"STRUCTURE-PROPERTY" RELATIONSHIPS OF POLYETHYLENE MATERIAL AND AT DIFFERENT CRYSTALLIZATION TEMPERATURES DEFORMATION PROCESS

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The article presents the results obtained from the study of the "structure-property" relationships of samples of high-density polyethylene material prepared under various technological conditions and the dependence of the deformation processes of samples prepared at different crystallization temperatures on the structural elements formed by macromolecular assemblies. It was determined that, depending on the structure formed by the assembly of macromolecules, significantly different properties and deformation processes of different nature are observed in polyethylene samples..

Keywords: polymer, amorphous, polycrystalline, spherulite, fibrillar structure.

INTRODUCTION

From the literature data [1-5], it is known that polyethylene sheets can be obtained by compressing polyethylene powder at temperatures higher than its melting temperature (200 ^{0}C) and pressures of 40-150 atm., and then by transferring the obtained alloy to temperatures lower than its melting temperature, at any thickness, and at the same time, it is known that the obtained sheets, regardless of their thickness, have isotropic properties and are characterized by spherulitic stricture. “Structure-property” relationships of polyethylene material prepared under different technological conditions.

The article studied polyethylene samples with thicknesses of 0.6, 1.2 and 1.6 mm. The choice of the research sample is due to the fact that, first of all, polyethylene material, as a typical representative of the linear polymer class, crystallizes with an amorphous-crystalline structure to form polycrystalline structures and is composed of spherulite structural elements in the isotropic state; since polyethylene material has been widely studied in a number of aspects, it is possible to provide univariate or multivariate explanations of the results obtained from the study of the issues raised in the article, using the information in the literature.

In the experiments, research samples of various thicknesses (0.6; 1.2; 1.6) were obtained by applying a pressure of 40-150 atmospheres using the above-mentioned method. The crystallization temperature of the samples was 20^{0}C. It is known from the literature [1, 2] that in the above-mentioned temperature-pressure regimes, the polyethylene material consists of spherulite structural elements of small dimensions.

Since the crystallization temperature is close to room temperature, the crystallization process in the material proceeds quite quickly, so the development of spherulite structural elements is limited and the spherulites have small dimensions. Considering that 20 ^{0}C acts more quickly on the thickness of the material in relatively thin layers, spherulites are characterized by smaller dimensions, while at the same time, at low values of the pressure P and in thick materials, the number of defects is greater.

It should be noted that the crystallization of polymer alloys goes through two main stages: the formation of crystallization centers and the growth of crystals from these centers. Crystallization centers are formed by a collection of polymer macromolecules or multiple folding of a single macromolecule. One of the main features of polymer alloys is that, due to the partially ordered structure in the amorphous state, heterogeneity is observed in the alloy.

The mentioned ordered structure is also observed at temperatures well above the melting temperature of the polymer material. For this reason, when polymer alloys are cooled, their crystallization ends very quickly. After the formation of crystallization centers in polymer alloys, the stage of development of a structural element from each crystallization center begins.

When the polymer alloy is cooled, the crystallization process initially proceeds rapidly (primary crystallization), and in the subsequent stage, crystallization ends at a somewhat slower rate (secondary crystallization).

In the primary crystallization process, a structural element formed by a collection of molecules is formed; in the secondary crystallization stage, the process of improving order occurs. It should be noted that both processes occur simultaneously, but the speed of the primary process is higher.

As mentioned, when the alloy is cooled, spherulite structural elements are usually formed in the material, since additives that do not participate in the crystallization process, end groups separated from the macromolecule, are removed to the surface of the formed crystals. The growth of crystals is in the direction of the pure alloy, since the additives removed to the surfaces limit the growth of the crystal.

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As a result, a radial spherulite composed of fibrils is formed.

The process of structuring in polymeric materials such as polyethylene, polypropylene, isotactic polystyrene, gutta-percha, polyacrylonitrile and other crystallizing polymers has been studied in detail by B.A. Kargin and his colleagues [6].

Based on the results of numerous theoretical and experimental studies conducted in the direction of morphological study of crystallizing polymers, monocrystalline, fibrillar and spherulite structural elements have been recorded as the main ones among the various structural elements formed in polymeric materials [2].

It has been established that the shape and size of spherulites also depend on the type of crystallization center (homogeneous or heterogeneous) and the rate of formation and development of the crystallization center.

A number of works have been carried out on the study of the internal structure of spherulites using radiography, electronography, electron microscopy, and monochromatic light optics methods [2, 7]. It should be noted that until now this issue has not been fully resolved.

