

WAXS studies of heat - mechanically modified amorphous PET fibers. Role of the tensile stress

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Abstract. The present work is devoted to the investigation of the structure developments in as-spun amorphous poly (ethylene terephthalate) (PET) filaments occurred as a result of heat mechanically modification. The degree of crystallinity of the untreated samples was 1,7 %. The thermal deformation experiments were carried out under isothermal conditions. PET yarn was annealed during 10 min at constant temperature of 80°C after which the sample is subjected to a well-defined constant tensile stress for 120 s at the same temperature. The mechanical load is gravitationally in the range from 0 MPa to 30 MPa and with increment step of 3 MPa. Using of wide angle X-ray scattering (WAXS) were investigated the structural rearrangements in the studied samples caused by the fibers treatments. Dependences between the strain force values and the running in the specimen's structure development are established. And in particular, it was found that a small increase of the tensile stress from 3 MPa to 6 MPa leads to a massive increase in the fibers degree of crystallinity with more than 33%.

1. Introduction

The flexible chain polymers are frequently used in different technological and commercial fields, but most often for the production of fibre-forming polymeric materials, films, etc. In the case of undrawn polymeric filaments, the final structure is determined mainly from the melt spinning conditions and of the subsequent heat-mechanically treatments, too. Depending on the forming conditions in the fibers are formed areas with an increased order of the macromolecular segments, meso- and crystalline phases with different perfection which under appropriate conditions can be converted into crystal nucleus, and they are the so-called semi- or quasi-crystalline nuclei. Another consequence of the filaments formation is the formation of regions with frozen stresses in them. The fibers formation 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 prepared 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 uniaxial drawing needs of special attention. There are described investigations of the relationships between treatments of PET with



different initial structures and the caused phase and structure evolution [1-5]. 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 [6-18] including the authors of the present article. It is studied the influence of the treatment and production conditions on the fibers deformation behavior [6, 7] mechanical properties [8, 9, 14] and spinning process [17].

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 preliminary fiber orientation and combined tension stress with thermal treatments in the temperature region just above the glass transition temperature on the deformation behaviour and super molecular structure development in uniaxially oriented PET remains not fully clarified.

The aim of the present study is the structural reorganization behaviour of amorphous PET fibers caused by combined thermal and mechanical treatments at constant temperature of 80°C and mechanical tensile loading with values from 0 MPa to 30 MPa .

2. Experimental

2.1. Materials

Amorphous PET as-spun multifilament yarns were used as precursor samples. The initial characteristics of the studied PET fibers were as follows:

- speed of fibrillate 1150 m/min ;
- number of single fibers in yarn 32;
- diameter of a single fiber $44\ \mu\text{m}$;
- degree of crystallinity $\alpha = 1,7\ \%$;
- birefringence $\Delta n \cdot 10^3 = 3,58$.

The filaments are produced by melt spinning on the industrial spinning machine of the company "Furnet" (France).

2.2. Methods

2.2.1. Simultaneous heat-mechanical modification. The filaments simultaneous heat-mechanical modification (SHMM) was performed using a specialized device designed and produced in the author's laboratory. Thermal deformation experiment consisted of annealing of the studied yarn during ten minutes at the required temperature of 80°C followed by the application of tensile stress for 120 seconds. The samples annealing temperature is closely above the filaments glass transition temperature, determined in our previous work of 74°C . The tensile stress values are in the interval from 0 MPa to 30 MPa with increment step of 3 MPa .

2.2.2. Wide-angle X-ray scattering. Structure of the treated PET fibers was studied by wide-angle X-ray scattering (WAXS) using apparatus 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 $\text{Cu}^{K\alpha}$ radiation with a wavelength $\lambda = 1,5418\text{ \AA}$.

3. Results and discussion

It is known that the wide-angle X-ray scattering method is geometric - structural sensitive therefore it was selected for the study of the treatments induced structural changes in the investigated PET objects. Due to the steric factor determined by the monomer composition, PET have narrow and hard defined options for mutual packing of the macromolecular chain segments. This determines his poor polymorphism and opportunities for the formation of various transient structural states and mesophases in improving of the quality and the packing density of the macromolecular segments in the crystallization process. The only known for now triclinic crystal modification of PET and the lack

of stable previously known pseudo crystalline states and mesophases determine in fact the complete absence of its polymorphism.

