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Molecular Order and Mechanical Properties of Polymer Plastics

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The main difference between polymer materials and low-molecular solids originates in the enormous difference of molecular size and shape in both cases. The linear structure of macromolecules introduces an unusually high degree of anisotropy in mechanical forces. In the amorphous plastics the long chainlike molecules are randomly coiled. Below the glass-transition temperature the chain mobility is so small that the polymer solid is quite rigid and behaves like glass. Above this temperature it exhibits rubberlike elasticity. The elastic forces are a consequence of entropy increase on stretching. Crystals act as permanent cross-links. The larger the ratio of crystals in a polymer plastic, the higher the mechanical strength, but also the greater the brittleness. Therefore a proper equilibrium between crystalline and amorphous areas is needed for obtaining useful properties of material under consideration. In addition, in many cases, particularly in fibers, a high alignment of crystals and of molecular chains in amorphous areas is desirable. This can be achieved by irreversible mechanical deformation (cold-drawing).

THE MAIN DIFFERENCE in properties between low- and high-molecular-weight solids originates in the peculiar chainlike structure of polymer molecules as contrasted with the nearly isometric molecules and atoms in the materials with low molecular weight. In metals, for instance, the cohesion forces between adjacent atoms are nearly isotropic and definitely of short range. As a consequence, crystallization easily proceeds by attachment of new atoms one by one on the surface of the growing crystal. On elastic deformation the potential energy of the crystal lattice increases reversibly as the atoms are displaced from equilibrium positions of local force fields. From knowledge of the interatomic potentials, elastic constants can be calculated. During irreversible plastic deformation a new minimum position is reached after translation by one or more lattice identity periods with practically no force tending to restore the initial position. Since the relevant forces and processes of readjustment are quite local in character, viscoelastic "anomalies" are negligible or of minor importance.

Polymer plastics, as for instance polyethylene or nylon, consist of long chainlike molecules in which the basic monomer unit— C_2H_4 in the case of polyethylene—is repeated many hundreds or thousands of times. The forces between consecutive monomers in the macromolecule are primary chemical forces. Resulting cohesion forces extend over just as long a range

as the geometrical extension of the polymer chain, i.e., over many hundreds or thousands of atomic distances. Intermolecular forces, however, as a rule are van der Waals forces of much lower strength and range. This spectacular anisotropy of the force field is reflected in the geometrical fine structure and hence in the mechanical properties of polymer solids. During any deformation, rearrangements on a local scale are relatively rapid just as in the case of low molecular solids, but very slow on a long-range scale where long sections of macromolecules have to find new equilibrium positions. As a consequence, there is a broad and continuous time scale covering the response of such a system to external stress.

Let us first look at the shape of a single macromolecule. The link between two consecutive monomers, or even smaller chain groups, permits at least partial rotation with respect to each other around the link. As a consequence, the linear macromolecule has no fixed shape. It can assume a nearly infinite number of conformations. The probability of any end-to-end distance is just given by the relative number of conformations having this end-to-end distance. The fully extended chain is very improbable because it can be obtained by only one conformation. If one has fully stretched all the macromolecules (by any means) and not hampered their mobility they will tend to assume more probable configurations, i.e., they will contract very markedly (let us say, by a factor of ten) and by doing so increase the entropy of the system. The corresponding elastic forces are a consequence of, and accompanied by, entropy changes, the energy of the system generally remaining nearly constant. Such forces occur in a polymer system whenever the average chain conformation deviates from the most probable shape. Reversible elastic deformation and stress-strain relationships are exhibited over many hundred percent elongation in striking contrast with but a few percent elastic deformation of metals where the forces originate in energy

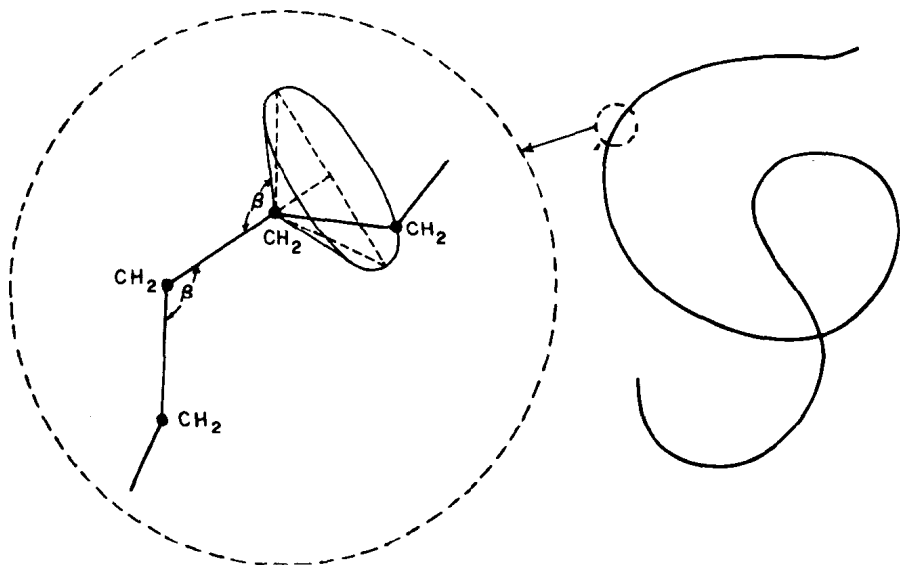


Fig. 1. Short- and long-range conformation of a flexible macromolecule (polyethylene).

changes of crystal lattice. The corresponding elasticity modulus, many orders of magnitude smaller than in metals, increases with temperature whereas in metals it decreases.

