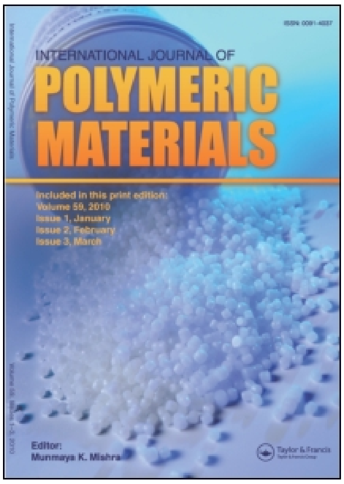

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Influence of Mechanical Vitrification on Flexible-Chain Polymer Drawing Process

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Factors, responsible for orientation interruption and polymer fracture under drawing are discussed in terms of molecular mobility. Mechanical vitrification, i.e. inhibition of micro-Brownian motion of chains during deformation and especially under tensile stress is considered to be the main physical factor limiting orientation processes. Broad-line NMR was used to study molecular motion in stretched polymers at different temperatures. Stretching results in the growth of virtual glass transition temperature and thereby in a dramatic deterioration in draw conditions. A simple theoretical model was used to describe the molecular dynamic processes in polymer under load. In this model nonvitrified regions of polymer were considered as the Newton liquid whose weight fraction was equal to the mobile fraction measured by NMR. The equation to describe the dynamics of the orientation process was proposed and specifically solved for nylon-6. The obtained diagrams enable one to choose optimal conditions for drawing. Instances when the draw process should be carried out in two or more steps are discussed.

KEY WORDS Drawing, molecular motion, NMR, mechanical vitrification.

INTRODUCTION

The dynamic heterogeneity and the molecular mobility change during stretching are considered as applied to the study on draw processes of flexible-chain polymers. As was observed previously,[1] the micro-Brownian mobility of polymer chains in amorphous regions is retarded by tensile stress. Plastic deformation and particularly stretching under stress result in decreasing micro-Brownian mobility even at temperatures much higher than the glass transition temperature T_g. The total disappearance of the motion under drawing points to the polymer passing from a highly elastic into a glassy state so that further molecular rearrangement becomes impossible.[2] It is the effect of molecular mobility inhibition under stress called "mechanical vitrification" that is very important for draw processes and we consider it to be the primary cause of polymer breakdown.

High temperature drawing, i.e. drawing at temperatures higher than T_g is a conventional method to produce high performance fibers. But does drawing which starts as a high temperature process always remain as such to the end? At least two glass transition temperatures must be taken into account T_g and T_g^{real}, which corresponds to the initial unloaded and stressed states respectively. The former is constant whereas the latter rises in consequence of mechanical vitrification as the orientation process develops.

A broadline NMR was used to study molecular mobility in stretched polymers. The fraction of narrow component in NMR spectra (mobile fraction C_m) is equal to a portion of

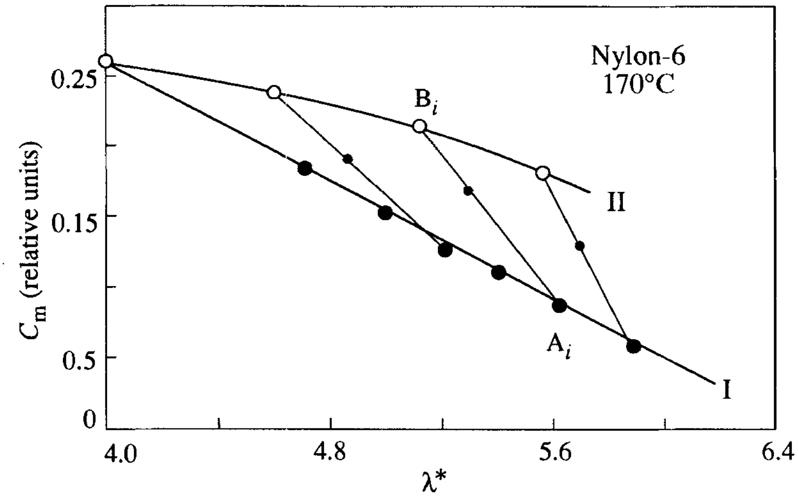

FIGURE 1 Variations of mobile fraction C_m under drawing.

microregions in which micro-Brownian motion takes place. Drop of C_m to zero indicates that the polymer becomes vitreous. Below, using a simple model, we carry out the quantitative estimation of the role played by the mechanical vitrification in the draw processes.

