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THERMO-MECHANICAL MODIFICATION OF AMORPHOUS POLYESTER FIBRES: III. STRUCTURE INVESTIGATIONS USING WIDE ANGLE X-RAY SCATTERING

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Abstract: *Amorphous poly (ethylene terephthalate) (PET) yarns were used as precursor specimens. The aim of the present experiment is to investigate the heat mechanically induced structural changes in the studied samples. The thermal deformation experiments were carried out on conditions of linear samples heating from room temperature up to 200^0C while they were subjected to a well-defined constant strain force. Using of wide angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC) methods ware investigated the structural rearrangements in the studied samples caused by the fibers drawing. Dependences between the parameters of the thermal deformation experiment and the running in the specimen's structure development are established.*

Key words: *poly (ethylene terephthalate), amorphous filaments, linear heating, tensile stress, extension, heat mechanical treatment, structure development, WAXS.*

1. INTRODUCTION

It is well known that the flexible chain polymers are widely used in the production of fibers, films and more. It is extremely important the study of their structure and structural transformation caused by different variants of heat mechanical modification. In this sense, a key issue is the study of structural transformation mechanisms in uniaxially orientation downloading. It is extremely important the investigation and understanding of the macromolecular chain segments orientation processes as well the accompanying processes of destruction, slip, tangling and untangling, relaxation of stresses, deformations, etc.

The present work is dedicated to investigation of heat-mechanical modification of poly (ethylene terephthalate) (PET) and in particular of PET fibers. PET is a polymer with good mechanical properties, high thermal resistance and consequently with a wide practical application. Realized are many experimental studies of induced both from heat [1-

4], and combined heat - mechanical modification [5-8] structural changes in PET fibers, including with the participation of the authors of this article. Regardless of the presence of many experiments, the relationship between the technological molding parameters and the subsequent thermal mechanical modification on the one hand and the change in the super molecular structural organization of PET fibers of the other is not fully understood.

In the present work we submit part of the results from large scale investigations of the relationships from the thermo-mechanical modification parameters and the structural changes in amorphous poly (ethylene terephthalate) fibers. Structural rearrangements occurred in the PET fibers as a result of the simultaneous thermal and mechanical treatments were studied using differential scanning calorimetry (DSC). It should be underlined that the performed structural analyses show that all of the heat mechanically modified PET filaments are partially crystalline. Moreover, the calorimetric studies show that the deformation behavior of the PET filaments is a direct consequence from the occurred as a result of the heat mechanical treatments phase transitions and especially of the strain-induced crystallization in the fibers. It was interesting to make additional structural analyzes in order to obtain information about the arrangement of the macromolecular chain segments in a crystalline phase of the fibers. Especially suitable for the study of the macromolecular chain segments arranged in the crystalline phase are the various X-ray methods [9].

2. EXPERIMENTAL

2.1. MATERIALS

PET undrawn multifilament yarns produced by melt spinning on the industrial spinning installation Furnet (France) have been selected as a precursor samples. The technological parameters and basic characteristics of the original filaments are spinning speed of 1100 *m/min* and a melt throughput of 50 *g/min*. Investigated complex threads contain 32 filaments and the single filament diameter was 44 μm. Filaments were characterized by their optical birefringence and flotation density. The values received, i. e., 0.006 for the birefringence and 1336 kg/m^3 for the density, showed that the samples were practically amorphous and oriented.

2.2. METHODS

2.2.1 THERMO-MECHANICALLY MODIFICATION

Simultaneous thermal and mechanical treatments of the studied yarns were performed using device constructed and produced in our laboratory. It involves a vertically located tubular heater, which can be moved to enclose the loop of the

studied PET- bundle. The fibers heat-mechanical treatments included linear heating from room temperature up to 200^0C accompanied by applied to the fiber bundle tensile force. The heating rate was 3.5^0C/min. During the filaments heating they were subjected to constant tensile stress in the range from 0 *MPa* to 3.0 *MPa* (increasing step of 0.12 *MPa*) without restrictions of the bundle deformation. The bundle length changes ware estimated from the position of the pointer as a function of time. Afterwards, the heater was removed and the sample was left at room temperature with dimensions acquired during the thermal treatment. Depending of the applied tensile stress values the samples are numbered from 1 to 26.

2.2.3 Wide-angle X-ray scattering (WAXS)

The structural characterizations of the studied fibers after the above described heat-mechanical treatments were realized by wide-angle X-ray scattering measurements.

The fiber structure was studied by WAXS, using diffractometer URD - 6 (under license of SIEMES) of the company "Freiberger Präzisionsmechanik" (Freiburg im Breisgau, Baden-Württemberg, Germany). Used is β-filtered with Ni-filter $Cu\ K_\alpha$ radiation with a wavelength $\lambda = 1.5418$ Å.

3. RESULTS AND DISCUSS

Depending on the deformation behavior the investigated samples were conditionally divided into three groups as follows. First one includes the bundles with numbers from one to fifteen. In the second one are the yarns from sixteen to twenty, and the third group includes the last six specimens which despite of the stress values increasing are extended less. As it was mentioned above the structural rearrangements occurred in the PET fibers as a result of the heat mechanical modification using WAXS.