Natural rubber is an excellent example for such behavior. Double bonds in the chainlike molecule permit adjacent monomer units to rotate rather freely, making the whole chain very flexible and of easily changing shape. At rest, rubber molecules are kinked at random and intertangled, forming an amorphous matrix. They tend to return to this condition whenever compression or extension of the sample causes the average coil dimensions to deviate from the most probable values. Young's modulus is extremely small, between 10^6 and 10^8 dyn/cm² as contrasted to 2×10^{12} for steel. Reversible extensions up to 1000% can be obtained.

Chain mobility, which is a consequence of the relatively small intermolecular cohesion forces, is a prerequisite for the rubberlike elasticity. In the nonstretched sample this mobility permits a slow diffusion of single sections of the molecular coils and enables the molecules to re-establish the equilibrium distribution of chain conformations after any deviation from that distribution owing to thermal fluctuation. In a stretched sample, however, such a diffusion is not at random but is unidirectional in character. The chains diffuse into new equilibrium positions (slippage), reducing the elastic restoring forces without any apparent dimensional change in the sample. By such stress relaxation, which is a consequence of material flow, the initially elastic deformation transforms into a plastic one. The flow effect is so prevalent with short chains that samples with less than about 500 monomer units in the average chain outwardly appear to become very viscous liquids. However, even elastomers of higher molecular weight exhibiting good rubber properties will gradually assume a liquidlike character with increasing temperature.

In order to prevent plastic flow, i.e., slippage, the chain ends have to be somehow fixed in the matrix. One achieves that by random *cross-linking* of the macromolecules in the amorphous matrix, in rubber for instance, by chemical vulcanization using sulfur or sulfur compounds (double bonds on adjacent molecules react with sulfur and create a sulfur bridge between them, the strength of this chemical bond being substantially greater than that of the cohesive van der Waals forces), by irradiation, or by introducing highly active particles (carbon black) into which adjacent macromolecules are strongly absorbed. Originally independent macromolecules are thus transformed into a network of practically infinite molecular weight. Such a cross-linked rubber exhibits a nearly reversible elasticity. As a rule, Young's modulus is enhanced with an increased number of cross-links partly as a consequence of a greater contribution of the energy term. The extension limits are markedly reduced due to the smaller effective average length of free molecular chains between two consecutive cross-links. One finally obtains a nearly rigid sample exhibiting no more extension before rupture than low-molecular solids. At the same time, as the deformation of short segments outweighs the contribution of large-scale conformational changes, the elasticity becomes more and more a consequence of energy instead of entropy increase during deformation.

During stretching the chains tend to become aligned. This effect, accompanied by a slight decrease in specific volume, can be quantitatively investigated by X-rays and optical birefringence. The increase in number

and extension of the areas of closer contact between the molecules and the resulting increase of intermolecular cohesion forces increases the modulus and at the same time reduces the extensibility of the network. Such an effect is favored by high regularity in polymer configuration and by a reduction in the temperature. It can be suppressed or delayed by diluents so strongly attached to the macromolecules that they are not displaced from the bulk of amorphous matrix during deformation. Any small molecules exhibiting sufficient interaction with the macromolecules of the rubber network may be used as the external diluent or *plasticizer*. The highest diluent stability, however, can be achieved by incorporating these molecules into the polymer chain, e.g., by producing copolymers, grafted polymers, branched polymers, and polymers with bulky side groups in every monomer. In many cases the low molecular weight fraction of a polydisperse sample already acts as an efficient plasticizer. A similar effect is obtained by mixing different, but compatible, polymers.

At sufficiently high alignment, adjacent chain sectors may be easily arranged in a *crystal* lattice. Raw rubber which has been quickly stretched to something like its maximum extension crystallizes to such an extent that it retains this extension for an indefinite time after removal of the stretching force. In this condition it is highly anisotropic in mechanical and optical properties. A characteristic fibrosity is developed. The state of rubber crystallized by extreme stretching is in all essentials comparable with that of a typical fiber. In practice, of course, there is the important difference that the crystalline state in rubber has not the permanence required for a technically valuable fiber because it is readily destroyed by moderate rise in temperature (30 to 40°C) or by swelling liquids. With such treatment the crystallized rubber reverts to the amorphous state and at the same time retracts to its original form.

The increase in crystallinity only slightly (by a few percent) decreases the specific volume but enormously, (by a factor of about 100) increases Young's modulus. Crystallization may also occur at sufficiently low temperature. In raw rubber the crystallization is easily detectable at 0°C and reaches a maximum at -25°C, crystallization being completed in about 10 days and in a few hours, respectively. The associated change in mechanical properties is of considerable industrial importance, particularly when rubber is used in cold climates. The effect of crystallization on the shape of the force extension curve is due to the reduction of the effective average length of free chain as crystallization proceeds. The crystals act as new cross-links and, in addition, longer parts of molecular chains are incorporated into the growing crystals.

