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Phenomenological Model of the Stress–Strain Behavior of Glassy Polymers

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ABSTRACT: Flow processes in glassy polymers under stress are identified with the orientation of chain segments which are large relative to a bond length but small relative to the chain length. A phenomenological expression is presented for the stress in terms of the strain and an order parameter characterizing the degree of segmental orientation. With this model, physical arguments are presented to describe qualitatively features of a stress–strain experiment including (1) the temperature dependence, (2) the initial time lag, (3) the effects of sudden changes in strain rate, and (4) the relationship between tension and compression.

I. Introduction

The response of a glassy polymer to an imposed stress is an important physical property of the plastic.[1] Of particular importance for the understanding of this behavior is the identification of the molecular processes accompanying the transition from the low-strain, elastic deformation regime to the high-strain, plastic-flow regime of a glassy polymer. To help in this task we present in this paper a phenomenological model of the behavior of a glassy polymer under stress. The model described below is still a long way from a proper theory of stress–strain behavior, primarily because we do not have an adequate mathematical realization of the physical ideas. However, even without the mathematics, we can show that the physical picture emerging from the model rationalizes a variety of experimental results. It is precisely this broad degree of qualitative agreement that convinces us that the physical picture we are presenting is reasonable. It is our hope that by presenting this qualitative picture we will stimulate the work that still needs to be done to obtain an adequate theoretical understanding of the stress–strain behavior of glassy polymers.

The next section presents the model we are proposing along with some discussion of the experimental results that support various aspects of the model. This will be followed in section III by a brief discussion of some of the existing theoretical models of stress–strain behavior. The object of this discussion is to point out why a new approach is necessary to explain the experimental results. We will then show that our model can explain qualitatively a wide variety of additional experimental results.

II. Basic Physical Model

A. Orientation of Chain Segments. The starting point for our model of the stress–strain behavior of glassy

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polymers is the well-known fact that when glassy polymers are stretched the polymer chains line up parallel to the direction of stretching. The recent infrared dichroism measurements on stressed polycarbonate by Jansson and Yannas[2] show that the tendency of the polymer to line up parallel to the applied stress not only occurs for large deformations (as has long been known) but also occurs at very small deformations. That is, even a small amount of strain introduces a small degree of ordering. These measurements unequivocally show that chain ordering (not just bond ordering) of some sort is a monotonic function of strain, even for low strain and low strain rate, under reversible conditions with no observable hysteresis. Plots of the dichroic ratio as a function of strain are linear in the strain with an apparent intercept at 0.6% strain. Below 0.5% strain the dichroic ratio lies in the range of the instrumental noise. (The apparent nonzero intercept of the dichroic ratio may perhaps be due to a finite elastic response of the system before ordering starts to occur. Alternatively, the dichroic ratio may be quadratic in the strain at small strains approaching zero at zero strain, but such a dependence is lost in the instrumental noise.)

The major assumption of our model is that the most important motion of a polymer under stress is the orientation of chain segments in the direction of the applied stress. This is not to say that the lining up is the only motion due to the applied field in all cases, but only that it is the dominant motion. We shall discuss other motions below.

B. Stress–Strain Relationships. In this section we shall discuss only simple uniaxial tension. A natural consequence of the picture that the strain entails the orientation of chain segments is to identify the stress (i.e., the applied force per unit area necessary to produce a given strain) as resulting from the resistance of the polymer system to the ordering of chain segments. Thus, the easier it is to orient the chain segments, the smaller will be the stress necessary to produce a given amount of strain. For a small strain, ϵ, the system is in the elastic regime and

$$\sigma = \kappa\epsilon/\chi \qquad (\epsilon \text{ small}) \tag{1}$$

where σ is the stress and κ is a system-dependent proportionality constant related to Young's modulus. χ^{-1} reflects the ease of ordering in response to the strain, where χ is the strain susceptibility. Since χ^{-1} reflects the ease of ordering only of those segments that are not already oriented, this linear elastic regime must saturate as the strain increases and hence as the degree of ordering $\langle M \rangle$ increases. M is an order parameter that characterizes the degree of orientation; the angular brackets denote the thermal ensemble average.

