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Molecular Interpretation of the Load-Elongation Curve of Crystalline Polymers

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The load-elongation curve of a semicrystalline polymer with lamellar structure may have four distinct parts: the initial elastic part, the yield area, the necking area where the lamellar morphology is transformed into the fibrous structure, and the drawing area of the fibrous material up to the failure of the sample. The neck formation stops the elastic deformation of the lamellar structure and hence reduces the upper yield load to the load needed for the continuous necking. The drawing of the fibrous structure extends the interfibrillar tie molecules and shears the crystal blocks. The increase of the contribution of taut interfibrillar tie molecule to the axial elastic modulus of the drawn sample comes to an end as soon as the tie molecule gets so far unfolded that at least one end is completely pulled out of the crystal block it was originally anchored in. Swelling of the amorphous regions so much weakens these areas that they are not able to exert enough force on the lamellae for their complete transformation into microfibrils. But the easy separation of the lamellae perpendicular to the direction of the applied tensile force creates a great many channels which are responsible for the high gas permeability. The bending of the same lamellae yields the high rubber-like strain behavior in the draw direction.

The fracture of the sample is caused by the growth and coalescence of microcracks up to a critical size crack. The process involves the rupture of most molecules which connect the opposite sides of any microcrack. This rupture increases the work per surface area of the microcrack but does not cause the failure of the sample.

1. INTRODUCTION

The most often measured mechanical property of a polymer sample is its load-elongation curve as obtained with a dog-bone shaped sample in a tensile tester. One measures the clamp displacement Δl_c at a constant displacement rate and the force F on the clamps. If the metal parts of the tester are rigid enough as compared with the elastic properties of the polymer sample

and the sample is properly shaped than the load-elongation curve of the polymer sample, F versus Δl , is practically identical with the load-displacement curve of the clamps.

Instead of having a constant displacement rate $\Delta l/\Delta t$ one can also keep the load F constant and measure the sample elongation. In such an engineering creep experiment the stress σ at any cross-section A is $F/A = \sigma_0 A_0/A$. The index 0 refers to the initial values when the load is just applied. Depending on the magnitude of the load one observes three types of creep curves.¹ At very small and at very large load the sample fails in a brittle manner while in the range of an intermediate load the sample deforms plastically and transforms from the lamellar into the fibrous structure. This new structure fails at a much longer time than one would expect in the case of the lamellar structure.

The disadvantage of all the engineering tests is caused by the substantial inhomogeneity of the deformation as soon as the neck forms at the most strained section of the probe. It propagates through the strained sample and transforms the original lamellar structure into the new fibrous structure. It is rather difficult if not completely impossible to derive the physically important mechanical response of the strained volume element from the observed load-elongation or creep curve. The curve obtained in such an engineering test is a superposition of the deformational behavior of the old and new morphology with the ratio of both steadily changing with the propagation of the neck. The mechanical properties of the two coexisting structures differ enormously. The fibrous structure has a substantially higher axial elastic modulus than the lamellar structure. The stress on them differs by a factor equal to the draw ratio in the neck which may quite substantially increase with the neck maturation.² As a rule it is between 5 and 10, at least in the case of linear polyethylene. Under a so much higher stress the fibrous structure deforms plastically to a much larger extent than the much softer lamellar structure which, however, is subjected to a much smaller stress. The just mentioned neck maturation means the transformation from the extremely gentle virgin neck into the much sharper final neck.

A study of the time and stress dependence of the mechanical properties of the volume element of the polymer sample is only possible by putting marks on the sample before the straining starts and to follow their displacement as a function of time. One obtains the strain of the volume element between two consecutive marks and by neglecting the sample compressibility also a sufficiently reliable value for the stress. This of course implies that one is so far from any substantial change of the cross-section that one can assume that the stress field is uniform in the volume element under consideration. This reduces the reliability of the information in the close vicinity of the neck which represents a substantial change of the cross-section of the strained sample. It also definitely excludes the ends of the narrow section of the dog-

bone shaped sample.

In that which follows one will neglect the time effects of the elastic modulus and the influence of the Poisson ratio of the elastic deformation on the cross-section of the sample. Hence the semicrystalline polymeric material will be treated as incompressible which yields the stress equal to F/A with $A = A_0/(1+l/l_0)$. This is perfectly correct for the plastic deformation but introduces an error in the elastic part of the deformation as a consequence of the deviation of the Poisson ratio of the elastic deformation from the value .5 of the incompressible material.

2. THE LOAD-ELONGATION CURVE

The load-elongation curve of a semicrystalline polymer with lamellar structure subjected to a constant displacement rate of the clamps may have four distinct parts (Figure 1):

1. the initial almost reversible elastic part,
2. the yield area,
3. the necking area which transforms the lamellar into fibrous structure,
4. the drawing area of the newly formed fibrous structure ending with the fracture of the sample.