With reduction in temperature in even noncrystallizable polymer systems, the cohesion forces between adjacent molecular segments increase so much that the macromolecules are nearly completely immobilized. The rubbery elastomer becomes harder and assumes a leatherlike character. Young's modulus drastically increases from 10^7 to 10^9 or 10^{10} dyn/cm²; the extensibility rapidly drops. Energy changes at deformation gradually replace entropy changes as the main source of elastic forces. In a relatively narrow temperature range with further cooling the leatherlike sample transforms into a hard solid of glasslike consistency. The stress-strain ratio has a high value, 10^9 to 10^{10} dyn/cm² or greater; the elastic deformation range is small; the elastic forces originate nearly exclusively in energy changes of almost

completely immobilized macromolecular chains. As a rule, polymer samples in the glassy state, in spite of their higher rigidity, are not as brittle as crystals, due primarily to the fact that the entangled long macromolecules connect volume elements that are separated by long distances. Also, the short-range mobility of chain segments is not completely impaired. Although they are much less mobile than in the rubbery state, they are substantially less rigidly fixed in their position than in the highly ordered crystalline lattice.

Below the *glass-transition* temperature with frozen-in long-range cooperative motion of molecular segments, the elastic properties prevail. Dissipation of mechanical energy may arise from micro-Brownian motion of small chain sections in less completely ordered areas, of side chains and groups, and of molecular free ends. The presence of traces of diluents of low molecular weight has a great effect in loosening the structure and shifting the relaxation time scale to shorter times. Rapid cooling resulting in higher specific volume has a similar effect, which can be removed by proper annealing and very slow cooling.

The glass transition is a second-order transition; neither density nor heat content change discontinuously. There is an abrupt change in thermal expansion coefficient, specific heat, mechanical strength and so on, however. Any of these effects can be used for the determination of the glass transition temperature T_g , which is one of the most important characteristics of polymer plastics (Table I). A fairly good comparison of different plastomers and elastomers may be obtained by plotting their mechanical properties against $(T - T_g)/T_g$.

The glass transition temperature of a polymer system may be varied over a very wide range of diluents (Table I). The influence of internal diluents can be well illustrated by the butadiene-styrene copolymer series (GR-S rubber). Pure polybutadiene, with $T_g = -85^\circ\text{C}$, properly vulcanized yields an excellent low-temperature rubber. The vulcanized 75/25 copolymer with 75 parts by weight of butadiene and 25 parts of styrene, having $T_g = -57^\circ\text{C}$, is the most widely used all-purpose man-made rubber. The 30/70 copolymer has $T_g = 18^\circ\text{C}$ and forms tough flexible films at room

TABLE I
Glass Transition Temperature T_g and Melting Point T_m for Some Elastomers

Elastomer	$T_g, ^\circ\text{C}$	$T_m, ^\circ\text{C}$
Silicone rubber	-123	
Natural rubber	-72	120
Polyethylene, branched	-68	105 to 115
unbranched	-20	132
6-Nylon	45	220
Polyvinylalcohol	80	190
Polystyrene	100	160
Polymethyl methacrylate	105	
Polystyrene with 20 wt. % of:		
nitrobenzene	50	
benzene	0	

temperature. The 10/90 polymer with $T_g = 68^\circ\text{C}$ is a rigid glasslike, hard plastic with modest impact strength. Pure, atactic polystyrene has $T_g = 100^\circ\text{C}$ and is still harder and more brittle.

A full description of mechanical behavior at any temperature has to include not only the stress-strain relationship but also its time dependence. Application of a periodic force causes the mechanical energy to be both stored and dissipated in correspondence with elasticity and viscosity, and the behavior is described as *viscoelastic*. In practice, several different methods may be needed to provide a complete picture over a broad time scale. The results may then be represented as the real and imaginary parts of the complex dynamic modulus as a function of frequency or as a distribution function of relaxation and retardation times. The procedure has to be applied to all temperatures of interest in order to obtain a complete picture of viscoelastic behavior of the sample under investigation. The mechanical parameters so obtained have to be plotted in a three-dimensional relief over time or frequency and temperature. Cross sections of this relief at different frequencies (times) or temperatures can be correlated owing to the fact that, with some minor restrictions and eventual change of the transforming constants, the relaxation processes all have basically the same temperature dependence. Therefore, the values can be reduced to a standard time or frequency or temperature.

The decay of the stress-elongation ratio with time for a polyisobutylene sample [1] ($M_w = 1,350,000$) between -83 and $+25^\circ\text{C}$ is shown in Fig. 2. The flow character at higher temperature gives way to the rubbery plateau between 0 and -40°C . At still lower temperatures the stress-elongation ratio rapidly increases and at the glass-transition temperature -80°C reaches values above 10^{10} dyn/cm² accompanied by a negligibly small decrease in time.

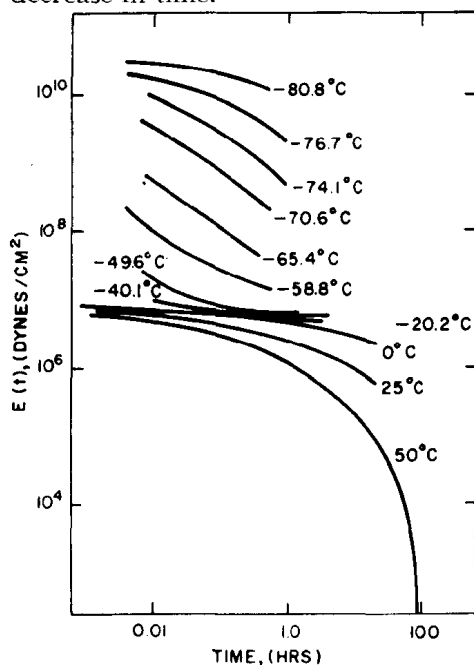


Fig. 2. Relaxation of stress-elongation ratio E with time for unfractionated polyisobutylene, $M_w = 1,350,000$. (After Catsiff and Tobolsky)