Away from the linear regime we expect a correction to eq 1 in the form of a function, $f(\langle M \rangle)$, multiplying the right-hand side; f must be a totally even function (since the chain segments have neither a "head" nor a "tail") and must go to zero as $1/\epsilon$ when $\epsilon \rightarrow \infty$ (and $\langle M \rangle \rightarrow 1$). This latter dependence is necessary so that $\lim_{\epsilon\rightarrow\infty} \sigma(\epsilon)$ is both finite and nonzero. A simple function that satisfies these criteria is $[1 - \langle M(\epsilon) \rangle^l]$, where $l = 1$ if M is an even function of the coordinates and $l = 2$ if M is an odd function. This is the first term in a Taylor expansion of any function f satisfying the above conditions and leads to

$$\sigma = \frac{\kappa\epsilon}{\chi}(1 - \langle M(\epsilon) \rangle^l) \tag{2}$$

C. Motional Unit. Before discussing further ramifications of our orientational model, we must step back and address the question of the nature of the motional unit. That is, what can we say about the segments that are lining up under strain? We can obtain some indirect evidence on the nature of the motional unit from NMR relaxation rates. Room-temperature spin–lattice relaxation rates (T_1's) are sensitive to the high-frequency (10^6–10^{12} Hz) internal, local motions of glassy polymers. Rotating-frame spin–lattice relaxation rates($T_{1\rho}$'s) are sensitive to the lower frequency (10^2–10^6 Hz) longer range motions. The measured room-temperature T_1(H), $T_{1\rho}$(H), and $T_{1\rho}$(C) of polycarbonate[3] are strain independent (within ±10%) for strains between 0.0 and 0.03 at a strain rate of 1.7×10^{-2} s^{-1}. (For polycarbonate, a strain of 0.03 is already beyond the linear regime.) This implies that the conformational changes responsible for the flow under stress allow the polymer chains to line up under an applied stress but for the most part do not affect the average local structure. Thus the major motional unit responsible for the flow under stress can be no smaller than the persistence length for the longer range, main-chain (kHz) motions, i.e., the distance over which these longer range motions damp out.

This persistence length should be of the order of a number of monomer units. Evidence for this sort of segment size can also be inferred from the dynamic mechanical loss spectroscopy of an extended series of chemically substituted and modified polycarbonates by Yee and Smith.[4] Their results provide only a lower bound on the size of the basic orienting unit. The only evidence we have on the upper bound to the segment size is that the stress–strain results are molecular weight independent for $M_w > 40000$.[5] Thus the segment size must be considerably smaller than the total chain length. This still allows for a range of possible segment sizes. For instance, we have no way at present of distinguishing between a model where the basic orienting unit is a set of persistence-length rods linked together end-to-end by flexible joints (these rods or segments being randomly oriented in the unstrained glass) and one where the basic orienting unit of the glass is a domain of locally parallel segments[6] (with the domain being randomly oriented in the unstrained glass). For simplicity we shall refer to the orienting units as a chain segment which must be large on the scale of the monomer unit and small compared to the chain length.

D. Cooperativity and Order–Disorder Transitions. A natural consequence of the large segment size is that the motion of the segments must be cooperative. It is quite reasonable that motion of small units (e.g., a bond conformational transition) takes place in the glass without the coordination of other neighboring chains. The dynamics of small units can be treated as incoherent motions taking place in some kind of mean-field average of the surrounding chains. However, large-segment motions such as we are considering here would be impossible without the cooperative motion of the surrounding segments. Hence, we picture the segmental motion under stress as a cooperative, many-body type motion similar to that arising in a disorder–order transition in the presence of an external field.[7,8] Pursuing this analogy of flow with an order–disorder transition, one can view the glass transition temperature, T_g, like a critical temperature—at least insofar as it is reasonable to use reduced temperature units, $|T - T_g|/T_g$. Above T_g, in the melt, the stress–strain behavior is quite different; the system does not order and the stress associated with a given strain is several orders of magnitude less than in the glass.[9] Note that we do not associate the yield point with a critical phenomenon since in our model ordering occurs for small deformations.

Although we shall pursue this analogy, we realize we cannot push it too far. We know there is no spontaneous ordering in the glass below T_g. By contrast, there is a spontaneous ordering (magnetization) in, for example, a ferromagnetic Ising lattice below the critical point. Also it is easier for a glass to flow[10,11] (order) as T increases to T_g, while in the usual order–disorder system (e.g., an Ising lattice in a magnetic field), it is easier to order the system as T decreases. Lastly, one should remember that the normal order–disorder systems are true equilibrium systems whereas the glass is a kinetically frustrated, nonequilibrium system.

E. Time Constant for Orientation. Another consequence of the large segment size is that there must be a relatively long time constant associated with segmental motion. Thus, the stress necessary to produce a given amount of strain must depend on the strain rate. The minimum amount of stress necessary to produce a given strain will be obtained at very slow strain rates and increases as a function of increasing strain rate. This behavior can be understood in several different ways. Perhaps the simplist explanation comes from realizing that the area under a stress–strain curve is the thermodynamic work necessary to produce a given (end point) strain. Since larger strain rates imply a greater departure from the equilibrium path (in the thermodynamic sense), the work (and hence the area under the curve) must increase at higher strain rates. This thermodynamic explanation of the monotonically increasing dependence of the stress on the strain rate is, of course, model independent and hence completely general.

