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Abstract

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On the Relation between the Mechanical Properties of Crystalline Polymers and Their Supramolecular Structures

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Structural investigations in recent years, chiefly by electron microscopy, have shown ($^{1-7}$) that polymers are not a chaotically entangled system of molecular chains, but a highly ordered system of bundles. Alongside bundles, in a number of crystalline polymers there is a portion of the substance that is in a globular state. Polymer bundles, being independent structural units, are capable of forming morphological forms of higher orders.

It is obvious that the macroscopic properties of polymer materials are closely related not so much to the relative fraction of ordered and disordered material as to the emergence and development in the polymer of one or another secondary structure. The formation of bundles of molecules with a definite ordering of the chains, the appearance of lamellar formations and other supramolecular structures is an important factor that to a considerable extent determines the macroscopic, in particular the mechanical, properties of polymer bodies.

We have attempted, using polyamide resin 68 as an example, to compare certain structural and mechanical properties in order to clarify the relative role of the local ordering of segments (“degree of crystallinity”) and of secondary supramolecular structures in determining the macroscopic properties of polymers. The object of study was an industrial polyamide resin 68 (polyhexamethylene sebacamide), widely used in technology, in particular for the manufacture of sliding bearings, and possessing good wear resistance. Specimens in the form of bars $4 \times 6 \times 55$ mm were cast under pressure on an LM-3 injection-molding machine according to the usual technological molding conditions and were then subjected to heat treatment in inert media (silicone oils) at various temperatures and holding times. For each series of specimens, changes were assessed both in the “degree of crystallinity” and in the spherulitic structure of the polyamide.

The “degree of crystallinity” was evaluated, as is generally accepted, from the integral intensities of the most characteristic interferences on the intensity curve of the object under study. The X-ray scattering intensity curves as a function of angle were recorded by us on a URS-50-I X-ray diffractometer using filtered copper radiation. The spherulitic structure of the polyamide was obtained by means of microphotography of the specimen surface, which had first been polished and then etched with tricresol. Microphotographs of the specimen surfaces were obtained with an MIM-8 metallographic microscope at 1000× magnification. At the same time, each series of specimens was tested for wear resistance, which was determined as a quantity inverse

of wear (wear was assessed by the loss of volume during abrasion), on a mesh in a Grasselli-type testing machine.

Temperatures of 150 and 190°C and various heating times, from 15 min to 30 h, were chosen as the technological heat-treatment regimes for each temperature. The transition we observed as a result of heating—the transformation of the original specimen from one form, characterized by a hexagonal cell, into another, triclinic, form—is well known and has been described in the literature ([8], [9]). The structure with a triclinic cell arose after as little as 15 min of heating. Further heat treatment caused a gradual improvement of the X-ray pattern, characterized by a noticeable increase in the (100) and (010) interferences and, consequently, in the "degree of crystallinity." At the same time an interesting observation was made: at long heating times, between the (100) and (010) reflections of the triclinic cell, an interference again appears that is characteristic of the hexagonal cell. After 8 h of heating at 190° and 12 h at 150°, the increase in crystallinity ceased, and no appreciable changes in the structure, according to X-ray data, were observed up to 30 h of heat treatment.

It was established that the spherulitic structure of the polyamide proved more sensitive to changes in the heat-treatment regimes than the "degree of crystallinity." At short heating times, a noticeable increase in the size of the spherulites was observed (from 1 to 5 μ); individual formations were considerably larger. After 8 h of heating at 190° and 10 h at 150°, gradual destruction of the spherulitic structures began, and after 30 h of heat treatment the surface of the specimens no longer gave a pattern typical of spherulitic formations.

Comparison of the structural data with the results of tests of the polyamide for wear showed that there is no definite correlation between the "degree of crystallinity"and the wear resistance of the plastic. Thus, for example, specimens with the same "degree of crystallinity" but treated under different temperature conditions do not have identical wear-resistance indices. For specimens which, during prolonged heat treatment, no longer changed their value of the "degree of crystallinity," a noticeable decrease in wear resistance was observed as a function of heating time.

Preliminary studies showed that the greatest resistance to wear is possessed by specimens whose spherulitic formations are characterized by a uniform size within the range of 2–3 μ. Thus, uniformity, size, and the fine structure of the supramolecular formations play an essential role in the wear of polyamide. Therefore, in studying the relationship between mechanical properties and the structure of crystalline polymers, it is important to clarify the role of secondary supramolecular formations in the development of these properties.

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