CHANGE OF STRENGTH OF POLYMERIC MATERIALS IN THE PROCESS OF ORIENTATION

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In the process of orientation the strength of polymeric materials changes as a result of a net increase in the number of ordered structural elements. It is shown that the model obtained can be used to predict the effect of orientation on the strength of polymers. The theoretical relations satisfactorily describe the available experimental data.

There have been numerous studies of the change in the strength of polymeric materials associated with orientation [1-4]. We propose to give a phenomenological description of the process. We assume that when a polymer is stretched, not only is there a certain increase in strength as a result of the orientation of the structural elements but also a certain loss of strength associated with the development of defects. The latter process leads in the limit to the failure of the material.

In evaluating the nature of the changes in mechanical properties during the orientation process it is very often necessary to compare different materials. Accordingly, it is desirable to normalize the change of length and strength. It is proposed to characterize the first of these parameters by the ratio of the variable elongation to the maximum elongation possible under the selected conditions

$$\lambda = \frac{l - l_i}{l_M - l_i},$$

(1)

where $l_i$ is the initial length of the specimen; $l$ is the length of the specimen at an intermediate stage of the process; $l_M$ is the maximum possible length; $\lambda$ is the normalized extension. It follows from relation (1) that $0 \leq \lambda \leq 1$. The strength normalization conditions are considered below.

The physical pattern of structural changes associated with polymer orientation has not been studied in sufficient detail. However, certain general laws can be established in relation to the various stages of the process. Thus, even when the material necks, the structure is transformed not instantaneously and uniformly over the entire section, but in the course of a certain interval of time and with a definite "gradient" of structural changes. Accordingly, in actual stretched polymers, not only before and after necking but also during the necking process itself, the structural changes are very complex and largely determined by the temperature conditions and related factors [5-8].

However, the structural changes also have certain features common to the different structural levels, for example, the time dependence of the transformation. Thus, with a certain approximation it is possible to simulate the structural changes responsible for the changes in properties in the different stages of polymer orientation by means of a certain general mechanism. One variant of this mechanism can be formulated as follows.

Polymeric materials are bodies with a very complex structure highly developed at various levels. However, with respect to the nature of their influence on the mechanical properties, in particular, the tensile strength, all the existing structural elements can be arbitrarily divided into two groups [9, 10]. The first group is that of the so-called "load-bearing" elements – formations with a high degree of order at
the molecular or supermolecular level and essentially asymmetric in shape. The second group consists of
elements that carry almost no load themselves, but assist in distributing the stresses among the load-
bearing elements. We shall refer to this material as the "matrix." The proposed terminology should not
be taken too literally. Stresses also develop in the matrix, but they are shear stresses, which do not make
a direct contribution to the normal stresses that determine the strength of the specimen. The shear
stresses lead to shear strains in the matrix.

The matrix is chiefly composed of structural forms with a low degree of order. In the process of
orientation the matrix may to some extent be converted into load-bearing elements and, as is pointed out
below, at sufficiently high elongations the opposite transition may occur.

The strength of the material, i.e., the system as a whole, depends on the difference in stiffness
between the load-bearing elements and the matrix, on their adhesion, and on the angle formed by the load-
bearing elements relative to the direction of the strain field. After necking, this angle is small, and the
stiffness of the ordered formations is one or two orders greater than that of the nonordered formations.
The fact that the load-bearing elements and the matrix have the same chemical composition indicates
quite high adhesion (essentially cohesion) between the components of the system. Accordingly, with a suf-
ficient degree of accuracy we may assume that the breaking load is proportional to the number of load-
bearing elements.

We assume that the number of load-bearing elements originating in the orientation process (or
rotated so that they become load-bearing) is proportional to the residual number of elements still not
oriented or not yet developed to the point at which they become load-bearing, but having the potential for
doing so. This condition can be formulated as follows:

$$dN = k_1(N_M - N)dx,$$

where $N$ is the number of load-bearing elements resisting the load in a given stage of the process; $N_M$
is the maximum number of load-bearing elements possible for a given polymer (when all are developed
and oriented along the direction of the field); $k_1$ is a constant whose value is determined by the orientation
parameters (temperature, stress, etc.).

We note, however, that the actual process of variation of the number of load-bearing elements is
more complicated and our assumption, strictly speaking, is valid only for that stage in which the system
is more or less already formed. Nonetheless, with a certain approximation it can still be extended to the
entire process, since, firstly, the remaining stages do not constitute a very large fraction of the process
(with respect to elongation) and, secondly, they do not play an important part in determining the mechan-
ical properties of the material.

Since, as assumed above, the strength is proportional to the number of load-bearing elements, we
obtain

$$P_1 = k_2N,$$

where $k_2$ is a constant determined by the orientation parameters; $P_1$ is the strength determined by the
load-bearing elements. Substituting (3) in (2) and setting $k_1k_2 = \alpha$, we find

$$dP_1 = \alpha(P_M - P_1)dx.$$

After integrating and determining the constant from the condition $P_1 = 0$ at $\lambda = 0$, we have

$$P_1 = P_M(1 - e^{-\alpha \lambda}),$$

where $P_M$ is the maximum possible strength. The constant $\alpha$ is the characteristic of the rate of orienta-
tion hardening.

For our strain normalization conditions, expression (5) requires refinement. The maximum value of
the normalized extension $\lambda_M = 1$ and an increase in $\lambda$ above this value is meaningless. At the same time,
the $P_M$ presupposes such a possibility. At $\lambda = 1$ the strength takes a certain value $P_K$ or $P_1 = P_K$; then
from relation (5) we find

$$P_1 = P_M(1 - e^{-\alpha}).$$