intimate connection between mechanical and chemical processes, which affect each other substantially.

Closely related discussions are to be found under ABRASION RESISTANCE; DEFORMATION; FRACTURE; HARDNESS; IMPACT RESISTANCE; REINFORCEMENT; TEST METHODS; VISCOELASTICITY. See also ANNEALING; CRYSTALLINITY; MORPHOLOGY; ORIENTATION. Values of properties of individual polymers are listed in their respective articles; see also BLOCK AND GRAFT COPOLYMERS; ELASTOMERS, SYNTHETIC; FIBERS; POLYBLENDS.

Thermomechanical Characteristics of Polymers in Different Physical States

To bring out the peculiar features of the mechanical properties of polymers it is necessary to study, apart from stress–strain diagrams (or diagrams of stress vs deformation rate in the case of liquids), the temperature dependence of the strains or stresses arising under given conditions of mechanical influence. Indeed, even stress–strain diagrams should be determined for various temperatures, covering as wide a range as possible.

The study of the temperature dependencies of the mechanical properties of polymers makes it possible to outline a number of physical states which differ substan-

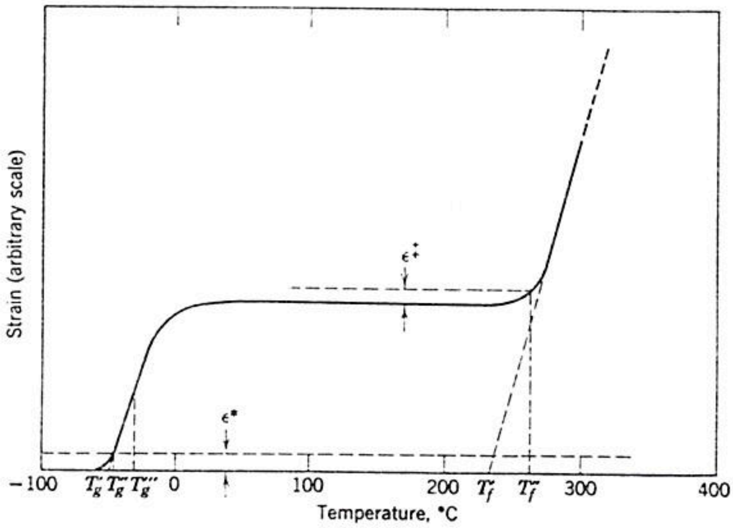

Fig. 1. Thermomechanical curve of a linear amorphous polymer. Stress and duration of application of stress are constant. Symbols are discussed in the text.

tially from one another in mechanical characteristics. It will therefore be useful to begin by discussing these states.

Polymers may be in the amorphous or in the crystalline state. Examples of amorphous polymers are polyisobutylene, uncured and cured elastomers under ordinary conditions, atactic poly(methyl methacrylate), atactic polystyrene and other glassy polymers. and very viscous polymeric resins. Examples of crystalline polymers are polyethylene, isotactic polypropylene, gutta percha, and polyamides and polyesters with regular structure, eg, nylon or poly(ethylene terephthalate).

Despite the pronounced diversity of mechanical properties of these and other polymeric bodies, they readily lend themselves to classification. The thermomechanical method of investigation (1,2) is especially convenient for this purpose.

This method consists essentially of determining the temperature dependence of the deformation caused by the action of a constant stress under given temperature–time conditions. The usual practice is to measure, every 3–5 min, the axial compression strain caused by a practically constant axial compressing stress acting for a short period (eg, 10 sec); the measurement is carried out with uniformly rising temperature (1–3°/min) beginning at a sufficiently low temperature of about −150°C and going up to a temperature of about 300–400°C or more, if necessary. The results of these measurements are then plotted as deformation-vs-temperature graphs known as thermomechanical curves. Some characteristic types of thermomechanical curves are shown in Figures 1–3.

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A related approach is offered by dynamic mechanical testing over a temperature range; this is discussed in the article on TEST METHODS.

Amorphous Polymers. The thermomechanical curve in Figure 1 is typical of a linear polymer which is amorphous at all temperatures, such as polyisobutylene. In this case the thermomechanical curve gives an idea of the temperature regions wherein the amorphous polymer exists in the glassy, rubbery (highly elastic), and viscofluid states. The glassy state corresponds to the low-temperature region to the left of the first rise on the thermomechanical curve. At these temperatures the deformability of the body is so low that on the scale used the curve merges completely with the abscissa axis. The rubbery state occupies the temperature region between the first and second rises of the thermomechanical curve. At these temperatures the polymer can develop high reversible deformations which reach their limit (under the given conditions of force action) at a distinct plateau. The viscofluid state exists in the temperature region to the right of the almost horizontal plateau up to the temperature of thermal degradation of the polymer. The characteristic feature of the viscofluid state is the development of indefinitely high irreversible deformations.

Attention should be drawn to the fact that no definite temperatures can be named for the transitions from one state to another. This is because the different physical states of amorphous polymers are due to differences in the mobilities both of the macromolecules as a whole and of their segments, which are capable of moving relative to one another in consequence of the flexibility of chain macromolecules. In the glassy state neither the macromolecules nor their segments can alter their relative arrangement under the action of thermal movement alone. (The energy of interaction of the segments, and, even more so, of the macromolecules, is much higher than the energy of thermal movement.) In the rubbery state the energy of thermal movement becomes sufficient to overcome the forces of interaction between segments, but is too low to overcome the interaction between macromolecules as a whole. Therefore, individual segments are displaced and the coiled macromolecules are able to straighten out under the action of external forces and coil up again under the action of their thermal movement after the external forces are removed. These changes in conformations of the macromolecules are observed as the large reversible (highly elastic) deformations characteristic of rubbery polymers (rubberlike elasticity). Naturally, a definite period of time is required for such deformations to develop, and the more intense the thermal movement, ie, the higher the temperature, the shorter is this time period. Since each point of the thermomechanical curve represents the same force acting through the same duration of time, the deformation increases with the temperature and reaches a maximum at the beginning of the plateau at which the temperature is so high that the deformation can develop fully in the course of the time interval accepted as standard for the measurement in question.

In principle, it may be expected that irreversible displacement of macromolecules also occurs in the rubbery state as a result of random movement of their segments under the action of the axial stress. However, owing to the very great length of the macromolecules, irreversible deformations occur practically only at the higher temperatures corresponding to the second rise of the thermomechanical curve. Therefore, in the viscofluid state both the segments and the macromolecules as a whole are displaced, resulting in the simultaneous development of irreversible and reversible deformations manifested as the rubber elasticity of the fluid polymer flow (3,4). This very essential feature of the mechanical properties of liquid polymers (melts and solutions) determines a number of important effects (see also FLOW BIREFRINGENCE; MELT VISCOSITY; SOLUTION PROPERTIES) and is responsible for the great ability of polymers to form fibers and films under isothermal conditions.

Thus, the three physical states of amorphous linear polymers, registered distinctly by means of thermomechanical curves, characterize the internal mobility of polymeric bodies, which increases continuously with rising temperatures. It is clear that the transitions from one of these states to another have nothing in common with phase

glassy
rubbery state
viscofluid

transitions, which involve a discontinuity in properties. That is why transition temperature ranges are observed rather than transition temperatures. It must be noted at this point that the widespread opinion regarding the transition from the glassy to the rubbery state as a "second-order phase transition" (5) is erroneous because it is not a thermodynamic transition.