According to modern concepts, the internal structure of spherulites consists of fibrils extending from the center along the radius. In fibrils, macromolecules are perpendicular to the radius. The crystallization of polymers in an isotropic state is not limited to the formation of spherulites, but also forms structural elements in the form of ribbons of larger sizes, in connection with spherulites and spherulite-like structures.

In the experiments, research samples of polyethylene materials with a length of 4 cm and a width of 0.8 cm were cut and deformed in a special device in the direction of one axis. The deformation process of the materials was carried out at room temperature.

The results obtained from the experiments are reflected in Table 1, the corresponding diagram (Fig. 1) and the graph (Fig. 2).

Table 1.

Results obtained from experiments on deformation of high-pressure polyethylene plates with different thicknesses d processed at a temperature of $T_{melt}=200^0C$, at different pressures P and at a crystallization temperature of $T_{kr}=22^0C$ and in one axis.

		d=0,6mm	**d=1,2mm**	**d=1,6mm**
№	P, atm	ε, %	ε, %	ε, %
1	40	110	80	50
2	60	150	120	95
3	80	190	150	120
4	100	290	220	190
5	120	350	300	270
6	140	320	280	250
7	150	300	270	200

It was found that as the thickness of the material increases, the mechanical fracture of polymer samples is observed at small values of deformation as a result of the deformation process.

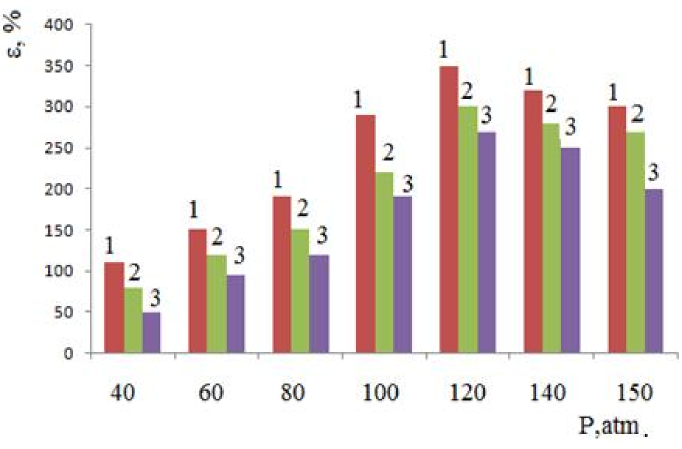

Fig. 1. Diagram of the results of the deformation process of polyethylene sheets.
1-d=0.6 mm
2-d=1.2 mm
3-d=1.6 mm

The initial results obtained from the deformation process of materials are explained by the fact that in samples with a small thickness, the crystallization process is completed at a faster rate at room temperature, and therefore the spherulite structures are smaller in size, and the distances between spherulites are also smaller, which leads to a more homogeneous material.

In samples with a greater thickness, the room temperature is unevenly distributed in the direction of the material thickness, and the degree of freedom of macromolecules in the volume of the material is greater, and therefore conditions are created for the development of spherulite structures and their sizes become larger.

In this case, since the distances between spherulites with a low density are large, the degree of inhomogeneity of the material is also high, and this leads to a decrease in the mechanical deformation of the material.

On the other hand, the greater number of defects in samples with a greater thickness also leads to a decrease in the mechanical deformation of the material.

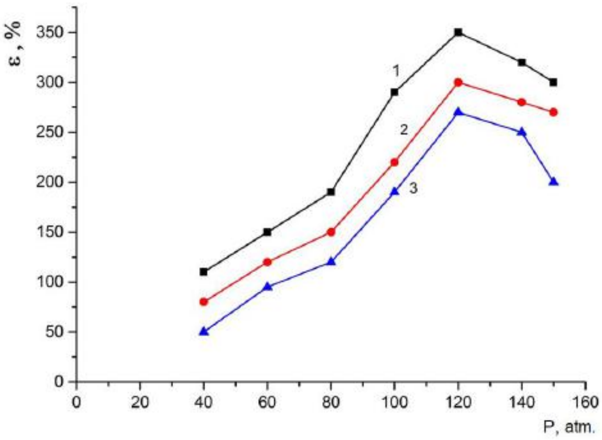

Fig. 2. Results of the deformation process of polyethylene plates

It should be noted that the mechanical deformation of the samples prepared at a pressure of 140-150 atm. was observed less than that of the samples prepared at a pressure of 120 atm. This result is explained by the fact that at a pressure of 140-150 atmospheres, the formation and development of structural elements in the material becomes more difficult, the degree of crystallization of the material decreases and the material has more defects.