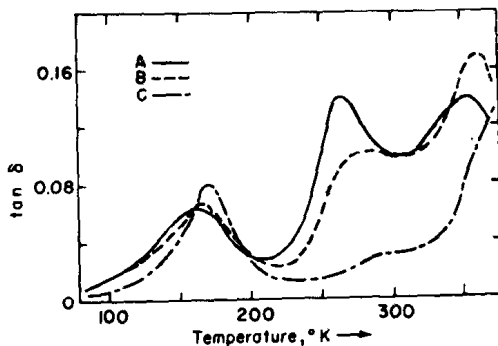


Fig. 3. Loss tangent plotted against temperature for polyethylenes with different amounts of branching: (A) $\text{CH}_3/\text{CH}_2 = 0.032$, (B) $\text{CH}_3/\text{CH}_2 = 0.016$, (C) $\text{CH}_3/\text{CH}_2 = 0.001$. (After Kline, Sauer, Woodward [3].)

Instead of plotting stress relaxation over time, one may plot the storage or the loss modulus (real and imaginary parts of the complex modulus) or the loss tangent (ratio of imaginary and real parts of modulus) over frequency of applied stress [2]. The loss modulus and loss tangent curves exhibiting well-developed maxima, corresponding to resonances with different types of motion of the polymer molecules and their parts, seem to give the best insight into the mobility of single groups in the plastomer. A plot of loss angle over temperature for polyethylenes [3] of different branching ratio between 1200 (at low temperature) and 200 cps (at high temperature) is shown in Fig. 3. The central peak measures the oscillations of the short side-chain branches, the low-temperature peak the torsional oscillations of CH_2 groups in the main chain, and the high-temperature peak, only appearing above T_g , the cooperative mobility of long chain segments achieving complete freedom in the melted sample.

The degree of crystallinity depends on the configuration of the macromolecules and on diluents as already mentioned above in connection with glass transition and crystallization of rubberlike samples at high extension. But since macromolecules are so bulky, their accommodation in the crystal lattice is a slow process. Therefore, the crystal growth in a sample cooled below the melting point requires much more time than in low-molecular melts. By rapid cooling the crystallization may be substantially depressed. However, on the other hand since the crystal nuclei formation rate increases with supercooling one obtains a larger number of smaller crystals by fast cooling. As a rule, such a material has better mechanical properties, a somewhat smaller Young's modulus, but is definitely less brittle than a slowly cooled sample with a smaller number of rather large crystals. By heating and annealing a quenched sample the crystals reform. The smaller crystals partly melt and become rearranged in larger crystals, and the crystallinity generally increases. The sample becomes harder but also more brittle.

The character of polymer crystals has undergone extensive investigation in the last few years. Originally the theory of bundlelike nucleation was favored. Either by chance or by applied stress long enough sectors of adjacent macromolecules become aligned to such a degree that they can be arranged in the highly ordered crystal lattice. The crystal nucleus grows by addition of new chains to the original bundle and by extending the order in chain direction, thus including more and more of the randomly coiled parts of those macromolecules which have already been partially incorporated in the crystal. According to this picture, the crystalline polymer solid

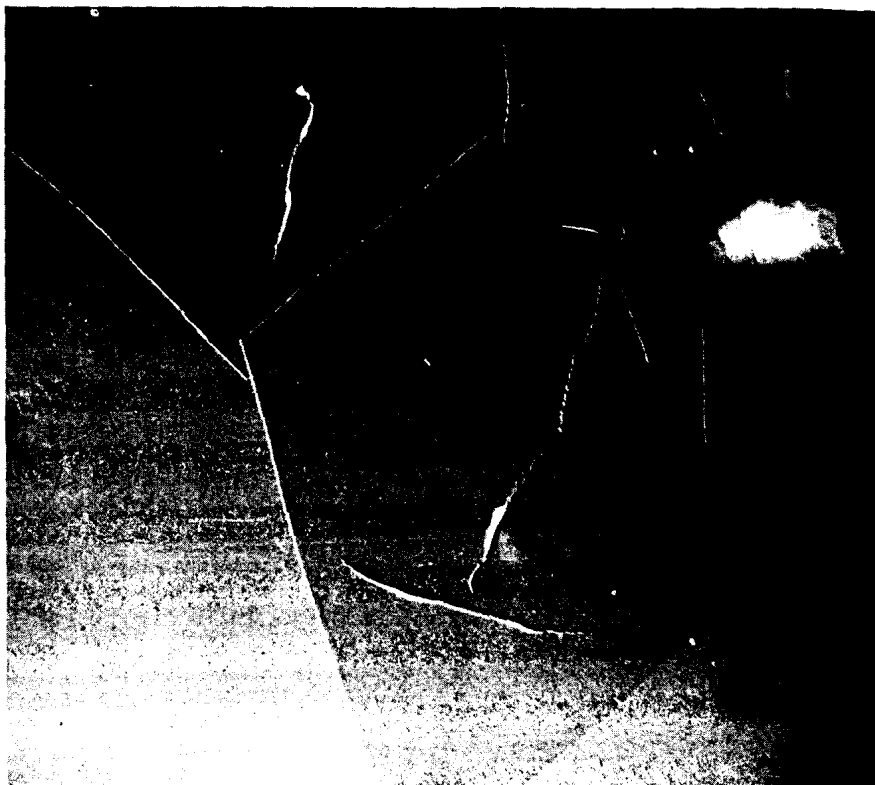


Fig. 4. Single crystals of polyethylene from dilute xylene solution. The distance between the marks is $10\ \mu$. (After P. H. Geil.)