Transition Temperatures. It follows, moreover, from the above considerations that the location of the region of transition from the glassy into the rubbery state (and from the rubbery to the viscofluid state) on the temperature axis depends on the duration of time of stress selected as standard for the measurements. Obviously, the longer the stress acts, the larger will be the deformation developed, and the lower the temperature region in which the transition occurs. Thus, transitions from one state to another are pronouncedly kinetic in nature. It should be pointed out that temperature regions of transitions from one physical state to another are usually about 20 or 30°C wide, but in the case of polymers with sufficiently rigid macromolecules they may sometimes expand to hundreds of degrees (see also FRACTURE).

These important transitions came to be characterized by the *glass-transition* and *flow temperatures*, which are rather conventional values. Unfortunately, so far no one has drawn attention to the desirability of simultaneously characterizing the width of the transition region. The values accepted as the glass-transition temperature, T_g, and the flow temperature, T_f, are temperatures lying within the corresponding transition range and determined by some stipulated principle. For example, a tangent may be drawn to the ascending branch of the curve in the region of the transition from one state to the other, as is shown by the sloping dashed lines in Figure 1. The temperatures corresponding to the intersection of these lines with the abscissa axis (T_g' and T_f') are considered the glass-transition and the flow temperatures. However, other procedures of determining these conventional temperatures are in use: A certain deformation value, ϵ^*, as small as possible, but easily determined, is selected; the temperature at which the deformation on the thermomechanical curve reaches the selected value is then considered the glass-transition temperature. (In Figure 1 this corresponds to the intersection between the lower horizontal dashed line and the thermomechanical curve at the temperature T_g''.) This temperature is analogous to the "heat distortion temperature" (5a) but differs from it in being measured under other conditions, primarily under other time conditions. Likewise, the flow temperature is determined as the temperature at which the thermomechanical curve rises above its plateau by a deformation value of $\epsilon^{\ddagger}$. (In Figure 1 this temperature corresponds to the intersection between the upper horizontal line and the thermomechanical curve at the point on the abscissa T_f''.) There are other procedures of determining conventional transition temperatures, one of which is estimation of the glass-transition temperature by the point of inflection of the thermomechanical curve (T_g'''). The glass-transition temperature may also be determined as the point at which the thermal expansion coefficient undergoes a discontinuity (5b). See also GLASS TRANSITION.

When considering published values of flow and glass-transition temperatures for various polymers it is always necessary to take into account the convention adopted by the author in defining these points, and the time conditions of the measurements, as these factors may affect the resulting transition temperature values substantially. Unfortunately, in many cases, no attention is paid to this in either thermomechanical or other methods of measurement, and therefore glass-transition and flow temperature

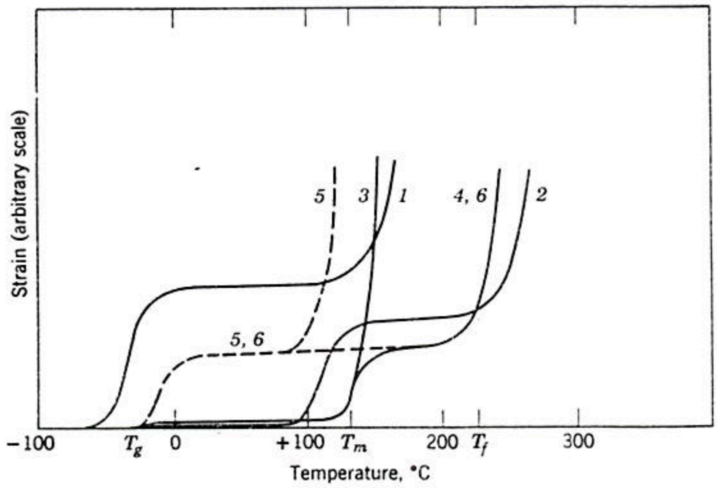

Fig. 2. Thermomechanical curves of various types of polymers: *1* and *2*, amorphous polymers; *3* and *4*, crystalline polymers; *5* and *6*, supercooled crystalline polymers.

data given in publications are, as a rule, of no definite sense and can therefore be used only conventionally.

Types of Curves. Reverting to a consideration of types of thermomechanical curves, Figure 2 will be seen to contain four such curves for amorphous and crystalline polymers. Curves *1* and *2* are typical of linear amorphous polymers, but differ substantially in arrangement on the temperature scale. An examination of these curves reveals that the region of the rubbery state of the polymer corresponding to curve *1* covers the entire range of low and slightly elevated temperatures usually encountered, whereas the polymer corresponding to curve *2* is in the glassy state at those temperatures. Therefore, a mere glance at these thermomechanical curves is enough to conclude that curve *1* belongs to a typical elastomer, whereas curve *2* is that of a polymer which can be used as a hard plastic. Such an appraisal is especially important in the synthesis of new polymers, when it is essential to determine at once the possibilities of application of a newly obtained polymer. Naturally, the final decision as to the applicability of such a polymer can be made only after a comprehensive study of all its mechanical, physical, and technological properties. However, the thermomechanical appraisal immediately makes it possible to outline the minimum of further investigations necessary.

Attention should be drawn to the fact that in the case of an elastomer the glass-transition temperature determines the temperature region below which the polymer cannot (under the system of influences in question) display elastomeric properties. Thus, in this case, the glass-transition temperature can serve as a criterion of the cold resistance of a rubberlike polymer. On the other hand, the glass-transition temperature of an amorphous polymer which is a solid at ordinary temperatures determines the temperature region above which the polymer softens: in the case of such a polymer the glass-transition temperature is a criterion of its heat resistance. It follows from this that the cold resistance or heat resistance of a polymer has no absolute value but depends on the conditions of deformation. Thus, rubber, which deforms quite readily at a certain low temperature when the deformations are slow (eg, during the operation of a conveyor belt), will be found to be very rigid and even brittle at the same temperature if the deformations are rapid (eg, during the operation of a very cold tire which has not had time to warm up). The same may be said of the behavior of hard plastics. With more rapid deformations the plastic will be more heat resistant. Hence, thermomechanical curves, usually obtained under conditions of sufficiently prolonged (~10 sec) stress action, characterize cold resistance and heat resistance for low deformation rates, ie, the lowest values of these resistances.

Crystalline Polymers. The thermomechanical curves of crystalline polymers may now be considered. Figure 2 contains two such curves. Curve *3* corresponds to a crystalline polymer with a melting point of T_m; this polymer gives a viscous melt above this temperature. The effect of this on the thermomechanical curve is that it rises abruptly immediately after melting. Curve *4* gives an idea of a polymer which becomes a rubbery amorphous polymer after melting, causing the appearance on the thermomechanical curve of a second almost horizontal plateau which starts just above the melting point and ends when fluidity appears, ie, in the region characterized by the flow temperature, T_f.

