Talipov (94) studied isotactic polystyrene above its glass-transition temperature, found that the tensile strength and elongation to break were decreased by adding plasticizer, and attributed these effects to the lower molecular orientation produced by stretching the plasticized polymer; in effect, he explained the change by the principle of instabilities of deformation.

In addition to these major and general effects of plasticizers, more specific effects can also be important. For example, (*1*) the quantitative effect of different plasticizers in the same polymer varies with the chemical composition of the plasticizer (95). (*2*) Some polymers absorb enough water, even from the atmosphere, for this to have a significant effect on their mechanical properties. For example, nylon-6,6 has a large modulus transition which is above room temperature when the polymer is dry, but which moves through room temperature as the water content increases (96). The mechanical properties of cellulose fibers depend on whether the specimens are wet or dry (97), and water decreases the tensile strength and impact energy of poly(methyl methacrylate) (98). (*3*) Poly(vinyl chloride) specimens with plasticizer contents between 0 and 10% behave in an anomalous manner. As the concentration of plasticizer increases in this range, the moduli and yield stresses at room temperature increase (Fig. 31), the impact strength decreases, and the material becomes more brittle (principle of variation of stress at constant strain) (99–101). Poly(vinyl chloride) is also embrittled by the addition of small quantities of soluble additives, such as some lubricants and stabilizers, other than plasticizers. Figure 31 shows the dependence of the room-temperature yield stress of poly(vinyl chloride) on the concentration of a

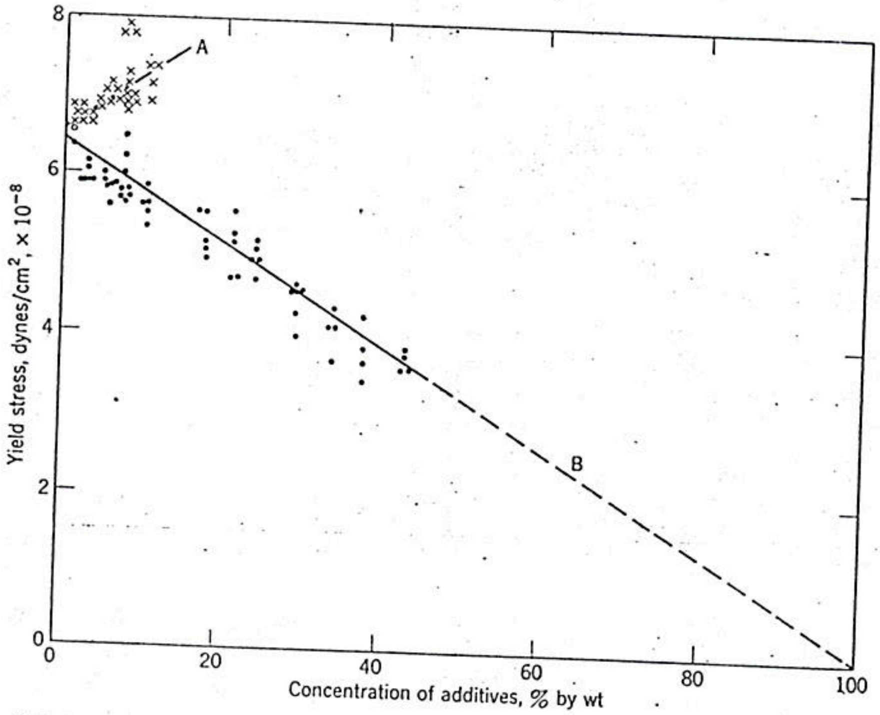


Fig. 31. Effect of additives on the tensile yield stress at 20°C for poly(vinyl chloride) (28). Key: A, soluble additives; B, insoluble additives.

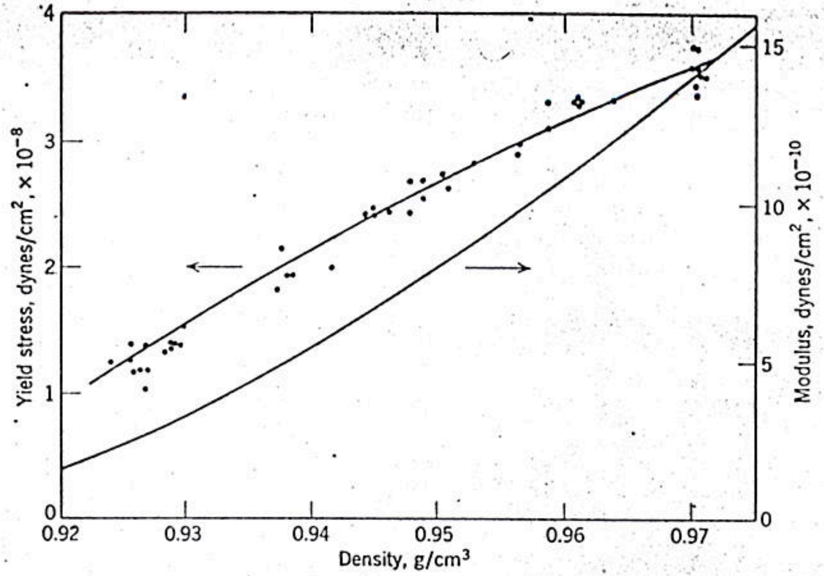


Fig. 32. A yield stress and a modulus at 20°C as functions of density for polyethylene.

variety of additives. (4) Contact with various substances has been observed to affect the stress–strain behavior of a variety of polymers (102–104).

Crystallinity (qv). It can be demonstrated that a crystalline or semicrystalline sample of a polymer has a consistently higher modulus and yield stress at a given temperature than does an amorphous sample of the polymer. From the principle of stress variation at a given strain it would be expected that as the moduli and yield stresses increase, the probability of fracture would increase as the proportion of ordered material increased. It follows that the amorphous form of a polymer can be expected to be more resistant to fracture at a given temperature than the semicrystalline material. In this way, the brittle temperatures of a polymer may be lowered to below room temperature on going from a crystalline to the amorphous form. For the same reason, the amorphous form may cold draw to high extensions whereas a semicrystalline specimen may fail by, for example, necking rupture; this behavior is shown by poly(ethylene terephthalate).

The proportion of ordered material in ethylene polymers can be varied by branching and by copolymerization as well as by thermal treatment (see also ETHYLENE POLYMERS). Figure 32 shows the dependence on density, taken as a measure of the proportion of crystallinity, of a modulus and a yield stress for samples of polyethylene (28,77). The curves bend in different directions and the yield stress does not increase as rapidly as the modulus with increasing density. In accordance with the principle of stress variation at a given strain, the high-density specimens are more brittle than the low-density specimens.

Starkweather and Brooks and their co-workers have published (105,106) the results of a thorough investigation of the effects of crystallinity and spherulites on the mechanical properties of nylon moldings. To a large extent, they were able to vary crystallinity and spherulite size independently. As the degree of crystallinity increased, the modulus and yield stress increased and the impact strength decreased, particularly above 35% crystallinity. As the spherulite size increased, the modulus

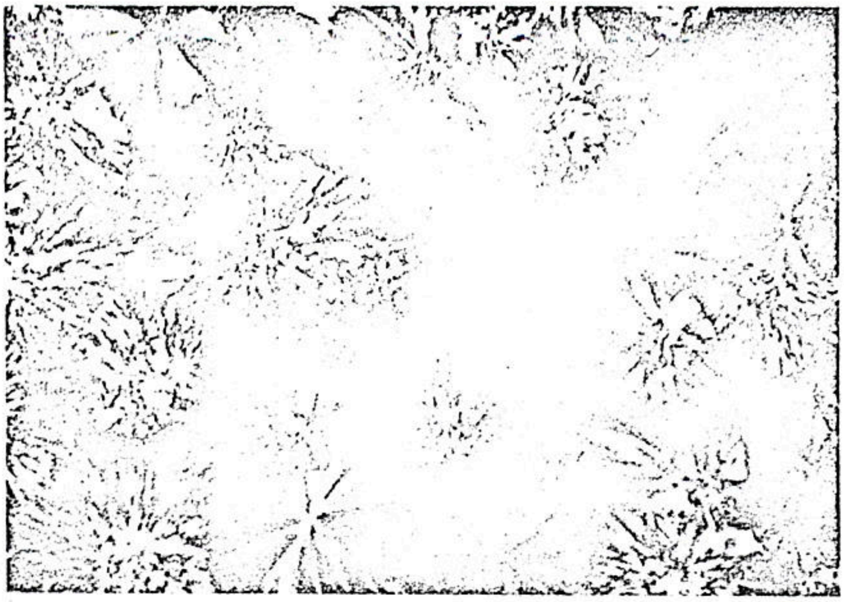


Fig. 33. Micrograph of a sample of polypropylene which was isothermally crystallized for an hour at 140°C.