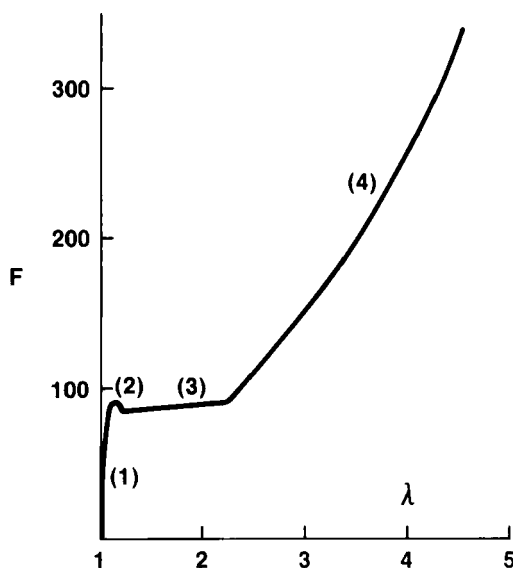


FIGURE 1 The load-elongation curve of nylon-6 showing the four distinct parts of the deformation.³

The deformation is homogeneous during part 1 and 4 with the whole sample in lamellar or fibrous structure, respectively, and inhomogeneous during parts 2 and 3 where the neck separates the material with lamellar from that with fibrous structure. One deforms the former structure in parts 1, 2, and 3 and the latter in parts 3 and 4.

At very high extension rates the sample is heated by the resistance of the friction forces opposing the rapid extension to such an extent that the temperature increase cannot be neglected any more. The heating effect is proportional to the square of the expansion rate. The heating makes the sample softer so that it deforms faster and may eventually flow and fracture in a liquid-like manner.¹ All such effects will be excluded in that which follows.

3. THE DEFORMATION OF THE LAMELLAR STRUCTURE

In the first region the material can be represented by a model with a parallel spring (E_1) and a viscous dashpot (η_2) with another spring (E_2) in series (Figure 2). The connection between the applied stress σ and the strain $\varepsilon = \dot{\varepsilon}_0 t$ reads

$$\begin{aligned}\sigma &= \varepsilon E_1 + \dot{\varepsilon}_0 \eta_2 (1 - \exp(-E_2 t / \eta_2)) = \varepsilon (E_1 + E_2) & t \rightarrow 0 \\ &= \varepsilon E_1 + \dot{\varepsilon}_0 \eta_2 & t \rightarrow \infty\end{aligned}\quad (1)$$

The influence of E_2 disappears completely after the transient is replaced by the limiting value of the stress. As a consequence of the finite viscosity of the polymer sample the observed stress at any strain is larger than the equilibrium stress at the same elongation. The difference is larger with a higher extension rate $\dot{\varepsilon}_0$ and only gradually disappears when with the start of the neck formation $\dot{\varepsilon}$ goes to zero.

The model corresponds to a parallel arrangement of crystals (E_1) and crystal-amorphous sandwiches (E_2, η_2). This represents sufficiently well the spherulitic sample with the randomly oriented stacks of parallel lamellae. The tendency of the amorphous layers to return to their prestressed state after the external load is removed is indirectly included in E_1 which is fully responsible for the return of the sample to the initial length. Since this effect may be relatively slow as compared with the relaxation of the parallel spring-dashpot system of the model one has to replace the spring E_1 by two springs E'_1 and E''_1 , the second one having in parallel a very highly viscous dashpot with a relaxation time τ'_1 much longer than τ_2 . With such a model one has a relatively rapid recovery corresponding to E'_1 while the rest of the recovery corresponding to the combination of E''_1 and η''_1 is substantially slower. The first part would correspond to the elastic and the second part to the recoverable plastic deformation. The designation elastic and plastic is