At temperatures below the melting point, T_m, the thermomechanical curve of the crystalline polymer has a relatively unsharp transition to a still harder state when cooled below the temperature marked T_g. This transition corresponds to a glass transition of the unordered regions present in any crystalline polymer. The less completely the polymer is crystallized, the higher the thermomechanical curve rises in the temperature interval between T_g and T_m. Naturally, if a molten polymer is cooled rapidly to the glassy state it will change into a rubbery body when reheated to a temperature T_g. The subsequent behavior of such a polymer specimen depends on the rate of its crystallization (see KINETICS OF CRYSTALLIZATION). If the polymer crystallizes so slowly that the entire thermomechanical curve up to its flow temperature can be obtained without any signs of crystallization appearing, such a supercooled polymer will not differ in any way from an amorphous polymer and its thermomechanical curve will be typical of such polymers. It will display a transition from the glassy to the rubbery state in the region of T_g, coinciding with the transition of the same polymer in the crystalline state, and a transition to the viscofluid state in the region of T_f. However, two alternatives are possible in the latter case: $T_f < T_m$ (curve *5*)

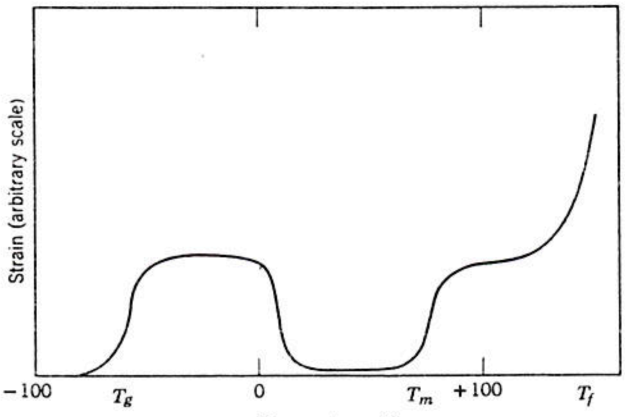

Fig. 3. Thermomechanical curve of a supercooled polymer rapidly crystallizing on heating

and $T_f > T_m$ (curve *6*). Curve *5* depicts the behavior of a supercooled polymer which has a thermomechanical curve like curve *3* in the crystalline state. Curve *6* corresponds to a supercooled polymer with a thermomechanical curve like curve *4* in the crystalline state. This correspondence is quite understandable, because in the former case melting of the crystalline polymer results in an amorphous polymer at a temperature above its flow temperature and, therefore, in the viscofluid state. In the second case, melting of the crystalline polymer results in an amorphous polymer below its flow temperature and, therefore, in the rubbery state.

However, if the rate of crystallization of the supercooled polymer when heated becomes sufficiently high, the supercooled polymer may begin to crystallize at a certain temperature and will crystallize out completely while the thermomechanical curve is being obtained. In this case, its rigidity begins to rise as it crystallizes and the thermomechanical curve acquires the shape shown in Figure 3. Naturally, the faster crystallization develops and the slower the specimen is heated during the thermomechanical measurements, the lower will be the temperature range wherein deformation decreases with rising temperature. The extent to which the thermomechanical curve drops will naturally be the greater, the more completely crystallization develops.

Thermal Degradation. Besides the glass-transition, flow, and melting temperatures, there are other important temperature characteristics which should be included in a general discussion of the mechanical properties of polymers over a wide range of temperatures. Two especially important ones are the brittle temperature (qv), or brittle point, T_b, and the thermal degradation temperature, T_d. Since brittleness is the property causing bodies to break at small deformations, questions relating to this property will be discussed together with the strength characteristics of polymers (p. 446). Regarding thermal degradation, it may be noted that the decomposition or chemical change of macromolecules alters the main properties of the polymeric body. Therefore the temperature of thermal degradation is always the upper boundary of the temperature range wherein the polymer exists and displays any particular sets of mechanical properties. In thermomechanical investigations of polymers, thermal degradation causes either (a) a sharp rise on the thermomechanical curve, owing to

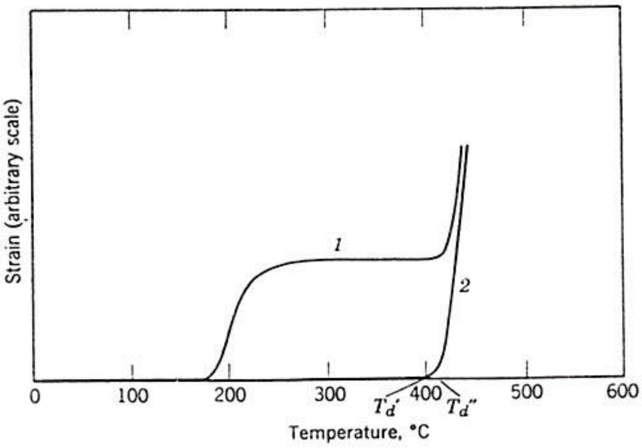

Fig. 4. Thermomechanical curves of polymers which degrade on heating; *1*, polymer with $T_f > T_d > T_g$ and T_d shown by T_d'; *2*, polymer with $T_d < T_g$ and T_d shown by T_d''.

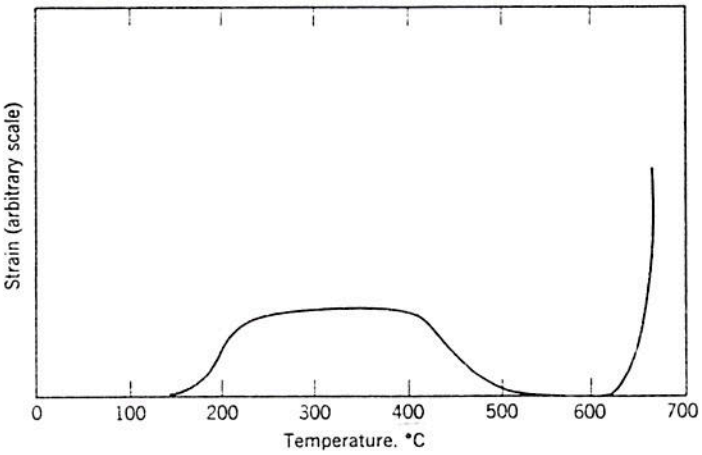

Fig. 5. Thermomechanical curve of a polymer which becomes crosslinked on heating.

decomposition of the macromolecules into low-molecular-weight substances, resulting in liquids of low viscosity or even in gaseous products (Fig. 4), or (b) a decrease or complete loss of deformability, owing to crosslinking and the attendant loss of molecular mobility. Figure 5 is a typical thermomechanical curve of a polymer which becomes crosslinked on heating. At temperatures above 400°C the polymer begins to change chemically, forming a harder body, which is manifested by the negative slope of the curve. Then at temperatures of about 600°C the macromolecules decompose and the body softens or even changes into a mixture of liquid and gaseous decomposition products: the thermomechanical curve sweeps upward, registering a rise in mobility of the body structure. See also DEGRADATION.

The sensitivity of thermomechanical curves to all changes in mobility of the structural elements of a body is of great importance in investigating any physical or chemical processes affecting the hardness of a polymeric body. One of the important applications of the thermomechanical method is the study of the thermal stability of polymers at high temperatures (6). Since any chemical reaction resulting in decomposition of macromolecules increases the deformability of the polymeric body, the corresponding thermomechanical curve will show a greater or smaller rise. On the other hand, for reactions resulting in crosslinking, ie, increasing the hardness of the polymer, the thermomechanical curve will show a decrease in deformability, ie, will descend. Curve *1* in Figure 6 shows the thermomechanical curve of an amorphous stabilized polymer which passes from the glassy to the rubbery state at about 130°C and to the viscofluid state at about 350°C. Curve *2* of the same figure represents the results of thermomechanical measurements of the same polymer without stabilizers. In this case the polymer begins to change chemically on passing into the viscofluid state. As the temperature rises, different chemical reactions develop in the polymer, as a result of which its hardness increases and decreases irregularly until the polymer reaches a temperature at which it decomposes completely. This is reflected in the complex shape of the thermomechanical curve, which shows a number of rises and falls; by studying this curve some characteristics of the reactions can be ascertained.