and yield stress decreased and the elongation to break increased. One cannot be certain that these effects are general and there is need for similarly thorough investigations on other polymers. Many workers (107–114) have concluded that samples with large spherulites are more brittle than samples with small spherulites. Starkweather and co-workers (105) found this for thin films but pointed out that large spherulites have an adverse effect on toughness only when the spherulite diameter is an appreciable fraction of the thickness of the test section.

In some cases the embrittlement of crystalline polymers on cooling slowly from the melt or annealing below the melting point may be a simple consequence of the increase in the yield stress, following the principle of stress variation at a given strain. In other cases the embrittlement may be more severe than the increase in yield stress can account for. For example, the brittle strength of polyethylene does not correlate directly with density, but is far more dependent on the rate of cooling than on the number of side branches (115). This reduction in brittle strength suggests that, as the cooling rate becomes lower, the samples contain more severe structural irregularities which, in accordance with the principle of stress concentrations, increases the probability of fracture. It has been observed that when nylon (108), polytetrafluoroethylene (108), and polypropylene (111–113) are cooled slowly from the melt or annealed, visible cracks may form in the structure. Clearly, such cracks are structural irregularities which tend to cause embrittlement. Figure 33 is a photograph of the microstructure of a sample of polypropylene which was isothermally crystallized for an hour at 140°C; it shows a large crack which developed between the spherulites.

The rate and time of crystallization affect brittle strength in that low temperatures cause rapid crystallization, leaving more links between crystallites and thus causing less reduction in brittle strength than slower crystallization at higher temperatures, which produces better ordered crystallization; this, in turn, reduces the links between crystallites and thus causes voids and cracks to form between the regions of ordered material. There is a minimum in brittle strength for a given crystallization time, however, since at still higher temperatures crystallization does not reach completion and links remain between crystallites.

There are two reasons for embrittlement on crystallization. First, the moduli and yield stresses increase and, therefore, the probability of fracture increases (principle of stress variation at a given strain). Second, at very high crystallization, cracks develop in the structure and, therefore, by the principle of stress concentrations, fracture becomes even more probable. Average tearing energies are not greatly affected by changes in crystallization temperature but the scatter in tearing energy reaches a maximum at the temperature of maximum crystallization rate.

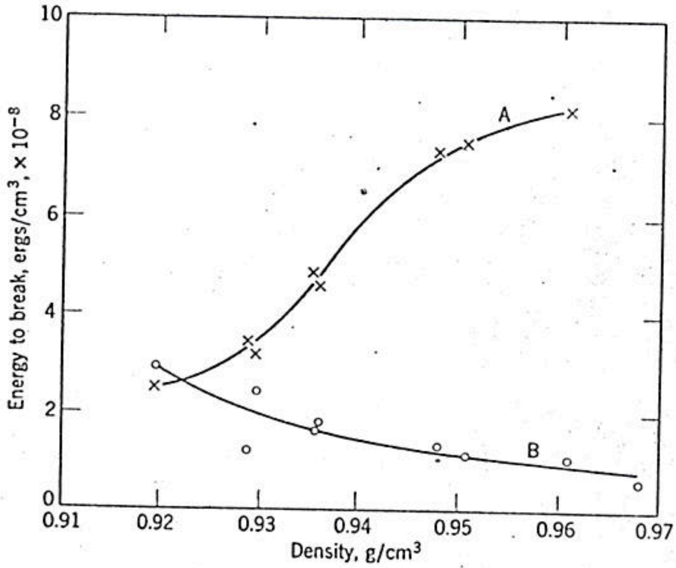


Fig. 34. Tensile energies to break per unit volume at 20°C as functions of density for ethylene polymers at two straining rates; A, slow, 0.8 cm-min^{-1} and B, fast, 30 cm-min^{-1}.

The results of various studies (28,116,117) demonstrate that it is too optimistic to expect the mechanical properties of semicrystalline polymers to correlate simply with some measure of their degree of crystallinity and that it is necessary to take account also of the way in which the crystallinity was achieved and the details of the texture. It appears significant that annealing at high temperatures below the melting point and also adding atactic polymer both introduce defects into the polymer structure, giving low brittle strengths. This suggests that polypropylene samples with a high concentration of atactic polymer, and samples highly crystallized by annealing, yield at unexpectedly low stresses because the specimens are beginning to tear apart at defects.

Crystallization on stretching greatly increases the slope of the stress–strain curve of an elastomer (118). Elastomers can be divided into two classes (119): (a) those which do not crystallize on stretching and therefore have a low breaking stress (1.5 to 4 × 10^7 dynes/cm^2), which can be increased to about 2 × 10^8 dynes/cm^2 by adding fillers, eg, sodium-catalyzed polyisoprene, polybutadiene, copolymers of butadiene with styrene or acrylonitrile, methyl rubber; (b) those which do crystallize on stretching and so have a high breaking stress (1.5 to 3.5 × 10^8 dynes/cm^2), which is not greatly increased by fillers, eg. natural rubber, polychloroprene, butyl rubber.

The tensile stress at break for elastomers has been found to be a linear function of the crystalline content at break (120). The mechanical properties of plastics can also be affected by changes in crystallinity during deformation. Greensmith and co-workers (27) have illustrated the striking differences in behavior between rubbers which do and do not crystallize on stretching by plotting tearing energy as functions of temperature and tearing speed for a natural rubber vulcanizate and a butadiene–styrene copolymer vulcanizate. Over wide ranges of the variables, the natural rubber had only a slowly changing tearing energy whereas the tearing energy of the copolymer was very sensitive to changes in test conditions.

The ductility of polyethylene, for example, is reduced in impact with increasing crystallinity. However, it must be noted that this effect can be reversed by varying the rate of deformation. Figure 34 shows tensile energy to break per unit volume of polyethylene at two rates of extension as functions of density (115). At high speeds, the ductility decreases as the crystallinity increases, but at low speeds the reverse is true. The pronounced drop in ductility of high-density polyethylene with increasing straining rate can be explained on the basis of the principle of instabilities of deformation. At high speeds the specimen heats up in the neck so that it cannot stabilize (see the section on Rates of Deformation). At low speeds the heat is lost, there is no temperature rise, the neck stabilizes, and the specimen cold draws to high extensions. Low-density specimens can cold draw even at high speeds because the yield stress is low; the strain energy is low, so that even under adiabatic conditions the temperature rise is not large enough to cause instability.

The main effects of crystallinity may be summarized as follows, in terms of the three principles listed on p. 315: (a) Increasing crystallinity increases moduli and yield stresses and tends to promote fracture through the principle of stress variation at a given strain. (b) High crystallization creates structural irregularities and so tends to promote fracture through the principle of stress concentration. (c) Crystallization during extension improves orientation hardening, and so tends to cause resistance to fracture through the principle of instabilities of deformation. Adiabatic effects may become more serious as crystallinity increases the yield stress.