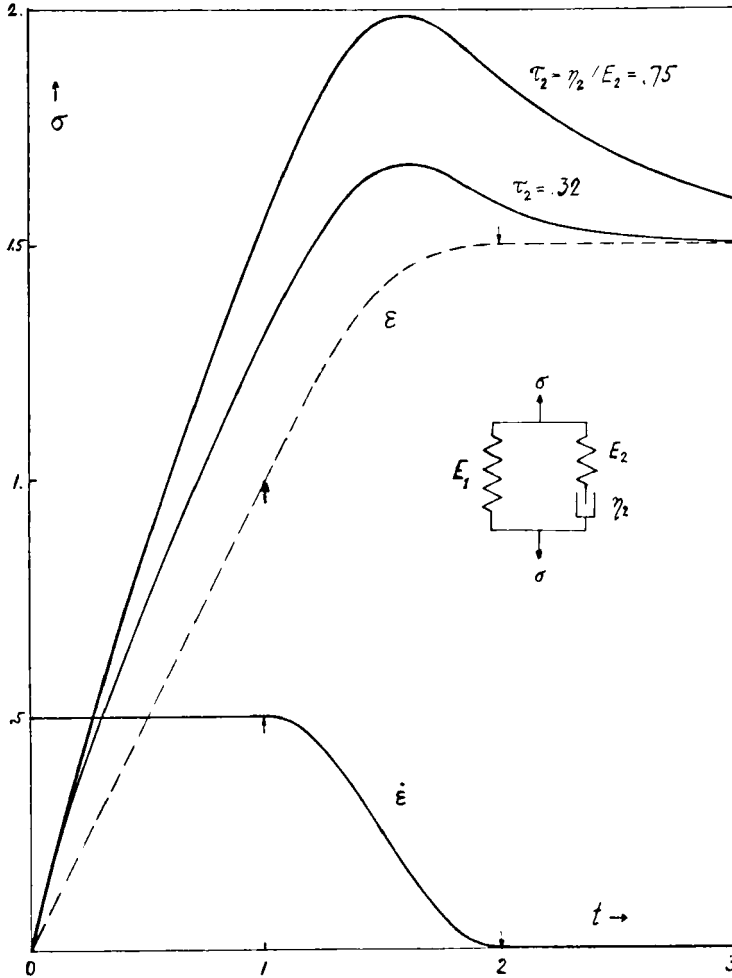


FIGURE 2 The calculated load-elongation curve of the linear model of the unoriented polymer (Voigt model with an additional spring E_2 in the dashpot branch) under the assumption that the neck formation starting at t^* gradually stops the deformation of the lamellar structure, i.e., makes $\dot{\epsilon}(t)$ to go to zero at $t^* + \tau$. Up to t^* the elongation rate is constant. The abscissa is plotted with $t^* = 1$ and $\tau = t^*$, and the ordinate assumes that the load at t^* is 1.

mainly based on the fractional free volume changes associated with each kind of deformation. The specific volume increases almost linearly in the former type of deformation and remains practically constant in the latter type as shown by the change of the sorption of vapors with the sample elongation.⁴

In the yield region the neck starts at the softest cross-section of the sample.

The softness means either a higher local stress as a consequence of a smaller cross-section or a smaller resistance of the material to a given stress. The reduction of the cross-section may be caused by any flaw, inclusion of some softer material or some poor machining of the dog-bone sample. The reduction of the resistance of the material to the plastic deformation may be caused by the structural inhomogeneity of the spherulitic sample, by the inclusion of some softer material or by some small local temperature increase as a consequence of the inhomogeneous heating by the internal friction forces during the elongation to the yield point.

As soon as the neck starts to form the lamellar section of the strained sample remains at a constant strain up to the time the neck transforms the lamellar structure into a fibrous structure. Hence the rate of the deformation $\dot{\epsilon}$ of this section vanishes and so does the viscous stress contribution $\dot{\epsilon}\eta_2$. The total load on the sample drops from the upper yield stress σ_y to the lower yield stress σ_d (stress to draw by necking). Since the final state is not reached abruptly one has a smooth decrease of the viscous stress from the initial value $\dot{\epsilon}\eta_2$ to zero. The nonlinearity of E_1 however, may modify the situation so much that there is no drop of the load during yielding. Toward the end of the initial almost elastic range, the load continues to rise at a steadily decreasing rate and ends in the long plateau of the necking region without any indication of the yield area.

If the draw ratio λ of the volume element in the necked zone remains constant, one has there also a constant stress so long as the neck can still propagate through the sample. A constant stress means also a constant load because the cross-section of the lamellar material remains practically constant during the neck propagation. Hence one expects in part 3 a horizontal load-elongation curve.

One has not explicitly considered the influence of the change of the shape of the neck on the load-elongation curve. The neck starts as a very gentle narrowing of the cross-section of the strained sample and as a rule ends as a very sharp reduction of the cross-section. The influence of such a shape change on the load-elongation curve is a less abrupt drop of the load from the upper to the lower yield load. The effect is much more conspicuous in the draw ratio of the volume element.² After a while, however, this effect levels off as it was explicitly observed in the drawing of branched polyethylene.⁵

The newly formed fibrous morphology is characterized by the long and narrow microfibrils.^{6,7} Their high axial elastic modulus is a consequence of the large fraction of taut tie molecules which originated from the destruction of the folded chain lamellae of the starting material. Most of the tie molecules are located at the outer boundary of the microfibrils. According to the molecular formation mechanism of the microfibrils by pulling folded chain blocks from the lamellae one does not expect any intrafibrillar tie molecule

inside the microfibril. An exception are the random reentry molecules of the original lamellae. If they connect areas which yield different blocks in the newly formed microfibril they act as intrafibrillar tie molecules not located at the outer boundary but in the interior of the microfibril. However, the tie molecules of the original lamellar structure which connected different lamellae, and the molecules reentering blocks which were incorporated in different microfibrils, now connect different microfibrils and thus act as interfibrillar tie molecules.

