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High Temperature Orientation Modification of Undrawn Polyester Filaments. Complex Influence of the Temperature and Tensile Stress

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Abstract* — *In the present work the complex influence of the temperature and tensile stress on the deformation behavior, birefringence and degree of crystallinity of undrawn poly (ethylene terephthalate) (PET) fibers was studied. Amorphous PET yarns were subjected on heat mechanical modification at constant temperatures in a narrow range above glass transition temperature from 80 ^{0}C to 95 ^{0}C combined with tensile stress with values from 0 MPa to 30 MPa. Birefringence measurements and differential scanning calorimetry (DSC) were used in order to identify the occurred as a result of the heat mechanical processing structural changes in the samples. The fibers birefringence was measured using a specialized device that allows quick and precisely determination of the birefringence of complex objects such as polymer fibers and films. It is established the influence of the superposition annealing temperature/tensile stress on the filaments dimensional changes, birefringence and degree of crystallinity.

Keywords* — *birefringence, deformation behavior, degree of crystallinity, filaments, tensile stress.

I. INTRODUCTION

The flexible chain polymers (FCP) are mainly used for the production of fibre-forming polymeric materials, films, etc. In the case of undrawn filaments, the final structure is mainly due to the melt spinning conditions and of the subsequent thermo mechanical treatments, too. Depending on the forming conditions in the fibers are formed areas with an increased order of the macromolecular segments, meso-phase and crystalline phases with a different perfection which under appropriate conditions can be converted into crystal nucleus, and they are the so-called semi-crystalline nuclei. Another consequence of the filaments formation is the formation of regions with frozen stresses in them.

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The uniaxially filaments download is accompanied by the alternative processes of the macromolecular segments orientation as well as from the destruction, tangling, untangling, stress relaxation, deformation, etc. The above-mentioned processes have a direct influence on the physical and in particular on the mechanical properties of the treated fibers.

At the same time the optimal realization of the high temperature orientation modification of polymer filaments remains complex and still insufficiently studied process. Therefore the study of the structural reorganization mechanisms during uniaxially drawing needs of special attention. The birefringence determination is a convenient and effective method for investigating of the orientation effects in the FCP. Representative of the FCP is the crystallizable thermoplastic poly (ethylene terephthalate) that in the form of fibres and foils has a widespread use. The applications of PET are based on its relatively high glass transition temperature and a low crystallization rate. There are described investigations of the relationships between treatments of PET with different initial structures and the caused phase and structure evolution [1-3]. The effects of the strain force, strain rate and temperature on the structure development of PET filaments have been well studied and reported by a number of researchers [4-6] including the authors of the present article. It is studied the influence of the treatment and production conditions on the fibers deformation behavior [4, 5] mechanical properties [6, 7] and spinning process [8]. Most often the birefringence measurement is used as a measure of degree of the fibers [7, 9-12] and films [14] orientation. Despite the large number of carried out investigations PET remains an interesting research object, intensively studied in the recent years. The complex effects of the combined tension stress with thermal treatments in the temperature region slightly above the glass transition temperature from 80^{0}C to 95^{0}C on the deformation behaviour and super molecular structure development in uniaxially oriented PET remains not fully clarified. The aim of this study is the structural reorganization behavior of amorphous as-spun PET fibers caused by combined thermal and mechanical treatments at four different temperatures ranging from 80^0C to 95^0C and mechanical tensile loading with values from 0 to 30 MPa.

II. EXPERIMENTAL

A. Materials

Amorphous as-spun multifilament PET yarns were used as precursor samples. PET threads are prepared by melt spinning on the industrial spinning machine Furnet (France) under basic production conditions as follows:

spinning speed 1150 *m/min*;
number of spinnerets in yarn 32;
single filament diameter 44 μm;
density ρ = 1338 kg/m^3;
degree of crystallinity α = 1,7 %;
birefringence Δn = 0,008;
coefficient of amorphous orientation f_a = 0,029.

B. Methods

The filaments heat-mechanical treatment was performed using a specialized device designed and produced in our laboratory. Thermal deformation experiment consisted of annealing of the studied yarn during ten minutes at the required temperature followed by the application of tensile stress for 120 seconds at the some temperature. The samples annealing temperatures are 80^0C, 85^0C, 90^0C and 95^0C in a temperature range closely above the filaments glass transition temperature, determined in our previous work of 74^0C. The tensile stress values are in the interval from 0 *MPa* to 30 *MPa* with increment step of 3 *MPa*. Structural characterizations of the tested fibers after the above described heat-mechanical treatments are realized using birefringence measurements and DSC analyses. The birefringence measurements of the heat mechanically processed PET fibers were performed using a specialized set-up developed and made in the author's laboratory. The gear involves polarizing interference microscope equipped with a CCD camera. The basic element of the experimental device is the system of a polarizer (*P*), analyzer (*A*) and birefringent fiber (*F*) in between and it is the so-called "*P-F-A*" system. The transmitting directions of the polarizers *P* and *A* are mutually perpendicular (crossed polarizers). The studied filament can be rotated around the optical microscope axis. The above-described experimental device allows quick and precisely measurement of the birefringence of complex objects such as polymer fibers and films. Based on the designed apparatus has been developed and the relevant methodology for quickly and effectively measurement of the birefringence of oriented polymers. Calorimetric analyzes were performed using a NETZSCH heat-flow calorimeter STA 449 F3 Jupiter (TG/DSC) in static air atmosphere. The temperature calibration was done using the onset melting temperatures of indium, tin, bismuth and zinc, and the energy calibration was based on the melting heat of the same metals. Fibers were cut in pieces of less than 1 *mm* and sealed in standard 85 μl platinum pans.

