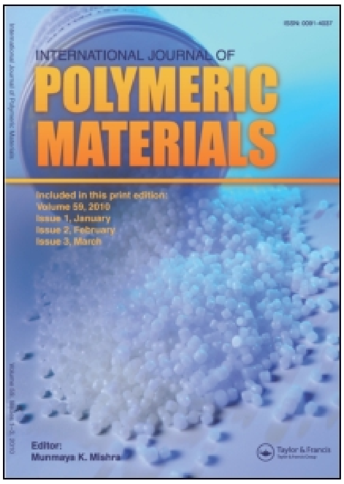

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Microprocesses Accompanying Deformation of Oriented Nylon 6

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Microprocesses Accompanying Deformation of Oriented Nylon 6

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Complex nature of tensile deformation of oriented nylon 6 fibers was investigated by broad-line NMR and IR methods. The first method was used for evaluation of a length distribution function for tie chains in amorphous regions of microfibrils and the second one—for chain scission detection. On the base of these results the stress-strain diagram and the elastic modulus dependence on deformation were calculated theoretically for an idealized model of polymer structure. From comparison between the theoretical curves and experimental ones the conclusion was drawn that deformation of fibers is due not only to stretching of tie chains in amorphous regions but to intermolecular interaction also. High values of modulus at small deformations were explained by existence of a rigid framework caused by interfibrillar interaction. External tensile load will be distributed between tie chains in amorphous regions only after destruction of this framework. Strength of the framework were estimated approximately as 70 MPa.

KEY WORDS Nylon 6, NMR, tie-chain length distribution, chain scissions, mechanical properties.

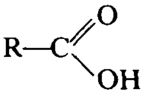
INTRODUCTION

The macroscopic deformation of polymers results from microprocesses which occur under load at different scale and structural levels. It has been shown[1] that in the idealized case macrodeformation of flexible-chain oriented polymers is approximately equal to the sum of deformations of intrafibrillar amorphous regions. Idealization consisted in the fact that the polymer was considered as the set of equally loaded microfibrils with alternating amorphous and crystalline regions inside them. The plastic effects such as the slippage of the microfibrils with respect to each other were not taken into account in this case. The real polymers often differ from such simplified model to some or other extent. The differences from "ideality" may influence the modulus value and the shape of stress-strain diagram as well as the fiber shrinkage, ageing, effect of active media, etc., since the latest phenomena are dependent on intermolecular interactions. But even for the idealized model it is impossible to predict the macroscopic extension behaviour of polymer if one does not know the details of amorphous region structure and primarily the chain amount and differences of tie-chain length within them.

The aim of this paper is to investigate the deformation behaviour of such oriented flexible-chain polymer as nylon 6, to compare the behaviour with that predicted for the idealized model and basing on this comparison to draw conclusions concerning real microprocesses determining the macroscopic mechanical properties of the fibers at different stages of strain.

EXPERIMENTAL

The objects of investigation were the oriented nylon 6 fibers with draw ratio $\lambda = 6.0$. The stress-strain diagrams $\sigma(\varepsilon)$ and dependences of elastic modulus E on relative deformation ε at room temperature have been obtained by the standard procedure using Instron. The number of molecular scissions have been evaluated by IR spectroscopy technique from the change in the intensity of 1718 and 1740 cm^{-1} absorption bands corresponding to



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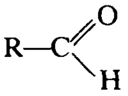

oxygen containing end groups respectively.[2] To evaluate length difference of tie chains in the microfibril amorphous regions the broad-line proton NMR has been used.[3] Beyond the glass transition temperature T_g one may observe the narrow component in NMR spectrum of the polymer. Its portion in the total spectrum area equals to relative number C_m of polymer units participating in micro-Brownian motion. As the temperature increases, C_m grows because new chains in the amorphous regions exhibit high elasticity.

The tensile stress causes decrease of C_m. Such effect, known as mechanical vitrification, results from impoverishment of the conformational set in tie chains during their extension.[4] Assume that all amorphous regions in fibrils are identical and their difference in chain lengths is described by the function of length distribution $W(l)$. As the polymer deformation proceeds at constant temperature (beyond T_g where the macromolecules under consideration are mobile in initial state) first the shortest chains and then more long ones lose their micro-Brownian mobility as a result of decrease on a number of possible conformations below a certain limit and start to contribute not to the narrow but to the broad component of NMR spectrum. Thus one may evaluate the difference of chain lengths based on C_m change. On the other hand the temperature dependence of C_m also contains information in the chain lengths difference. The higher temperature will be the more straightened chains with fixed ends in amorphous regions can take part in the narrow component of NMR spectrum.