4. THE DEFORMATION OF THE FIBROUS STRUCTURE

The last part of the load-elongation curve corresponds to the drawing of the fibrous material up to the final break of the sample.⁸ Such a drawing which may start already in the neck is only possible by shear displacement of microfibrils and fibrils which represent a dense packing of all microfibrils originating from the same stack of parallel lamellae. A macroscopic draw ratio of the fibrous structure can only be explained if the microfibrils and fibrils have a finite length. Any shear displacement of infinitely long elements does not change the aspect ratio of the sample.

The load-elongation curve during the drawing of the fibrous structure has to be interpreted in a similar manner as the first section corresponding to the almost elastic deformation of the lamellar structure. In both cases the sample is uniform so that the data observed are directly applicable to the volume element. The main difference between the two cases is in the character of the deformation. It is almost purely elastic in the first region and almost completely plastic with the fibrous material which is formed under the high tension in the necking zone. The deformational model in the latter case therefore may not include the spring with E_1 . It only contains the extremely high viscosity dashpot in series with a very strong elastic spring E_f . Such a model completely neglects the high elastic modulus of the fibrous structure which yields a recoverable strain of a few percent which is substantially smaller than the irreversible plastic strain of a few hundred percent.

This yields

$$\begin{aligned} F &= \sigma A_f = \varepsilon E_f A_f + (\dot{\lambda}/\lambda^*) \eta_f A_f = \varepsilon E_f^* A_f^* + (\dot{\lambda}/\lambda') \eta_f A_f^* \\ A_f &= (\lambda^*/\lambda) A_f^* \\ E_f &= f(\lambda/\lambda^*) E_f^* \sim (\lambda/\lambda^*) E_f^* \end{aligned} \quad (2)$$

The superscripted asterisk denotes the properties of the sample at the moment when the necking process is just terminated, i.e. all the lamellar material is transformed into the fibrous structure. The subsequent deformation of the fibrous structure is plastic. The cross-section of the sample

decreases as the inverse of the relative draw ratio λ/λ^* of the fibrous structure. As a rule the elastic modulus increases a little faster than the draw ratio but finally reaches a limit. This limit is approached faster if the drawing is performed close to the melting point of the sample and at a high draw rate which by itself increases the temperature of the strained sample. As soon as this limit is approached the elastic modulus does not increase substantially with further drawing.

From the last equation one gets the impression that most of the eventual increase of F with the elongation is a consequence of a more than linear increase of the viscous resistance of the fibrous structure against the plastic deformation. Such a resistance has two sources; the work for pulling out chain stems from the crystal blocks in which the interfibrillar tie molecules are anchored, and the viscous resistance of the boundary between adjacent fibrils and microfibrils. Since the number of interfibrillar tie molecules does not increase with drawing and the same applies to the force for the pulling out a single stem one has to blame the frictional force between adjacent microfibrils and fibrils for almost all the increase of the load with increasing plastic deformation.

The liquid type friction force for any shear displacement of adjacent fibrillar elements is proportional to the product of the area, the friction coefficient, and the shear gradient. Since the first and the last factor remain practically constant the whole increase of the frictional resistance must be the consequence of the increased friction coefficient. The interfibrillar material must increase its specific viscous resistance more than linearly with the draw ratio λ/λ^* . This may be the consequence of a better chain alignment which approaches that in the crystals. Such internal ordering may go locally so far that the blocks on adjacent microfibrils are almost completely in a crystallographic register which shows up in an increase of the lateral coherence length for the wide angle x-ray scattering. This effect was indeed observed by Hosemann and Wilke⁹ and more recently by Cakmak.¹⁰ Presently one has not yet any direct indication what causes this increase.

The drawing of the fibrous structure enormously extends the length of the interfibrillar tie molecules by unfolding the sections by which they are anchored in the crystal blocks of adjacent fibrils and microfibrils. The drawing also irregularly shears the crystal blocks of the microfibrils and may thus create sporadically crystalline bridges between consecutive blocks separated by the intervening amorphous layer. The first effect increases the number of taut tie molecules per amorphous layer while the second one not only adds new bridges in the central part of the microfibril which is practically without taut tie molecules but also by doing so homogenizes the stress field in the crystal blocks. Both effects may increase the axial elastic modulus faster than one would expect from the almost linear increase of the fraction of taut

tie molecules with the draw ratio.

