

STRUCTURE-PROPERTY RELATIONSHIPS IN LINEAR POLYMERS

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Abstract- In the article, an overview of the electrical and mechanical strength of the upper molecular structure of polymer systems is described. 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 electrical and 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 was determined that electrical and mechanical strength are 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.

Keywords: Upper Molecular Structure, Linear Polymer Systems, Electrical and Mechanical Strengths, Amorphous, Crystal, Spherulite, Fibril, Crystallization.

1. INTRODUCTION

Physics of macromolecular compounds is a rapidly developing field of knowledge. Unlike a number of other areas of modern physics. The physics of polymers arose under the direct influence of technology that widely uses polymer materials. The technical application of polymers itself is based mainly on their specific physical properties. Thus, the technical value of rubber-like substances is determined by their ability to undergo large reversible deformations with a low elastic modulus - high elasticity.

In modern electrical engineering, the dielectric properties of a number of polymers play a significant role. The use and search for new fibrous materials are associated with their high mechanical strength and elasticity. The most clearly formulated applied problem of polymer physics to date can be formulated as establishing a connection between the physical properties of a polymer, its supramolecular organization and the structure of individual macromolecules [14]. 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 [5-7]. Currently, many studies have been carried out to establish a correlation between the type of supramolecular organization (SMO), (as well as its changes) and various external influences [1, 3, 4].

Many structural and mechanical issues related to crystallizing polymers were solved in studies of changes in structure when these polymers are exposed to external mechanical force (mostly tensile, sometimes compressive). To solve structural-mechanical issues (and often for structural issues themselves), it turns out to be especially fruitful to conduct research on polymers that are directly in a loaded state or in a non-stationary mode. Many authors have studied crystallizing polymers according to the following scheme: elastic (reversible) changes in structure in the original, non-oriented polymers; the gradual transition of reversible changes in structure into irreversible ones, when the original structure is reconstructed into a new, oriented one; reversible and irreversible structural changes in oriented polymers. At present, many theoretical and experimental results have been obtained characterizing individual key moments of the above scheme. In some cases, certain structural details and their connection with the properties of specific polymers have been established quite convincingly [10, 11, 12, 15].

2. SPHERULITE STRUCTURAL ELEMENTS

The idea of the atomic structure of chain molecules and their mutual arrangement in polymers, as well as the basis for solving the central "structure-properties" problem, was formed mainly on the basis of X-ray diffraction analysis data. However, to date there is no unified approach to the theoretical analysis and calculation of the scattering of X-rays from aggregates of chain molecules, and there is no generally accepted point of view on the structure of polymers. Because of the latter, the interpretation of the results obtained often suffers from a lack of unambiguity. Many structural issues generate debate in the literature. Due to the specific structure of oriented amorphous-crystalline polymers, X-ray studies of their behavior at different levels of structural organization under the action of an external force along the orientation axis are of particular interest.

In this case, the effect of tensile force is of greatest interest, since it is in this case that those changes that are associated with the increased strength inherent in such polymers are realized [16]. The study of supramolecular order in polymers is one of the youngest and most rapidly developing areas of work in the field of polymer physics in the last decade, which not only gave numerous new results, but also forced a critical revision of old ideas about the structure of polymers and the relationship between their structure and properties.

In recent years, as a result of detailed studies of crystallization processes from solutions and melts, a picture of the complex morphology of block polycrystalline polymers is gradually emerging. Thus, in block polymers, crystalline and non-crystalline regions are distinguished. Crystalline regions are single or aggregated folded or nonfolded crystals, and noncrystalline regions include fold fold surfaces, crystal linking molecules ("chains"), noncrystallizable components, and contaminants not involved in crystallization. Crystalline and non-crystalline regions are often associated into large ordered formations of various shapes: spherulites, dendrites, lamellas, axilites, hedrites, etc. arxaca yaz.