EXPERIMENTAL RESULTS AND DISCUSSION

Semicrystalline polymers such as polyethylene and nylon-6 in the form of fibers and films were studied. A broadline NMR spectrometer[1] was used to record the spectra in the form of their first derivatives by means of a small modulation technique. A special device enables the drawing of samples in the spectrometer coil along its axis perpendicular to the magnetic field over a wide temperature range.

We shall define T_g as the temperature at which the narrow component appears in the spectrum. This is physically reasonable since marked micro-Brownian motion signifies the transitions of noncrystalline regions from the glassy to a highly elastic state. NMR is a high-frequency method, and the glass transition temperature thereby determined may be higher than that determined by other methods. The value of C_m increases with temperature.[3] Consequently, for noncrystalline regions of semicrystalline polymers there is a certain distribution of glass transition temperatures of which T_g is the lowest. The increase of mobile fraction with temperature points to progressive softening of amorphous regions. The decrease of C_m under tension may be regarded as the reverse process; we shall refer to it as mechanical vitrification. Mechanisms of this phenomenon have been considered previously.[1,3] The orientational process is a complex phenomenon associated with both plastic and elastic deformation. The two modes of deformation give rise to retardation of molecular mobility. The hindrance of the micro-Brownian motion with increasing draw ratio λ in unloaded polymers was well known earlier.[4] However the motion inhibition caused by the action of the force in the range of elastic deformation ϵ is a much stronger effect. To describe the change of molecular dynamics upon stretching we have chosen as

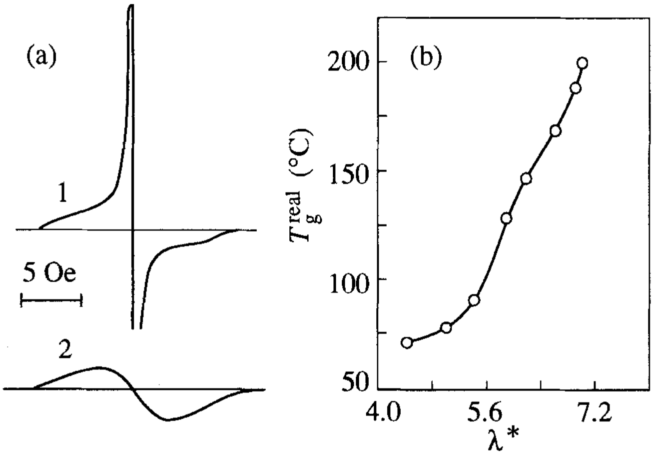

FIGURE 2 Inhibition of molecular mobility in nylon-6 as a result of mechanical vitrification. (a) Changes of NMR spectra at 170°C: unloaded polymer ($\lambda = 1$, curve 1); stretched polymer ($\lambda^* = 6.3$, curve 2). (b) Increase of the actual glass transition temperature under stretching.

an argument the degree of elongation $\lambda^* = \lambda(1 + \epsilon)$ instead of the draw ratio λ. Such a choice takes into account both the residual and the elastic deformation. Curve I in Figure 1 shows a total decrease in molecular mobility as a result of stretching, whereas curve II corresponds to the unloaded state and characterizes the effect of orientation proper. If in a certain stage (point A_i) stretching is stopped and the sample is unloaded its mobile fraction greatly increases after quasi-elastic contraction (point B_i). In the A_iB_i range only the reversible change in $C_{\rm m}$ takes place. After the second loading the system returns to point A_i and mobile fraction changes further in accordance with curve I. Therefore, under stress amorphous regions are vitrified to a greater extent than as a result of morphological changes. Let us introduce the real glass transition temperature $T_g^{\rm real}$ as a temperature, at which the cessation micro-Brownian motion occurs ($C_{\rm m} < 1$–3%).