The first effect has a serious limitation in the finite length of the inter-fibrillar tie molecules. As soon as any such molecule is so much extended by unfolding that it is pulled out of at least one of the two crystal blocks it is originally anchored in it drops out as a contributor of new tie molecules per amorphous layer. From this moment on its effective length does not increase any more and hence the molecule cannot bridge any new amorphous layer as it did before. This means that sooner or later the increase of the axial elastic modulus with increasing draw ratio must come to a halt at least as far as the contribution of the inter-fibrillar tie molecules is concerned.

The effect may occur earlier if the expansion forces are resisted by very soft crystals so that the unfolding is incomplete. One or more loops are pulled out together from the crystal block. Each loop corresponds to at least two strands. The ideal complete unfolding pulls out a single strand only.

The incomplete unfolding is in many respects similar to that taking place at the transformation of the lamellae into microfibrils when folded chain blocks are pulled out of the lamellae and incorporated in the newly formed microfibrils. One may ask why in the same temperature range such pulling out of blocks occurs in the micronecking process and not with the inter-fibrillar tie molecules which as a rule pull only one single strand out of the block they are anchored in. The cause for the difference seems to be the different morphology of both cases. As a rule the inter-fibrillar tie molecule is acting alone as a single molecule while in the micronecking zone the microcrack is bridged by a full layer of molecules. Hence the former molecule is not able to pull out of the crystal block more than its own chain while the layer of chains bridging the crack is able to pull out of the lamella a larger number of folded chains. Moreover and more important, the microfibril morphology protects the crystal blocks against any large scale deformation by the strong axial connections of all the blocks by the great many taut intrafibrillar tie molecules. A large deformation of any block is only possible if also some subsequent blocks of the same microfibril cooperate with almost the same kind of deformation. Such a cooperativeness makes the pulling out of a single chain rather easy because it affects only one block. But it strongly opposes the shear displacement of a larger group of chain stems which is the prerequisite for pulling out any block of folded chains as requested in the incomplete unfolding. In the drawing of microfibrils in the micronecking zone such a cooperation between the lamellae of the same stack is much less likely to occur because the lamellae are not tightly connected by taut tie molecules as are the blocks of each microfibril. Hence there is nothing which would prevent the pulling out of lamellae full blocks of folded chains in contrast to the case of the inter-fibrillar tie molecule which pulls out only its own stem.

If such an incomplete unfolding takes place the end of the interfibrillar tie molecule is reached much faster. This brings earlier to a halt the increase of the contribution of the interfibrillar tie molecule to the axial elastic modulus. As a consequence of this effect the modulus increases more slowly with increasing draw ratio and may sooner reach a limit than in the case of complete unfolding. This was actually observed¹¹ on polyethylene and polypropylene drawn at a high temperature close to the melting point and at a high draw rate which also increases the actual temperature of the sample by the measurably increased work of the friction forces between sheared microfibrils.

If the drawing occurs sufficiently below the melting point the incomplete unfolding seems to be more an exception than the rule. The unfolding has to compete with the chain rupture. The former effect increases the fraction of taut tie molecules per amorphous layer while the latter effect acts in the same way as the just mentioned reaching of the end of the interfibrillar tie molecule, i.e., it stops the increase of this fraction. It seems that at a given draw rate the steady increase of the maximum draw ratio and the attainable axial elastic modulus of the drawn material, e.g., linear polyethylene, if one goes from room temperature to higher temperature, are a good indication that the increase of the temperature makes easier the unfolding and thus reduces the chances for a premature chain rupture or sample failure. As a consequence one obtains a higher draw ratio and a higher elastic modulus at 60°C, up to $\lambda = 28$ and $E = 30$ GPa, and between 70 and 80°C, up to $\lambda = 45$ and $E = 70$ GPa, than at room temperature with $\lambda \sim 6$. Such an enhancement of the axial mechanical properties of the drawn material comes to a halt if one approaches the melting point where the incomplete unfolding seems to prevail.

5. ENVIRONMENTAL EFFECTS

The effect of the temperature was studied in most investigations of the plastic deformation of semicrystalline polymers. It turns out that the main effect occurs in the amorphous regions which with increasing temperature become more rubbery while the crystals as a rule still remain practically unaffected almost up to the melting point. As a consequence of the reduction of the melting point by the small thickness of the lamellar crystals such effects may occur far below the extrapolated melting point of the infinite ideal crystal lattice. The polydispersity of crystal thicknesses results in a finite temperature range where the melting phenomena show up in an apparent softening of the crystal component.