Blending and Copolymerization. The primary effects of copolymerization and blending can be illustrated by consideration of the properties of polymers from styrene and butadiene. The glass-transition temperature of polystyrene is about 100°C and the polymer is normally brittle at room temperature. The glass-transition temperature of *cis*-1,4-polybutadiene is about −70°C and the polymer is rubbery at room temperature. Random copolymers of the two monomers have glass-transition temperatures between −70°C and 100°C, the actual temperature and breadth of the transition depending on the relative concentrations. The mechanical properties of the copolymers at room temperature depend primarily on the temperature of the glass transition. By copolymerizing increasing quantities of butadiene with styrene, it is possible to make materials which are increasingly softer and tougher at room temperature, but only at the expense of lowering the softening point. If, on the other hand, polystyrene and polybutadiene are blended in such a way that particles of polybutadiene are embedded in a matrix of polystyrene, the blend has two transitions, one near the glass transition of each homopolymer. In this way it is possible to obtain a material which, at room temperature, has lower moduli and yield stresses than polystyrene (and therefore is tougher, by the principle of stress variation at a given strain) without seriously reducing the softening point.

In the simplest situation, yield stresses of blends are intermediate between those of the homopolymers and depend on the relative concentrations. Figure 35 gives the yield stresses as functions of temperature for poly(methyl methacrylate) and a blend of this polymer with a rubbery polymer (28), showing the reduction in yield stress over the whole temperature range examined and also indicating changes in the temperature dependence of the yield stress. If it is assumed that blending has not changed the brittle strength, it can be deduced that blending has lowered the brittleness temperature by about 50 C°. Also, when the yield stresses are reduced by copolymerization and blending, the impact strengths are increased but the gain becomes less pronounced as the temperature decreases. Impact strength is not determined solely by the yield stress but there is a general tendency for the impact strength to increase as the yield stress decreases (principle of stress variation at a given strain).

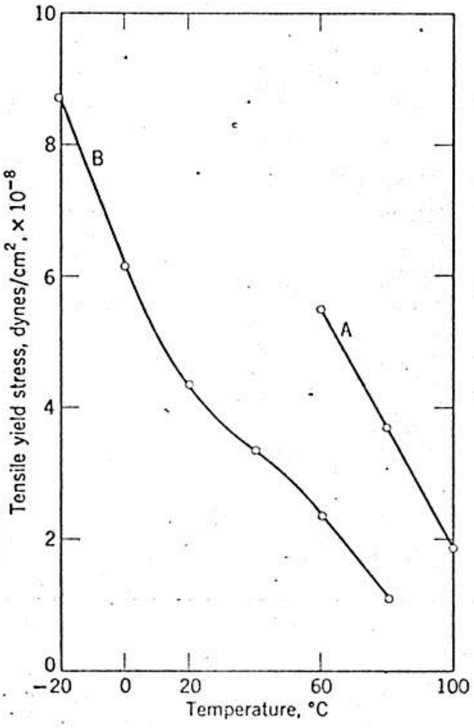


Fig. 35. Tensile yield stresses as functions of temperature for A, poly(methyl methacrylate) and B, a blend of A with a rubbery polymer.

The actual values of the stresses, strains, and energies to break of copolymers and blends do not depend only on the properties of the homopolymers and the relative concentrations. Haward and Mann (121) have proposed that the properties of a blend depend on the size and shape of the dispersed rubber particles, which can be controlled by the manufacturing process. For example, copolymerization gives higher impact strength than direct blending; the particle size of rubber required to reinforce a polymer matrix depends on the nature of the matrix; the impact and flex resistance of a blend depend on the compatibility of the components (122); the impact strength at 0°C of notched specimens of copolymers of vinyl chloride and octyl acrylate depend not only on the relative concentrations, but also on the point during polymerization at which the octyl acrylate was injected and therefore on the nonuniformity of the copolymers (123); the brittleness of high-density polyethylene is reduced by mixture with small quantities of low-density polyethylene, provided they are thoroughly mixed in the melt (124). See also IMPACT RESISTANCE.

Besides the relative concentration of two components in a blend, it is therefore necessary to control also the dispersion of the rubber in the resin and the adhesion between the two polymers (125). One important method of varying adhesion is to chemically graft part of the rigid phase onto the elastic phase. Haward and Mann (121) propose that in a blend the rubbery particles tend to bunch, giving poor impact strength, whereas, with grafting, the particles are dispersed better and impact resistance is improved. Varying the proportion of grafted polymer has a particularly noticeable effect on the impact strength of sharply notched specimens. It can be observed from polymer specimens used in impact tests that it is necessary to have interphase adhesion which is high, but not too high, to obtain the maximum impact strength in sharply notched specimens. Bobalek and Evans (126) concluded that it was desirable to have an intimate mixture, but not a solution, of the high- and low-modulus components of a blend. The prescription for optimum impact strength does not necessarily give the best results in other fracture tests such as tensile tests and dynamic fatigue. Lee and co-workers (127) concluded from their dynamic fatigue tests, in which changes in the material could be detected mechanically and electrically before visible failure, that fatigue resistance can be poor in some compositions which have superior impact resistance.

When two monomers, at least one of which would give a semicrystalline homopolymer, are copolymerized, it may happen that the copolymer molecules are unsymmetrical so that copolymerization reduces the proportion of ordered material. In such a case, the moduli and yield stresses of copolymers may be less than those of either homopolymer. For example, Folt (128) and Huff and co-workers (129) studied the copolymers of ethylene and propylene with α-olefins and found that, as the proportion of higher olefin increased, the density, crystallinity, moduli, and yield stresses decreased and the impact strength of notched specimens increased. A similar effect can be obtained when polyethylene is chlorinated. The chlorine atoms can reduce the symmetry, and therefore the crystallinity, until the chlorinated polyethylene is rubbery at room temperature. With further increase in chlorine content, the glass-transition temperature increases and the polymer becomes harder (higher moduli and yield stresses) at room temperature.

It will be clear from the foregoing discussion that the effects of copolymerization and blending on the fracture properties of polymers cannot be neatly summarized. To a certain extent the results obtained can be understood on the basis of the principle of stress variation at a given strain but there are examples of changes in the fracture properties without parallel changes in moduli and yield stresses.

Orientation(qv). Molecular orientation is frequently introduced into a film or fiber during the manufacturing process. (See BIAXIAL ORIENTATION; MAN-MADE FIBERS, MANUFACTURE.) Also, most ordinary fabrication processes for plastics involve some flow in the molten state which causes a certain amount of molecular orientation in the flow direction. Besides the draw ratio, degree of orientation is dependent

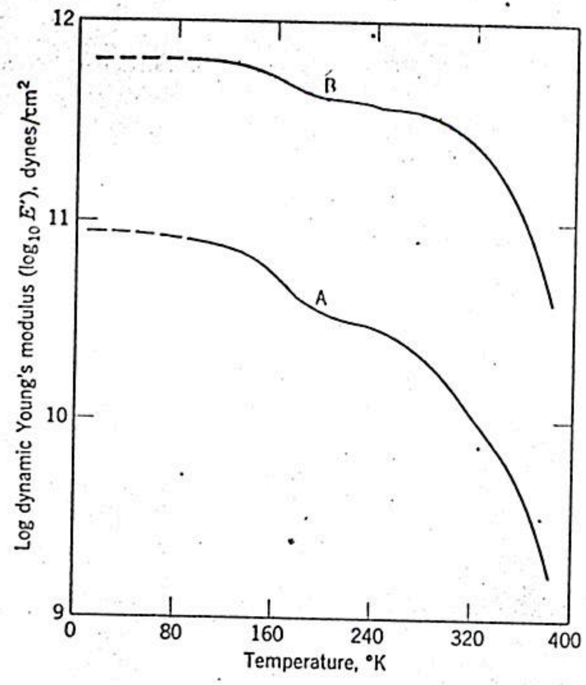


Fig. 36. Moduli as functions of temperature for A, isotropic polyethylene and B, oriented polyethylene.

upon other factors, such as temperature (132, 133). In a molded article, orientation may vary considerably from point to point as the result of complex flow paths.

Neither the draw ratio nor the birefringence characterizes orientation entirely adequately (134,135). Shishkin and co-workers (136) have suggested that either all the molecules in a sample or only the longer molecules may be oriented and that the relations between mechanical and optical properties depend on what proportion of the molecules have taken part in the orientation process.