However, as is noted above, depending on the conditions, and other specific characteristics of the crystallization processes, the quality and perfection of the crystalline phase can be found in many structural states. Right from the beginning of the emergence of some distant three-dimensional order in separate micro local areas in the polymer volume the specifics of the registered X-ray diffraction pattern reflecting the geometry package of the macromolecular segments on atomic - molecular (crystallographic) level reflect any change and it is criterion for its evaluation.

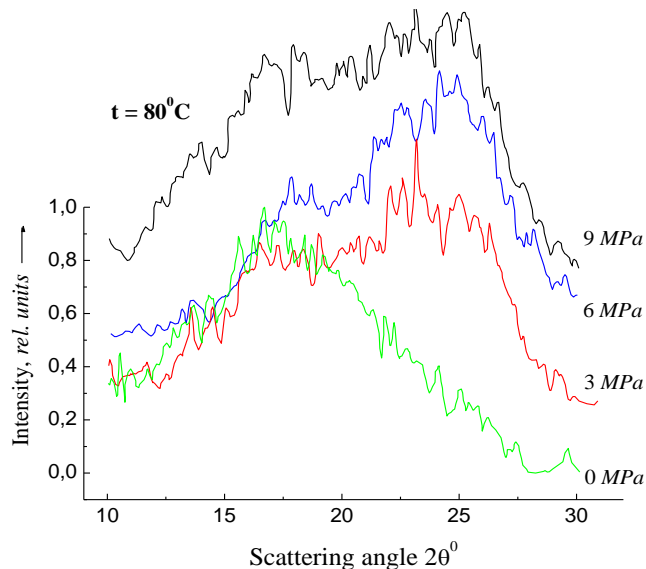


Figure 1. WAXS curves of amorphous PET yarns heat mechanically modified at isothermal conditions and under tensile stress with different values.

All major structural characteristics of that a finely-crystalline, not morphological, crystallographic elementary level is described by the angular positions and deviations, intensity ratios and profile changes in X-ray diffraction reflections in the angle range from $16^{\circ}2\theta$ to $28^{\circ}2\theta$.

At thermo-mechanically modified (TMM) objects the infrastructure of the intensity distribution of diffracted X-ray looks more similar to the known highly oriented or well-crystallized objects therefore the structure of TMM samples can be assumed and proved more easily, precise and unambiguously. At heat mechanically-initiated destruction the supporting factor "free volume" also exist around the overstressed in the state before destroying macromolecular segments. Comparing the Kilian's model [19] with the received diffraction patterns can be suggested the structural changes in their mutual pickings of the macromolecular chain segments in the heat-mechanically modified PET fibers.

The obtained wide-angle X-ray scattering curves of TMM PET fibers under tensile stress values from 0 MPa to 9 MPa, from 12 MPa to 21 MPa and from 24 MPa to 30 MPa are presented respectively in figures 1, 2 and 3.

The observed effects of the SHMM on the geometry of the intensity distribution of the diffracted X-ray in the objects diffraction patterns (figures 1-3) is expressed in angular deviations of intensity changes in the angular range from $10^{\circ}2\theta$ to $30^{\circ}2\theta$. The starting amorphous sample of undrawn fibers shows on the diffraction pattern increased intensity about $16,5^{\circ}2\theta$ (figure 1).

This is the reflex 010 which reflects the width of the macromolecules folds, which is a thermodynamic dependent value and is relatively stable over a wide range of conditions. Application of tensile stress of 3 MPa leads to the occurrence of intensity peak (figure 1) at an angle of about