A more detailed, model-dependent explanation of the strain-rate dependence of the stress can also be obtained from the relatively slow time scale of segmental motion. At higher strain rates, the segmental motion (and hence segmental flow) cannot keep up. Since the system is being pulled at this faster rate, the glass must still be flowing (neglecting the possibility of failure) and this flow must be by a mechanism other than segmental reorientation. We shall call all such mechanisms internal. Examples of internal flow mechanisms are local conformational transitions, flexing of segments, etc. These internal mechanisms of flow must, in the main, be higher energy modes than segmental reorientation; otherwise there would be evidence of changes in local NMR relaxation parameters on stretching and evidence of strain *un*accompanied by ordering at slow strain rates. Thus, more work is required to strain the glass at a higher strain rate.[10–12]

III. Comparison with Previous Models of Stress–Strain Behavior

Most of the earlier theoretical treatments of the stress–strain behavior of polymers stem from the work of Eyring,[13] who used a transition state treatment in which the stress induced a bias in the energy barrier between potential minima. This treatment was essentially a static approach in that it was assumed that the applied stress introduced no structural or conformational changes in the polymer and was in fact just the standard transition state theory of viscosity.

Thirty years later Robertson[14] introduced the idea of stress-induced conformational changes to explain the stress-induced flow in glassy polymers. His model basically asserted that under the influence of a stress field more "flexed bonds" were introduced into the chain configuration; these flexed bonds resulted in a liquid-like structure and thus produced increased flow. Hence, Robertson's model assumed that the observed large-strain behavior is caused by an increase in the "disorder" of the glass due to the imposed stress field.

In the Eyring and Robertson theories of polymer stress–strain behavior, one has to assume either that the flow lines up the molecules (i.e., the molecules begin to flow and then ordering results) or that the ordering is somewhat independent of the flow properties. While hydrodynamic streaming will of course line up molecules, as in flow birefringence in liquids, it is difficult to see how the extremely slow rate of flow in the stretched polymer can have any sizeable effect. In fact, Jansson and Yannas' experiment[2] is essentially in the limit of zero strain rate. As to the ordering being somehow independent of the flow properties, the ubiquitous coincidence of ordering and flow makes such a viewpoint unappealing.

Argon[15] introduced a model that assumed that the polymer molecules thread through each other in a randomly zig-zagging fashion. He then proposed that the local strain rotates small molecular segments from a random orientation to one parallel to the applied stress. Using this model, he constructed a potential energy surface and then applied Eyring theory to calculate the flow properties of the plastic. Argon assumed that the observed large-strain behavior is caused by an increase in the "order" of the glass (opposite to the assumption of the Robertson model).

The basic physical picture that the flow behavior of glassy polymers under stress involves the lining up of chain segments parallel to the applied stress underlies both Argon's model and ours. The major physical difference between the approaches is in the size of the segments that make up the motion. Argon assumed that the segments that move from an unaligned to an aligned configuration are small—of the order of a monomer repeat distance (actually they turn out to be somewhat less than a repeat distance). As we discussed in the previous section, in order to be consistent with NMR relaxation studies of polycarbonate[3] and with the dynamic mechanical loss studies of modified polycarbonates,[4] we assume large-size segments. In addition, the assumption of a large segment size brings with it the necessity of viewing the segmental motions as being cooperative. Argon, on the other hand, did not treat the effect of one segment's moving on its neighboring segments. Hence alignment in his picture is the result of the incoherent ordering of many small segments.

The use of a cooperative model to explain the stress–strain behavior of glassy polymers has been used by Brereton, Joseph, and co-workers,[16] who invoked an Ising lattice type model to explain polymer yield. Despite some success, their model has intrinsic problems in its formulation such as, for example, the necessity for the glass below T_g to have an ordering, which increases as the temperature decreases, a nonphysical result. Clearly, a new picture of the stress–strain behavior of polymer glasses is needed.