All mechanical properties can be affected by molecular orientation (130,131). Figure 36 shows moduli as functions of temperature for polyethylene both in the isotropic state and in oriented states (28). Moduli obtained by extrapolation to 0°K are shown in Table 6. The moduli of the isotropic specimens are in the expected range for solids whose moduli are primarily determined by van der Waals bonds (33). They also agree reasonably with the values of lateral moduli (for single crystals in the *a* and *b* directions) computed by Miyazawa and Kitagawa (139) who gave them as 2.1 and 5.7 $\times 10^{10}$ dynes/cm^2. On the other hand, the modulus of oriented polyethylene is less

Table 6. Effect of Orientation on Modulus

Polymer	Modulus at 0°K, dynes/cm^2		Ref.
	Extrapolated	Theoretical	
isotropic polyethylene	9.0×10^{10}	10^{10} to 10^{11}	33
oriented polyethylene	6.3×10^{11}	3.4×10^{12}	137
isotropic polypropylene	5.0×10^{10}	10^{10} to 10^{11}	33
oriented polypropylene	2.7×10^{11}	4 to 5×10^{11}	138

than the calculated value (137) by a factor of 5 to 6; the discrepancy for the highly oriented polypropylene is less than a factor of 2. In order to reach the theoretical values for highly drawn specimens, it would be necessary to have perfect molecular orientation. Evidently the low-temperature modulus increases as the number of covalent bonds in the test direction increases, but does not reach the theoretical value because the specimens break in the drawing process before the molecules attain perfect orientation.

No doubt the influence of the orientation of covalent bonds is still important at temperatures above 0°K but, as the temperature increases, it eventually becomes necessary to take account also of the influence of orientation on the magnitude of relaxation processes. For crystalline isotactic polypropylene it has been demonstrated that above 20°C the modulus is affected by the variation in amplitude of the relaxation process which first increases in magnitude and then decreases, eventually disappearing as the orientation (as shown by birefringence) increases. In general, the moduli usually increase in the direction of molecular orientation but there may be complicating effects on relaxation processes.

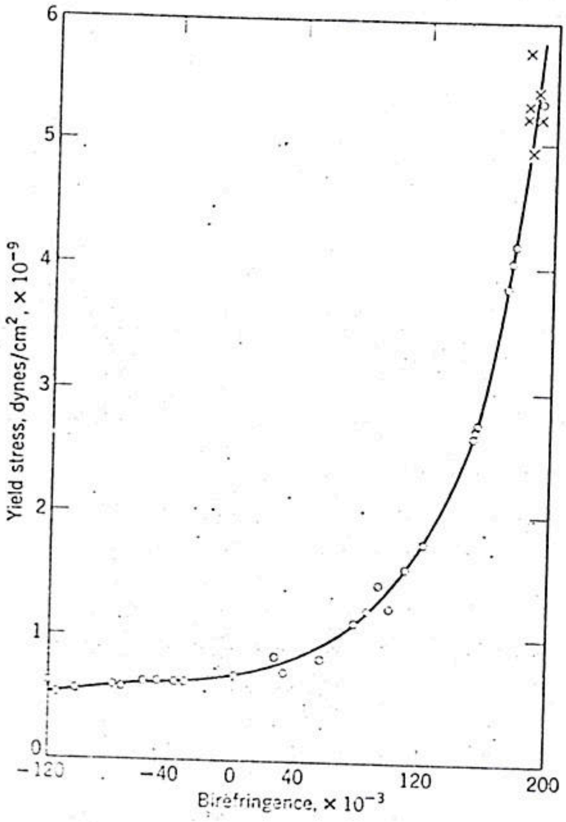


Fig. 37. Tensile yield stress at 20°C for samples of poly(ethylene terephthalate) as a function of birefringence. Negative birefringence indicates perpendicularity to the draw direction.

Yield stresses are affected by molecular orientation in broadly the same way as moduli are affected. They may increase or decrease slightly at low draw ratios but they invariably increase at high draw ratios (Fig. 37). A curve of yield stress as a function of previous draw ratio has a significant, and not unexpected, relation to the true stress–strain curve beyond yield. Values of yield stress of specimens which were predrawn, relaxed, and then retested lie close to yield stresses in the true stress–strain curve. It is not to be expected that these two curves, which may be called $\sigma_T(R)$ and $\sigma_Y(R)$, are always exactly the same, regardless of the temperature of preorientation. However, provided that the temperature of preorientation is not too high, $\sigma_T(R)$ and $\sigma_Y(R)$ can be regarded as having useful similarity. The curve of yield stress against draw ratio is important because it gives the upper limiting stress which cannot be exceeded by that material at that temperature. If the curve is reached, the specimen yields and extends to higher draw ratios along the curve, eventually breaking on the curve. Of course the upper limiting curve may not be reached because the specimen breaks at a stress below this curve. The curve may be regarded as expressing a more basic property of the material whereas breaking stresses falling below it must be regarded as more accidental features representing premature failures at faults in the specimens. This is similar to the behavior observed when the yield stress of isotropic specimens is increased in other ways, such as by lowering the test temperature. Thus the change may be regarded as a tough–brittle transition.

Moseley (140), working with drawn samples of nylon and poly(ethylene terephthalate), showed that the fracture behavior could be divided into two regions. At low temperatures the breaking stress was independent of temperature but dependent on faults in the specimen. At higher temperatures the breaking stress was dependent on temperature but independent of faults. In Moseley's temperature-dependent region, the specimens break at stresses on the curves of yield stress against draw ratio, whereas in his temperature-independent region, the specimens break prematurely at faults before reaching the yield stress.

In the discussion of the effect of reduction of temperature on isotropic polymers, it was pointed out (p. 320) that at low temperatures fracture occurs prematurely at faults before the macroscopic yield stress is reached; at higher temperatures the polymer yields before fracture. It is now clear that the situation is similar for highly oriented polymers. There are two types of fracture which must be clearly distinguished. In one type the specimen reaches the macroscopic yield stress and then follows the true stress–strain curve for some time before breaking; the true breaking stress and draw ratio at break define a point which lies on the true stress–strain curve. In the other type the specimen breaks before yielding and the true breaking stress and draw ratio at break define a point which lies at a lower stress than the true stress–strain curve. This second type of fracture seems rather more fortuitous than the first.

The amount and direction of molecular orientation have an effect on energies to break which has a particular significance in the practical testing of plastics. In order to obtain results which can be relied upon when evaluating materials to be used in injection molding, it is necessary to test samples which have been injection molded (see Injection Molding under MOLDING). It is quite a common practice to measure Izod impact strengths on specimens which have been end-gated so that the tensile stress is applied along the direction of molecular orientation. Although such results may be adequate for quality control, they may well be unreliable for comparison of materials for other purposes. The results are considerably affected by the molecular orientation and may rate materials in the wrong order. In practice, articles are more likely to break in their weakest direction which is ordinarily such that the crack travels along the flow direction; therefore, for realistic predictions, they should be tested with the applied tensile stress perpendicular to the flow direction.