The thermomechanical method of estimating thermal stability has another advantage; besides characterizing the behavior of the polymer prior to its chemical

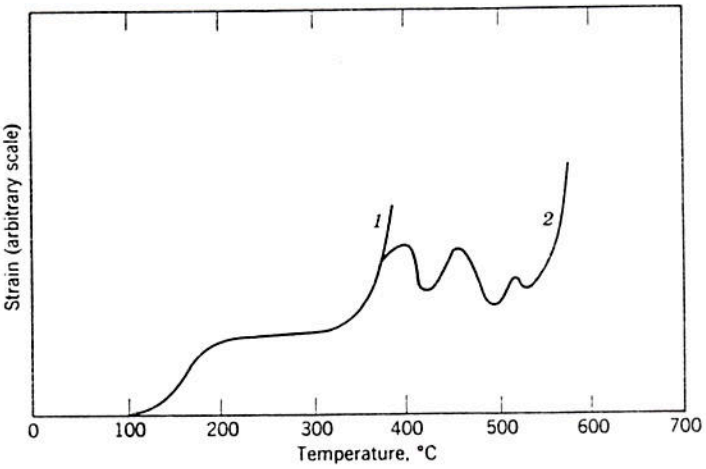

Fig. 6. Thermomechanical curves of stabilized (*1*) and unstabilized (*2*) polymer.

changes, it makes possible an estimate of the behavior of the polymer during its manufacture into finished articles by methods requiring transference of the polymer to the viscofluid state (casting (qv), molding (qv), etc). An examination of the thermomechanical curve immediately reveals the temperature to which the polymer can be heated without undergoing chemical change and makes it possible to see whether the polymer is stabilized.

It should be noted that far from all linear amorphous polymers are capable of existing in three physical states. If the flow temperature is so high that thermal degradation of the polymer occurs before fluidity is reached, the polymer will have glassy and rubbery states but will exhibit no viscofluid state owing to decomposition of its macromolecules. A pertinent thermomechanical curve is shown in Figure 4 (curve *1*, degradation temperature T_d'). But if the glass-transition temperature is very high, which may be the case with rigid macromolecules and macromolecules which interact strongly with each other, the polymer can exist only in the glassy state at all temperatures below T_d. The thermomechanical curve of such a polymer, which is a solid right up to the decomposition temperature T_d'', is represented by curve *2* in Figure 4.

Effects of Molecular Weight. It is quite obviously very important to know the dependence of the glass-transition and flow temperatures on the molecular characteristics and various other factors. It is therefore appropriate to discuss the most important dependencies of T_g and T_f on the molecular weight of the polymer and on the content of plasticizer in the polymer.

The molecular-weight dependence of a number of amorphous polymer homologs is illustrated by Figure 7. The lowest members of the series exhibit no rubbery state at all, passing from the glassy directly into the viscofluid state. These are the low-molecular-weight members of the series. Beginning from some given molecular weight, characteristic for each homologous series of polymers (ie, a series of monodisperse polymers differing only in degree of polymerization), a horizontal plateau appears on the thermomechanical curve, the length of which on the temperature scale is determined by the interval $T_f - T_g$. When this rubbery-state region appears, a substantial change occurs in the dependence of the glass-transition temperature on

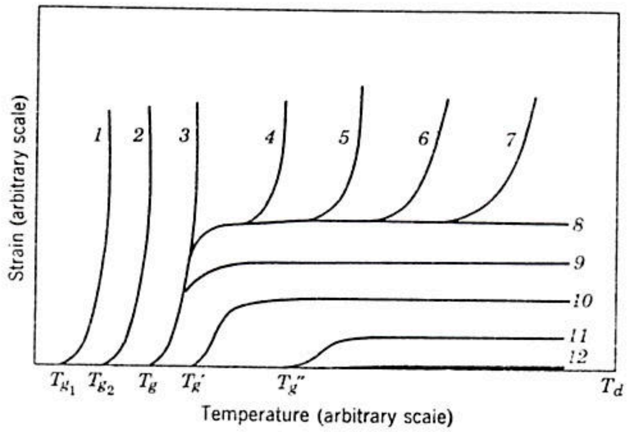

Fig. 7. Dependence of the shape of the thermomechanical curve on the molecular weight (for polymer homologs, curves *1–7*) and on the degree of spatial crosslinking (curves *8–12*).

the molecular weight. For the low-molecular-weight members of the series that are incapable of displaying rubbery properties, the glass-transition temperature rises with increasing molecular weight, owing to the increase in the energy of interaction of the molecule in question with its neighbors as it grows in size. The higher the interaction energy, the greater must also be the energy of thermal movement of the molecules required to overcome the interaction forces and to displace the molecules. Therefore, the higher the molecular weight of the molecules, the higher the temperatures at which they exhibit mobility.

However, as the length of linear macromolecules grows, the nature of their thermal movement changes. As soon as they reach a length sufficient for them to display flexibility, their thermal movement begins to take the form of shifts of separate sections of the flexible macromolecules, and rubberlike elasticity appears. Since the thermal energy required for the displacement of such sections is the same, independent of the total length of the macromolecules, the appearance of rubberlike elasticity corresponds to the temperature at which the thermal energy is sufficient to displace such segments. This signifies that the transition from the glassy to the rubbery state always occurs in the same temperature range, ie, the glass-transition temperature becomes independent of the molecular weight (curves *3–7* in Fig. 7). Naturally, the location of this temperature on the temperature scale depends on the energy of interaction of the segments, ie, on their composition and length. It should be pointed out that in the case of polymers based on monomers with the same empirical composition, the segment length may differ if the flexibility of the macromolecules is different. (This accounts for the difference in glass-transition temperatures of polymers of isomeric monomers, eg, poly(methyl methacrylate) and poly(ethyl acrylate), poly(methyl acrylate) and poly(vinyl acetate), etc.)

The flow temperature has a different dependence on the molecular weight. For the low-molecular-weight members of a series, T_f is always close to the glass-transition temperature (because softening immediately results in fluidity), and increases with T_g as the molecular weight rises (curves *1–3* in Fig. 7). The appearance of rubberlike elasticity does not affect this dependence. The appearance of fluidity means that the macromolecules have begun to be displaced as a whole. The longer the macromolecule, the more difficult it is to displace it and the higher the flow temperature. Indeed, the longer the molecule, the larger the number of segment displacements that have to be accomplished to displace a flexible macromolecule. Therefore, to obtain a displacement equal to that obtained with shorter macromolecules during a given time of action of a constant stress, a more intensive thermal movement is required.

Thus, the rubbery state appears as a result of the divergence of the dependencies of the flow temperature and glass-transition temperature on the molecular weight, owing to the flexibility of the macromolecules.

The flow temperature is dependent on the molecular weight of homologous polymers but the glass-transition temperature is independent of it; this makes it possible to determine the molecular weight of polymers by the thermomechanical method (1,2,7–11), by using equation 41, given on p. 488. An advantage of this method worth stressing is that it makes possible determination of the molecular weight without dissolving the polymer. However, it is necessary for the polymer to be capable of flowing, ie, for it to be linear and for the condition $T_f < T_d$ to be observed.

