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ANALYSIS OF RADIOGRAMS AND MODELS SUPRAMOLECULAR STRUCTURES OF POLYMERS

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Abstract- The work involves the categorization of small-angle X-ray patterns discovered through the investigation of orientated, amorphous-crystalline polymers. The suggested one-dimensional model may be utilized to analyze the shape of various small-angle reflections, according to an examination of the work done.

Keywords: Polymer, X-ray, Reflex, Classification, Intensity, Small-Angle X-ray Patterns, Macromolecule, Texture, Crystallization.

1. INTRODUCTION

Numerous studies have been conducted (both domestically and internationally) on small-angle X-ray scattering on oriented polymers of different types that are produced and processed under a variety of different circumstances. This research resulted in the identification of numerous types of small-angle X-ray diffraction patterns. [1-7].

Figures 1 and 2 show diagrams of the most common types of such X-ray diffraction patterns characteristic of polymers. Of course, it is not possible to describe all the small-angle radiographs observed so far within the framework of this article: this would require compiling an entire album (which, undoubtedly, could be one of the handbooks for specialists in this field). Consideration of a large number of small-angle X-ray patterns allowed D. Ya. Tsvankin to classify them for the first time and distinguish two groups of reflections [1].

Figures 1 and 2 schematically show the small-angle X-ray diffraction patterns that are typically seen in the investigation of materials with a high degree of orientation. Figure 1a shows a reflex in the shape of a stroke that intersects the meridian of the X-ray diffraction pattern, with the meridian itself acting as the stroke's point of highest intensity. This is the simplest reflection possible because the macromolecules' axes and the sample's texture axis are in line with one another. This reflection is particularly common in orientated samples with a C-texture [5, 8].

The term "four-point" refers to a small-angle radiograph that is formed when the intensity maxima are symmetrically situated on both sides of the meridian and are moved from it.

The term has come from the fact that there are a total of four reflexes seen on the x-ray. The literature has a sufficient number of references to these radiographs. The existence of planes inclined with respect to the texturing axis in the structure is the most common theory used to explain the four-point radiograph. There are yet further structural interpretations of the four-point, several of which conflict with one another. We will discuss this issue in more detail in the next article, but already now we can express the opinion that due to the ambiguity of the existing interpretations of four-point radiographs, the four-point problem requires further research [5, 8].

A rarer case is when instead of four reflections on a small-angle X-ray pattern, only two centrally symmetric reflections are formed, the centers of which are displaced from the meridian.

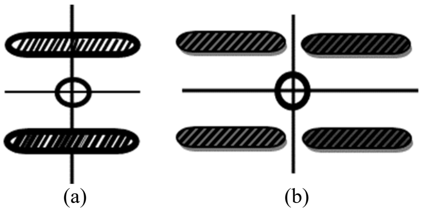

(a) (b)

Figure 1. Schemes of tangential reflexes [5, 8]
(a) dashed reflex, (b) four-dot

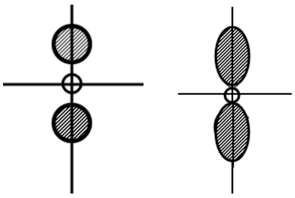


Figure 2. Schemes of radial reflections [5, 8]

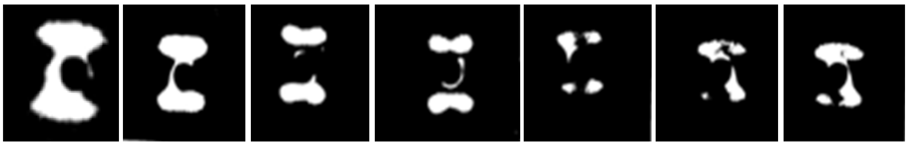
In the works, a radiograph of this type is called a two-point radiograph or "two-point". Two-spot radiographs are obtained from samples subjected to shear deformations. All reflections are situated on layered lines, which is a characteristic shared by the two kinds of small-angle X-ray diffraction patterns schematically depicted in (Figure 1) shows that these layer lines are usually located perpendicular to the meridian of the small-angle radiograph. If the sample has a complex texture, the axes of which are pointing in the direction of the X-ray pattern, the layer lines may also be positioned at an angle to the meridian. This radius must be simultaneously the axis of the sample texture. Therefore, a stroke, a four-point and a two-point are called tangential reflections, meaning their location tangentially relative to any radiograph radius. Along with such maxima, X-ray diffraction patterns often reveal reflections that have a completely different form.

Frequently, maxima on a small-angle radiograph's meridian take the shape of a "circle" or "drop," stretched toward the radiograph's center (Figure 2). During the annealing of orientated samples, this sort of diffraction maxima develops.

These reflexes have a high level of intensity. Particularly strong circular reflections have tremendous intensity. The strength of this particular collection of reflexes is typically focused close to the radiograph's meridian or another radius that extends to its center. The equatorial diffuse scattering, which appears in cold drawing at the equator and is angled perpendicular to the texture axis off the sample, has to be distinguished from these radial reflections.