There is a number of evidence in the literature confirming the assumption that polymers can crystallize to form regular molecular folds and that low molecular weight fractions, the ends of molecules and all "disordered" inclusions are pushed out of the crystal growing by folding macromolecules [12]. In block crystallizing polymers in a non-oriented state, one of the most typical and widespread morphological units are spherulites (Figure 1). Spherulites are spherical formations consisting of rays ("radii") diverging from a central core. The center of the spherulite usually has a sheaf-like elongated shape. The rays diverging from it are, as a rule, branched like Christmas tree branches.

Figure 1 presents an electron microscopic image of a spherulite element characterizing the structure of isotropic amorphous-crystalline, linear polymer systems.

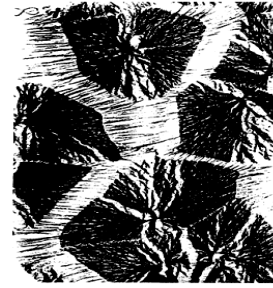


Figure 1. Spherulite structural element in amorphous-crystalline polymer systems [17]

At a high nucleation frequency, growing spherulites collide with each other and therefore, in a system of densely packed spherulites, 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 rays is 50-100 Å and the axes of macromolecules are usually perpendicular or almost perpendicular to the radii. It is assumed that in spherulitic crystalline formations the macromolecules are folded, although individual rays and spherulites can be connected by passing molecules and strands in which the macromolecules are located parallel to the axis of the strand. Typical sizes of spherulites in systems crystallized from a melt are 1-10 microns. According to some models, spherulite rays are ribbons twisted into a spiral. Such ideas are especially plausible in the case of ring spherulites.

Recently, however, views have emerged that claim that 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, another mechanism for the formation of ring spherulites in polymers exhibiting polymorphism is possible if the spherulite growth occurs near the transition temperature from one modification to another [17].

The process of transition from a non-oriented structure to an oriented fibrillar structure is one of the key ones 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 transforming 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 one. The transition conditions and the nature of the initial structure are determined by the properties of oriented fibers and films and products made from them. The process of stretching unoriented 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 mechanism of transformation of a block sample into an oriented fibrillar structure has not yet been definitively established (Figure 2).



Figure 2. Fibrillar structural element in polymer systems [17]

At the initial stages of stretching high-pressure polyethylene, the crystallites in the polymer remain almost unchanged, turning somewhat with their c-axes towards the axis of action of the tensile force. This occurs due to elastic deformation of intercrystalline areas. At a deformation of 40-150%, the process of crystallite grinding occurs. In this deformation region, an irreversible intracrystalline rearrangement is observed. The work shows that, depending on the preparation of the initial samples, they can have different "degrees of connectivity" of NMO elements. The "degree of connectivity" largely determines the properties of the NMO resulting from orientational stretching, although some elements of the NMO (for example, large periods) may be the same for oriented samples, regardless of the initial NMO [6-9].

In conclusion, we can say that the problem of structural changes during stretching of polymers is still far from being solved. There is no doubt that some 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 ability to undergo large deformations itself 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 of obtaining highly oriented polymer systems is the drawing operation. The final structure and properties of the resulting products depend on the selected process conditions - temperature, stretching speed, degree of stretching, or more precisely, on the temperature-time regime of the deformation process as a whole, conditions of sequentially performed operations of drawing [2, 8, 9].

Table 1. Made by hot (200 °C) pressing method, spherulite structure electrical and mechanical strengths of polyethylene [18]

Electrical Strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kV/mm		
1	20	34.3	37.2	36.5
2	60	35.4	38.6	37.1
3	95	34.5	36.2	35.3
Mechanical strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kgs/cm ²		
1	20	95	110	105
2	60	98	120	114
3	95	92	103	100

Table 2. Electrical and mechanical strengths of polyethylene material with a fibrillar structure subjected to *l*=300% tensile deformation in the direction of one axis [18]

Electrical Strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kV/mm		
1	20	34.3	37.2	36.5
2	60	35.4	38.6	37.1
3	95	34.5	36.2	35.3
Mechanical strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kgs/cm ²		
1	20	95	110	105
2	60	98	120	114
3	95	92	103	100