Now let us consider the influence of increase of the molecular weight on the values of T_g and T_f when continuous, spatially crosslinked polymeric bodies are formed. In regard to T_f, it may immediately be noted that crosslinked systems are incapable of flowing and therefore no fluidity is observed in them (see p. 508) up to their decomposition temperature (curves *8–12* in Fig. 7). The effect of crosslinking on the glass-transition temperature, T_g, is somewhat more complex. At degrees of crosslinking that are not very high and when the macromolecular sections between crosslinked points (ie, between their nodes) are large relative to the size of the macromolecular segments, T_g does not change, but the height of the rubbery plateau begins to decrease (curves *8* and *9* in Fig. 7). This reflects the gradual increase in rigidity of the system as crosslinking progresses. Further increase of the degree of crosslinking brings the distances between nodes close to the size of a segment. As a result, the segments lose their independence of movement, and have to move in groups, which requires a larger amount of thermal energy. Therefore the glass-transition temperature begins to rise, and the height of the plateau continues to decrease (curves *10* and *11* in Fig. 7). Finally, at a very high degree of crosslinking, when no movement of the segments relative to one another is possible, the thermomechanical curve comes very close to the temperature axis (curve *12* in Fig. 7); this corresponds to complete solidification of the polymer at all temperatures right up to that of thermal degradation. In this case, the glass-transition temperature becomes higher than the degradation temperature and cannot be determined.

Effects of Plasticizer. At this point it is appropriate to consider how plasticization of polymers, ie, the addition of low-molecular-weight substances to a polymer, affects the thermomechanical curve.

If the plasticizer is soluble in the polymer and forms a solution, then, obviously, the more plasticizer is added to the polymer the lower should be the viscosity of the plasticized polymer. This means that both T_g and T_f should decrease. At the same time, owing to the decrease in the number of macromolecules contained in a unit volume, the hardness of the polymer should also decrease. As is evident from Figure 8 all these effects actually occur. With the addition of more and more plasticizer, T_g and T_f decline and the plateau on the thermomechanical curve rises. At high plasticizer contents the solution of the plasticizer in the polymer changes into a solu-

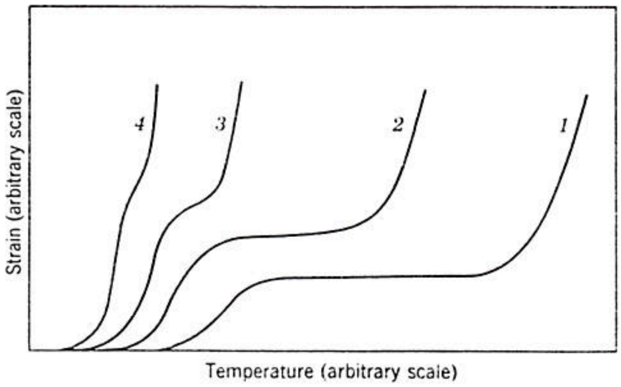

Fig. 8. Effect of plasticizing a polymer with flexible macromolecules on the shape of its thermomechanical curve (content of plasticizer increases with ascending numbers of the curves).

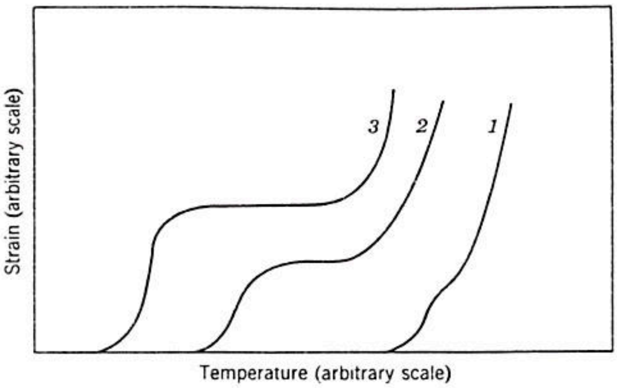

Fig. 9. Effect, on the shape of the thermomechanical curve, of plasticizing a polymer with rigid macromolecules which soften on interacting with the plasticizer (content of plasticizer increases with ascending numbers of the curves).

tion of the polymer in the plasticizer, this being reflected in a gradual shortening of the plateau and its complete disappearance on passing over to a dilute solution of the polymer.

Such a picture of the change in thermomechanical properties of a polymer is characteristic of polymers with flexible macromolecules that possess a rubbery state. In the case of polymers consisting of rigid macromolecules the behavior becomes much more complex. Here, only the important case will be considered where the addition of a low-molecular-weight substance to such a polymer causes a change in the flexibility of its macromolecules as a result of the change in nature of the molecular interactions.

Softening of the polymer as more and more plasticizer is added results in the appearance of a rubbery state if the polymer had none before (or in expansion of the temperature region of this state if it was not very pronounced in the polymer to begin with), ie, in a considerable lowering of T_g and a less considerable lowering of T_f with a simultaneous decrease in the hardness of the body (Fig. 9). Later, when the macromolecules become soft, increasing the plasticizer content has an effect similar to its action on polymers with flexible macromolecules.

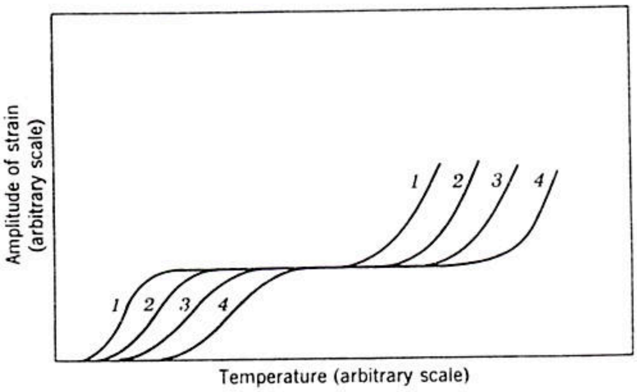

Fig. 10. Temperature dependence of the amplitude of deformation under sinusoidal stresses of different frequencies (frequency increases with ascending numbers of the curves); stress amplitude is constant.

Frequency–Temperature Studies. The thermomechanical method of polymer investigation has found wide usage for primary assessment of newly synthesized polymers, for investigating processes affecting the mobility of the structural elements of a polymeric body, for controlling polymer quality, etc. However, it should be pointed out that instead of the temperature dependence of the deformation at a constant stress, some authors (12,13) consider the temperature dependence of the modulus of elasticity determined under preset time conditions of stress action. Obviously, both dependencies are quite equivalent.

Of great importance are the conditions of action of the forces on the polymer sample. As has already been said, the faster the action, the less deformation has time to develop and the higher the temperatures of transition of the polymer from one physical state into another. The thermomechanical method which uses constant stresses acting over periods of a few seconds to a few tens of seconds cannot be employed for determining the deformation properties of polymers under rapidly recurring influences which last for small fractions of a second. Meanwhile, many engineering applications of polymers (for example, in automobile and aircraft tires) require knowledge of the mechanical properties of polymers under stresses alternating at frequencies on the order of from 1 to 10,000 cycles/min. For this reason study of frequency–temperature behavior (14,15) has found application alongside the thermomechanical method.