III. RESULTS AND DISCUSSION

With purpose to investigate the role of the complex superposition temperature/mechanical stress for achieving of optimal orientation effect the studied amorphous sample was subjected to combined heat mechanical treatments under the above described experimental conditions. During the thermal deformation experiments was registered and the relative elongation of the objects. The dependencies of the relative change of the yarns length $(L - L_0)/L_0$ (L_0 is the initial length of the fibers bundle) from the tensile loading values and temperature are shown on the "stress-deformation" diagram (Fig.1). From the Fig. 1 we can see the role of the temperature in the samples deformation process. Insignificant temperature increase from 80^0C to 85^0C resulted in leads to a tenfold increasing of the fibers elongation at the same values of the applied strain stress.

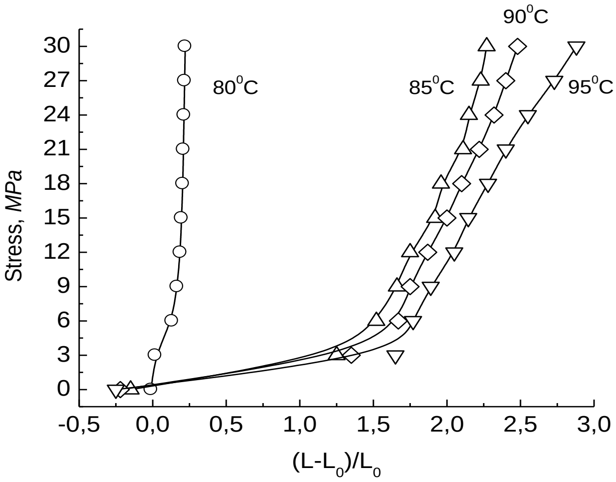

Figure 1. Tensile stress – relative elongation diagram.

Also were measured and the diameters of the modified fibers. The obtained data is present on Fig.2. Influence of the heat mechanical modification on the structural changes in the treated samples was examined by measurement of the fibers birefringence as well as with using of differential scanning calorimetry.

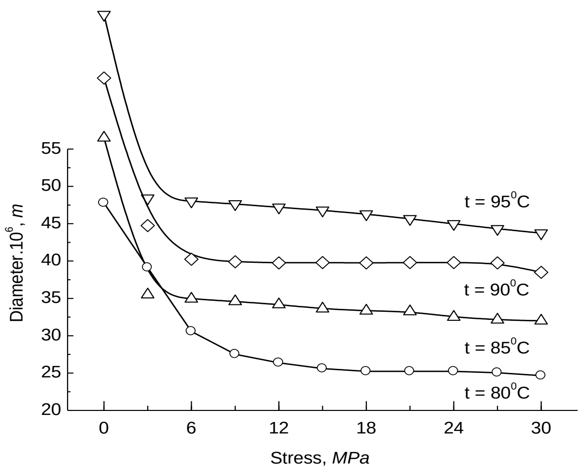

Figure 2. Fibers diameter.

The curves are shifted vertically for clarity.

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It is known that the birefringence measurement is convenient, effective and therefore preferred method for characterizing of the orientation effects in the amorphous areas of the flexible chain polymers. Using the above described specialized device and the relevant methodology have been performed the birefringence measurements of the processed PET objects. Filaments birefringence was measured by transmission of linearly polarized monochromatic light with wavelength λ = 590 *nm* across the P-F-A system. The obtained birefringence data depending on the applied to the yarn tensile stress are present in Fig. 3.

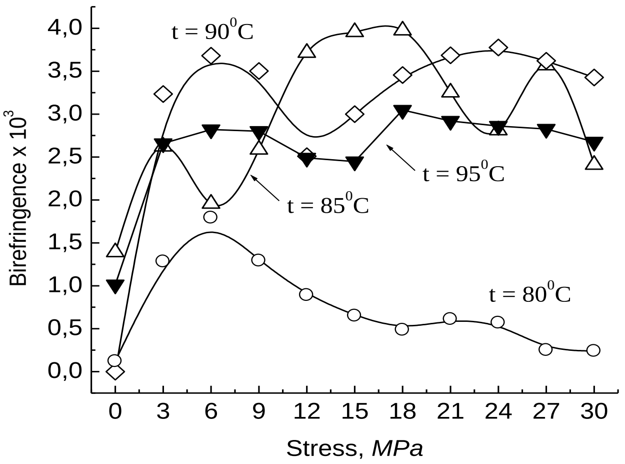

Figure 3. Birefringence of the heat mechanically processed at different temperatures PET filaments depending on the applied tensile stress.