Table 3. Electrical and mechanical strengths of polypropylene with a spherulite structure [18]

Electrical Strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kV/mm		
1	20	34.3	37.2	36.5
2	60	35.4	38.6	37.1
3	95	34.5	36.2	35.3
Mechanical strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kgs/cm ²		
1	20	95	110	105
2	60	98	120	114
3	95	92	103	100

Table 4. Electrical and mechanical strengths of polyvinylidene fluoride with spherulite structure [18]

Electrical Strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kV/mm		
1	20	34.3	37.2	36.5
2	60	35.4	38.6	37.1
3	95	34.5	36.2	35.3
Mechanical strength				
No <i>P</i> , atm.	<i>T_{kr}</i> , °C	<i>P</i> ₁ =50 atm.	<i>P</i> ₂ =100 atm.	<i>P</i> ₃ =150 atm.
		kgs/cm ²		
1	20	95	110	105
2	60	98	120	114
3	95	92	103	100

From the results mentioned in Tables 1-4, it is known that hot pressing *P*=100 atm. and crystallization temperature *T_{kr}*=60 °C of polyethylene material with spherulite structure, *T_{kr}*=100 °C, hot pressing *P*=100 atm. and *T_{kr}*=100 °C. electrical and mechanical strengths of polypropylene and polyvinylidene fluoride materials are higher than in other cases. It should be noted that the indicators obtained from the experimental study of the electrical and mechanical strength properties of polyethylene material with a fibrillar structure subjected to *l*=300% tensile deformation in the direction of one axis differ from the indicators of polyethylene with a spherulite structure. So, in this case, at high values of crystallization temperature, hot pressing pressure and deformation percentage, the mechanical strength properties show higher indicators.

3. DISCUSSION

In the materials prepared under the mentioned processing conditions, the orderly parallel arrangement of the set of macromolecules that make up it increases, the degree of crystallization increases, and this leads to an increase in the electrical and mechanical strength of the material. From the results of the conducted studies, it is known that the mechanical strength of linear polymer systems is related to the structural elements that are repeated with a large period, formed by a set of macromolecules that make up the materials. The specified properties of materials depend on the parameters of their preparation and processing technology.

Thus, by changing the parameters of the processing technology, the properties of polymer materials can be adjusted in the direction required by their fields of application. The widespread practical use of polymers in the oriented state, due mainly to the high strength properties of oriented systems along the orientation axis, increasingly requires information about the structure of such systems. Numerous electron microscopy and x-ray studies have shown that highly oriented crystalline polymers consist of anisometric supramolecular formations with a width of the order of 10^2 - 10^3 Å, 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 later turned out) of mechanical and electrical properties, are called fibrils. Fibrils in flexible chain synthetic crystalline polymers most often represent a more or less regular one-dimensional alternation of regions with different densities. This alternation is observed in electron micrographs and also appears in the form of meridional reflections in low-angle X-ray photographs [17].

When hot pressing is used in the preparation of polymer materials, it depends on 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 indicators of mechanical and electrical properties of polymer materials with an amorphous-crystalline structure, has found its place in the relevant literature [8, 9, 14, 15, 17, 18].

In the literature, the deformation process of polyethylene samples with a thickness of 0.6, 1.2, and 1.6 mm obtained from experimental studies are given. It was determined that as the thickness of the material increases, the breaking of polymer samples is observed at small values of the relative deformation. At the same time, the

weakening of the deformation process at low (40 atm) and high (150 atm) pressures of the hot pressing of the material was explained by the amount of defects, the dimensions of the structural elements, the degree of crystallization of the material, and the uneven distribution of the crystallization temperature along the thickness of the material. It was determined that in polymer samples, the relative deformation process is characterized by small values as the crystallization temperature increases. It is known that larger spherulites are observed in polymeric materials as the crystallization temperature and crystallization time increase.