The frequency–temperature method is based on obtaining the temperature dependence of the amplitude of strain during a steady process of deformation under the action of a sinusoidal mechanical stress of given amplitude. As a rule, these dependencies are obtained for several frequencies. Figure 10 is a schematic representation of a family of such dependence graphs. It is evident from the figure that increasing the frequency shifts the curve toward higher temperatures. Conventional values of T_g and T_f can be indicated, corresponding to each frequency. The data obtained by the frequency–temperature studies also make it possible to consider the dependence of the amplitude of strain on the stress frequency at constant temperature. Figure 11 shows the corresponding family of curves, an examination of which reveals that the effective stiffness of the polymer increases with increasing frequency. Figures 10 and 11 show vividly that the effects of rate of action (measured by the frequency) and temperature on the strain amplitude can completely compensate one another.

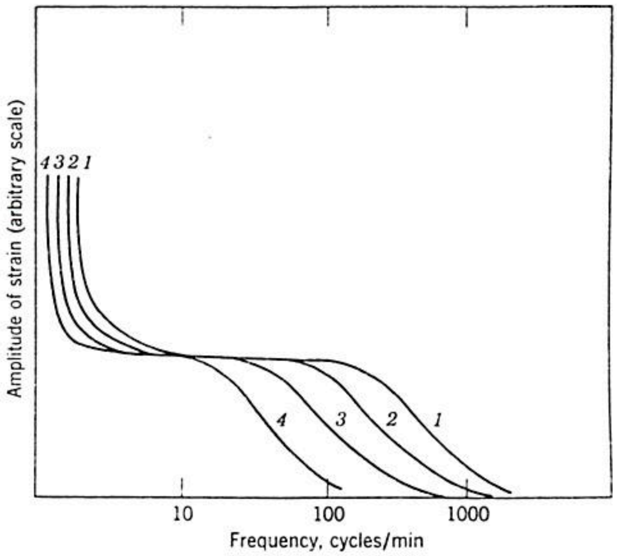

Fig. 11. Dependence of strain amplitude on frequency of a sinusoidal stress at different temperatures (temperature decreases with ascending numbers of the curves); stress amplitude is constant.

Attention was drawn to this fact as long ago as 1937–1939 (12,14,15) and correctly interpreted at that time as a consequence of the kinetic nature of the deformation of a polymeric body. Indeed, for the segments of macromolecules to be displaced enough to result in a rubbery deformation, and for irreversible displacements of the macromolecule as a whole to occur in the case of viscous flow of the polymer, a definite length of time is required. The higher the temperature, the smaller is this time period. Therefore, the same regrouping of structural elements of a polymeric body can be accomplished either during a longer time period at a lower temperature, or during a shorter time at an elevated temperature. Outwardly this is manifested as the possibility of obtaining the same strain value at corresponding pairs of values of time of stress action (or frequency) and temperature. Figure 12 demonstrates how the same

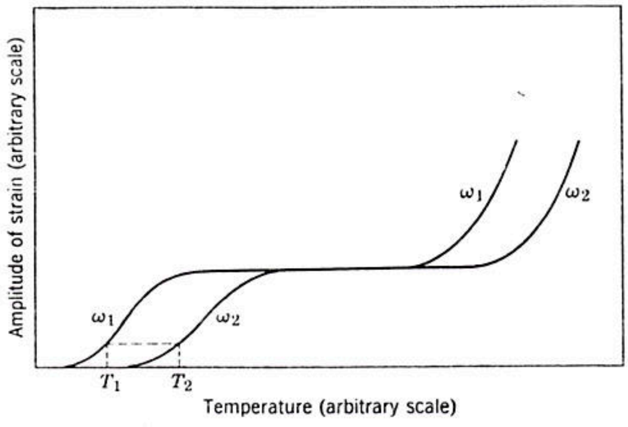

Fig. 12. Equivalent effects of frequency, ω, and temperature on deformation.

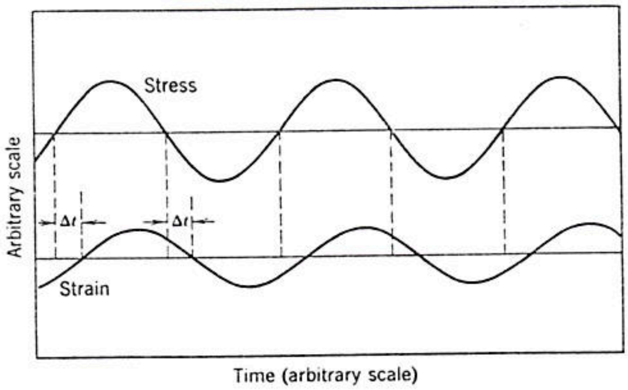

Fig. 13. Phase shift $\Delta\varphi$ between stress and strain: $\Delta\varphi = \omega\Delta t$, where ω is circular frequency and t is time.

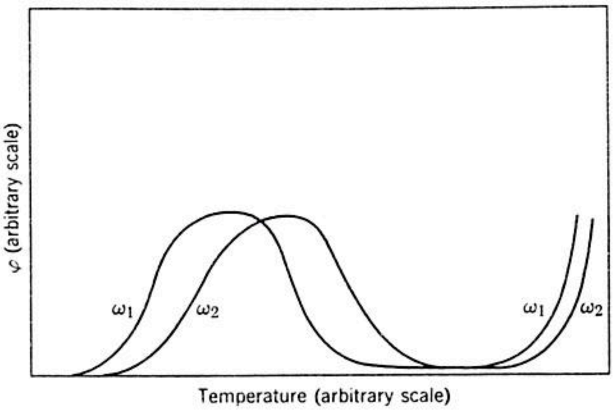

Fig. 14. Dependence of the angle of phase shifts between stress and strain on temperature ($\omega_1 < \omega_2$).

deformation amplitude is obtained at a temperature of T_1 and a frequency of ω_1 as at the temperature T_2 and the frequency ω_2.

Owing to this interchangeability of the influence of temperature and of frequency, measurements of the deformation properties of polymers obtained in different frequency and temperature regions become compatible, and characteristics obtained at one set of frequency and temperature values can be recalculated for other frequencies and temperatures.

Calculations of this kind have been practiced extensively in recent years, and the corresponding principle has become known as the *time–temperature superposition principle* (16,17).

The consequence of the lag of deformation behind stress is that these two values, while varying sinusoidally, are shifted in phase with respect to one another (Fig. 13). This phase shift determines the value of the mechanical losses characterizing heat generation in the deforming polymer due to the thermodynamic irreversibility of the mechanical deformations. For this reason, the temperature and frequency dependencies of the phase shift angle between stress and strain are measured along with the temperature and frequency dependencies of the modulus of elasticity (18–20). Figure 14 shows this dependence of phase shift in the form of curves with maxima in the regions of transition of the polymer from one state to another. It will easily be appreciated that such dependencies make possible an estimate of the glass-transition and flow temperatures, as well as their dependence on the frequency.

Stress–Strain Diagrams

The discussion so far has referred to the temperature dependence of the mechanical properties of polymers exhibited during small deformations due to constant or intermittent stresses. Also of major importance, however, are the mechanical properties of polymers in the case of large tensile strains. Stress–strain dependencies under conditions of isothermal extension are usually studied on various types of tensile testing machines (see TEST METHODS). However, for such measurements of the dependence of the mechanical properties of polymers on the time and temperature of stress, either the rate of application of the force or the rate of deformation (depending on the type of test) must also be indicated, and tests must be performed within as wide a range of temperatures as possible. Only then will the data obtained yield an insight into the physical nature of the specific mechanical properties of the polymers and a correct estimate of the efficiency of the polymeric products for the particular conditions of their usage.