For the idealized fibrillar model of the polymer one can write[3,5]

$$C_m(\varepsilon, T) = A \int_{l_{cr}(\varepsilon, T)}^{\infty} l W(l)\, \mathrm{d}l \qquad (1)$$

where A—normalizing factor; $l_{cr} = r(\varepsilon)/\beta_{cr}(T)$—the chain critical length; r—

distance between adjacent crystallites along the microfibril depending on the sample deformation; β_{cr}—the critical degree of chain uncoiling (chain micro-Brownian motion is possible only at $r/l < \beta_{cr}$). The method for calculation of $\beta_{cr}(T)$ dependence and its form for nylon 6 are given elsewhere.[5]

Thus the function chain length distribution can be calculated by two ways: from the experimental $C_m(\varepsilon)_{T=\mathrm{const}}$ or $C_m(T)_{\varepsilon=0}$ curve. Note them W_ε and W_T, respectively. If the polymer structure and deformability are adequately described by the idealized model, then W_ε and W_T should be the same. Some differences point to incomplete adequancy of the model and the real system. At last, substantional differences between W and W_T means that this model can not be used.[3]

RESULTS AND DISCUSSION

In Figure 1 the stress-strain diagram $\sigma(\varepsilon)$ is given for the sample at room temperature (curve 1) as well as the relationship between the elastic modulus $E = \partial\sigma/\partial\varepsilon$ and deformation (curve 2). Curve 3 in this figure shows that the amount of macromolecule scissions sharply increases at final stages of deformation.[6] The experimental dependences of C_m on deformation and temperature do not principally differ from those given earlier.[5]

The length distribution functions W_ε and W_T calculated from NMR data using the expression (1) are given in Figure 2 (the functions are normalized to unity; the lengths are expressed in relative units l/r_0, where r_0—the initial length of undeformed amorphous regions). In calculation of W_ε the correction for chain ruptures during testing has been introduced,[7] therefore both distribution functions under consideration correspond to the initial before loading state of the polymer. It is suggested that the structure of amorphous layers does not change and the distribution function characterizes the amorphous regions at temperatures below T_g as well.

As seen, W_ε and W_T are rather similar in shape but still there is some difference

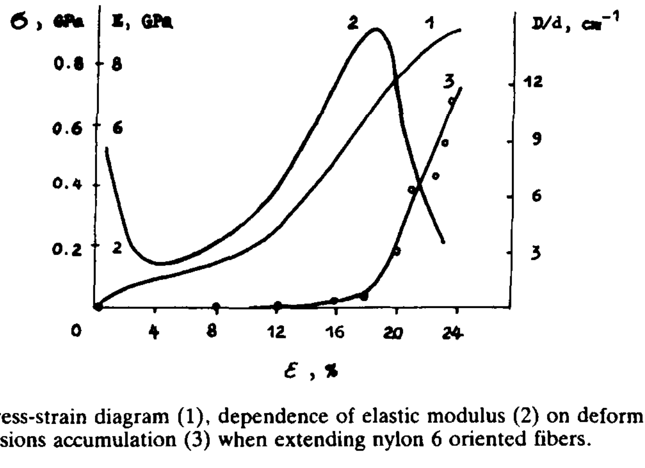

FIGURE 1 Stress-strain diagram (1), dependence of elastic modulus (2) on deformation, and curve of molecular scissions accumulation (3) when extending nylon 6 oriented fibers.

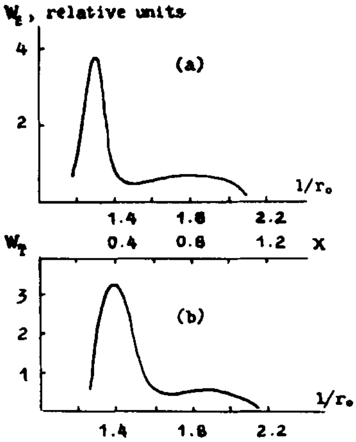

FIGURE 2 Function of the tie-chain length distribution in amorphous regions nylon 6 oriented fiber (λ = 6.0) obtained with deformation (a) and temperature (b) C_m dependences.

between them. Let us assume that the idealized model of structure may be taken only as first approximation. The aim of the experimental data analysis is to evaluate "deviation from ideality." Further we shall use only W_T (without index). To find the above function there is no need in apriori specifying the relationship between macro- and microdeformation and, hence the plastic deformation which is not taken into account has no effect on W_T, but it can distort W_ε.[5]