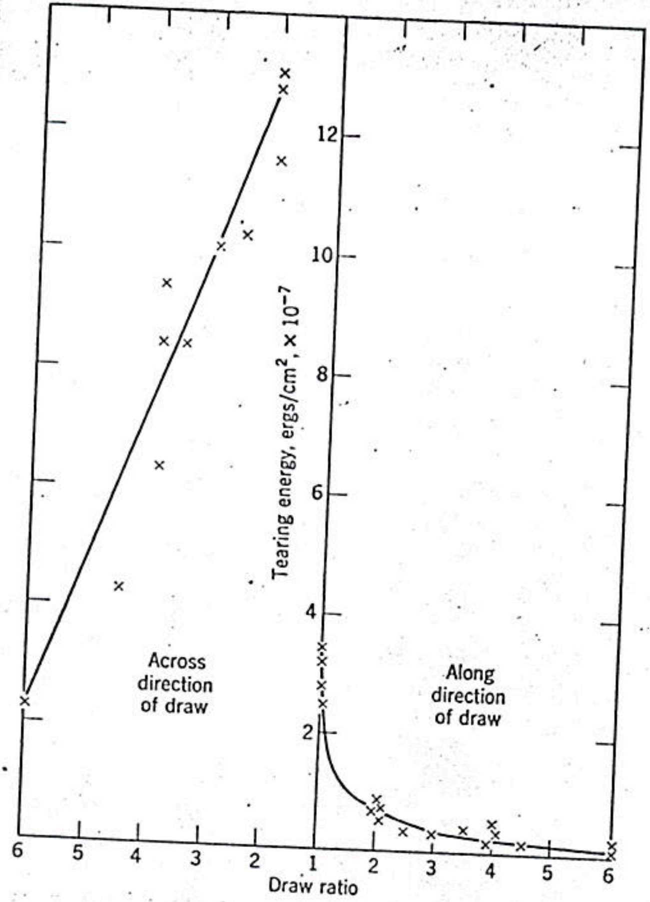


Fig. 38. Tearing energies (−10 to −80°C) of poly(ethylene terephthalate) film as functions of draw ratio.

The results shown in Figure 38 demonstrate that the tearing energy reaches a maximum for partially drawn film torn across the draw direction and that highly oriented film has low tearing energies in both directions.

Figure 39 shows the effect of draw ratio on uniaxially and biaxially drawn poly(methyl methacrylate) (141). The broken specimens (Fig. 40) showed that, in these cases, fracture occurred at right angles to the draw directions; as can be seen from curve C in Figure 39, the specimens have low brittle strengths in directions perpendicular to the draw. This reduction in strength perpendicular to the draw direction becomes particularly plain when highly oriented specimens fibrillate; for an unusually clear example, see Figure 41.

The brittle strength of specimens cut at angles other than 0° and 90° to the draw direction of uniaxially drawn samples may be calculated on the assumption that the specimen either cracks across the draw direction when the stress is $\sigma_1 \sec \theta$ or along the draw direction when the stress is $\sigma_2 \csc \theta$, whichever is less (142). (Here, σ_1 is the breaking stress along the draw direction, σ_2 is the breaking stress across the draw direction, and θ is the angle between the applied stress and the draw direction.) Although the assumptions are not proved, they represent the results reasonably. Significantly, it was observed that when the samples were cut at small angles to the draw direction they cracked across the draw direction; otherwise they cracked along the draw direction (Fig. 42).

The effects of molecular orientation on various fracture properties of polymers have been the subject of a number of studies. For example, the torsional strength of uniaxially drawn polystyrene has been found to decrease and the tensile strength to

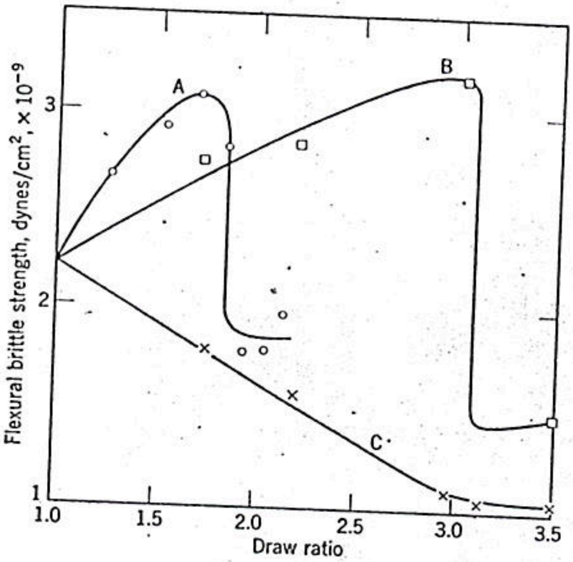


Fig. 39. Effect of draw ratio on brittle strength of poly(methyl methacrylate) (141). Tested after dipping samples in liquid nitrogen. Key: A, biaxially drawn; B and C, uniaxially drawn; B, tested along draw and C, tested across draw.

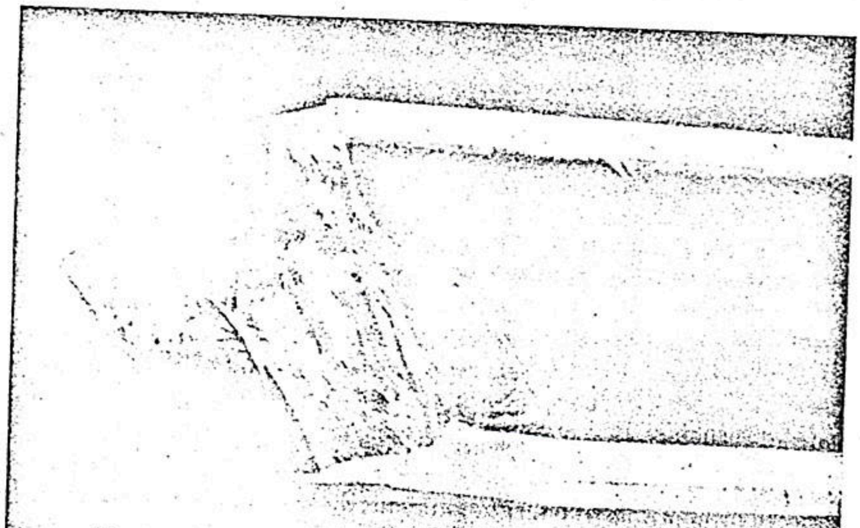


Fig. 40. A biaxially drawn sample of poly(methyl methacrylate) with a draw ratio greater than 1.7 × 1.7 showing fracture occurring by delamination.

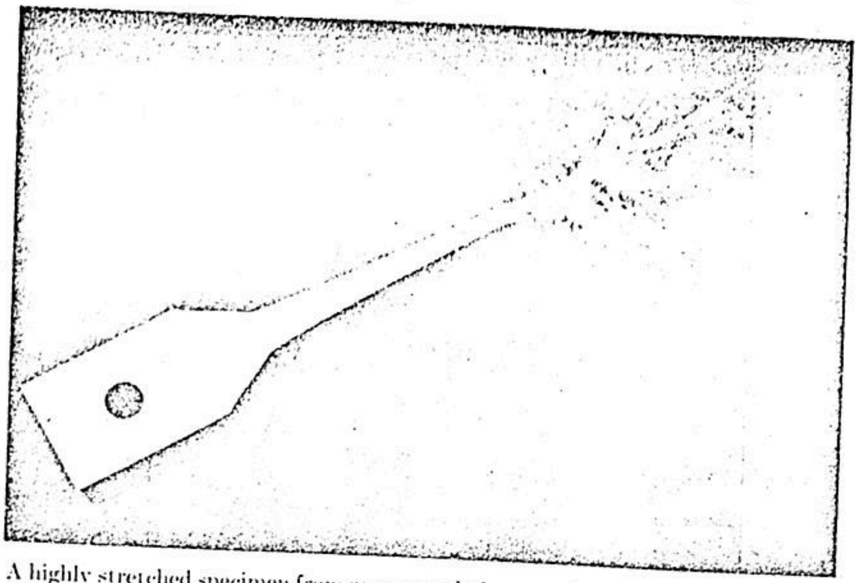
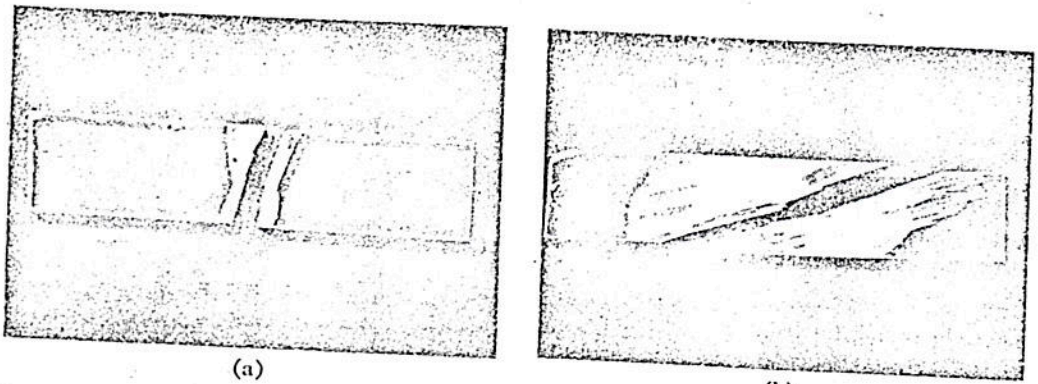


Fig. 41. A highly stretched specimen from an oxymethylene copolymer showing fibrillation occurring on fracture.



