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AN OVERVIEW OF THE MACROMOLECULAR STRUCTURE AND MECHANICAL PROPERTIES OF POLYMERS

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At the same time, information about the results obtained from the investigation of the relationships between "upper molecular structure-property" was given. As a result of the research, it was determined that the important mechanical properties of polymer systems depend to a significant extent on the upper molecular structure formed on the macromolecules of the materials.

High-density polyethylene, polypropylene and polyvinylidene fluoride materials, produced in different technological modes, having a chemical linear structure and therefore crystallizing, were used in the research. In the case of samples of polyethylene materials, in the case of other polymers with spherulite and fibrillar upper molecular structures, only samples with a spherulite structure were studied. It has been established that the mechanical strength is characterized by higher indicators in materials with small geometric dimensions of structural elements and, therefore, a high degree of primacy. In terms of the mechanical strength of the studied polymers, the optimal variants of the technological modes of sample preparation were determined.

The physics of macromolecular compounds is a rapidly developing field of knowledge. The physics of polymers arose under the direct influence of technology, which widely uses polymeric materials. Thus, the technical value of rubber-like substances is determined by their ability to large reversible deformations with a low modulus of elasticity - high elasticity. In modern electrical engineering, the dielectric properties of a number of polymers play an important role. The use and search for new fibrous materials are associated with their high mechanical strength and elasticity. As a result of many studies carried out in recent years, it has been established that the mechanical, optical, electrical, information ("anti-entropy"), and other properties of polymer objects are largely determined by the structure of supramolecular aggregations, i.e., aggregations consisting of hundreds and thousands of macromolecules organized in a certain way. To solve structuralmechanical problems (and often also for structural problems proper), it turns out to be especially fruitful to carry out studies on polymers that are directly in a loaded state or in a non-stationary regime. The concept of the atomic structure of chain molecules and their mutual stacking in polymers, as well as the fundamentals for solving the central "structure-property" problem, were formed mainly on the basis of X-ray diffraction analysis data. Due to the specific nature of the structure of oriented amorphous-crystalline polymers, the X-ray diffraction study of their behavior at different levels of structural organization under the action of an external force along the orientation axis is of particular interest. In this case, the action of the tensile force is of greatest interest, since it is in this case that the changes associated with the increased strength inherent in such polymers are realized. The study of the supramolecular order in polymers is one of the youngest and rapidly developing areas of work in the field of polymer physics in the last decade, which not only yielded numerous new results, but also made it necessary to critically reconsider the old ideas about the structure of polymers and about the relationship between their structure and properties.

In recent years, as a result of a detailed study of the processes of crystallization from solutions and melts, a picture of the complex morphology of block polycrystalline polymers is gradually emerging. So, in block polymers, crystalline and non-crystalline regions are distinguished. The crystalline regions are single or aggregated folded or non-folded crystals, and the non-crystalline regions include fold surfaces, crystal-binding molecules ("pass chains"), non-crystallizing components, and non-crystallizing contaminants. Crystalline and noncrystalline regions are often associated into large ordered formations of various shapes: spherulites, dendrites, lamellae, axilites, aedrites, etc. There is a number of evidence in the literature supporting the assumption that polymers can crystallize with the formation of regular molecular folds and that low molecular weight fractions, molecular ends, and all "disordered" inclusions are pushed out of the crystal growing by folding macromolecules. In block crystallizing polymers in an unoriented state, one of the most typical and widespread morphological units are spherulites. Spherulites are spherical formations consisting of rays ("radii") diverging from the central core. The center of a spherulite usually has a sheaf-like elongated shape. The rays emanating from it, as a rule, are branched like Christmas tree branches. At a high nucleation frequency, growing spherulites collide with each other and, therefore, in a system of densely packed spherulites, they most often have the shape of a distorted polyhedron. Their density, as a rule, decreases from the center to the periphery, due to the branching of the rays. The width of individual beams is 50-100, and the axes of macromolecules are usually perpendicular or almost perpendicular to the radii. It is assumed that in spherulitic crystalline formations, macromolecules are also folded, although individual rays and spherulites can be connected by passing molecules and strands, in which the macromolecules are parallel to the axis of the strand. The usual sizes of spherulites in systems crystallized from a melt are 1–10 microns. According to some model, the rays of a spherulite are ribbons twisted into a spiral.Such representations are especially plausible in the case of ring spherulites. Recently, however, views have appeared that state that the spherulite does not consist of radially diverging continuous ribbon-like fibrils, but of concentric aggregates growing around the core according to a spiral mechanism. Apparently, one more mechanism for the formation of ring spherulites in polymers exhibiting polymorphism is possible if the growth of the spherulite occurs near the transition temperature from one modification to another.

The process of transition from an unoriented structure to an oriented one is one of the key issues in the problem of supramolecular formations in polymers. The importance of a detailed study of this transition is determined by the fact that in the process of transformation of the initial unoriented structure into an oriented one, all the properties of the polymer change. The resulting oriented structure is completely different from the original. The transition conditions and the nature of the initial structure are determined by the properties of oriented fibers and films and articles made from them. The process of stretching nonoriented samples and transition to an oriented structure is studied by different methods at different levels of the structural organization of the polymer. A large number of works have been devoted to this issue, but even the basic mechanisms for the transformation of a block sample into an oriented structure have not yet been finally established. At the initial stages of stretching of high-pressure polyethylene, the crystallites in the polymer remain almost unchanged, somewhat turning their c - axes towards the axis of action of the tensile force. This occurs due to the elastic deformation of the intergranular regions. At a deformation of 40-150%, the process of grinding crystallites occurs, i.e. in this region of deformation, an irreversible crystalline rearrangement is observed. It was shown in the works that, depending on the preparation of the initial samples, they can have different "degrees of bonding" of the SMO elements. The "degree of bonding" largely determines the properties of the SMO resulting from orientational drawing, although some elements of the SMO (for example, long periods) may be the same for oriented samples, regardless of the initial SMO.