The softening of the amorphous component by increased temperature makes easier the sliding and rotation of the crystal lamellae, i.e., it favors

the start of the plastic deformation which destroys first the most favorably oriented lamellae and transforms them into microfibrils. Higher temperature also makes easier the sliding motion of the microfibrils which is the main mechanism of the plastic deformation of the fibrous structure. Hence one can achieve a higher draw ratio if one increases the temperature of drawing. This is very clearly demonstrated in the case of the linear polyethylene which at room temperature can be only drawn to a draw ratio about 6 while at 60°C the draw ratio of 30 is easily obtained.² At a still higher temperature of drawing one reaches $\lambda = 45$ and calls this process superdrawing¹² in contrast to the drawing with $\lambda = 30$.

As soon, however, as the temperature is so high that it affects substantially the mechanical properties of the crystals by partial melting, the incomplete unfolding of the strained interfibrillar tie molecules starts to prevail to such an extent that the axial elastic modulus does not increase any more with the increasing draw ratio. In such a case one draws the sample to higher and higher draw ratio without increasing the elastic modulus.¹¹ Too many interfibrillar tie molecules have one end completely pulled out of the crystal block they were anchored in and can even contract in the highly mobilized amorphous matrix so that at further drawing they cease to act as taut tie molecules which make the main contribution to the axial elastic modulus.

Much less study was devoted to the influence of surface active and swelling agents on the mechanical properties of crystalline polymers during drawing. One does not expect very much of an influence on the draw properties from a surface active agent which does not penetrate the sample. The drawing properties are based on the effects in the bulk of the sample. Nevertheless one expects some influence of the surface active agents since they can accelerate or impede the formation of shear bands which start at the surface of the sample. Such shear bands are a prerequisite of the plastic deformation. If the formation of the shear bands is impeded the sample will choose other ways of deformation under the tensile load and will avoid necking. But since the same consideration may apply also to the formation of the crazes which are the first precursor of a crack leading eventually to sample failure one expects an effect of the surface active agent on the plastic deformation mode only in the case that such an agent influences in an observably different way the formation of the shear bands and the crazes, respectively.

The swelling agents act on the bulk of the sample if they have sufficient time to diffuse into its interior up to the thermodynamically equilibrated sorption. They act as a rule uniquely on the amorphous component without affecting the crystals. Hence their effect is in many respects similar to that of an increased temperature although it seems to be more extreme. The softening of the amorphous regions and the preservation of almost intact crystals may change completely the mode of the plastic deformation.

The load-elongation curve of polypropylene swollen in xylene is shown in Figure 3. It is not basically different from that of the dry sample. It shows a reduction of the elastic modulus and of the upper and lower yield load with a more gentle transition which is indicative of a smaller η_2 . But the draw ratio is severely limited to a value between 2 and 3 which means that the necked sample cannot be drawn to any substantial amount.¹³

The forces transmitted through the amorphous matrix on the crystals may be too weak for a complete destruction of the crystal lamellae and the formation of the microfibrils which are the basic constituent of the fibrous structure. On the other hand the softened amorphous regions are unable to resist the forces exerted upon them by the crystals. Hence one observes a separation of the crystal lamellae oriented more or less perpendicular to the applied tensile stress with only partial microfibril formation in the stacks with the lamellae oriented parallel to the stress. The achievable draw ratio remains small as a consequence of the incomplete transformation of the lamellae into microfibrils so that large sections of the sample remain practically unchanged. The maximum observed draw ratio in polypropylene, between 2 and 3,

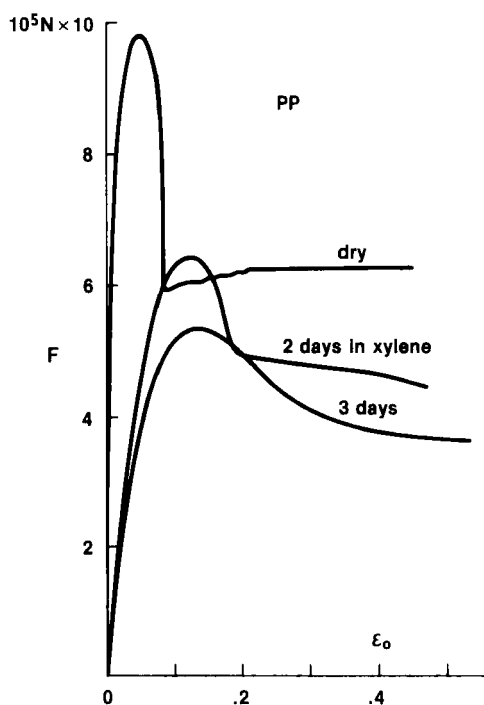


FIGURE 3 Load-elongation curve of polypropylene dry and swollen to equilibrium in xylene at room temperature.

corresponds to a region where in the dry polypropylene the transformation to the fibrous structure is in full progress but is not yet finished.¹⁴