Therefore, it is necessary to consider the relationship between the stresses and strains obtained at various temperatures under conditions of axial tension at a constant rate. The corresponding families of curves for amorphous and crystalline polymers are shown in Figures 15 and 17.

When discussing stress–strain relationships it must be agreed beforehand to which cross-sectional area of the specimen the force acting on that cross section will be referred. Owing to the very high values of the strains actually obtained when elastomeric, crystalline, and glassy polymers are extended, the cross-sectional area of the strained specimen may vary severalfold. For this reason two values are ordinarily considered, namely, the actual stress and the nominal stress. The former is the quotient of the applied force divided by the actual cross-sectional area, and the latter, divided by the cross-sectional area of the original specimen.

The stress–strain dependencies of polymers are complex. It can be seen from Figures 15 and 17 that these dependencies are not linear in nature, and therefore Hooke's law is, generally speaking, inapplicable to polymers. However, at temperatures below T_g and at deformations that are not very large the stress–strain curves (curves *1–4* in Figs. 15 and 17) approach straight lines, giving the impression that under such conditions polymeric bodies obey Hooke's Law. Nevertheless, the dependence of the mechanical properties of polymers on the time conditions of force action must not be forgotten. If the slopes of such linear stress–strain dependencies are measured, ie, their Young's moduli are determined, it is found that they are the larger, the higher the rate of extension of the sample. Only at very low temperatures, ie, far below the glass-transition temperature, can the rate of deformation be neglected and such a polymeric body be considered a quasi-Hookean solid (curves *1* and *2* in Figs. 15 and 17).

At temperatures above T_f the stress–strain dependence of amorphous linear polymers at first glance also tends to linearity. However, here the curve, on rectifying, approaches the strain rather than the stress axis, as is the case when the temperature is lowered. This is due to the fact that as the temperature rises the polymer passes into the viscofluid state, ie, irreversible deformations begin to develop. Accordingly, the stress–strain dependence comes closer and closer (curve *9* in Fig. 15) to the dependence characteristic of viscous liquids, ie, to Newton's viscosity law. Naturally, the lower the rate of extension, the smaller the resulting stress.

Amorphous Polymers. At temperatures between T_g and T_f the stress–strain dependence curve for an amorphous polymer is S shaped (curves *6–8* in Fig. 15), corresponding to the appearance of a rubbery state. At these temperatures and at a given rate of extension, rubbery strains develop, caused by straightening of the flexible macromolecules. As a result of the development of these strains the value of the stress required to cause the deformation reached by a given moment of time decreases, and therefore the curve bends toward the strain axis. On further extension, when the macromolecules have practically exhausted their capacity for straightening, ie, when the rubbery strain reaches values close to the maximum possible, the mechanism of deformation changes; further extension occurs only by extension of the straightened macromolecules, and this requires very large stresses. That is why the curve passes through a point of inflection and bends sharply upward, ending at the point corresponding to failure of the extended polymer specimen.

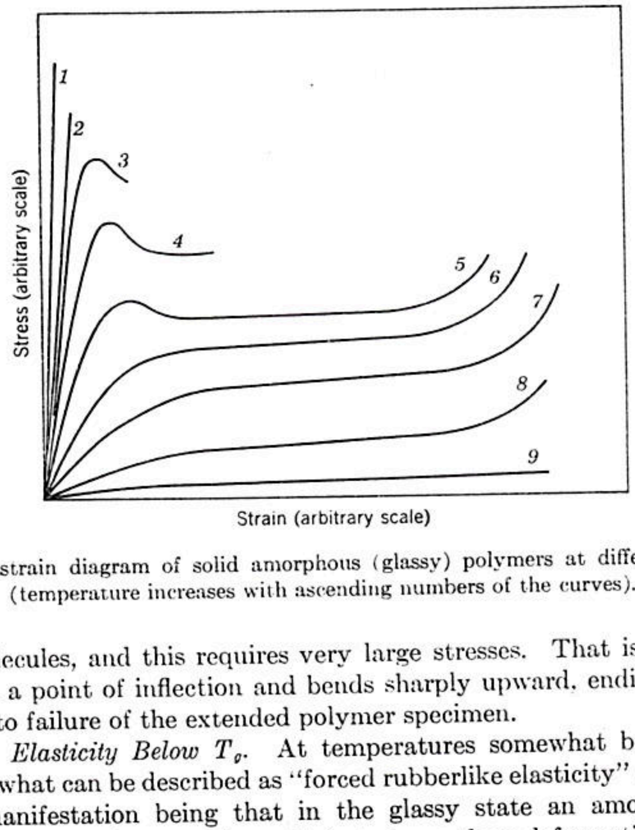

Fig. 15. Stress-strain diagram of solid amorphous (glassy) polymers at different temperatures (temperature increases with ascending numbers of the curves).

Rubberlike Elasticity Below T_g. At temperatures somewhat below T_g (curves *3–5* in Fig. 15) what can be described as "forced rubberlike elasticity" (21–24) appears, its outward manifestation being that in the glassy state an amorphous polymer becomes capable of very large strains. At first glance these deformations seem mainly residual, because after the extending forces have ceased to act the specimen contracts only to the extent of the strain corresponding to the ascending portions of the stress–strain curve. However, they are of the same nature as the rubbery deformation, ie, are due to straightening of the coiled macromolecules. This is demonstrated by the fact that when such a polymeric body, first extended and then freed from the action of the external forces, is heated, it regains its initial shape as soon as the temperature reaches values above T_g, ie, as soon as the flexible macromolecules become sufficiently mobile.

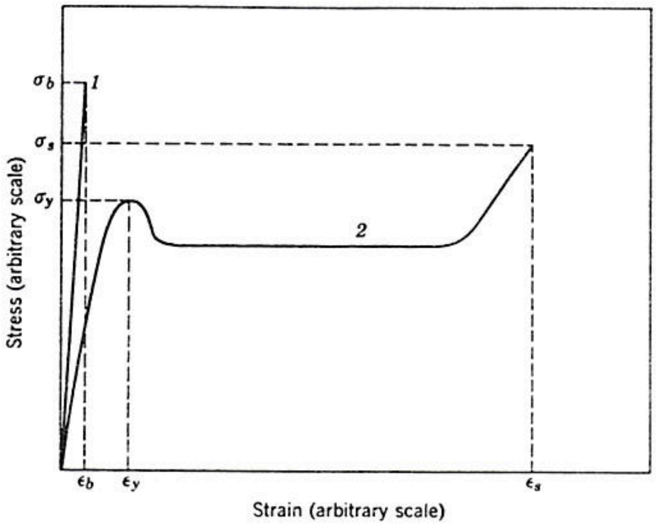

Fig. 16. Stress–strain diagrams of a polymer at brittle failure (*1*), and on development of forced rubbery deformation before breakdown (*2*). Symbols are discussed in the text.

The development of forced rubberlike elasticity (forced high elasticity) possesses several characteristic features. It can be seen from curves *3–5* in Figure 15 that during extension, almost direct proportionality is at first observed between stress and strain. However, subsequently, a small maximum appears at not very large strains but at fairly high stresses, following which the curve runs almost parallel to the strain axis. After a certain strain value is reached (the horizontal section corresponding to the development of "forced rubbery deformation" is usually several hundred percent long), the curve sweeps sharply upward and ends at the point where the specimen fails.