consists of single crystals of very different shape and size embedded in an amorphous matrix consisting of unoriented, randomly, coiled parts of macromolecules which are to some extent also partially incorporated in one or more adjacent crystals. Recent investigations, however, have revealed that polymers crystallize in platelike crystals exhibiting a surprisingly uniform thickness which for a given polymer seems to depend primarily on the temperature of crystal formation. The polymer chains are perpendicular to the platelet surface. Because their average length ($\sim 2000\ \text{\AA}$ and more) is many times larger than the crystal thickness ($\sim 100\ \text{\AA}$), one has to assume that the chains fold back on themselves at the platelet surface. This peculiar phenomenon is well proven for single crystals grown from solution (Fig. 4). It seems chain folding also occurs in crystals growing from the melt and eventually prevails to such an extent that these crystals can in many respects be closely identified with those grown from solution. The fully crystallized polymer solid consists of spherulites containing many layers of twisted plateletlike single crystals which give the impression of being independent of each other to a large extent (Fig. 5). Of course, one certainly has a non-negligible ratio of molecules which become

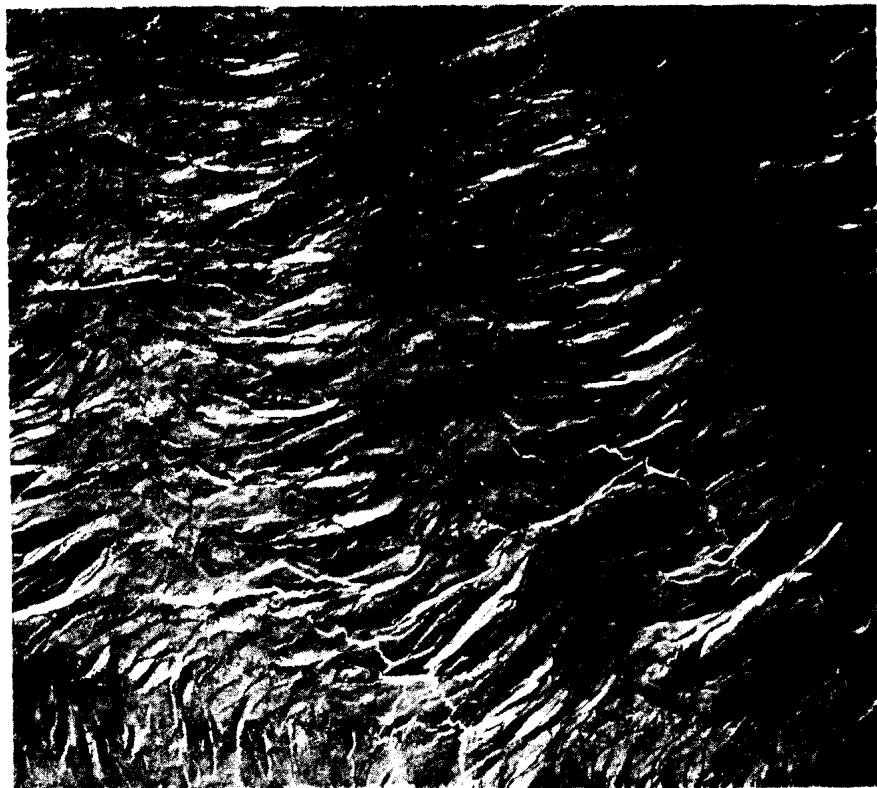


Fig. 5. Fine structure of a spherulite showing the twisted plateletlike single crystals. The distance between the marks is 1μ . (After P. H. Geil.)

incorporated into two different crystals during crystallization and because of this cannot be completely included with the crystal lattice. The non-incorporated part remains amorphous. However, when crystallization occurs while a sample is being stretched then very likely the bundlelike nucleus is more probable than the single macromolecule nucleus. Even in this case some folding must occur in order to explain the density difference between crystallized and amorphous areas.

It is believed that secondary nucleation occurs on the surface of a crystal growing from the melt. The splaying or separation of the secondary crystals leads to a spherulitic crystal arrangement. The number and size of spherulites depend on the ratio of crystal growth rate to primary nucleation rate. Samples of easily-crystallizable polymers, as for instance polyethylene, consist of spherulites filling out the whole sample (Fig. 6).

A special case is that of *fibers* and *films*. The highly viscous liquid or very soft solid polymer material is extrusion molded or drawn under simultaneous cooling or removal of diluent. The increased cohesion between partially aligned macromolecules prevents complete randomization after removal of the applied stress so that the orientation and eventual crystallization induced by mechanical deformation is preserved. As a consequence,