Figure 2 demonstrates the hindering of molecular mobility due to stretching. The actual temperature of vitrification greatly increases with λ^*. If the experiment is carried out at a temperature below $T_g^{\rm real}$, drawing can no longer be considered as a high temperature process, since under these conditions one deals with a solid glassy body. In our opinion mechanical vitrification is the main physical reason for stretching termination and for accumulating breaks in the last stage of drawing.[2] These breaks emerge when a considerable deformation of a glassy body is attempted. For instance, at 105°C in NMR spectra of PE the narrow component remains noticeable till the draw ratio λ of about 25 and disappears under load at larger λ^*. After complete mechanical vitrification the stress increases sharply and internal fracture processes can be detected. Thus kink bands in such PE samples were observed by scanning electron microscopy[2] after stretching. In order to shift intensive destruction to higher λ^*, one ought to increase chain mobility by heating or plasticization. The existence of mechanical vitrification leads to an important conclusion: the solid state destruction mechanism[5] can be extended on rubber-like bodies, since the most stressed regions vitrify before destruction. It is evident that the gradual character of mobility hindrance upon stretching reflects a fine structure of amorphous layers responsible for macroscopic deformation and mechanical strength. For the theoretical description of

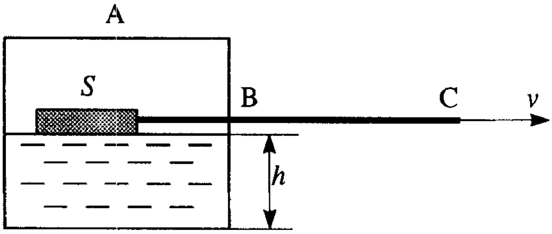

FIGURE 3 The model for describing draw process.

mechanical vitrification effects in the stretching process a model is proposed (Figure 3) consisting of a shock-absorber A and a rigid part BC. Point C moves at a constant speed v_c. Let the element BC strengthens with increase of λ^*, and its cross section decreases: $S = S_0/\lambda^*$ (here S_0 and S are the initial and the current cross sections, respectively). This model describes not only a macroscopic fiber but also a separate fibril. The shock-absorber resistance depends on the liquid level h. The force F required for displacing a plate of an area s in a medium with viscosity depends η on the rate gradient:

$$F = s\eta|\mathrm{grad} v_c| = s\eta\frac{v_c}{h}. \tag{1}$$

This is a tensile force for the BC element. The failure of BC element is the failure of the sample as a whole. The liquid in the shock-absorber is a model for softened microregions. A decrease in the liquid level corresponds to mechanical vitrification upon stretching. It would be more correct to describe polymer deformation with a series of numerous (n) cells similar to that presented in Figure 3. Then the speed of the motion of the sliding element in these cells will be n times less than that of the sample stretching. This effect can be described by a model with a single cell, if v_c is assumed to be proportional to the stretching rate v and inversely proportional to the initial sample length l_0. This assumption is natural, since the longer the real sample, the less its elements displace in a time unit with respect to each other. Let $v_c = (L/l_0)v$ (L is a coefficient of the unity order with length dimensionality), $s_0 = s/V_0$ is the total area of sliding elements in a volume unity and C_m is proportional to h $(C_m = bh)$. Then the tensile stress is given by

$$\sigma = \frac{F\lambda^*}{S_0} = \frac{(s_0 bL\eta)\lambda^* v}{C_m(\lambda^*)}. \tag{2}$$