The large size of spherulites in block polymers leads to the brittleness of the material, which in turn results in a decrease in the deformation properties of the material. The process of breaking of brittle polymer material was explained by the fact that it occurs at the boundary of spherulites and in numerous internal defects of large spherulites. It has been shown that structural changes intensify in the high-temperature deformation process, deformation and disintegration of amorphous parts as well as crystalline parts in the deformation process, formation of new additional defects in the material, and expansion of defects in the direction of the applied force result in the weakening of the deformation process.

At the same time, increasing the speed of the deformation process also led to the weakening of the deformation process. In this work, the dependences of the samples of high-pressure polyethylene material with a thickness of 0.25-1.75 mm on the thickness and the cooling rate of the alloy were studied, and it was determined that as the thickness increases, the number of voids, microcracks in the samples, and the size of the structural elements similar to spherulites affect the deformation process of the material, relative causes a reduction in deformation.

On the other hand, the weakening of the deformation process can be attributed to the cooling of the polymer alloy at speeds lower than 200 °C. In this case, the size of the spherulite structural elements is larger and, again, leads to a higher degree of heterogeneity of the material. When the crystallized polymer materials are subjected to the deformation process in the direction of an axis, the recrystallization process actually takes place in the material, so that the initial spherulite structure is disintegrated and a fibrillar structure is formed in the material. The multitude of factors affecting the recrystallization process makes it impossible to establish a single theory that covers the deformation process in all cases. Polyethylene material with spherulite structure at $T_{kr}=60$ °C, $T_{kr}=100$ °C, hot pressing $P=100$ atm. electrical and mechanical strengths of polypropylene and polyvinylidene fluoride materials are higher than in other cases. The above-mentioned temperature-pressure indicators can be considered optimal processing parameters of polyethylene PP and PVDF materials with a spherulite structure, from the point of view of electrical and mechanical strength [12, 15].

It is known from the analysis of the mass spectrogram of the emission process from the surface of

polytrifluorochlorethylene (60%) and polyvinylidene fluoride (40%) composition material exposed to the effects of gas discharge in the ozone gas environment. As a result of the effect of gas discharges in the ozone gas environment, intensive emission of F^+ atoms from the surface of the material into the volume, along with ozone gas in the gas environment of the system, F^+ atoms are intensively involved in the surface bombardment process and rapid gas reactions.

From the results of the research carried out in this work, it is known that as a result of the effect of electric gas discharges on polymeric materials in the ozone gas environment, atoms and molecules undergoing the emission process in the materials, in gaseous form, rapid gas among the residual gases of the atmospheric air (hydrogen, oxygen) and other system gases present in the closed system. Reactions take place and the gas environment formed in the closed system differs sharply from the initial gas environment. By studying the emission processes from polyethylene terephthalate material in the SF_6 gas environment under the influence of electric gas discharge, it was determined that the emission process from the surface of the polycrystalline material was significantly weakened compared to the amorphous material. The intensity of the emission process decreased sharply due to the fact that the processing time of the material is long and the crystallization temperature is close to the melting temperature of the material.

It should be noted that the results obtained in the performed studies are of scientific importance for the study of "structure-property" relationships in polymer materials, and at the same time, they are a physical device in industries where there are effects of strong electric fields and electric gas discharges on polyethylene terephthalate and polymer materials in general. and its use as an electro-insulating material in technical equipment is also of practical importance in terms of predicting the service life. From the results of the conducted research, it was found that the process of emission of atoms and molecules occurs from the surface of linear polymer systems exposed to the effects of torch-shaped electric gas discharges, and as the temperature of the material increases, the intensity of the emission process is observed to increase. The obtained results are explained through structural concepts.