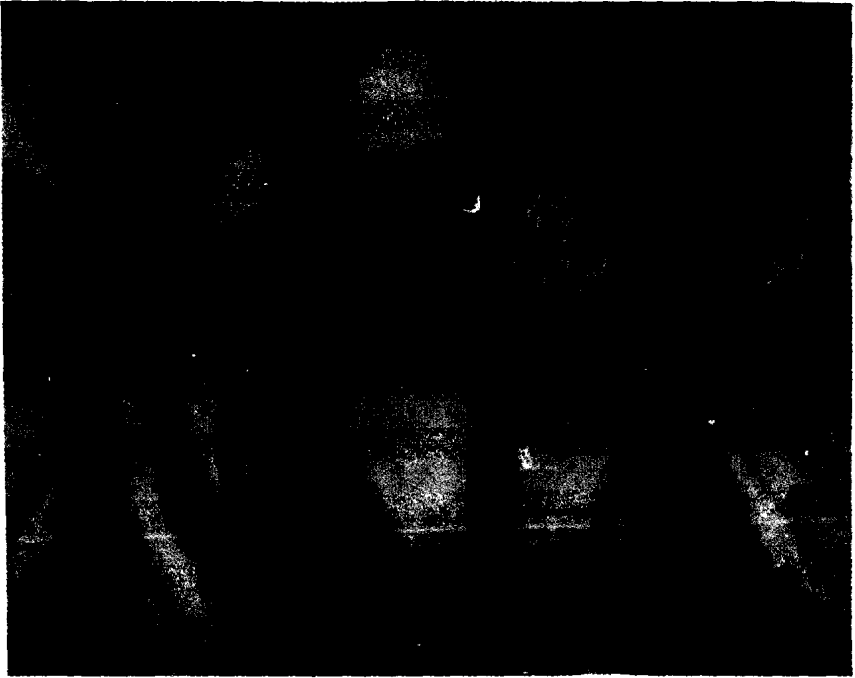


Fig. 6. Spherulite structure of polyethylene film viewed between crossed polaroids. (After P. H. Geil.)

fibers and films are anisotropic in their mechanical properties. Oftentimes this anisotropy is increased by drawing the sample after it has crystallized.

The stress elongation curve for a cellulose fiber, for instance, consists of an initial rather steep and reversible section (I) which is related to the increase in potential energy (Fig. 7). The elongation in this section is small, about 2 to 3%. The slope then drops rather sharply and remains nearly constant over an extended elongation range (about 30%). This second deformation section (II) is not completely reversible. After removal of the applied stress the elongation drops to less than half of its original amount with a characteristic short relaxation time (spontaneous recovery). The remaining quasi-permanent elongation can be nearly completely reduced by the action of an appropriate swelling agent (latent recovery). The amount of quasi-permanent elongation after the spontaneous retraction has a marked value only in the case where the initial elongation sensibly surpassed the range of reversible elasticity (I). The second section is closely related to rubber elasticity. After the applied stress reaches a value sufficient for breaking the secondary bonds (for instance, hydrogen bonds) between adjacent molecules in the amorphous areas the mobilized molecular chains give rise to entropy-connected elasticity. With increasing elongation the parallelization of chain sectors again favors crystallization or at least creates areas of enhanced cohesion with new secondary bonds which after removal of applied stress slowly decay in a way similar to rubbery plastics. However,

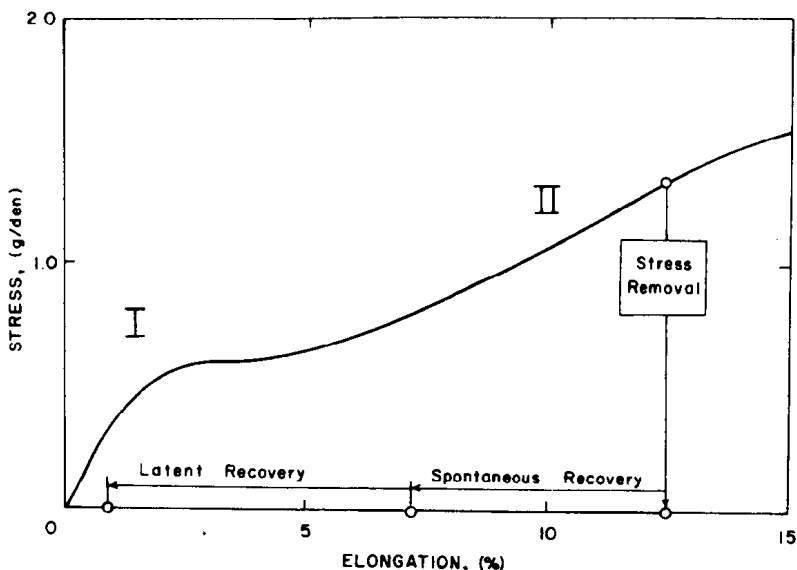


Fig. 7. Stress-elongation curve and recovery diagram for viscose rayon. (After De Vries [4].)

ne secondary bonds are more stable than ordinary interchain cohesion bonds between two hydrocarbon chains and hence cannot be broken spontaneously. When the sample is immersed in a swelling agent, the latter succeeds in breaking these bonds and hence re-establishes the initial random distribution. Eventual crystal formation during high enough elongation, of course cannot be destroyed by the swelling liquid and accounts for the remaining permanent deformation after swelling retraction.

Fibers containing macromolecules of high regularity, as for instance 66-nylon, which is able to form a well-ordered system of hydrogen bonds, can be substantially improved by *cold drawing*. After increasing the stress a little over the range of the initial elasticity domain the elongation irreversibly proceeds to several 100% yielding a much stronger fiber with many times increased elasticity. With special fibers, as for instance Dacron, one can even fix different elongation ratios and although starting with the same soft, nearly isotropic fiber obtain fibers of different strength and elastic modulus. During cold drawing, the mechanical work done may be sufficient for nearly complete melting of the sample in the plastically deformed transition zone where the original cross section is reduced to the final one.