Viscosity can be roughly estimated from the width of the narrow component in the NMR spectrum.[6] Evidently $\sigma \to \infty$ when $C_m \to 0$. The tensile stress increases with stretching time t. This is related to λ^* as follows:

$$t = \frac{l_0(\lambda^* - 1)}{v}. \tag{3}$$

Since the stress on BC element is not constant the time of fracture t_f can be estimated according to Baily's principle[5]

$$\int_0^{t_f} \frac{d\tau}{\tau[\sigma(t)]} = 1. \tag{4}$$

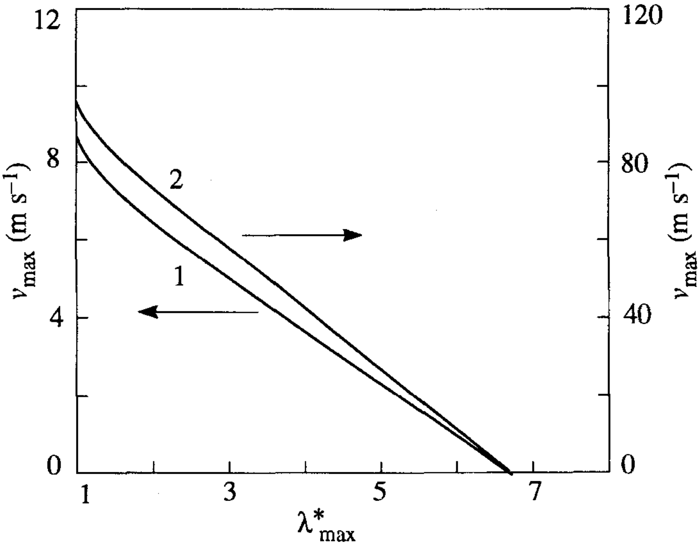

FIGURE 4 Relationship between draw ratio λ_{max} and the maximum rate of the orientational stretching process. $p = 10$ (curve 1), $p = 1$ MPa s m^{-1} (curve 2).

The dependence of sample life time τ upon stress is given by Zhurkov's equation

$$\tau = \tau_0 \exp \frac{U_0 - \gamma\sigma}{RT}. \tag{5}$$

Here U_0 is the activation energy of destruction, $\tau_0 = 10^{-13}$ s, γ is the strengthening coefficient, and R is the universal gas constant. Combining Equations (2), (4), (5) and replacing the variable of integration according to Equation (3) one obtains the final integral equation relating draw ratio to the maximum permissible rate v_{max} of stretching at constant temperature

$$\frac{l_0}{v_{max}} \int_1^{\lambda^*_{max}} \exp\left(\frac{p\gamma(\lambda^*)\lambda^* v_{max}}{RTC_m(\lambda^*)}\right) d\lambda^* = \tau_0 \exp \frac{U_0}{RT}, \tag{6}$$

where $p = s_0 b L \eta$ is the parameter characterizing the resistance of the system to rearrangement.

We will now attempt to clarify the physical sense of this equation. Its right-hand side is the sample life-time determined by thermal destruction only and independent of λ^*. The left-hand side reflects the accumulation of breaks upon stretching. The equality of left- and right-hand sides at $v = v_{max}$ corresponds to sample destruction. The real stretching rate must be less than v_{max}. The solution of Equation (6) is plotted in Figure 4 for the case of nylon-6 (at $T = 170°\text{C}$). Strengthening corresponds to the dependence[7] $\gamma = 5 \times 10^{-4}/\lambda^*$ J mol^{-1} Pa^{-1} and $U_0 = 171$ kJ mol^{-1}. Mechanical vitrification can be expressed by the equation $C_m(\lambda^*, 170°\text{C}) = 0.65 - 0.1\lambda^*$.

The values of p (1 and 10 MPa s m^{-1}) were chosen so that after the substitution of p into Equation (2) the calculated stress would be equal to the real tensile strength.