IV. Further Qualitative Deductions

Armed with our picture of orienting segments as the dominant mechanism of the stress–strain behavior of glasses, we make the following qualitative deductions:

A. Temperature Behavior of the Stress–Strain Curve. From eq 1 it is apparent that in the small-strain regime, the temperature behavior of the stress–strain curve should be given by the temperature behavior of the inverse of the strain susceptibility. If one pursues the analogy of flow with an order–disorder transition and identifies T_g with a critical temperature, then the susceptibility increases as the temperature increases toward T_g and finally diverges at T_g. Thus one expects the stress necessary to achieve a given strain to decrease with increasing temperature, finally going to zero at T_g. This behavior with temperature is only altered slightly in the large-strain regime since the saturation effect only multiplies the small-strain behavior by a factor of order unity. Experimentally[9-12] this is in essence what happens: Plots of the yield stress as a function of temperature essentially go to zero at T_g.[10,11]

B. Initial Lag Time. Following the imposition of a stress on a glassy polymer, there is an initial lag time as the solid responds. That is, there is an inherent relaxation time for the ordering to occur and the glass to begin to flow. Since the ordering segments themselves are large, they require en masse a considerable time to move. A lag time on the order of seconds has been observed in constant-load experiments,[1,17] supporting the idea of large segment size.

C. Sudden Changes in Strain Rate: Slow to Fast. If the glass is pulled at a slow strain rate and then suddenly the strain rate is increased, our model predicts the following behavior: at the changeover point the average orientation is larger for the slower strain rate than it would have been if the system had been strained to the same point at the faster strain rate. This difference is due to the nonzero response time of the system (section IIE). When the strain rate is suddenly increased, the orienting segment can no longer keep up, and the stress necessary to obtain a given amount of strain becomes larger than if the tension had continued at the slower rate. However, at the changeover point, the average orientation is greater for the system which had initially been pulled at the slow rate than it would have been for a system which had been pulled continuously at the (new) faster rate. Starting out (at the changeover point) with a greater average orientation, the system now continues to have a greater average orientation. Hence, after the strain-rate jump the system requires a lower stress to obtain a given strain than a system which had been pulled continuously at the fast strain rate, but a higher stress than one being pulled continously at the slow rate. This is in agreement with the observations by Yee and De Torres[18] on polycarbonate.

D. Sudden Changes in Strain Rate: Fast to Slow. If the glass is pulled at a fast strain rate and then suddenly the strain rate is decreased, our model predicts the following behavior: at the changeover point the average orientation is smaller than if it had been pulled at the slower rate and hence the stress is larger. After the rate change, it is now being pulled so slowly that the average orientation can not only keep up with the strain but can in fact quickly catch up to where it should have been if it were being pulled constantly at the slow rate. Thus, the stress is expected to fall rapidly from its high value at the changeover point to a value on the slow strain rate, stress–strain curve and then continue along the slow strain rate curve. Experimentally Yee and De Torres[18] observe the quick drop to the slow-rate curve as the model predicts, but the experimental curve falls slightly below the slow-rate curve and remains slightly below it over the duration of the run. This slight undershoot is not observed in similar experiments on non-polycarbonates.[19] Within our model there is no explanation of this slight undershoot.

E. Compression. Our model is capable of treating compression in the same way as tension. For simplicity let us fix on a cylinder compressed longitudinally; the compressive force is on the plane faces of the cylinder. The flow under compression must be radially outward, perpendicular to the compressive force. If our model is correct in treating flow as an orientation of segments, the segments will align themselves with radial symmetry. This forms the basis of our treatment of uniaxial compression. That is, we can replace the uniaxial compressive strain ϵ_z by an equivalent radial strain in tension, ϵ_r. In doing this, we are idealizing the system by assuming that the radial flow is completely uniform. We allow no bulging or bowing of the cylinder. While in tension we ignored the dependence of volume on strain, we cannot ignore it in compression; that is, we require an explicit relationship between ϵ_r and ϵ_z, and these are related through the volume. Experimentally in the small-strain regime, polymer glasses have a Poisson ratio, ν, that decreases from $^1/_2$ to $^1/_3$ with increasing strain rate.[20-22] Beyond the yield point, $\nu \simeq {}^1/_2$; in other words, the volume is essentially constant near and beyond yield.