Representative wide-angle X-ray scattering curves of treated PET fibers from the above defined three groups of samples are present in Figures 1, 2 and 3. The diffraction curves are presented to illustrate the change in the fibers degree of crystallinity and orientation with the samples load increasing as well as their accordance with the DSC curves of the same objects for comparison of the structural information from the both methods which are respectively geometric and energetically-structural sensitive. The first group of samples is characterized by a monotonic, although nonlinear elongation increase with the strain stress increasing up to the specimen with number 15. As is evident from Fig. 1, with the load increasing within this group the intensity distribution in the diffraction pattern shows noticeable changes with the stress increase,

which is evidence for the significant structural reorganization without strict consistent trend observed in a specific type of alteration.

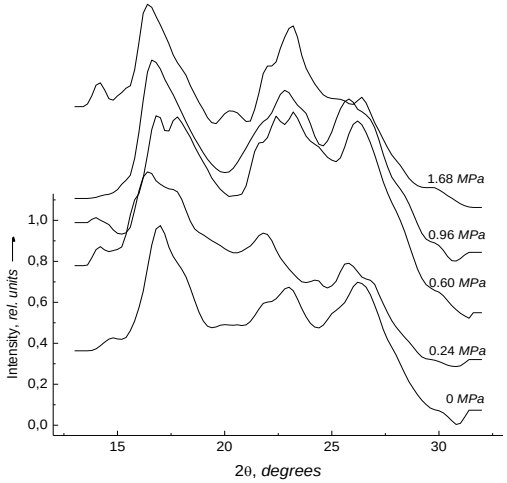

Fig. 1. Representative WAXS curves of heat-mechanically treated PET fibers from the first group (the curves are shifted vertically for clarity).

In the second group of WAXS curves (Fig. 2) it can be seen more stable trend of increase in the intensity of the diffraction radiation from improved crystalline and oriented regions in the samples.

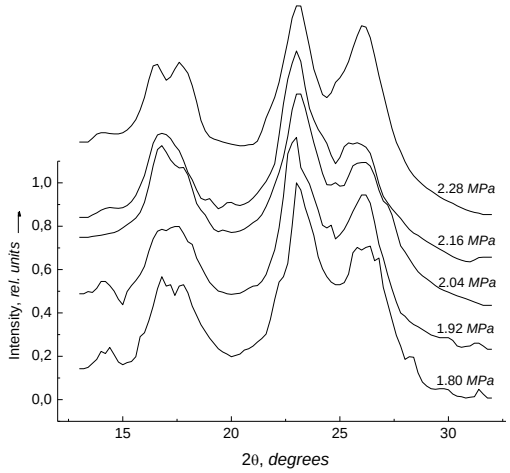

Fig. 2. Representative WAXS curves of heat-mechanically treated PET fibers from the second group (the curves are shifted vertically for clarity).

The DSC curves from the same group also showed a stable trend of deviation of the melting process to higher temperatures which confirms the suggestion for improvement of the crystalline phase. The same is valid and for the oriented amorphous regions. As from the diffraction and DSC curves, as well as from the stress - deformation dependence is confirmed the assumption for additional objects orientation

allowing improvement of the crystalline phase and the supporting fraction in amorphous sections, which leads up to decrease in the total relative fibers deformation.

With the strain stress increasing at the samples with numbers from 20 up to 26 in which the relative fibers deformation almost does not change the intensity of the diffraction reflections significantly increase (Fig. 3). Probably for the account of low elastic deformation is realized a significant improvement of the crystalline phase on the surface of the lamellae or in the newly oriented regions.

The exception occurs only in the sample subjected of the biggest tension stress of 3.0 *MPa*, where the intensity of the diffraction pattern falls strongly. Perhaps the increased destruction of separate fractions of macromolecular segments partially distorts the degree of the orderliness in the polymer system. At the same time the indestructible part of additional downloaded segments further improves their arrangement

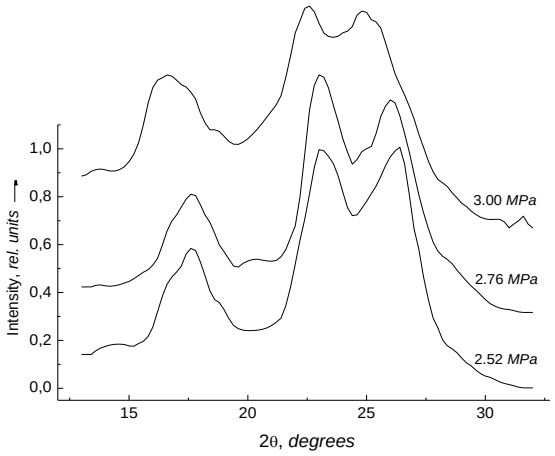

Fig. 3. Representative WAXS of heat-mechanically treated PET fibers from third group (the curves are shifted vertically for clarity).

so that is realized more detailed infrastructure of distribution of the intensity of the powder diffraction pattern.

4. CONCLUSIONS

Based on the carried out thermal deformation experiments and structural investigations it can be concluded:

The WAXS research confirmed the obtained by DSC result that all of the investigated amorphous specimens after the heat - mechanically treatment are partially crystalline.

Was confirmed and the role of the applied to the fibers tensile stress in the adjustment of the interacting processes of fluid like deformation and stress-induced crystallization

kinetics clearly manifested in the ultimate samples deformation.

At tensile stress values up to 1.68 *MPa* predominates the fluid like filaments elongation, while the further stress increasing leads to the earlier crystallization start and therefore to reduce of the final fibers length.

About us stays interesting and unclear the question about the role of heat mechanical treatment at tensile stress values above 3 *MPa* and therefore such experiments are coming.

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