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On the Plastic Behavior of Polycrystalline Aggregates

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The complete understanding of the physical origin and nature of the plastic behavior of polycrystalline aggregates constitutes one of the major problems in materials science. It has as its major objective the predictions of the plastic behavior of polycrystals from the known behavior of single crystals. The possibility of making such a prediction rests on the tacit assumption that the mechanisms of plastic deformation in aggregates are substantially identical with those observed in single crystals. The steps involved in the solution are: (a) mechanisms of deformation in single crystals; (b) interactions at grain boundary; (c) statistical averaging; and (d) contained plasticity.

I. INTRODUCTION

ONE OF THE major objectives of physical metallurgy is the rationalization of the plastic behavior of metals in terms of the atomistic mechanisms of single-crystal deformation. As a result of the basic scientific importance as well as the technical significance of this subject, an extensive literature has developed, and numerous surveys [1-3] have already been made on various aspects of metal plasticity. It is now recognized that four major processes are responsible for deformation in crystalline aggregates: (1) crystallographic glide, (2) twin formation, (3) grain boundary shearing, and (4) stress-directed diffusion of vacancies. Stress-directed diffusion of vacancies contributes significantly to creep straining of polycrystalline materials only at low stresses and at temperatures approaching the melting points [4]. For polycrystalline materials that exhibit numerous glide systems [e.g., face-centered cubic (F.C.C.) metals] grain boundary shearing is usually restricted to temperatures above about one-half of the melting temperature, where creep is controlled by the climb of dislocations. On the other hand, in systems [e.g., hexagonal close-packed (Hex.C.P.) such as Mg] which have only relatively few operative glide systems, grain boundary shearing has been observed at temperatures as low as 78°K [5]. Although twinning may be induced in many metals, the deformations that can be achieved by this mechanism are limited geometrically [6]. Crystallographic glide

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qualifies as the principal process of deformation in F.C.C. metals at low and intermediate temperatures. Twinning indeed affects in a major way the strain-hardening that is observed as a result of interferences to slip but precise knowledge on this aspect is meagre. From this point of view it is reasonable to attempt to limit this discussion principally to examples of plastic deformation by slip in F.C.C. metals. Such a limitation is further justified by the fact that most of the currently available research results on mechanisms of deformation and analyses of strain hardening have been made on F.C.C. metals at low temperatures.

Although the mechanical behavior of aggregates of several phases might be included in a general discussion of the behavior of polycrystalline materials, this subject is indeed a separate chapter, involving the introduction of additional concepts and it will therefore be excluded from the present review.

The plastic behavior of polycrystalline metals appears to be somewhat different from that exhibited by individual single crystals. Frequently, polycrystalline metals have about the same rates of strain hardening as single crystals undergoing multiple slip, but their flow stresses are invariably somewhat higher than those for single crystals; the flow stress increases linearly with the reciprocal of the square root of the grain diameter. In the past it has generally been assumed that, at least in the absence of grain boundary shearing, the basic mechanisms of deformation in single and polycrystalline metals are the same. If this were so, the behavior of polycrystalline aggregates could be deduced from a complete knowledge of single-crystal behavior. We will therefore consider in the next sections (II, III, and IV) the status of our knowledge of single-crystal behavior and in section V the behavior of bicrystals, which begin to approach more closely the behavior of polycrystals. In Section VI we will demonstrate that the existing attempts to deduce the behavior of polycrystalline aggregates in terms of the behavior of single crystals suggest that the flow stresses are only a few times greater than those for single crystals and are independent of grain size. Undoubtedly, new factors not inherent in single-crystal deformation enter the picture. These will be discussed in Section VII. We will show that, in contrast to the usual assumptions of homogeneous deformation by multiple slip, deformation is highly localized. Consequently, dislocations pile up against the boundaries of unfavorably oriented grains and, depending on their relative orientations, either produce slip on the usual slip planes or on uncommon planes only operative in polycrystals. The stresses at the head of piled-up arrays depend on grain size in such a way that the flow stress becomes proportional to the reciprocal of the square root of the grain diameter. The plastic behavior of polycrystals therefore cannot be deduced exclusively from single-crystal data because new factors such as heterogeneous behavior, new slip mechanisms, and piled-up arrays of dislocations, enter the picture. More effort must therefore be devoted directly toward understanding these auxiliary features of the deformation in polycrystalline metals.

II. THEORIES OF SINGLE-CRYSTAL BEHAVIOR

Although some aspects of the theory of the plastic behavior of single metal crystals are yet under discussion, there is general agreement relative