(a)

(b)

Fig. 42. Uniaxially drawn samples of poly(methyl methacrylate) stressed in (a) 15° and (b) 20° to the draw direction.

increase with increasing draw ratio; crazing was reduced and eventually eliminated as orientation increased (143). Hurst (144), studying biaxially stretched poly(methyl methacrylate), found improvements in craze resistance, reduced notch sensitivity, and increased impact strength, as well as a reduction in shear strength parallel to the plane of the sheet. Biaxially stretched high-density polyethylene pipe, with reduced wall thickness, has been found to have the same burst strength as isotropic pipe (145). Biaxial orientation doubles the creep rupture strength of high-density polyethylene pipe (146). A study of the effects of orientation and crystallinity on the properties of cellulose acetate fibers showed that, for draw ratios up to 4:1, the fine structure changes, the modulus and tenacity increase, and the elongation to break decreases. For increasing draw ratio between 4:1 and 21:1, the modulus and tenacity increase but there is little change in fine structure or elongation to break (147).

Some understanding of the effects of molecular orientation on fracture can be obtained through the principle of instabilities of deformation. Consider an isotropic

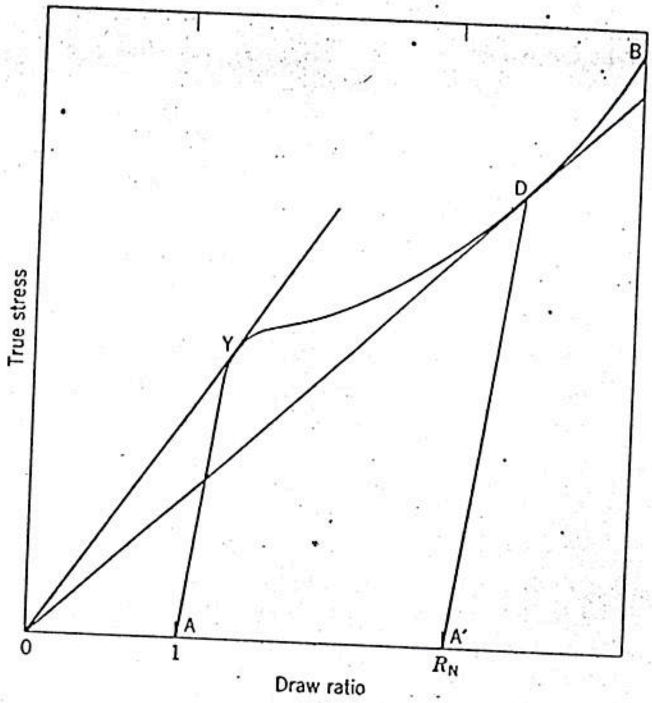


Fig. 43. True stress–strain curve, AYDB, of an isotropic polymer specimen. A′DE is the true stress–strain curve of a predrawn specimen. R_N is the natural draw ratio.

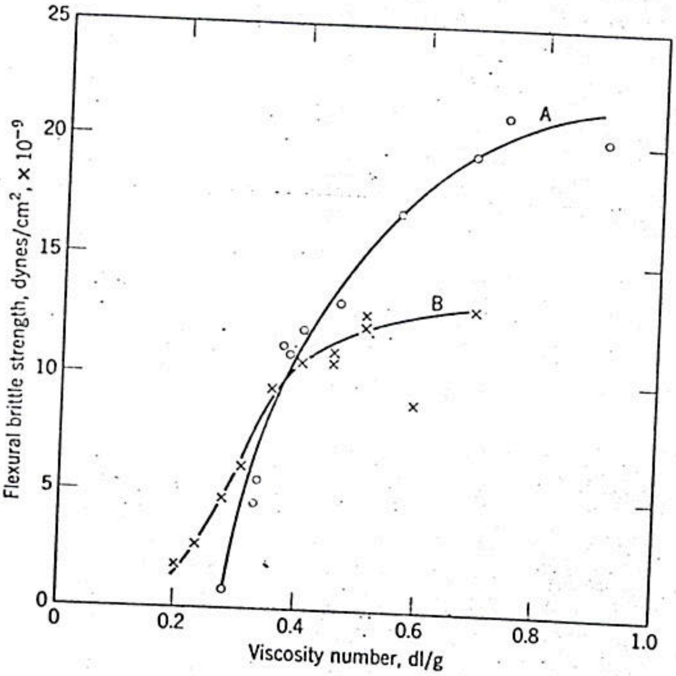


Fig. 44. Flexural strengths of poly(methyl methacrylate) samples as functions of viscosity number. Key: A, tested at about −180°C (after dip in liquid nitrogen) and B, tested at 20°C.

specimen whose tensile true stress–strain curve has the shape AYDB shown in Figure 43 with a natural draw ratio R_N (p. 299). Suppose that such a specimen is preoriented with a draw ratio R_N. Then the oriented material has, in tensile stress, a true stress–strain curve of the shape A′DB. It follows that, whereas the isotropic specimen necked beyond its yield point Y, the preoriented specimen does not neck because the true stress–strain ratio ($d\sigma/dR$) does not fall below σ/R. Consequently, the preoriented specimen extends uniformly. This demonstrates that deformation can be more stable in partially oriented material as an immediate consequence of the behavior expressed in the upward curvature of the true stress–strain curve beyond yield. It follows, from the principle of instabilities of deformation, that partially oriented material has a better resistance to fracture than isotropic material: this is shown, for example, in the tearing energies in Figure 38. It can also be seen in Figure 38 that the tearing energy is low in highly oriented film; this appears to be a consequence of the high yield stress (Fig. 37) (principle of stress variation at a given strain).

Molecular Weight. The average molecular weight of a polymer sample can be characterized approximately by some measure of its solution viscosity or of its melt viscosity (qv). As the average molecular weight of a sample decreases, there is a tendency for the breaking stresses, strains, and energies to decrease, but for little or no change to take place in the moduli and the yield stresses (148). Figure 19 indicated how a reduction in brittle strength, such as is observed with decreasing molecular weight, leads to a movement of the brittle point to higher temperatures when the yield stresses are unchanged.

In general, brittle strength can be observed to increase with increasing molecular weight (Fig. 44) (28,115,141). However, this tendency can be modified or even reversed by high degrees of crystallization or by orientation (see the sections on Crystallinity and on Orientation). These latter factors appear in the effects of molding techniques and cooling rate on test specimens or articles prepared from the same polymer by different techniques. For polyethylene, it has been observed that the brittle strengths of branched polymers and of linear polymers of the same melt viscosity do not differ significantly.

Because reduction in molecular weight generally leads to some reduction in brittle strength without directly affecting the yield stress, the brittle point moves to higher temperatures; it thus leads to a reduction in the values of other fracture properties such as impact strength, tearing energy (28), and energy to break (115). Berry (15) has shown that, for poly(methyl methacrylate), the fracture surface energy in controlled cracking decreases as the viscosity-average molecular weight decreases. Cooney (149), working with high-density polyethylene, found that the stress level at which the mechanism of fracture changed from ductile to brittle decreased as the melt flow index increased (ie, as molecular weight decreased). Polyethylene becomes more susceptible to environmental stress-cracking as the melt flow index increases (89,90); it is thus advantageous to extract low-molecular-weight material (89) and disadvantageous to add low-molecular-weight material (91). When molecular weight is increased, fibers can be drawn to higher orientation; since tenacity is also greater at a given orientation, the tenacity of fibers can generally be increased by increasing their molecular weight (150–155).

