EFFECT OF MOLECULAR WEIGHT ON STRENGTH AND DEFORMATION CHARACTERISTICS OF ORIENTED AMORPHOUS POLYMERS

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Tensile tests were carried out on uniaxially oriented films of several amorphous linear polymers (polymethyl methacrylate, polystyrene, and poly-2,2'-octamethylene-6,6'-dibenzoimidazol) of various molecular weights. It was shown that molecular weight has no direct effect on polymer strength, which is determined by structure. However, when polymer fibers and films are formed and stretched, the molecular weight of a given material affects the orientation of macromolecules and so predetermines the structure of the products obtained and, consequently, their strength.

Published data on the influence of molecular weight (when it is not too low) and molecular weight distribution on the mechanical properties of polymers, both isotropic [1-8] and oriented by stretching [9-20], are contradictory. Thus, it was reported in [12] that the strength of capron fibers is linearly related to the reciprocal of its molecular weight. The most substantial variation in strength was observed in the range of molecular weights $3 \cdot 10^3 - 15 \cdot 10^3$, i.e., the range in which sharp changes in the strength of isotropic polymers take place.

A linear relation between the logarithm of strength of several polymer fibers and reciprocal molecular weight was observed in [14-16, 18]. According to [10], the strength of oriented polyvinyl acetate films increases linearly with their molecular weight. Unlike [12], this relationship was observed in a range of molecular weights in which the strength of isotropic polymers (polymethyl methacrylate, polystyrene, and polyvinyl acetate), although the relation we observed was not linear.

Some time ago we attempted to determine the effect of molecular weight on the strength and deformation characteristics of oriented polymers [11]. This attempt was not successful, however, probably because we ignored the possibility of detecting parameters of the polymer structure likely to determine the mechanical properties of polymers.

Definite progress in this direction was made with amorphous polymers in [21-27]. The structure of oriented polymers was described not only by the degree of orientation $f$ of the macromolecule links but also by another parameter characterizing the degree of interlocking of macromolecules, which determines the quasi-recticular structure of block polymers. In [23] the concentration $N_c$ of stressed chains of the quasi-recticular structure in a unit polymer volume was used as this parameter. Analysis of a large volume of experimental data showed [23] that the strength and deformation characteristics of oriented glasslike amorphous polymers are more or less precisely determined by these two parameters. The molecular weight of the polymers varied within wide limits, but no direct relation between this property and polymer

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*Here and henceforth the strength discussed is that at room temperature.*
strength was observed. On the other hand, if parameters \( f \) and \( N_c \) were known it was possible accurately to predict the form of the tensile stress–strain dia-

![Image: Maximum attainable strength \( \sigma_b(M) \) of PMM films plotted against their molecular weight. Notation as in Fig. 2.](image)

gram, the breaking stress \( \sigma_p \), and elongation at rupture \( \varepsilon_p \) for specimens of any molecular weight.

This may appear to contradict the results of many investigations in which the influence of molecular weight on the mechanical properties of oriented fibers or films was definitely proved. However, it can be shown that this contradiction does not, in fact, exist. Let us analyze the results of mechanical tests on oriented polymethyl methacrylate (PMM), polystyrene (PS), and poly-2,2'-octamethylene-5,5'-dibenzimidazol (PBI) films cited in [28].

The PMM and PS specimens had a narrow fractional composition and were characterized by the following values of the average molecular weight \( M_v \): PMM—88 • 10^3, 260 • 10^3, 680 • 10^3, 1.42 • 10^4; PS—160 • 10^3, 660 • 10^3, 1 • 10^4, 2.34 • 10^4.

The characteristic viscosity \( \eta \) of PBI specimens measured in formic acid was 2.0, 4.7, 6.0, 9.0, and 13.0. (It is not yet possible to calculate the molecular weight of PBI.)

The characteristics of the starting polymers and the preparation of the oriented films were described in [24, 29]. In most cases the polymers were oriented by "zone" stretching of the films [29]. When zone stretching is used, deformation takes place in a limited zone of the film, and it varies, at various instants of time. Some oriented specimens were produced by "global" stretching, whereby a film specimen is placed in its entirety in a heated chamber and stretched by its end so that all portions of the film are uniformly deformed. These methods will be referred to as methods No. 1 (zone stretching) and No. 2 (global stretching).

The behavior of films during orientation stretching may vary considerably from polymer to polymer depending on their molecular weight. This variation is particularly noticeable if the stretching is done at a high temperature (say, a score of degrees higher than the softening temperature \( T_{SO} \)). The stretching of high–molecular–weight polymer films is done at higher stresses than those used for low–molecular–weight materials. The stretching stress \( \sigma_{st} \) is equal to the maximum stress on the isometric heating curve [21]. The latter is known to be related in a definite way to the average degree of orientation of macromolecule links [21]. Given the same degree of stretching \( \lambda \), other factors being equal, the degree of orientation of high–molecular–weight polymers is therefore higher than that obtained in low–molecular–weight materials. As a result, their birefringence effects are also more pronounced* (Fig. 1, curves 1–3). When the stretching temperature is reduced, the differences in the degree of orientation of specimens of different molecular weights are leveled (Fig. 1, curve 4).

Furthermore, \( \lambda_m \), the maximum degree of stretching a specimen can withstand under given conditions without rupturing, depends on the molecular weight of a given polymer. The relation between \( \lambda_m \) and \( M_v \) can vary considerably depending on the stretching conditions. Data reproduced in Fig. 2 for PMM films show that with method No. 1 at \( T_{ST} = 160^\circ C \), the value of \( \lambda_m \) rapidly decreases with increasing \( M_v \) (curve 1); when \( T_{ST} = 120^\circ C \), increasing \( M_v \) leads initially to a sharp increase in \( \lambda_m \) which subsequently reaches a practically constant level (curve 2). When method No. 2 is applied at \( T_{ST} = 160^\circ C \), the \( \lambda_m \) increases with \( M_v \) (curve 3). Thus, changing only the method of stretching leads to a substantial change in the dependence of \( \lambda_m \) on \( M_v \).

According to data cited in [11], when nonfractional polymer films are oriented by method No. 2 at \( T_{ST} = 160^\circ C \), \( \lambda_m \) decreases with increasing \( M_v \) (curve 4 in Fig. 2). Comparison of curves 3 and 4 shows that the molecular weight distribution plays an important part. [A slight difference in the stretching temperatures (160 instead of 170° C) could not produce such a large difference in the response of the polymer to stretching.]

It may therefore be concluded that the outcome of the orientation stretching of polymers in a highly elastic state depends to a large extent on their molecular weight and on the distribution of this property. Polymers characterized by different molecular weights and molecular weight distributions assume different structures (i.e., have different values of \( f \) and \( N_c \)) even when the stretching conditions are the same. As shown in [28], the strength and deformation properties of oriented polymers are fully determined by parameters \( f \) and \( N_c \). Consequently, polymer fibers or films of different molecular weights produced under identical conditions should have different mechanical properties. For the breaking stress \( \sigma_b \) we may write

\[
\sigma_b = \sigma_b(f,N_c).
\]

Since \( f = f(M_v, \lambda, T_{ST}, \ldots) \); \( N_c = N_c(M_v, \lambda, T_{ST}, \ldots) \), we finally obtain

\[
\sigma_b = \sigma_b(M_v, \lambda, T_{ST}, \ldots).
\]

Analysis of a relation of type (2) makes it possible to compare the strength of specimens obtained under

* Birefringence \( \Delta n \) is proportional to the average degree of orientation of macromolecule links [30].