4. CONCLUSIONS

It was determined in the work that the mechanical and electrical strength of the studied polymer materials depends to an important extent on the parameters of the technological process of their preparation. Thus, depending on the P-pressure of hot pressing applied in the technological process of the upper molecular structure formed in the materials, and T_k - the crystallization temperature of the sample, different sizes of mechanical and electrical mechanical strength were recorded in the materials. explained with An increase in the degree of crystallization of the material with the formation of a fibrillar structure in a polyethylene sample deformed in

one axis direction led to an increase in its mechanical strength. From the results of the conducted studies, it is known that the electrical and mechanical strengths of linear polymer systems are related to the structural elements that are repeated with a large period, formed by a set of macromolecules that make up the materials. The specified properties of materials depend on the parameters of their preparation and processing technology. Thus, by changing the parameters of the processing technology, the properties of polymer materials can be adjusted in the direction required by their fields of application.

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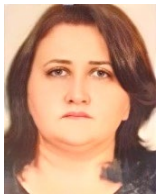
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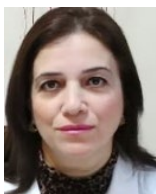
Master: Faculty Electrical Insulation, Cable and Capacitor Technology, Azerbaijan Technical University, Baku, Azerbaijan, 2003

Ph.D.: Chemical Technology and Engineering, Institute of Petroleum Chemical Processes, Baku, Azerbaijan, 2022

The Last Scientific Position: Teacher, Energy Department, Mingachevir State University, Mingachevir, Azerbaijan, Since 2023

Research Interests: Electrical Engineering and Electromechanics

Scientific Publications: 47 Papers



Name: **Zenfira**

Middle Name: **Adikhan**

Surname: **Tagiyeva**

Birthdate: 03.12.1974

Birthplace: Baku, Azerbaijan

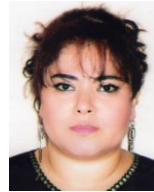
Bachelor: Faculty of High Voltage Technology and Electro Physics, Azerbaijan State Oil Academy, Baku, Azerbaijan, 1998

Master: Faculty of High Voltage Technology and Electro Physics, Azerbaijan State Oil Academy, Baku, Azerbaijan, 2000

The Last Scientific Position: Leading Engineer, Institute of Physics, Ministry of Science and Education, Baku, Azerbaijan, Since 2023

Research Interests: Electrotechnics, Electromechanics, Electro Technologies

Scientific Publications: 30 Papers



Name: **Sabina**

Middle Name: **Aghakazim**

Surname: **Huseynova**

Birthdate: 24.07.1977

Birthplace: Baku, Azerbaijan

Bachelor: Faculty of High Voltage Technology and Electro Physics,

Azerbaijan State Oil Academy, Baku, Azerbaijan, 1998

Master: Faculty of High Voltage Technology and Electro Physics, Azerbaijan State Oil Academy, Baku, Azerbaijan, 2002

The Last Scientific Position: Leading Engineer, Institute of Physics, Ministry of Science and Education, Baku, Azerbaijan, Since 2023

Research Interests: Electrotechnics, Electromechanics, Electro Technologies

c: 22 Papers



Name: **Vafa**

Middle Name: **Musa**

Surname: **Hajiyeva**

Birthdate: 18.08.1986

Birthplace: Bolnisi, Georgia

Bachelor: Physics Teaching - General Technical Subjects and Physics,

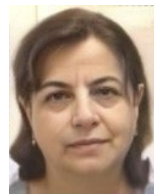
Azerbaijan State Pedagogical University, Baku, Azerbaijan, 2008

Master: Physics Teaching Methodology, Azerbaijan State Pedagogical University, Baku, Azerbaijan, 2017

The Last Scientific Position: Researcher, Institute of Physics, Ministry of Science and Education, Baku, Azerbaijan, Since 2018

Research Interests: Electrotechnics, Electro-Physics,

Scientific Publications: 25 Papers



Name: **Sevil**

Middle Name: **Sadiraddin**

Surname: **Ahadova**

Birthdate: 16.10.1962

Birthplace: Qabala, Azerbaijan

The Last Scientific Position: Laboratory Assistant, Institute of Physics, Ministry

of Science and Education, Baku, Azerbaijan, Since 2004

Research Interests: Electrotechnics, Electro-Physics

Scientific Publications: 16 Papers