If the molecular weight is increased very greatly, there are secondary effects caused by the high melt viscosity (156). Very viscous melts are difficult to mold satisfactorily so that the samples may have unexpectedly low brittle strengths because of poor welding and molding faults. Also, high melt viscosity may reduce the rate of crystallization for semicrystalline polymers, and thus reduce moduli and yield stresses.

One method of controlling the molecular weight is by adjustment of polymerization conditions, but it can also be affected by treatments that the polymer receives during fabrication or in use. Molecular weights, and consequently fracture stresses, can be reduced by the following: (a) Irradiation by γ-rays, neutrons, etc (Charlesby, Ref. 15); (b) High temperatures during melt processing and in use (see, for example, Refs. 157–160); (c) Weathering and ultraviolet irradiation (161–163); (d) Chemical attack (Jellinek, Ref. 15). Attack on elastomers by ozone is particularly important, since this is the principal cause of cracking at low strains (164,165). See also ANTI-OZONANTS. (e) Severe mechanical working in the melt. See also DEGRADATION.

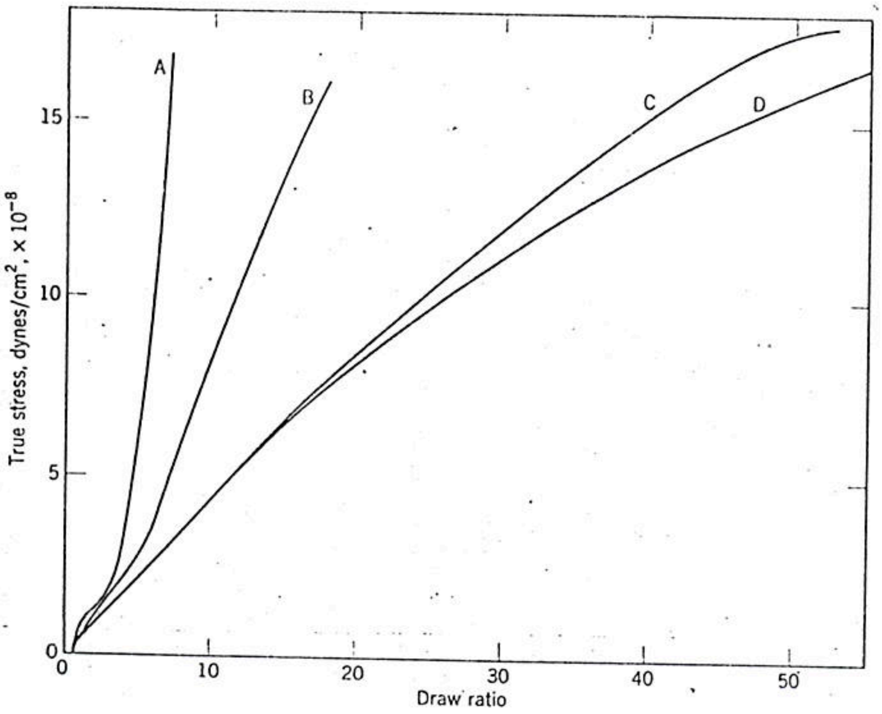
Fig. 45. A film of poly(methyl methacrylate) (η_{sp}/c = 0.2 dl/g) cast from a solution of ethylene dichloride.

There are a variety of ways of measuring or assessing molecular weight, eg, light scattering, ebulliometry, osmometry, and melt and solution viscosities; however, it is not certain that any of them provides a measure of molecular weight which correlates well with fracture properties. Measurement of the tenacity and breaking extension of regenerated cellulose fractions and blends indicates that the point of fracture is determined by neither the number-average molecular weight nor the weight-average molecular weight (166). Evidence supports the suggestion that

$$\bar{T} = \sum_{1}^{n} w_i T_i \qquad (24)$$

where T is the tenacity of a material with a broad molecular-weight distribution, w_i is the proportion by weight of the ith molecular-weight fraction of a polymer of n molecular-weight fractions, and T_i is the tenacity of the fraction w_i.

It is clear that changes in molecular weight often have effects on the fracture properties but that the exact change found depends on the test conditions. There is no complete quantitative theory known to explain the effects observed but some indications can be given which are consistent with the principles of stress concentrations and of instabilities of deformation. In Figure 44 it was shown that samples of poly(methyl methacrylate) with a viscosity number in chloroform of about 0.3 dl/g had very low breaking stresses. When such samples are compression molded, they crack during solidification. In an attempt to create a crackfree sample, thin films were cast from chloroform and ethylene chloride solutions by very slow evaporation of the solvent. Even under these conditions, the films cracked during solidification; Figure 45 shows an example. This result suggests that very low-molecular-weight samples have very low strengths because they contain many serious structural irregularities: an example of the principle of stress concentration.



	Melt index	*Density*
A	$\sim 10^{-7}$	0.945
B	0.02	0.95
C	0.2	0.96
D	5.0	0.965

Fig. 46. True stress-strain curves at 100°C for polyethylene (melt index determined according to ASTM E 1238).

Flory (167), working with butyl rubber fractions of varying molecular weight, demonstrated that the rate of orientation hardening decreased as the molecular weight decreased. Figure 46 shows the true stress–strain curves at 100°C for four samples of high-density polyethylene (28). As the melt flow index increases (molecular weight decreases), the rate of orientation hardening decreases. In general, increasing molecular weight favors cold drawing rather than necking rupture, and so it follows that increasing molecular weight increases orientation hardening and therefore promotes stability of deformation. On the basis of the principle of instabilities of deformation, therefore, the effects of molecular weight on fracture can be explained as consequences of the effects on orientation hardening. In addition, it may be that cracking on solidification, as exemplified in Figure 45, is also a consequence of low orientation hardening. As the sample solidifies, stresses are set up by differential contraction. In a material with a complete lack of orientation hardening, such as low-molecular-weight poly(methyl methacrylate), there is nothing to prevent these stresses causing local fracture and developing into visible serious cracks. In this view, therefore, the effect of molecular weight on fracture is a consequence of the effect of molecular weight on orientation hardening. It remains only to explain this effect. The course of the stress–strain curve for a rubbery polymer depends on the proportion of crosslinks (2). As the number of crosslinks increases, the stress rises more rapidly on extension, ie, there is more orientation hardening. For linear polymers, the true stress–strain curves beyond yield are similar to those of crosslinked rubbers in spite of the absence of chemical crosslinks. It is likely that even linear polymers deform as networks with physical crosslinks such as entanglements and intermolecular secondary bonds. When the molecular weight of such a polymer is decreased, the number of entanglements is reduced (168) and so it behaves like a rubber with reduced crosslink density.

Crosslinking (qv) (15,169–172). One effect of crosslinking in polymers is to increase the glass-transition temperature of the polymer (see, for example, Refs. 173 and 174). It follows that, at some temperatures, crosslinking increases moduli and yield stresses and, therefore, in accordance with the principle of stress variation at a given strain, decreases strains and energies to break. As a thermosetting resin is cured (crosslinked) it becomes harder and more brittle. A small amount of crosslinking may increase the breaking stress of brittle polymers such as polystyrene and poly(methyl methacrylate) but more than a few percent of the crosslinking agent reduces the breaking stress to much lower values (169,170,175–177).

According to Gee (178), the degree of crosslinking is the most important single factor determining the tensile breaking stress of rubbers. It has been well established that, as the degree of crosslinking of a rubber is increased, the tensile breaking stress rises to a maximum and then decreases (179–182). This maximum becomes less obvious as the straining rate is decreased (183). Landel and Fedors (184) have pointed out that the maximum is an artifact and that increasing crosslink density can, within certain limits, be regarded as equivalent to decreasing the temperature or increasing the rate of extension. It follows that the decreases in tensile strength and elongation to break observed at high degrees of crosslinking are consequences of the principle of stress variation at a given strain; that is, they are caused by the increased resistance to deformation. The initial rise in tensile strength is a consequence of the principle of instabilities of deformation. As the degree of crosslinking increases, the rubber molecules become more oriented on stretching (2) and also, in a rubber which can crystallize, the crystallization sets in at a lower extension. Thus the rate of orientation hardening increases as the degree of crosslinking increases.