The deformed material is extremely inhomogeneous. It shows practically undeformed areas where the lamellae are more or less parallel to the applied tensile load and extremely porous areas where the lamellae are almost perpendicular to this direction. The latter structure is in many respects rather similar to that in hard elastomers as far as the mechanical and transport properties are concerned. The material has a low apparent density as a consequence of the great many holes. It is completely stable if it is dried with fixed ends so that it cannot partially contract when it is still in the swollen state. Enough of the holes extend through the sample from one surface to the other one thus permitting an easy passage to gas molecules. Hence the permeability follows the rules of the Knudsen type flow through channels with lateral dimensions comparable with the average free path of the molecules. Hence the permeability is proportional to the average velocity of the gas molecule, i.e., to the square root of the inverse molecular weight of the gas. Helium diffuses much faster than oxygen or nitrogen which in turn diffuse much faster than carbon dioxide.¹⁵

The mechanical properties are also very similar to those of the hard elastomers.¹⁶ The strain is recoverable up to about 300%. The elastic modulus decreases with the temperature which is a good indication that its origin is not entropic as in the case of rubber but energetic caused by the bending of the crystal lamellae. The material is extremely anisotropic in its mechanical properties. While in the machine direction the material behaves like a rubber it has a very limited strain range in the perpendicular direction. The elastic modulus is much higher and the strain to break drastically lower in this direction than in the direction of the drawing. But the tearing stress in this direction is larger than in the case of the conventional hard elastomers as a consequence of the large almost unaffected quasispherulitic areas which have the lamellae prevalently in the direction of the initial draw.¹⁷

6. THE FRACTURE OF THE FIBROUS STRUCTURE

The drawing of the fibrous structure comes to an end with the failure of the strained sample. According to the small angle x-ray scattering (SAXS) investigation of the rupture of the fibrous sample, the strained material before the failure is characterized by the gradual appearance of a great many microholes distributed all over the sample.¹⁸ With increased straining new microholes are formed while they seem not to grow larger. At the fracture the average ratio between the hole diameter seems to be almost constant independent of the chemistry and fine structure of the sample. The chemistry

and the morphology determine the stress needed for the formation, distribution, and growth of the microholes. Hence they are extremely important in those factors which determine the strength of the sample. But the actual fracture takes place only after a sufficiently large number of sufficiently large microholes is obtained. The failure of the sample is caused by the coalescence of microcracks which finally leads to a critical size crack.

The critical size crack grows so fast, in a catastrophic manner, that the sample fails almost instantaneously as soon as the critical size is reached. The fractured sample retains all those microcracks which were not involved in the final crack which developed at only one location while the rest of the sample remained coherent. At a subsequent tensile experiment these microcracks open more easily than in the first run during which they had to be created and opened. This explains the lower stress-strain curve during the second run as compared with that of the first run and practically the same or even a higher stress to break because the microcrack coalescence and growth to the critical size crack has to be induced at another place which did not fail during the first straining.

The fibrous structure is rather homogeneous. But it contains plenty of structural defects at both ends of each microfibril where the axial connection with the rest of the sample by taut tie molecules is substantially reduced or even completely interrupted. Such defects cannot transmit the tensile stress as efficiently as the rest of the sample. If they are imagined as holes one has in the adjacent material at the equator three times as high a stress as in the bulk of the sample. The poles, however, are stressfree. Hence the ends of the microfibrils do not carry any load and may even return to the unstrained state if the viscous resistance on their boundaries with the adjacent microfibrils is not high enough to prevent such a shear displacement. In the defect areas the adjacent microfibrils are so much strained by the additional load they have to carry that they are the first to break. In such an event they rupture all the tie molecules bridging the amorphous layer where the break of the microfibril takes place. In such a way a great number of microholes oriented perpendicular to the fibre direction are formed. They are detected by the broadening of the zero orders SAXS. From the shape the average size and from the scattering intensity the number of microcracks can be derived.

Such a microhole is so much easier to form from the strained defect at the end of the microfibril and even from an amorphous layer between the consecutive blocks of the same microfibril the smaller the fraction of tie molecules the defect or the amorphous layer contains. This number seems to increase with the molecular weight of the sample and the draw ratio λ . Hence both factors increase the axial strength of the drawn sample although the increase of the strength with the draw ratio is less rapid than that of the elastic modulus.²