5% 10% 15% 20% 25%

Figure 3. Small angle radiographs of high-pressure polyethylene (LDPE) stretched at room temperature after orientation at T=1000 °C [5, 6, 8]



1% 2% 3-10% 4-15% 5-20% 6-30% 7-40%

Figure 4. Small-angle radiographs of LDPE oriented at room temperature (1) then free-shrunk at T=100 °C (2), re-stretched at room temperature (3)-(7) [5, 6, 8]

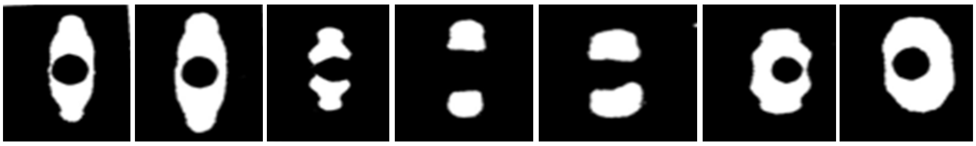


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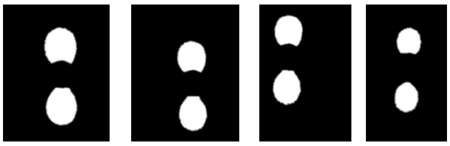
Figure 5. Small angle X-ray patterns of medium pressure polyethylene PESD lightly irradiated ($n\gamma$ radiation) in the reactor at T=200 °C, stretched at T=1600 °C and crystallized at T=600 °C [5, 6, 8]



a b c d

Figure 6. Patterns of small-angle X-ray diffraction of samples of polyamide 6, annealed in the free state at T=850 °C and deformed at room temperature [5, 6, 8]

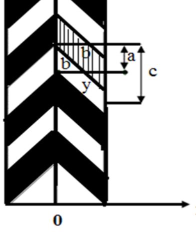


Figure 7. Scheme of the longitudinal section of the model of fibrils with sinuous layers [1, 5, 8]

Issues related to four-spot radiographs, indicating that there are diagonal grating planes that are tilted with respect to the texture axis, are also considered in a model in which elementary fibrils are more independent of each other, i.e., independent to such an extent that they can move relative to each other. In this case, as shown in Figure 9, it is easy to imagine how inclined lattice planes can be formed if the crystalline regions of neighboring fibrils are not located at the same level. Indeed, such an arrangement of crystalline regions should be considered normal, because, due to steric hindrances, the location of such regions in planes perpendicular to the texture axis is very unlikely [4].

A more thorough interpretation of four-point X-ray patterns is contained in the work of D.Y. Tsvankin, where a new model of oriented systems is proposed. A feature of the model is that it contains crystallites in the form of oblique parallelepipeds adjacent to the transition zones and monotonically changing density. The model has a lateral smooth surface [1].

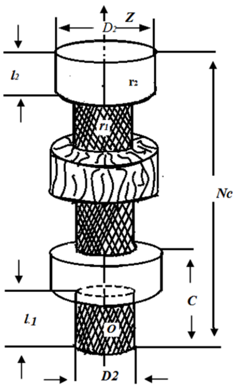
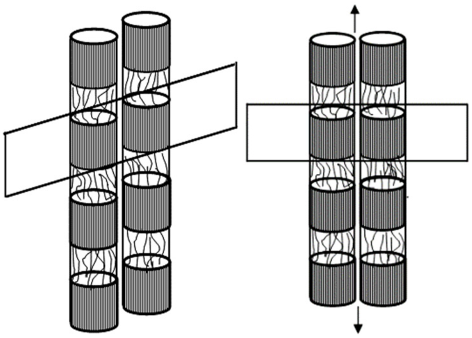


Figure 8. Schematic representation of fibrils with antinodes [5, 8]



(a) (b)

Figure 9. The elementary cylinders were moved in such a way that the distortion vanished in the following diagram showing changes in the supramolecular structure during stretching of the three samples: (a) initial state, (b) sample will stretch [5, 8]

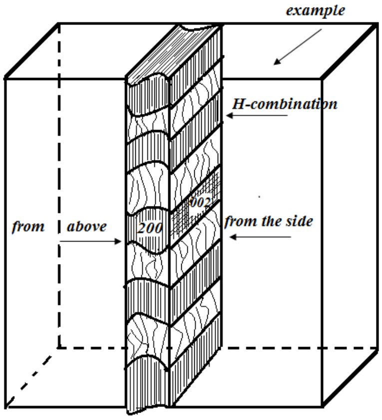


Figure 10. Scheme of the supramolecular structure of an oriented polyamide 6 film annealed in a free state [5, 8]

The suggested fibril model and an oblique crystallite are shown in Figure 7. With the use of the suggested model, small-angle scattering can be calculated, and its origins can be explained for different kinds small-angle X-rays patterns. The intensity distribution in the full reciprocal space for different values of the parameters describing the shape and dimensions of the oblique crystallite may be calculated by using the general formula for the form factor that was deduced in the study under review. The author of shone through an analysis of the form factor formula that the parameter bt/a is the primary parameter representing the impact of the crystallite shape on the intensity distribution. The calculations carried out and the intensity distribution graphs built on their foundation demonstrate that the occurrence of small-angle reflections of different sorts may be explained by a simple the bt/a value was increased from 0.6 to 2.0 [1, 2].