As the temperature decreases, the horizontal section of the curve rises, and the entire stress–strain curve becomes gradually shorter (curves *3* and *4*), ie, the lower the temperature, the smaller the deformations at which failure occurs. Finally the specimen fails at the very first section of the stress–strain curve with very small deformations, ie, brittle failure occurs.

Figure 16 shows two stress–strain curves, the first of a glassy polymer displaying forced rubbery deformation (curve *2*) and the second, of one undergoing brittle failure (curve *1*). In the latter case the strength of the polymer can be sufficiently well characterized at the given rate of extension and temperature by indicating the values of the stress and the strain at the moment of brittle failure (σ_b and ϵ_b). In the former case it is important to know two pairs of values: the stress and strain at the moment of failure (σ_s and ϵ_s) and the stress and strain at the moment when forced rubbery deformation begins to develop (σ_y and ϵ_y). The quantity σ_y has become known as the yield stress. Another quantity of interest for characterizing deformability is the length of the horizontal section of the diagram, ie, the region of the forced rubbery deformation. See also FRACTURE.

The appearance of forced rubbery deformation is related to the fact that in the glassy state the mobility of the macromolecular segments is suppressed by the forces of their interaction. For this reason thermal movement by itself is not capable of displacing them and the body remains solid. However, when the body is in a stressed state less energy is required to overcome the forces of interaction, because a part of these forces is compensated by the mechanical stresses tending to extend the body. Therefore, when a sufficiently high stress value has been reached, thermal movement begins to overcome the forces of interaction between the macromolecular segments, and regrouping of the latter becomes possible. Thus, when a stress equal to the yield point is reached, the glassy polymeric body acquires an internal mobility similar to that involved in the rubbery state. Naturally, this results in rubbery deformations. However, after the body has been relieved of the external forces, mobility of the segments again becomes impossible; the reason for this is that now only thermal movement is acting again, and the deformation which has appeared is "frozen" until the body is reheated to a temperature at which the thermal energy is sufficient to move the segments. At this temperature, which is, of course, above T_g, the shape of the specimen is restored.

Necking. Forced rubbery deformation develops in a very characteristic manner. At a certain cross section of the specimen a narrowing suddenly appears, which then grows at the expense of the gradually diminishing initial thick part of the specimen. The formation of such a "neck" corresponds to the transition to the horizontal part of the stress–strain diagram. From this point to the end of the horizontal part of the graph the specimen is nonuniform, because it has a thick and a thin part, ie, cross sections of two different areas, the initial one and that corresponding to the neck, coexist in the specimen. After complete conversion of the specimen into the neck, ie, at the end of the horizontal section, the specimen again becomes uniform and is subsequently extended as a whole. This is accompanied by a sharp rise of the curve, and very soon failure occurs.

Naturally, the development of forced rubbery deformation causes anisotropy in the specimen. If the initial glassy specimen is isotropic, the neck and, hence, the entire specimen at the last stage of the extension process is a highly oriented glassy body (see ORIENTATION), possessing pronounced mechanical, optical, and other kinds of anisotropy. This anisotropy is due to straightening of the macromolecules during the development of forced rubberlike elasticity and remains as long as the forced rubbery deformation attained is preserved. It disappears after the specimen has contracted to its initial size on heating.

A characteristic feature of the rise of forced rubberlike elasticity is the small maximum preceding the horizontal section of the graph. This maximum is the less pronounced, the slower the extension occurs and the more efficiently heat exchange is effected between the specimen and the thermostat during extension. It may be due to disturbance of the isothermal conditions of extension, because at the moment the neck appears the nonuniformity of the deformation causes overheating in the zone of narrowing of the sample, which lowers the stress required for further development of the neck. Other explanations have been offered to account for the appearance of this maximum; one of them concerns a possible drop in stress on appearance of the neck owing to breakdown of the elements of supermolecular structure at sufficiently high stresses, making possible development of larger deformations at lower stresses.

Crystalline Polymers. Stress–strain diagrams of crystalline polymers at different temperatures should now be considered. It is evident from Figure 17 that these dependencies bear a general resemblance to those just considered for glassy polymeric bodies. At very low temperatures crystalline polymers behave like quasi-Hookean solids (curves *1* and *2*); at higher temperatures they become similar to glassy bodies

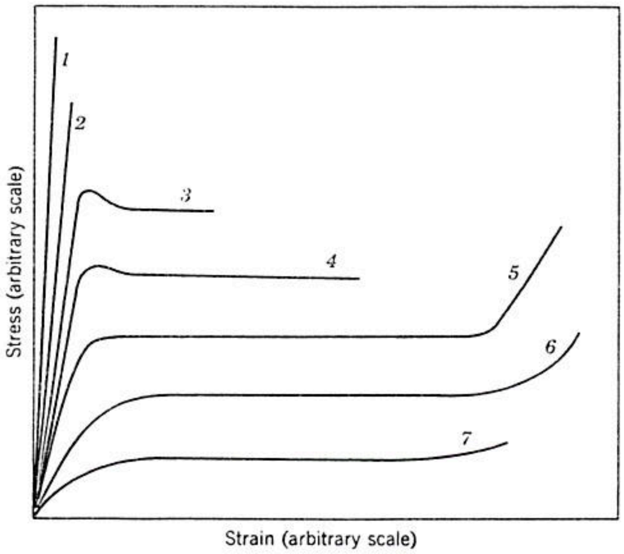

Fig. 17. Stress–strain diagrams of crystalline polymers at different temperatures (temperature increases with ascending numbers of the curves).

capable of forced rubberlike elasticity (curves *3–5*); and at still higher temperatures (below the melting point of the crystalline polymer, however) they approach the behavior of rubbery bodies in regard to the shape of their curves (curves *6* and *7*).

It should be pointed out that on extension of crystalline polymeric bodies neck formation is still more pronounced than that in the case of glassy polymers, and involves all the peculiar features mentioned above. However, when the temperature is lowered, neck development is cut off owing to premature failure, and at a fairly low temperature brittle failure occurs with small strains when the specimen is still quite uniform. On the other hand, if the temperature is raised sufficiently, neck formation becomes less distinct owing to the crystalline specimen becoming progressively amorphous, and the features of deformation of a rubbery body are exhibited more and more strongly: the previously horizontal section of the curve begins to slope, reflecting the growth of the stresses upon extension: the regions of neck appearance and of transition to extension of the fully anisotropic specimen become blurred; the value of the forced rubbery deformation, ie, of the apparent residual deformation, decreases, and the value of the reversible part of the deformation increases; and the stress required to cause large deformations decreases sharply. After the melting point is reached the polymer becomes rubbery or viscofluid, and all effects of crystallinity disappear entirely.

In the temperature range wherein the crystalline polymer possesses pronounced forced rubberlike elasticity its mechanical properties can also be characterized by the yield point and the breaking stress, and by the corresponding strain values, as in the case of glassy polymeric bodies.

However, the mechanism of development of forced rubberlike elasticity in crystalline bodies is of a somewhat different nature. In this case the mobility of the flexible macromolecules is suppressed by the crystalline state of the body, ie, by their ordered arrangement, and they can be regrouped only by rebuilding the crystal structure, ie, 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, ie, 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, ie, 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,