Microholes at the strained structural defects and some amorphous layers form already during drawing, i.e., during the plastic deformation of the sample to a higher λ . At the beginning only the defects with the smallest fraction of tie molecules are affected. With increasing axial stress this gradually applies to defects with a larger fraction of tie molecules. When the drawing continues and λ increases up to just short below the fracture point one opens these defects and even some amorphous layers with the smallest fraction of tie molecules in very much the same way as it happens during the straining up to fracture of the drawn material. The same applies to the lateral extension of the microholes which proceeds by the gradual fracture of the adjacent microfibrils. Hence the number and the lateral dimensions of the microholes increase with λ in spite of the fact that the simultaneous increase of tie molecules per amorphous layer or per defect reduces the number of areas with few tie molecules which can be easily opened and transformed into microholes. With increasing draw ratio the distribution function of the amorphous layers and defects shifts toward a higher fraction of tie molecules per defect or amorphous layer. Since the increase of tie molecules comes to a halt as soon as the tie molecules are fully extended one finds with increasing molecular weight a longer lasting increase of the number of tie molecules per defect or amorphous layer, i.e., a longer lasting shift of the distribution function toward a higher fraction of tie molecules per defect or amorphous layer. This in turn requires a higher stress for the formation of a microhole. The drawn material at a given draw ratio has a higher stress to break the higher the molecular weight.

Jarecki and Meier¹⁹ have shown in electron micrographs of the surface replicas of highly drawn polyethylene the existence of a great many such cracks or crazes perpendicular to the fiber direction. Their lateral dimensions are a few μm . Their number increases with λ and decreases with increasing temperature of drawing. This means that they need a high longitudinal stress for formation. According to the rather rudimentary report in the paper quoted such cracks or crazes seem to occur at almost the same temperature and draw ratio as the longitudinal voids which are mainly assumed to be responsible for the opacity of the sample. But the fluctuation of their ratio is quite substantial so that in some cases the voids appear earlier than the perpendicular cracks or crazes while in other cases the opposite is true. The appearance of the lateral and longitudinal cracks or crazes and voids is in perfect agreement with the above mentioned mechanism of the failure of the fibrous structure under load²⁰ which assumes that each defect of the microfibrillar structure may trigger the formation of lateral and longitudinal microcracks as soon as the local stress becomes large enough.

The tie molecules must be strained to between 35 and 42% in order to break.^{21,21a} This is much higher than the bulk strain to break of the sample

which usually fails at an elongation between 10 and 15%. This high figure is the consequence of the zigzag conformation of the fully extended polymer chain, i.e. of the valency angle of about 109° of the carbon-carbon bond. This angle has to be first stretched to 180° before any substantial straining of the chemical bond takes place. The corresponding elongation is about 22.5%. If the bond stretching up to failure is about 10% one reaches the chain rupture at an elongation of about 35%. Any model of fibrous structure which does not yield such a high straining of taut tie molecules at a substantially smaller bulk strain is unable to explain the observed chain rupture as monitored by the electron spin resonance of the radicals formed during the tensile testing of a highly drawn polymer sample, e.g., a high tenacity fiber.

The rupture of chains starts to be observable in 6-nylon at a strain of 40% of the strain-to-break of the sample which is about 15%.²² At a bulk strain of about 6% one must have at least some structural defects where the adjacent areas are strained to about 35% because only in such a case the tie molecules will be ruptured. With a 50% crystallinity the average amorphous area is strained to about 12% which is far below this critical value. It is only in some defect areas where some tie molecules may be overstrained even at zero bulk strain that a strain of 35% is reached at such a small bulk strain. Even at the strain-to-break, i.e. at a strain of 15%, the average strain in the amorphous areas is only 30% which is too low for any substantial chain rupture. It is only in the defect areas that the strain is high enough²³ to provide the large number of ruptured chains, between 10^{17} and $10^{18}/\text{cm}^3$, as reported in nylon 6 strained to break.²² All the rest of the sample, however, is practically free of chain rupture. In spite of the high local stress and strain enhancement at the defects of the fibrous structure the bulk of the sample is hardly damaged at all even when the sample breaks.

7. CONCLUSIONS

The linear models of the semicrystalline polymer solid with lamellar or fibrous structure adequately describe the main features of the engineering load-elongation curve, i.e., the difference between the upper and the lower yield load and the drawing of the fibrous structure up to failure.

The swelling of the amorphous component changes the load-elongation curve. The elastic modulus and the yield load are much reduced. The transformation from the lamellar to the fibrillar structure is incomplete because the forces transmitted through the swollen amorphous layers are not strong enough for the complete destruction of the lamellae. The incompleteness of the transformation makes understandable the limited range of drawing of

the necked material. The final product behaves like a hard elastomer with an extremely high recoverable strain and a high permeability to gases.

The drawing of the fibrous structure is performed by the shear displacement of the adjacent fibrils which have a finite length. The ends of the microfibrils display such a reduction of the axial connection with the rest of the sample by taut tie molecules that under the influence of a tensile force they open and form microcracks. The growth and coalescence of such microcracks leads to the formation of a critical size crack which makes the sample fail in a catastrophic manner. The opening and growth of the microcrack ruptures the connecting taut tie molecules. The lax tie molecules are not strained enough to rupture. The same applies to taut tie molecules in the conventional amorphous layers of the microfibrils in the sample away from the microcracks.

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