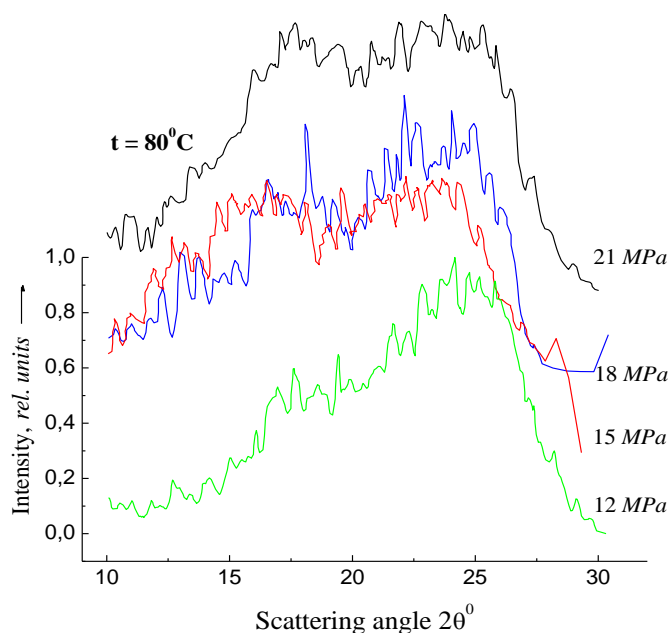


Figure 2. WAXS curves of amorphous PET yarns heat mechanically modified at temperature of 80°C and under tensile stress with values of 12, 15, 18 and 21 MPa .

$23,7^{\circ} 2\theta$ (reflex 100) reflecting the distance between the planes on folding of the macromolecular chain segments equaling to about $3,5 \text{ \AA}$. At the same time there is an intensity increase and on the positions of the diffraction reflections from the type of 1-1-1, 1-10 and 011.

The tensile stress increasing to 6 MPa enhances this effect (figure 1) and further load increase equalizing the intensity throughout the observed range of $16\text{-}28^{\circ} 2\theta$. The last two effects are related to improving the quality and packing density of the macromolecular chain segments and the order disturbing of the distance between the folding planes. These effects appear consecutively two more times with the next tensile stress increasing up to value of 24 MPa (figure 2).

As can be seen from figure 3 the increase in gravitational load up to 30 MPa did not causes significant changes in the course of the diffraction curves that shows rather the absence of further structural reorganization than the development of the above mentioned processes.

In conclusion it can be said that TMM has a major impact on the structural reorganization of PET in solid phase state. Depending on the objects and conditions of the thermo-mechanical treatments significant redistribution of the intensity of the scattered and diffracted X-ray radiation is observed.

The registered effects may be explained by an increase in the width of the folds, respectively, decrease the distance between the planes of the folding of the chain segments. From a geometric standpoint, these two effects are interrelated, and even highly mutually dependent. There is observed a marked increase in the orientation and overall degree of the objects crystallinity, which is a confirmation of the suggested mechanism of TM modification. Registered effects are evidence of the crystallization of the studied PET fibers and especially of the impact of the strain stress on the crystallization process. Tensile stress is the factor which prevents the destruction of the quasi-crystalline nuclei and turns them into crystal nuclei thus starting the crystallization.

In addition to the above described studies it was examined and the deformation behavior of the PET fibers during the thermal deformation experiments [18]. The obtained results show large increase of the final yarns length with only minor increase of the stress level increasing from 3 MPa to 6 MPa .

Furthermore, with purpose to determine the effect of TMM on the structural changes in the studied PET objects the heat mechanically treated amorphous samples were tested by differential scanning

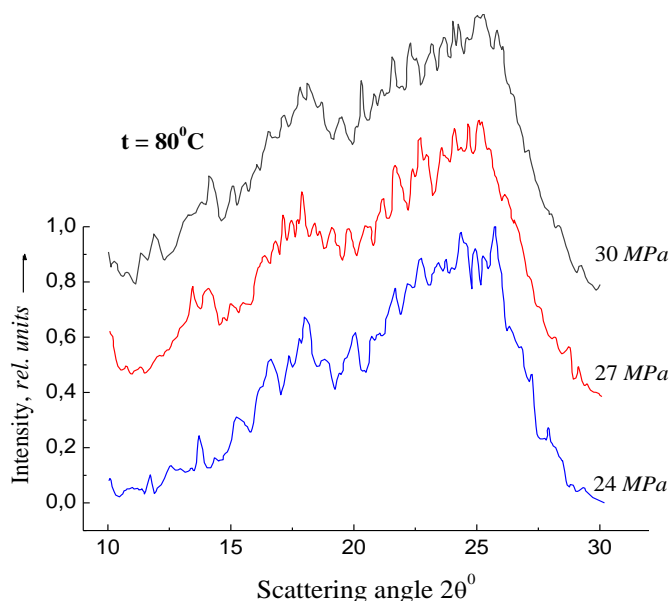


Figure 3. WAXS curves of amorphous PET yarns heat mechanically modified at temperature of 80°C and under tensile stress with values of 24, 27 and 30 *MPa*.

calorimetry (DSC), too. On the basis of the obtained DSC data it was calculated and the degree of crystallinity of the studied PET fibers [18].