In Figure 2 on X-axis the second scale is given apart from the major one: $x = (l/r_0) - 1$. X value may be considered as relative tensile strain of the amorphous regions. If they are deformed up to a certain x_i value, then the chains with a length $l_i = r_0\,(1 + x_i)$ will be completely straightened, shorter chains will be taut (or ruptured) and longer chains will remain sagged. Further we shall neglect the entropy forces and consider only elastic forces stipulated by deformation of chemical bonds in the chain skeleton. Then in extending the amorphous layers by x_i value only the chains correspondent with the left part of distribution with respect to x_i will make a contribution to the polymer force constants.

In the first approximation (not considering the slip) at certain current macrodeformation ε the relative tensile strain of amorphous layers makes up[1]

$$\varepsilon_\mu = \varepsilon/(1 - \varkappa), \qquad (2)$$

where $\varkappa$ is the crystallite part in the long period ($\varkappa \simeq 0.6$). Then the chains with a length $l < r_0\,(1 + \varepsilon_\mu)$ will be taut; for the present we shall exclude the scissions of short chains from consideration. For chains which the length corresponds to x_i coordinate in the distribution (Figure 2b) the relative strain due to only chemical bonds is equal to $(\varepsilon_\mu - x_i)/(1 + x_i)$ at $x_i < \varepsilon_\mu$ and it is equal to zero at $x_i \geqslant \varepsilon_\mu$. The tensile stress applied to these taut chains is $E_\mu(\varepsilon_\mu - x_i)/(1 + x_i)$, where E_μ is the elastic modulus of the completely extended macromolecule. The summation over all taut chains in distribution leads one to the expression for stress-strain diagram (without taking ruptures into account)

$$\sigma^{\text{theor}}(\varepsilon) = E_\mu q \int_0^{\varepsilon_\mu} W(x) \frac{\varepsilon_\mu - x}{1 + x} \, \mathrm{d}x, \tag{3}$$

where σ^{theor} is the theoretical value of stress corresponding to microdeformation ε_μ; relationship between the latter and strain of the sample ε is given by Equation (2). q is the portion of tie chains which may be evaluated from the chain length distribution function as[5]

$$q = \frac{\rho_a}{\rho_c} \frac{r_0}{l_{av}} \tag{4}$$

here ρ_a/ρ_c is ratio of densities of amorphous and crystalline regions; l_{av}—is an average chain length (averaged over length distribution).

To obtain the theoretical dependence $E^{\text{theor}}(\varepsilon)$ it is sufficient to differentiate the expression (3) with respect to ε taking (2) into account. The expression (3) can not describe the decrease in the slope of $\sigma(\varepsilon)$ curve or $E(\varepsilon)$ drop under large deformations which are observed experimentally since the chain scissions occurring during extension are not considered. Let us assume that the chains break on attaining the maximum relative elastic deformation δ. Then in deformation of the amorphous layers ε_μ those chains from the distribution will be ruptured for which $x \leq (\varepsilon_\mu - \delta)/(1 + \delta)$. These chains are no longer under load, therefore from the part of equation (3) one should subtract the contribution of ruptured chains; the above contribution is described by equation like (3) but with the upper limit $(\varepsilon_\mu - \delta)/(1 + \delta)$. Then remembering (2) we obtain in a general form:

$$\sigma^{\text{theor}}(\varepsilon) = E_\mu q \int_B^{\varepsilon_\mu} W(x) \frac{\varepsilon_\mu - x}{1 + x} \, \mathrm{d}x \tag{5}$$

where $B = 0$ at $\varepsilon_\mu \leq \delta$ (no scissions) and

$$B = \frac{\varepsilon_\mu - \delta}{1 + \delta} \quad \text{at} \quad \varepsilon_\mu > \delta.$$

The value of δ lies in the range of 0.1–0.2.[8–10] Let us take the least value at which good agreement between NMR and X-rays data has been observed.[8] In this case the amount of ruptures under large deformations, both the theoretical and experimental, correlate well.