Bonotto (185) has studied the effect of crosslinking on the mechanical properties of polyethylene and copolymers of ethylene and ethyl acrylate. Although crosslinked ethylene polymers may have some superficial similarities to reinforced rubber vulcanizates, this author emphasizes that there are significant detailed differences in the shapes of the load–extension curves and in the temperature dependence of the mechanical properties. At ambient temperatures, crosslinked polyethylene is reinforced by crystallization, whereas above the crystal melting point it is a lightly crosslinked rubber.

Insoluble Additives. A variety of substances are added to polymers, either in deliberate attempts to change the mechanical properties or for other reasons, with secondary effects on the mechanical properties. Additives which dissolve in the polymer have been considered in the section on Plasticizers and Other Soluble Additives; this section is concerned only with additives which do not dissolve in the polymer but remain as a separate phase. When the modulus of the polymer is lower than that of the additive, the modulus of the composite is intermediate between the two, provided the applied strain is sufficiently small. Turner (186) has defined a quantity called the "reinforcement factor" as the ratio of the modulus of the filled polymer to the modulus of the unfilled polymer at the same strain. As the strain increases, the reinforcement factor decreases (187). However, a single measurement of low-strain modulus is insufficient to characterize the stiffness of a composite. If the composite yields before breaking, its yield stress may be greater than, less than, or the same as that of the polymer. Figure 31 shows the yield stress of poly(vinyl chloride) as a function of the concentration of additives. As the amount of insoluble additives (fine spherical particles) decreases, the yield stress decreases (curve B).

The values of fracture stresses, strains, and energies depend on a variety of factors: (a) The nature of the additive (188,189). Different fillers may vary widely in the degree to which they affect the properties of a polymer. (b) Particle size (190–192). The mechanical properties of composites have been found to be inversely proportional to the particle size of the filler (190). (c) Bond between polymer and additive (127, 191–195). (d) Particle shape. Long thin additives reinforce better than spherical particles (9,196,197). The properties of composites with fibrous additives depend also on the orientation of the fibers (see, for example Ref. 198; see also FIBERS, INORGANIC).

A comprehensive examination of the effect of adding various amounts of chopped strands of glass fiber to polycarbonate showed that the elongation to break decreased as the resistance to deformation increased (199). (This study demonstrates the superiority of detailed investigation of behavior over the simple tabulation of the results of standard tests.) See also FILLERS; REINFORCEMENT.

Faults. According to the principle of stress concentration, the probability of fracture is increased by increasing the severity of faults in the structure. Such faults may be deliberate notches or holes (p. 328) or they may be caused by very high crystallization (p. 337), low molecular weight (p. 350), high crosslinking (p. 353), or contamination by insoluble additives (p. 354).

Structural irregularities may also be introduced by the use of poor fabrication techniques. The brittle strength decreases at low molding temperatures; Figure 47 is a photograph of a low-temperature molding in which the structural irregularities can be clearly seen. Too low a molding temperature can lead to inadequate bonding

Fig. 47. Micrograph of poly(methyl methacrylate) molded at 130°C.

and so to structural irregularities and brittleness. Low molding pressure can have a similar effect (200). When two sheets are welded, the weld may have a low brittle strength because of low welding temperature or pressure or because holes are left in the material (201,202).

Faults, such as notches, holes, cracks, contamination, and the effects of poor molding, reduce the brittle strengths of polymers. Figure 19 shows how a reduction in brittle strength leads to an increase in brittleness temperature. Apart from the obvious practical implications, faults of this type can cause a particular difficulty in the initial evaluation of small quantities of experimental polymers; in this case, brittleness may be caused by contamination or by unsuitable molding conditions, rather than by any fundamental brittleness of the polymer.

Chemical Composition. It will be appreciated from the examples in the previous sections that the stresses, strains, and energies to break of polymer specimens can be substantially altered by changes in any one of a large number of variables. It is, therefore, difficult to compare the fracture behavior of two or more polymers of different chemical composition. Changes in test conditions can often have different effects on different polymers and therefore cause reversals in the order in which materials can be rated. Furthermore, even if test conditions are carefully standardized and controlled or, preferably, tests are made over a wide range of conditions, it is not easy to be certain that any differences found are caused by a change in chemical composition rather than by changes in other factors, such as molecular orientation, molecular weight, faults, etc. In spite of these difficulties it is possible to note certain general tendencies.

As the length of a side chain is increased, the glass-transition temperature decreases and, at room temperature, the material becomes softer (lower moduli and yield stresses) and less brittle (principle of stress variation at a given strain). Rehberg and Fisher (203) showed that, as the length of the side group increased, the brittleness temperature of *n*-alkyl methacrylate and acrylate polymers decreased to minima at poly(*n*-dodecyl methacrylate) and poly(*n*-octyl acrylate). Yield stresses of *n*-alkyl methacrylate polymers at a given temperature decrease with increasing length of the alkyl group (28). A similar effect can be observed with α-olefin polymers, although, in this case, variations in crystallinity can cause confusion. For example, at room temperature, ordinary polypropylene is harder and more brittle in impact than poly-1-pentene.

When the side group is nonlinear, with branches or rings, the glass-transition temperature is increased and, at room temperature, the material is harder and more brittle. At room temperature, poly-4-methyl-1-pentene is harder and more brittle than poly-1-pentene. Bulky side groups tend to increase yield stresses and so tend to lead to embrittlement. However, polymers with very bulky side groups, such as polystyrene, poly(cyclohexyl methacrylate), and poly-*N*-vinylcarbazole, have substantially lower breaking stresses than linear polymers. It is possible that, because of the bulky side groups, such polymers contain natural faults which reduce their brittle strengths.

Methylene groups are small and have low secondary bonding forces. When the polymer chains contain other groups, such as CH_2Cl, CH_2CN, CONH, and C_6H_4, which are larger and have higher secondary bonding forces, the glass-transition temperature is increased and, at room temperature, the material is harder and more brittle in impact.

Table 7 compares a number of polymers in two ways. First, they are grouped into three classes according to their characteristic behavior in impact tests at room temperature. It is not possible to quote precise values of the impact strengths because

Table 7. Some Polymer Properties at 20°C

Class of behavior in impact	Polymer	Approximate tensile yield stress, dynes/cm²
not brittle even when severely notched	rubbers	$<10^8$
	low-density polyethylene	10^8
	polytetrafluoroethylene	1.5×10^8
	poly-1-butene	2×10^8
	poly-1-pentene	$<10^8$
not brittle when unnotched; brittle when severely notched	poly(*n*-hexyl methacrylate)	$<10^8$
	high-density polyethylene	3×10^8
	polypropylene	3.5×10^8
	chlorinated polyether	4×10^8
	poly(vinyl chloride)	6×10^8
	polyoxymethylene	7×10^8
	poly(ethylene terephthalate)	6×10^8
	polycarbonate of bisphenol A	6.5×10^8
	poly(phenylene oxide)	7.5×10^8
	polydiphenyl ether sulfone	7.5×10^8
brittle even when unnotched	nylon-6,6 (dry)	9×10^8
	poly-4-methyl-1-pentene	3×10^8
	polystyrene	$7–10 \times 10^8$
	poly(methyl methacrylate)	1.1×10^9
	poly(cyclohexyl methacrylate)	too brittle
	polyacrylonitrile	too brittle
	poly-*N*-vinylcarbazole	too brittle

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these are dependent on so many factors, but the classification remains valid for ordinary polymers without a gross change in secondary factors. Also, typical values are given for the tensile yield stress at room temperature; again this cannot be regarded as absolutely fixed because of the dependence on crystallinity, etc. A study of Table 7 provides examples of the effects of side groups and substituent groups discussed above.

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