It should be noted that when a polyethylene material with an amorphous-crystalline structure is subjected to a deformation process in the direction of one axis, structural changes occur in the amorphous and crystalline parts of the material, so the nature of the structural changes mainly depends on the parameters of the material preparation technology: the temperature of the environment in which the deformation process is carried out, the internal structure of the spherulite structural elements, the circular or radial arrangement of the spherulite elements in the material, whether the spherulites are highly defective or less defective, the nature of the distribution of macromolecules from the center of the spherulite along the radius, the chemical structure of the material and other parameters characterizing the material.

Taking into account the above, it can be concluded that the explanation of the mechanical strength of polymers and the mechanisms of deformation processes is not determined only by the dimensions of the structural elements (spherulites) and depends on a number of factors, therefore, the results we obtained in the initial experiments characterize the "structure-property" relationships of high-pressure polyethylene processed under the indicated temperature and pressure conditions.

If it is possible to determine the dependence of deformation processes on the dimensions of the spherulite in a one-valued manner, if the internal structure of the spherulite is the same and the influence of other influencing factors on the sample is eliminated, then a one-valued opinion can be made about the nature of the dependence of the material properties on the dimensions of the structural element.

It is precisely for the above reasons that it is difficult to give a general theory covering all cases of deformation processes of polymeric materials. In this regard, the collection of statistics of the results obtained from the experimental study of the deformation process in individual cases can help to eliminate the limitations existing in the theory of the deformation process.

RESEARCH METHODS

Deformation process of polyethylene material processed at different crystallization temperatures:

It is known that [8-12] spherulite is formed from morphologic elements based on crystallized block polymers. In the literature [8, 9], information about spherulites was first given by A.B. Shubnikov and H. Keith.

Spherulites are described as rays distributed from the center of spherical shapes along the radius.

Studies on the number of spherulite centers in the material show that as spherulites develop, they collide and form images of polygons in the material. Under the influence of spherulite, the distribution of rays, the density of spherulite, the flow of radius from the center, gradually decreases to the edges. A polymer with a spherulite structure is deformed again along one axis, a recrystallization process occurs in the material, and the polymer material at the final stage of deformation is formed from fibrillar structures.

The process of transition from a spheroidal structure to a fibrillar structure in chemical polymers due to deformation along one axis poses a threat to the study of the physical structure and physicomechanical properties of polymers.

The new fibrillar structure formed by this process is built up sharply from the initial spherulite structure. The minimum temperature-time conditions of the transition process and the initial structure determine the properties of a certain polymer material.

From the literature, it is known that the transition material has the following effects: the breakdown of crystallites, the replacement of amorphous parts, the breakdown of crystallites, the stretching of macromolecules in amorphous parts, the occurrence of a phase transition, the formation of cracks in the material, the formation of cracks in the material, etc., such that it undergoes deformation.

At the beginning of the process, some elastic deformations of the spherulites, the strength of the applied force is dissipated, as the deformation continues, the stretching of macromolecules in the amorphous parts and finally the removal of crystalline parts and the formation of a new amorphous-crystalline, fibrillar structure occur.

Note that, depending on the different initial structure, when a polymer with a harmful, linear structure is subjected to a limited temperature, deformation process, they have the same fibrillar at the final stage of deformation.

In crystallizing linear polymers, the fibrillar structure is formed by the repetition of the axis of deformation of the crystalline and amorphous parts with high density, so the repetition period, called the large period, is 50-1000 Å units, depending on the parameters of the sample processing technology.

The deformation process of crystallizing polymer materials is a complex problem, resulting from the influence of a number of factors:

- Polymer processing temperature;
- Material crystallization temperature;
- Polymer deformation process temperature;
- Deformation process speed;
- Internal structure of spherulites;
- Polymer surface;
- Spherulite internal configuration of macromolecules;
- Voids (gas bonds), microcracks, spherulite defects in the material;
- Thickness of the study;
- The molecular weight of the polymer and other factors are factors that affect the structure, physical and mechanical properties of the polymer material.

The presented article studies the dependence of the deformation process of polyethylene material prepared at a high-density crystallization temperature on the crystallization temperature. For this purpose, polyethylene samples with thicknesses of 0.6 mm, 1.2 mm and 1.6 were processed at a pressure of P=120 atm., crystallized at a crystallization temperature of T_{cr}~20-100 ^{0}C, and subjected to a single-axis deformation process at a temperature of T=20 ^{0}C.

Table 2, the necessary diagram (Fig. 2) and graph (Fig. 3) obtained from the experiments are given.

The presented results show that in polymer samples prepared under the above-mentioned technological conditions, the deformation process is characterized by smaller values as the crystallization temperature increases. It is known that as the crystallization temperature and crystallization time increase, larger spherulites are observed in polymer materials.