In conclusion, we can say that the problem of structural changes during polymer stretching is still far from being solved. Undoubtedly, some of the elements of the original structure can be completely preserved during orientation, while other elements are completely or partially changed. The study of the supramolecular organization of polymers is closely related to the study of the mechanism of large deformations, since the very capacity for large deformations seems to be the most important specific property of polymers, closely related to all levels of their structural organization. It is known that one of the last stages in the production of highly oriented polymer systems is the pulling operation. The final structure and properties of the resulting products depend on the selected process conditions - temperature, stretching rate, stretching degree, or, more precisely, on the temperature-time regime of the deformation process as a whole, i.e. conditions for sequentially performed operations of drawing, heat treatment, etc. From the results shown in tables 1, 3 and 4, it is known that at hot pressing P=100 atm and crystallization temperature Tcr=600C, polyethylene material with a spherulitic structure, polypropylene and polyvinylidene fluoride materials at Tcr=1000C, hot pressing P=100 atm and mechanical strength is higher than in other cases. It should be noted that the indicators obtained in the experimental study of the electrical and mechanical strength characteristics of a polyethylene material with a fibrillar structure subjected to tensile deformation 1=300% in the ddirection of one axis differ from polyethylene with a sspherulite structure. So, in this case, at high values of the crystallization temperature, hot pressing pressure and percentage of deformation, the mechanical strength properties show higher rates. In materials prepared under the specified processing conditions, the ordered parallel arrangement of a set of macromolecules that make up its composition increases, the degree of crystallization increases, which leads to an increase in the electrical and mechanical strength of the material. It is known from the results of the studies that the mechanical strength of linear polymer systems is associated with structural elements repeating with a large period, formed by a combination of macromolecules that make up the materials. with the parameters of the technology, it is possible to control the properties of polymer materials in the direction required by their fields of application. The wide practical application of polymers in the oriented state, which is mainly due to the high strength properties of oriented systems along the orientation axis, requires more and more information about the structure of such systems. Numerous electron microscopic and X-ray studies have shown that highly oriented crystalline polymers consist of anisometric supramolecular formations with a width on the order of 102–103 elongated along the direction of orientation; in this case, the axes of macromolecules, with a sufficiently high orientation, are elongated in the same direction. The observed extended supramolecular formations, with a pronounced anisotropy (as it turned out later) of mechanical and optical properties, are called fibrils. Fibrils in flexibly chain synthetic crystalline polymers most often represent a more or less regular one-dimensional alternation of regions with different densities. Such an alternation is observed in electron micrographs, and also appears as meridional reflections in small-angle X-ray diffraction patterns.

Table 1. Mechanical strengths of hot (200°C) pressed spherulitestructured polyethylene [13].

N₀	Mechanical strength					
		P ₁ =50 atm.	P ₂ =100 atm.	P ₃ =150 atm.		
	$T_{\rm kr}{}^0{\rm C}$	kqs/sm ²				
1	20	95	110	105		
2	60	98	120	114		
3	95	92	103	100		

 Table 3. Mechanical strengths of polypropylene with spherulite structure [13].

	Mechanical strength						
№		P ₁ =50 atm.	P ₂ =100 atm.	P ₃ =150 atm.			
	$T_{kr}^{0}C$	kqs/sm ²					
1	50	130	148	142			
2	100	180	210	200			
3	150	172	184	179			

Table 2. Mechanical strengths of polyethylene material with a fibrillarstructure subjected to l=300% tensile deformation in the direction of
one axis [13].

	Mechanical strength				
N⁰		<i>l,</i> %	P ₁ =50 atm.	P ₂ =100 atm.	P ₃ =150 atm.
	T _{kr} ⁰ C			kqs/sm ²	
1	20	100	110	125	123
2	60	200	127	135	132
3	95	300	140	145	149

Table 4. Mechanical strengths of polyvinylidene fluoride with
spherulite structure [13].

	Mechanical strength					
N⁰		P ₁ =50 atm.		P ₂ =100 atm.	P ₃ =150 atm.	
	T _{cr} ⁰ C	kqs/sm ²				
1	50	340	352	343		
2	100	348	356	350		
3	150	344	349	346		

CONCLUSIONS

When hot pressing is used in the preparation of polymer materials, the upper molecular structure and properties of the material, the P-pressure of the technological process, and the t-temperature of crystallization. It is known from the literature that polymer systems with a chemical linear structure, depending on the parameters of the production technology, are composed of lamella, spherulite, fibril and other structural elements of different sizes and are characterized by an amorphous-crystalline-polycrystalline structure. It should be noted that detailed information on the parameters of each of their processing processes, suitable for obtaining high, optimal and stable values of the mechanical properties of polymer materials with an amorphous-crystalline structure, has been found in relevant literature. It was determined in the work that the mechanical strength of the studied polymer materials depends to an important extent on the parameters of the technological process of their propersing applied in the technological process, T_k - depending on the crystallization temperature of the sample, spherulite structures of different sizes are formed in the materials, and in the case of small-sized spherulites, higher mechanical strength was recorded in the material. The mentioned result is explained by the homogeneity of the material and the small amount of defects in the case of small-sized spherulites. An increase in the degree of crystallization leads to an increase in mechanical strength. strength.