From Fig. 3 it is seen that at a temperature of heat mechanical samples treatment of 80 ^0C with an increase of the tensile stress to 6 *MPa* was observed a strong increase of the orientation effects in the filaments registered by measurement of the birefringence. At tensile stress values higher than 6 *MPa* is observed not monotonically orientation decrease to the whole of the load range up to 30 *MPa*. In the range 18-24 *MPa*, occurs arrest of the birefringence decrease and is observed a less pronounced extremum at stress of 21 *MPa*. The observed course of the birefringence could mean that the stress levels exceeding 6 *MPa* are unsuitable for the given test temperature. I.e. for these tension values the fiber deformation is accompanied with more destructive than with orientation processes. The rise of the samples treatment temperature up to 85^0C leads to the appearance of three extreme regions of the filaments birefringence values namely at 3 *MPa* in the range of 12-18 *MPa* (highest) and at 27 *MPa*. It means that at these values of the gravimetric loading (respectively deformation speeds) are created suitable conditions for the fiber drawing accompanied with the increase of the orientation effects. As can be seen from Fig. 3, the temperature rise to 90^0C, shows increased fiber birefringence in the whole range of the gravimetric load values except the range 12-15 *MPa*. Birefringence of the fibers heat mechanically modified at the maximum temperature of 95^0C (Fig. 3) shows decrease and tendency of deterioration of the orientation processes in the whole studied range of tensile stress values. The probable cause for the observed effect at this temperature is the appearance of plastic deformation in the studied objects. This means that the temperature of 95^0C is not optimal to improve the fibers super molecular structure using uniaxial orientation drawing at the studied tensile stress values. Except by the birefringence measurement for evaluation of the structural changes in the modified objects have been also used and DSC. On the basis of the obtained data it was determined and the degree of crystallinity of the treated samples. The results are impressive and are presented in Table 1. It should be noted that the precursor sample subjected to heat mechanical treatments is practically amorphous.

Table 1. Degree of crystallinity of the heat mechanically modified amorphous PET filaments.

№	σ, *MPa*	α, % (80^{0}C)	α, % (85^{0}C)	α, % (90^{0}C)	α, % (95^{0}C)
1	Raw	1.7	1.7	1.7	1.7
2	0	2.0	11.8	4.0	13.7
3	3	2.9	39.5	36.1	40.7
4	6	34.7	38.5	39.2	42.1
5	9	34.9	39.3	41.3	43.3
6	12	35.0	41.6	42.5	45.0
7	15	34.0	42.5	43.3	44.7
8	18	33.3	41.8	42.6	44.5
9	21	33.7	41.5	41.5	44.4
10	24	34.0	39.7	40.6	44.6
11	27	35.8	40.5	40.0	44.9
12	30	34.2	40.7	40.9	43.8

As it can be seen from Table 1 the samples annealing at the experimental temperatures (80^0C-95^0C) without application of tensile stress (0 *MPa*) has little effect on the fibers degree of crystallinity. This fact proves the minor role of the temperature in the range 80^0C to 95^0C on the structural changes in the studied samples. But at a modification temperature of 80^0C combined with tensile stress, the small change of the tensile stress from 3 *MPa* to 6 *MPa* causes a sharp increase in the fibers degree of crystallinity with more than 30%. Moreover, the degree of crystallinity remains almost constant throughout the all tested range of the applied pulling stress. Similar picture was observed and at the other three temperatures of the fibers heat mechanical modification only with the difference that the jump of the samples crystallinity appears at tension of 3*MPa*. Analysis of the data shown in Fig. 1, 2 and Table 1 shows the existence of a clear correlation between the deformation behavior and the crystallization process in the studied PET filaments. The course of the crystallization process is fully in line with yarns deformation and this is another proof of the control role of mechanical tension in these interrelated processes.

IV. Conclusions

Has been carried out a large study of the effect of heat mechanical treatment of amorphous PET fibers within the temperature range from 80^0C to 95^0C under different tensile stress on their deformation and phase behavior.

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The complex influence of the tensile stress and temperature on the orientation behavior and degree of crystallinity on the studied PET fibers is not simple. The superposition annealing temperature/tensile stress, at a given stress values leads to strong increase of the filaments birefringence and consequently of the orientation effects in the samples. Relationship between the samples deformation behavior and the crystallization process in the studied PET filaments has been found. The effect of the annealing temperature on the fibers degree of crystallinity is minor. At best, there is observed only a small increase of the crystallinity with increasing of the annealing temperature. In contrast, the applied tensile stress strongly influences the structure development of the studied specimens. It is established a major increase on the filaments degree of crystallinity only with minor increment of the stretching stress values.

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