The large size of spherulites in block polymers causes the brittleness of the material, which in turn results in a decrease in the strength and deformation properties of the material.

Table 2.

Results obtained from experiments on deformation of high-pressure polyethylene plates at different T_{cr}-crystallization temperatures, prepared at a temperature of T_{melt}=200 ^{0}C, a pressure of P=120 atmospheres, and a temperature of T_{dif}.=20 ^{0}C and in the direction of one axis.

		d=0,6mm	d=1,2mm	d=1,6mm
№	**$T_{кр}$.^{0}S**	**ε, %**	**ε, %**	**ε, %**
1	20	375	370	300
2	40	265	210	170
3	60	200	180	160
4	80	150	120	110
5	100	100	100	100

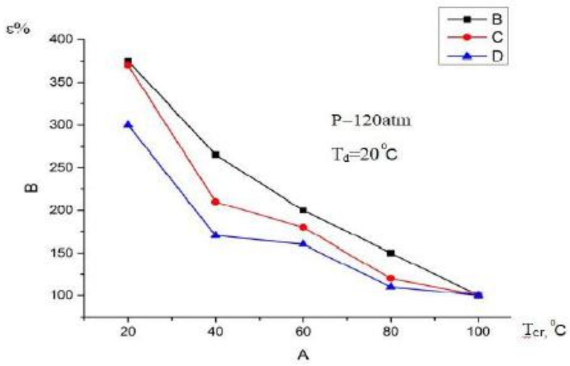

Fig. 3. Diagram of the results of the deformation process of polyethylene plates
1-d=0.6mm
2-d=1.2mm
3-d=1.6mm

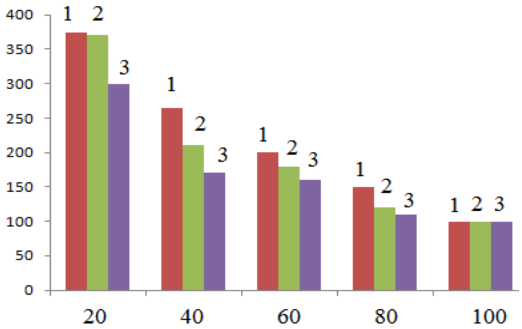

Fig. 4. Results of the deformation process of polyethylene plates.
1-d=0.6mm
2-d=1.2mm
3-d=1.6mm

The process of destruction of a brittle polymer material is possible to occur at the boundaries of spherulites or in numerous internal defects of large-sized spherulites. It should be noted that the results obtained in the experiments characterize the structural-deformation properties of polyethylene samples prepared under the above-mentioned technological conditions and the results obtained cannot be applied to polymer materials processed under different conditions.

Thus, the investigation of "structure-deformation properties" relationships in polymers necessitates continued experimental research.

It was determined that as the thickness of the material increases, the mechanical fracture of polymer samples as a result of the deformation process is observed at small values of deformation. The initial results obtained from the deformation process of materials are explained by the fact that in samples with a small thickness, the crystallization process is completed at a faster rate at room temperature, and therefore the spherulite structures are smaller in size, and the distances between spherulites are also smaller, which leads to a more homogeneous material. In samples with a greater thickness, the room temperature is unevenly distributed in the direction of the material thickness, and the degree of freedom of macromolecules in the volume of the material is greater, and therefore conditions are created for the development of spherulite structures and their sizes become larger. In this case, since the distances between spherulites with a low density are large, the degree of inhomogeneity of the material is also high, and this leads to a decrease in the mechanical deformation of the material. On the other hand, the greater number of defects in samples with a greater thickness also leads to a decrease in the mechanical deformation of the material. The article comments on the results characterizing the deformation process of PE material processed at different crystallization temperatures. From the presented results, it was determined that in polymer samples prepared under the above-mentioned technological conditions, the deformation process is characterized by small values as the crystallization temperature increases. It is known that as the crystallization temperature and crystallization time increase, larger spherulites are observed in polymer materials.

CONCLUSION

1. From the study of the deformation process of samples made of polyethylene material with a thickness of 0.6, 1.2 and 1.6 mm prepared under different technological conditions, it was found that as the thickness of the material increases, the mechanical fracture of the samples as a result of the deformation process is observed at small

values of deformation. This experimental result is explained by the non-uniformity of the structure in samples with a greater thickness and the presence of more defects in thick samples;

2. By studying the dependence of the deformation process on the crystallization temperature, crystallization rate and deformation rate of the polymer material, the dependence of the deformation process on the supermolecular structure of the polymer was determined and the structural concepts of the explanation of the above results were given.

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