On differentiating the expression (5) with respect to ε we obtain

$$E^{\text{theor}}(\varepsilon) = \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon} = \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon_\mu} \frac{\mathrm{d}\varepsilon_\mu}{\mathrm{d}\varepsilon} = \frac{E_\mu q}{1 - \varkappa} \left[\int_B^{\varepsilon_\mu} W(x) \frac{\mathrm{d}x}{1 + x} - \frac{\delta W(B)}{1 + \delta} \right]. \tag{6}$$

Evidently the theoretical values σ and E may be calculated with an accuracy of the factor E_μ. One should not accept E_μ to be equal to the crystallite elastic modulus. According to References 11 and 12 even minor chain bending (deviation from trans-zigzag) substantially reduce the elastic modulus. So the chain contraction with respect to trans-zigzag length by 1.3% decreases the modulus by an order. It is difficult to expect that in the amorphous regions the extended tie chains will be the ideal trans-segments: twisting of trans-zigzag planes, presence of kinks, displacement of chain with respect to extension axis within the crystallite cross-section are probably available. Thus E_μ should be lower than the modulus of chain crystal.

Let us appreciate it in a following way. The theoretical $\sigma^{\text{theor}}(\varepsilon)$ relationship calculated from equation (5) has the maximum determined by balance between scissions and newly added long chains. Let us impose the condition: the maximum value of the theoretical curve $\sigma_{\max}^{\text{theor}}$ should be equal to the highest experimental value σ in Figure 1 (curve 1), i.e. $\sigma_{\max}^{\text{theor}} = 0.9$ GPa, and then $E_\mu = 70$ GPa (quite reasonable value compared to nylon 6 crystallite modulus—200 GPa[11]). The theoretical $\sigma(\varepsilon)$ and $E(\varepsilon)$ dependences at $E_\mu = 70$ GPa are presented in Figure 3 as well as the experimental relationships transferred from Figure 1. The discrepancy between the theoretical and experimental relationship reflect inadequancy of the "idealized" model and the real polymer. Let us discuss this in more detail. The theoretical dependences are more steep: the maximum of the theoretical modulus is shifted to the left and its value is twice that of the experimental modulus. We attribute the above differences to the fact that along with the reversible deformation of intrafibrillar amorphous layers the irreversible plastic deformation takes place which results in "smearing" of deformation region compared to the model. Assume that the plastic strain ε_p may be evaluated as the difference between the experimental and theoretical curves in Figure 3a in the case of not too low ε values to the right of $\sigma(\varepsilon)$ and $\sigma^{\text{theor}}(\varepsilon)$ intersection: $\varepsilon_p = (\varepsilon - \varepsilon^{\text{theor}})_{\sigma=\text{const}}$. The relation between the plastic and total deformation of the sample is given in Figure 4.

Consideration of the plastic strain will lead to the approach of the theoretical modulus to the experimental one, and also to a decrease in its absolute value. In

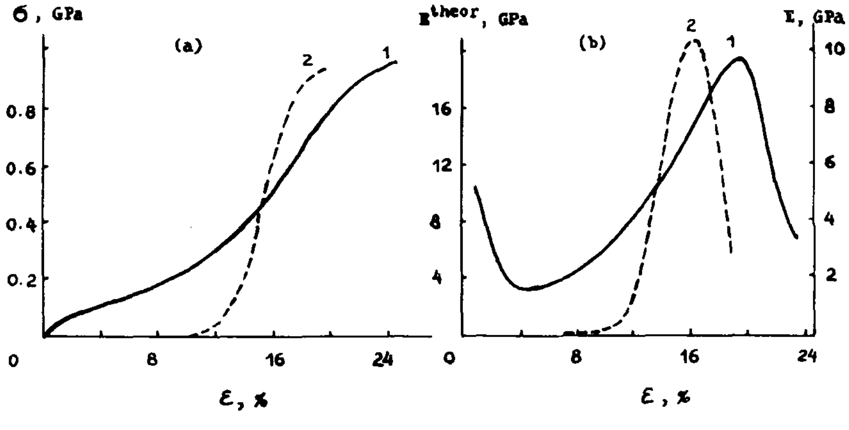

FIGURE 3 Experimental (1) and theoretical (2) stress-strain diagrams (a) and current modulus strain curves (b) for oriented nylon 6 fiber.

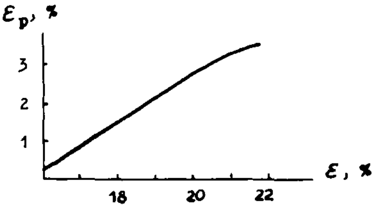

FIGURE 4 Dependence of plastic deformation on total strain of oriented nylon 6 fiber.

fact, if $\varepsilon = \varepsilon_\mu (1 - \varkappa) + \varepsilon_p$ then using expression (6) for evaluating the modulus it is necessary to take into account plasticity substituting into (6)

$$\frac{d\varepsilon_\mu}{d\varepsilon} = \frac{1}{1-\varkappa}\left(1 - \frac{d\varepsilon_p}{d\varepsilon}\right). \tag{7}$$

It is the second term in the brackets that causes decrease in the absolute value of the theoretical modulus in case of slippage.