When it comes to axial textures, there is a progressive change from a dash to a four-dot and finally to an X-ray diffraction pattern of the "oblique four-dot" type as bt/a rises. When bt/a1.7-2.0 has large values, a radial-type reflex that is angled toward the meridian occurs. Because of this, it can be shown from the findings in that the suggested one-dimensional model may be used to categorize and explain the form of different small-angle reflections [3].

Unlike a number of other areas of modern physics, polymer physics arose under the direct influence of technology that widely uses polymeric materials. The very technical application of polymers is based mainly on their specific physical properties. The most clearly formulated applied problem of polymer physics to date can be formulated as establishing a relationship between the physical properties of a polymer, its supramolecular organization, and the structure of individual macromolecules.

Currently, many studies have been carried out establishing a correlation between the type of supramolecular organization (SMO) (as well as its changes) and various external influences. Many structural-mechanical issues related to crystallizing polymers were solved in studies of changes in the structure under the action of an external mechanical force on these polymers. To solve structural-mechanical issues, it turns out to be especially fruitful to conduct research on polymers that are directly in a loaded conformity or in a non-stationary mode.

Many authors have studied crystallizing polymers according to the following scheme: elastic (reversible) changes in the structure in the initial, nonoriented polymers; the gradual transition of reversible changes in the structure to irreversible ones, when the original structure is rebuilt into a new, oriented one; reversible and irreversible structural changes in oriented polymers.

At present, many theoretical and experimental results have been obtained that characterize individual key moments of the above scheme. In some cases, certain details of the structure and their connection with the properties of particular polymers have been convincingly established.

For many years, the X-ray diffraction method has been successfully used in the study of the structure of polymers. However, until now there is no one approach to the theoretical analysis of the calculation of X-ray scattering 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-mechanical questions cause discussion in the literature.

In most works, research is used using diffraction at large and small angles. The experimental material obtained for a particular polymer sample using small-angle X-ray diffraction is very limited. On small-angle radiographs, there is one, or less often, two orders of reflections. The method of direct analysis of the intensity distribution using the Fourier transform, which is used in radiography, in this case can hardly give certain results [1]. In this case, the simulation method is the most suitable or, perhaps, even the only possible (so far) method for interpreting small-angle scattering and large periods. Most of the facts now available are satisfactorily explained by means of a linear scheme, which can therefore be used as the basis for constructing a specific model.

Therefore, the general problem of this study can be defined as minimizing the ambiguities that remain when using a linear scheme: in methodological terms, this means choosing additional types of experiments (usually rediffractive ones), which make it possible to narrow the range of possible structural-mechanical interpretations and then in a "secondary series » additional experiments, acting by the method of exclusion, - to select if not the only possible, then the most probable models of the structure.

This approach is associated with a revision of some of the usual ideas, for example, with the uniqueness of the Hosemann-Bonard model for oriented crystallizing flexible-chain polymers, the impossibility of implementing the fibrillar Statton model in such systems, the invariance of the size and shape of crystallites under reversible (elastic) loading, etc. As a starting point, the computational works of Tsvankin deserve the most attention, in which a number of experimentally observed X-ray diffraction patterns [1] were explained by a variation in the shape of crystallites.

It was shown in the work that if the original oriented system (s-texture), which gives two dashed reflections on the meridian of a small-angle X-ray diffraction pattern, is subjected to shear deformation (for example, by reorientation at some acute angle to the primary orientation axis), then the "strokes" are strongly displaced from the meridian in opposite directions, which, according to Tsvankin's calculations, means that the crystals are skewed, Since in real systems there is always some misorientation of crystallites relative to the texture axis, it should be assumed that when such systems are stretched along the texture axis, some of the crystallites will also undergo shear deformation, and the corresponding distortions should appear in small-angle X-ray diffraction patterns. Moreover, at a not very high orientation of the initial structure, stretching along the texture axis, apparently, can lead to the destruction of some of the initial crystallites; to irreversible changes in the structure [1, 2].

Note that reversible changes in the structure and the corresponding changes in the diffraction patterns from samples under load make it possible to significantly refine the models of the supramolecular organization of the initial (unloaded) samples. According to a review of the data from the literature, most experts believe that the four-point small-angle X-ray diffraction pattern is what causes the structure's planes to be inclined with respect to the texturing axis. Thus, the results presented in show that the proposed one-dimensional model can be used to classify and interpret the shape of various small-angle reflections. An analysis of the literature data shows that most researchers explain the four-point small-angle X-ray diffraction pattern by the existence of planes inclined with respect to the texture axis in the structure [1].

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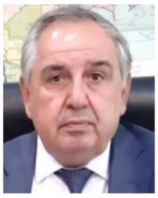
BIOGRAPHIES



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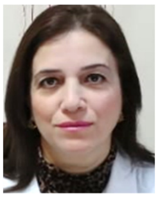

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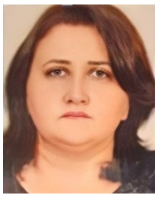

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