In order to obtain the compressive stress σ_z we first realize that

$$\epsilon_r = -\nu\epsilon_z \tag{3}$$

for small strain. (One can obtain a more complicated general expression that is correct beyond yield, but it is not necessary for the present argument.) Now, (i) treating compression as an equivalent radial tension, (ii) equating the total compressive forces (force on the two faces of the cylinder) to the total radial force, (iii) requiring that Young's modulus, κ/χ, be the same in tension and compression, and (iv) requiring that this whole thought process is invertible, i.e., uniaxial compression can be treated as an equivalent radial tension, yield

$$\sigma_z = \frac{\kappa\epsilon_z}{\chi}(1 - \langle M_r \rangle^l) \tag{4}$$

Note that this is the same expression for the compressive stress as for a tensile stress, except that one now has in the saturation term the radial ordering parameter for compression instead of the parallel ordering parameter that appears in tension (and of course the overall sign is reversed). The ordering parameter increases with increasing strain, but the radial ordering depends on the effective radial strain ϵ_r, which is always less than ϵ_z for strains in the region of interest. Hence we obtain the result that

$$\sigma(\text{compression}) > \sigma(\text{tension})$$

Moreover, since the saturation term itself is always a term of order unity, the difference between the stress in compression and tension cannot be too large. Remember that when $\langle M \rangle$ gets too large, i.e., when most of the segments are already ordered, the system must find other, higher energy ways to flow in order to relieve the stress; our present model breaks down in this regime.

Experimentally as pointed out by Matsuoka,[23] the stress–strain curve in compression is an approximate mirror image of the stress–strain curve in tension, but σ(compression) is always greater than or equal to σ(tension) at a given value of the strain. The difference between σ(compression) and σ(tension) at yield is ca. 30%. Furthermore, as discussed in section II.B and IV.A, the yield stress in both compression or tension is expected to go to zero at T_g in the same way as $1/\chi$. The difference between the yield stress in compression and tension must decrease therefore with increasing temperature. This is in agreement with yield stress data[9] on poly(methyl methacrylate). The same argument shows that the slope of the yield stress vs. temperature curve is larger in compression than in tension. This also is in accord with the experimental poly(methyl methacrylate) data.[9]

V. Summary

Identifying flow processes in glassy polymers as the orientation of segments whose size is large relative to a bond length and small relative to the chain length provides a unifying picture for a great variety of experimental observations. In view of this success we believe this qualitative picture should be pursued further by the development of a rigorous mathematical formulation. The outstanding unsolved problem is the derivation of an expression for M, the orientation parameter, in terms of the nature of the chain segment, the temperature, the geometrical constraints, and the applied forces. This derivation must recognize the nonequilibrium cooperative character of the glassy state, and so is a substantial undertaking.

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Kinetics of Free Volume and Physical Aging in Polymer Glasses

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ABSTRACT: A recently developed molecular kinetic theory, based on the idea that the glass relaxation is a result of the collapse of a series of free volumes having different levels of energies of hole formation, is applied to the phenomenon of physical aging in polymer glasses near the glass transition. Detailed comparisons between the prediction of the theory and a well-known experiment on the volume recovery of poly(vinyl acetate) are made. Defining the relaxation spectrum by a single Williams–Watts parameter β enables us to derive a new expression linking the relaxation of a macrosystem to that of localized state on the basis of scaling concept. This apparent relaxation serves as the basis of kinetic calculations. The favorable comparison between theory and experiment supports the pertinent introduction of β and substantiates our basic physical picture of linking the equilibrium and nonequilibrium behaviors of free volumes to the distribution of hole energies, its mean value, and the reference conditions. The reference free volume fraction is interpreted as the ratio of the mean hole energy and the local activation energy. Functional relationships are presented to show that the structural parameters in Tool's equation should not be constants but a function of β and temperature. The study improves our understanding that the physical aging in polymer glasses is dominated by the nonequilibrium structural dependent part of the relaxation time.

Introduction

The phenomenon of physical aging that occurs in amorphous materials annealed below the glass transition temperature (T_g), and exhibits sensitive and complicated nonequilibrium characteristics, has been extensively investigated in recent years.[1-10] Attributing the volume relaxation in amorphous polymers near the glass transition to free volume collapse, a molecular kinetic theory[1] based on the existence of free volume distribution has been recently developed to provide a coherent interpretation of some recent models. They include the molecular theories advanced by Robertson[3] and Curro, Lagasse, and Simha[4] and the phenomenological model developed by Kovacs and co-workers.[8] The kinetics of free volume are regarded as a series of relaxational processes in the present statistical theory. The departure from equilibrium is treated by a nonequilibrium transition-state theory where the structural contributions to the relaxation times are considered as the result of nonequilibrium fluctuations of the system and are related to the change of entropy.[1] The present theory can readily be extended to include the effects of stress and stress rate[2] and be incorporated in a nonequilibrium criterion[11] for the determination of T_g in a self-consistent manner.

In this paper, a calculation based on the molecular kinetic theory[1] is made and is compared with the well-known data[7] on volume recovery of poly(vinyl acetate). The equilibrium free volume fraction defines the equation of state. The mean energy of hole formation, the reference free volume fraction, and the coefficient of free volume

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