Further refinement of the calculated $\sigma^{\text{theor}}(\varepsilon)$ and $E^{\text{theor}}(\varepsilon)$ relationships is not reasonable because of necessity of extra assumptions. Thus if the deformation is not too low the stress-strain diagram for nylon 6 fibers and $E(\varepsilon)$ dependence are determined by successive tension and scission of tie chains with different length in the amorphous regions accompained by the plastic effects.

Let us now draw our attention to low deformations at which the modulus and stress should be approximately equal to zero if they result from the tie chains only. There is no reason to take into account the entropy forces.[13]

Two assumptions may be made concerning the nature of mechanical behaviour at low values of ε: 1) The above behaviour results from highly straightened or extended in the initial state tie chains; they are not registered as mobile by NMR technique and hence are not considered in the distribution function.[14] The amount of such chains should be rather great since the modulus at $\varepsilon \rightarrow 0$ is only twice less than the modulus maximum value. These short chains have to be ruptured even at strain of some per cent. This amount of scissions should be sufficient for its reliable registration by IR spectroscopy method; however, at low deformation values the scissions have not been observed (Figure 1, curve 3). Hence the above assumption has not been confirmed experimentally. For the same reason one should not relate the high initial modulus to interfibrillar straightenened chains connecting crystallites of the neighbouring fibrils—their ruptures should have been also registered at low values of ε. 2) The initial tensile stress and modulus are related to adhesive intermolecular forces between the crystallites of adjacent microfibrils. Until these interactions are disturbed, the intrafibrillar amorphous regions are not loaded (they are mechanically shunted) and the load is borne by the crystalline framework. It is the framework that defines high modulus. In this case the chemical bond scissions should not take place. Only after framework failure the tie chains begin to bear the load. The minimum on $E(\varepsilon)$ curve (Figure 1, curve 2) may be explained by transition from the framework elasticity to the tie-chain one. Such assumption is not at variance with all set of experimental data; it is known that decrease of adhesional forces in storage of nylon 6 under wet conditions results in the substantional drop of the initial modulus.[6] Thermal treatment of the fibers affects the modulus as well. Thus in case of low deformations the nature of fiber elasticity may be considered as "nonpolymeric" one, namely it is not directly related to the chain structure of macromolecules. Based on the obtained experimental data one may attempt to evaluate the framework strength (shearing stress which cause its failure). Let us suppose that the minimum of the elastic modulus corresponds to destruction of the major framework. According to Figure 1 the modulus minimum is observed at the tensile stress of 100 MPa. Let the crystallite cross section in microfibrial be about 4 x 4 nm^2. Then the total length of boundaries between microfibrils in 1 m^2 of section perpendicular to the orientation axis amounts to $5 \cdot 10^8$ m. Assume that the crystallites form the framework overlapping along the axis of microfibril in an average by a half of their length (about 3 nm). Then the area of crystallite contacts in 1 m^2 of the fiber cross-section is 1.5 m^2. If the framework destroys at tensile stress of 100 MN/m^2 its shearing strength is about 70 MPa. This value seems to be rather realistic one because it is of the same order but still less than the shear stress destroying an individual crystallite (the shear stress holding back an individual chain into the crystallite is not less than 200 MPa[15]).

CONCLUSION

So it may be concluded that not only deformation of intrafibrillar amorphous layers defines stress-strain diagram of nylon 6. Substantional part of work on deformation, especially at low strain involves overcoming the adhesional forces. Difference between the theoretical and experimental curves in Figure 3 can be used for evaluating the relation between intra- and interfibrillar (plastic) effects. There is reason to believe that plasticization of the nylon 6 fiber is due to deterioration of the conditions for transmitting the external load on microfibrils. Indeed, for samples with different previous history (see Reference 6) it may be noted that as a result of plasticization and thermal treatment the tensile strength is little affected but the breaking strain and elastic modulus are changed to a great extent. It may occur if the structure of the microfibrillar amorphous regions remains constant but adhesional properties of structural elements are changed: the tie chains are loaded at the final stages of deformation which includes ε_p as well. The decrease of the elastic modulus in this case may be described considering Equation (7).

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