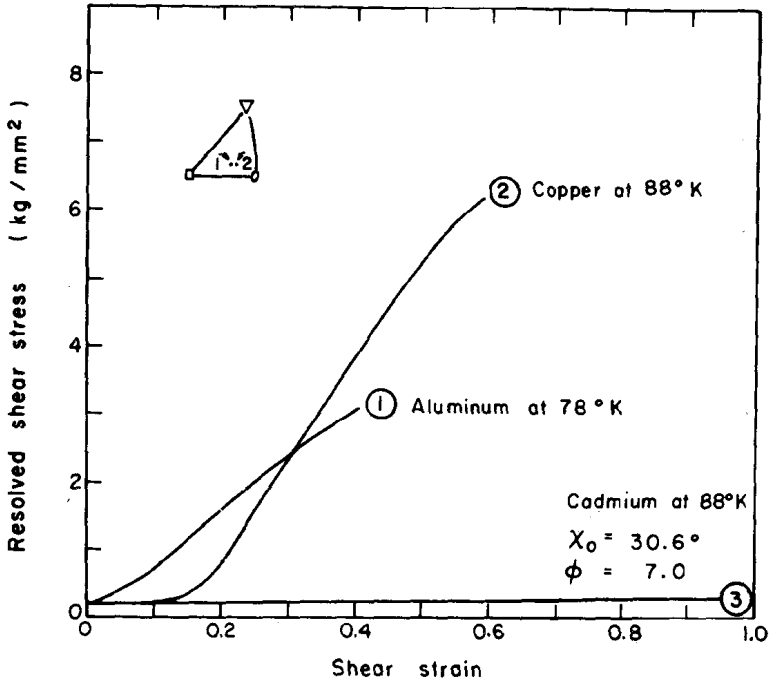


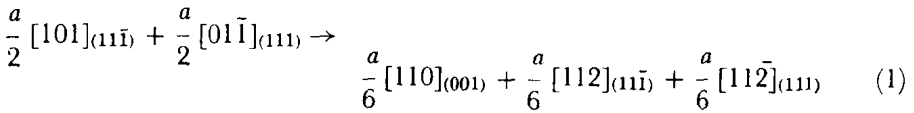
Fig. 1. Shear-stress vs. shear-strain curves for Cd [7], Al [8], and Cu [9] single crystals of similar orientation.

to the shape of experimentally determined stress-strain curves [1-3]. In Fig. 1 are shown the resolved shear stress vs. resolved shear strain curves for Cd (0001) [1120][7], Al (11 $\bar{1}$) [101][8], and Cu (11 $\bar{1}$) [101][9] for the temperatures and orientations indicated.

Whereas the Cd (Hex.C.P.) crystals exhibit only a modest amount of strain hardening over the entire range of deformation, the Cu and Al crystals have an initial range, Stage I, of mild linear hardening (also known as easy glide), a Stage II of rapid linear strain hardening, and a Stage III over which the rate of strain hardening decreases. The low rate of strain hardening over Stage I in the F.C.C. metals approximates that for Hex.C.P. metals insofar as it suggests substantially unperturbed slip on the principal slip system. Over this region the slip bands are usually continuous over the entire crystal surface. Over Stage II, however, the principal slip bands become progressively shorter [9-12] implying that some interference to easy glide takes place. The absence of Stage II in Hex.C.P. metals reveals that the mechanism of hardening in Stage II is uniquely associated with the multiplicity of possible operative slip systems in F.C.C. metals leading to blockage of slip on the principal slip plane. The lower strain-hardening rate that is observed over Stage III must be ascribed to some process that allows a moderation of the higher rate of strain hardening operative earlier over Stage II. It has been shown that the reduced rate of strain hardening in Stage III arises from the stress-assisted thermal activation of cross-slip [2].

Stages I and II of the low-temperature plastic behavior of F.C.C. metals has been ascribed to an intersection model which was introduced

by Mott [13] and Cottrell [14] and extended in detail by Friedel [15] and Seeger [16]. According to the general assumptions of this model, the interruptions of easy glide at the terminus of Stage I was ascribed to the formation of Lomer-Cottrell sessile dislocation blocks produced by reactions of the form



Since the energy decreases, a stable sessile arrangement is obtained of dislocations lying on the three designated planes. Thus, two stacking faults are formed on the $(11\bar{1})$ and the (111) planes, respectively, which issue from the $(a/6)$ $[110]$ dislocation and terminate at the two partial dislocations. On the basis of electron microscopical evidence [10], which reveals that continuously decreasing lengths of slip bands are produced during the same interval of deformation as the shear strain increases, Seeger concludes that the formation of Lomer-Cottrell dislocations continues throughout Stage II. The theory further postulates that dislocations on the primary slip system pile up against the Lomer-Cottrell sessile dislocations producing in this way long-range back stresses. The energy that is required to move dislocations against such long-range stress fields is very large and consequently this process is not thermally activatable. Therefore, the component of the flow stress necessary to overcome the long-range stress fields is substantially independent of the temperature. As the dislocations move away from their Frank-Read sources, however, they must intersect dislocations of the Frank network that thread through the slip plane; thus, they form jogs.

The energy for intersection depends on the geometric details of the process as well as the stacking fault energy. But estimates of these energies for intersection usually range from a fraction to several electron volts, and therefore the intersection process is thermally activatable. Consequently, the flow stress τ must equal the temperature-insensitive long-range back stress τ_G^* plus the temperature-dependent activation stress τ_i necessary for intersection. The initiation of Stage III is attributed to the nucleation of cross-slip among the highly stressed leading dislocations in the piled-up arrays. Since cross-slip is thermally activatable, the stress $\tau_{II, III}$ must decrease with increasing temperatures as shown in Fig. 2 [12].

Although this theory has been reasonably successful in accounting for the observed plastic behavior of single F.C.C. metal crystals, recently documented evidence, primarily that which has been obtained by transmission electron microscopy has cast doubts on the validity of several major assumptions that were made. Much of this evidence was discussed at the Fifth General Assembly of the International Union of Crystallography (University of Cambridge, August, 1960). And a preliminary analysis of the newer concepts was reported by Mott in the 1960 Institute of Metals Lecture [17]. The critical observations, primarily due to Hirsch, are as follows:

1. Although detailed searches have been made, there is no direct transmission electron microscopical evidence for the formation of