Degree of crystallinity of the PET filaments heat treated without applied strain stress (0 *MPa*) marks negligible growth from 1,7 % to 2,0 %. But only the insignificant increase of the tensile stress from 3 *MPa* to 6 *MPa* leads to a massive increase in the samples degree of crystallinity with more than thirty percents reaching value of 34,7%.

Further more, at loadings above 9 *MPa* both the filaments crystallinity and final bundle length almost no changed and reach to a plateau up to the load value of 30 *MPa*. The above mentioned additional results confirm the established by X-ray diffraction experimental fact for the decisive role of the tensile stress in the process of crystallization of the tested amorphous PET yarns.

4. Conclusions

It is investigated the structure developments in as-spun amorphous poly (ethylene terephthalate) filaments occurred as a result of heat mechanically modification at isothermal conditions in rubbery state.

Using wide-angle X-ray scattering it was found that the heat mechanically modification has a major impact on the structural reorganization of PET in solid phase state and leads to the crystallization of the studied objects.

The effect of the annealing temperature of 80°C on the fibers degree of crystallinity is minor; In contrast, the applied tensile stress strongly influences the structure development of the studied specimens.

It is established that only the insignificant tensile stress increasing leads to a massive increase in the fibers degree of crystallinity with more than thirty percents.

Remains interesting and unclear the question about the role of the superposition annealing temperature/tensile stress in the temperature range between 80°C and 100°C on the structure development of preliminary and additionally oriented PET materials and objects and such experiments are coming.

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References

- [1] Todorov L V and Viana J C 2008 *International J. Material Forming* **1** 661
- [2] Göschel U 2005 *Handbook of Thermoplastic Polymers: Homopolymers, Copolymers, Blends, and Composites*, Weinheim: Wiley-Vch Verlag GmbH **Ch. 6**
- [3] Todorov L V, Martins C I and Viana J C 2012 *J.of Appl. Polymer Sci.* **124** 470
- [4] Todorov L V, Martins C I and Viana J C 2011 *J.of Appl. Polym. Sci.* **120** 1253
- [5] Bouti S, Kieffel Y, Pohlink K, Hiver J M, Dahoun A and Etienne S 2009 *Journal of Physics, Conf. Series: Materials Science and Engineering* **5**, doi:10.1088/1757-899X/5/1/012006
- [6] Desai P and Abhiraman A S 1986 *J. of Polym. Sci. Part C: Polymer Letters* **24** 135
- [7] Betchev Ch 1995 *Polym. Testing* **14** 163
- [8] Rudolf A, Geršak J and Smole M S 2012 *Textile Research Journal* **82** 161
- [9] Rudolf A and Geršak J 2012 *Textile Research Journal* **82** 148
- [10] Velev V, Androsch R, Dimov T, Popov A and Radusch H-J 2010 *J. of Optoelectronics and Advanced Materials* **12** 958
- [11] Haji A, Rahbar R S and Kalantari B 2012 *Materials Research* **15** 554
- [12] Velev V, Popov A, Androsch R, Dimov T, Angelov T and Radusch H-J 2012 *Journal of Physics: Conference Series* **398** 012055
- [13] Vibhor J 2009 *A thesis presented to the academic faculty*, Georgia Institute of Technology
- [14] Haji A and Rahbar R S 2012 *Chemical Industry & Chemical Engineering Quarterly* **18** 233
- [15] Murthy N S and Grubb D T 2003 *Journal of Polymer Science: Part B: Polymer Physics* **41** 1538
- [16] Minqiao R, Zhiying Z, Shizhen W, Jia W and Xiao C 2006 *Journal of Polymer Research* **13** 9
- [17] Ziabicki A and Jarecki L 2007 *Journal of Applied Polymer Science* **105** 215
- [18] Velev V, Popov A and Bogdanov B 2011 *Thermodynamics - Systems in Equilibrium and Non-Equilibrium* ed Moreno-Pirajan J C (Rijeka: INTECH) **Ch.5** 89
- [19] Kilian et. al 1960 *Koll. Zeitschrift* **172** 166