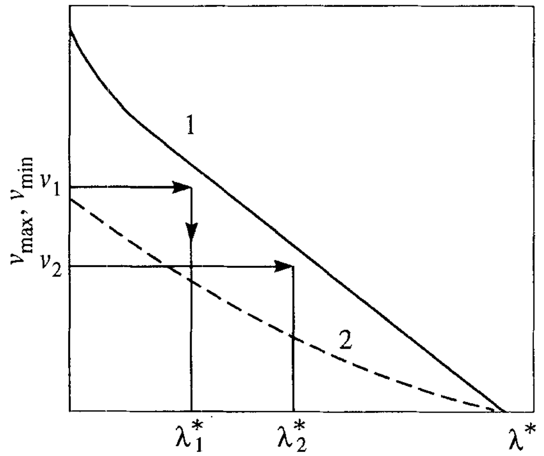

FIGURE 5 Diagram for a selection of optimal regimes of orientational drawing of polymers at a constant temperature. Drawing rate v_{max} (curve 1), drawing rate v_{min} (curve 2).

Curves in Figure 4 describe the upper limit of stretching rates. Below this limit there is a sufficient amount of liquid in the shock-absorber and the tensile force will not cause significant destruction.

We foresee a possibility to relate the dynamic characteristics to supermolecular structure which will provide a complex approach to the problem of orientational strengthening. Evidently there are factors limiting the stretching rate not only from above but also from below. First, we mean the local process of recrystallization. During the extension of a polymer the structure can be "spoiled" because of high temperature.[8] The higher the molecular mobility in polymer, the more probable is their recrystallization. Let us assume that the minimum "safe" stretching rate $v_{\min}$ (from the viewpoint of recrystallization) can be expressed as follows: $v_{\min} \sim (C_{\mathrm{m}})^k$, where k is an empirical index. The condition of the optimal stretching rate $v_{\min} < v < v_{\max}$ is schematically shown in Figure 5 for constant temperature. This diagram demonstrates the cases in which drawing should be carried out in several steps. For instance, in order to stretch polymer to λ_2^* one chooses at first the rate v_1 (up to λ_1^*) and then stretching is completed at rate v_2. This scheme can be complicated for optimizing the real process. Here only general considerations are presented and the decisive role of mechanical vitrification is emphasized. Figures 4 and 5 show that it is desirable to draw a polymer at a decreasing rate. It seems promising to use drawing machines with variable stretching rates and temperatures, for example, machines with conic rollers.[9] The above ideas can be a basis to calculate a program for polymers strengthening.

CONCLUSION

To summarize we should like to consider the cases when the narrow component in NMR spectra does not completely disappear prior to polymer fracture. The narrow component preserved in the spectra just before the fracture state of polymer may be due to the following reasons.

(i) Rather a narrow component can appear and rise sharply at the final stages of the deformation. It is neither subjected to the stress action not is it temperature-dependant over a wide range. We observed that for PE and explained it by macromolecule ruptures in the kink bands after a total mechanical vitrification of amorphous regions at high temperature.[2] We believe the narrow component to be associated with broken chain ends which like "cilia" cover the surface of inner cracks. This component is indicative of a fracture process.

(ii) A narrow component in the NMR spectrum can be due to the recrystallization discussed above. It is related to the increase in the number of coiled chains in a sample. These are interlocked by crystal regions and are not affected by the external load. The narrow component of such kind points to the polymer "deterioration" which makes its drawing ineffective.

(iii) Presence of low-molecular compounds (moisture, plasticizer) in polymer leads to the appearance of the proper, rather a narrow component in the spectra as well, which, on the contrary, increases upon stretching. For nylon-6 fibers and oriented rods ($\lambda = 4$) of PMMA containing some percentage of water the growth of the narrow component under stress at room temperature was observed. However it increased gradually reaching the maximum of magnitude in about 20 minutes after tension. With the sample unloaded, the narrow component intensity decreased, the delay-time constant remaining unchanged. We believe this effect results from desorption-sorption processes on microscopic level and must be taken into account when studying plasticized polymers under stress.

Evidently any kind of narrow component such as these discussed above must be subtracted from the NMR spectra when characterizing the mechanical vitrification phenomenon quantitatively. In the absence of low molecular impurities in polymer coiled chains alone can contribute to a narrow component. These chains have never been under external load and therefore have no influence on the mechanical properties of stretched polymer. So mobile fraction corresponding to the state before fracture may be used as a measure of nonutilized reserve for improving macroscopic mechanical properties.

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