International Journal of Recent Technology and Engineering (IJRTE)
ISSN: 2277-3878 (Online), Volume-4 Issue-1, March 2015

Structural Changes in Amorphous Poly (Ethylene Terephthalate) Fibers Caused by Combined Heat Mechanical Treatment

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Abstract — The article submits new experimental data pertaining to the role of combined heat-mechanically treatments on the birefringence and degree of crystallinity of amorphous uncrystallized but crystallizable poly (ethylene terephthalate) (PET) filaments. The heat-mechanically treatments of the investigated objects as well as the optical measurements were realized by specialized installations designed and built in the author's laboratories. Undrawn PET yarns were subjected on heat-mechanically modification at constant temperature of 90^{0}C above their glass transition temperature (T_g) combined with tensile stress with values from 0MPa to 30MPa. Birefringence measurements and differential scanning calorimetry (DSC) were used in order to identify the occurred as a result of the heat mechanical processing the specimens' structural evolution. The optical measurements were carried out using the so called "P-F-A" system involving polarization microscope and a CCD camera. It was established the influence of the superposition "annealing temperature/tensile stress" on the filaments birefringence as well as the dominant effect of the tensile load on the fibers degree of crystallinity.

Keywords — birefringence, degree of crystallinity, fibers, poly (ethylene terephthalate), tensile stress.

I. INTRODUCTION

Object of the present studies is poly (ethylene terephthalate) (PET) as a crystallizable thermoplastic polymer, which is widespread in many high-volume usages very often in orientated forms such as filaments and folios. The widely applications of PET are founded on its crystallization ability, relatively low crystallization velocity and comparatively high glass transition temperature. Its high glass transition temperature allows the keeping of the filaments orientation at room temperature and to study the tensile induced structure development at higher temperatures. It is known that the final characteristics of the anisotropic polymer systems are directly related to their super molecular structure [1-3].

Revised Manuscript Received on 30 March 2015.
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The final structure of the polymeric fibers depends primarily on the melt spinning conditions as well as from the subsequent heat-mechanical modifications, too [4-6].
Deformation behavior and the super molecular structure development in PET fibers caused by thermal and mechanical treatments have been investigated in the recent years. Part of the experiments have been carried out in non-isothermal conditions [7, 8] while in other of them the structural changes of PET filaments are investigated at different temperatures without application of stress [9] and under tensile stress [10, 11]. Nevertheless the role of the combined mechanical and thermal treatments on the structure development, phase and relaxation transitions of the amorphous PET yarns remains insufficiently clear. With purpose to clarify the role of the temperature and tension stress values on the structure development in amorphous PET filaments were carried out thermal deformation experiments at constant temperatures of 80 ^0C and 85 ^0C under precisely defined tensile stresses from 0 *MPa* to 30 *MPa* with increment step of 3 *MPa* [11]. The structural investigations of the heat mechanically modified PET objects show very important results concerning the role of the temperature and the applied stress on the specimens deformation behavior, birefringence and degree of crystallinity. Therefore it was very interesting to continue the investigations of the same PET filaments at enhanced temperature of 90 ^0C. The experiment includes annealing of PET yarns at temperature 90 ^0C above its glass transition temperature determined of 74 ^0C [9] while the fiber bundle is subjected to a well defined strain stress from 0 *MPa* to 30 *MPa* with increment of 3 *MPa*.

II. EXPERIMENTAL

A. Materials

Undrawn PET multifilament yarns produced on the industrial spinning installation Furnet (France) have been selected as a precursor samples. The basic filament characteristics and formation conditions were 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 fibers density was determined using a density gradient column filled with a tetra chloromethane and *n*-heptane mixture. The samples degree of crystallinity was calculated using the obtained filaments density data. Birefringence of the untreated fibers was measured by an Amplival POL D (Karl-Zeiss Jena) polarizing microscope, equipped with Bereck compensators. The coefficient of amorphous orientation was calculated using the obtained birefringence data and the Stein's equation [13]. Filaments heat-mechanical treatments were implemented using a specialized instrument designed and manufactured in our laboratory. The thermal deformation experiment includes rapidly sample heating from room temperature up to temperature of 90^0C with subsequent annealing for ten minutes. After annealing time the studied yarn was loaded with well-defined tension stress from 0 *MPa* to 30 *MPa* with increment step of 3 *MPa* during two minutes. The heat mechanical filaments treatment was followed by a simultaneously taking down of the applied strain stress and yarn moving from the oven to room temperature. The birefringence measurements of the heat mechanically treated PET fibers were performed using a specialized set-up constructed and made in the author's laboratory. The gear involves polarizing interference microscope equipped with a CCD camera [9]. The basic element of the experimental device is the system including a polarizer (P), analyzer (A) and birefringent filament (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 fiber can be rotated round the optical microscope axis. Calorimetric analyzes were performed using a NETZSCH heat-flux 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

The occurred because of the heat mechanically modification structure developments in the fibers were studied 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 tension stress are present in Fig. 1. Experimental results presented on Fig. 1 allow to trace the role of the temperature of the heat mechanically treatments of the same PET filaments. The birefringence received at temperature 80^0C is characterized by the presence of "resonance" dependence with pronounced peak [12]. Filaments birefringence obtained at 85^0C show a wide basic peak with two attendant smaller peaks. Unlike from these results here we can see initially sharply increase with a peak at 6 *MPa* followed by a second broad peak with maximum at 24 *MPa*. The overall birefringence picture on figure 1 shows a steady state mode of increased orientation in the entire range of gravimetric load with the exception of the range 12-15 *MPa*.

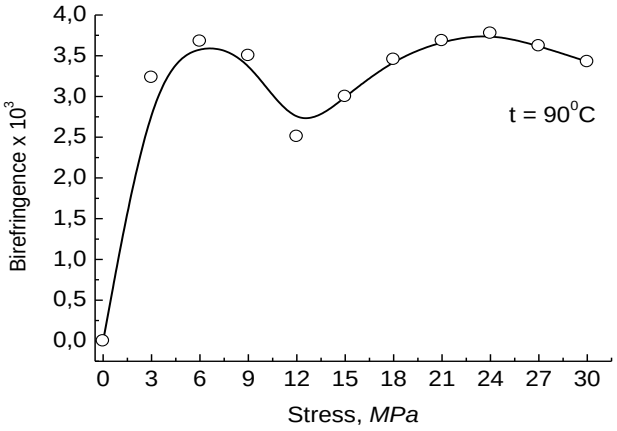

Figure 1. Birefringence of the heat mechanical treated PET filaments depending on the applied strain stress.

During the thermal deformation experiments was registered and the specimen's deformation behaviour. The fibers diameter changes are shown in Fig. 2. The relative change of the fibers length $(L-L_0)/L_0$ are present in the "stress-deformation" diagram in Fig. 3, where L_0 is the initial length of the fibers bundle. As it can be seen from the Fig. 1, 2 and 3, the filaments' birefringence changes are in a good agreement with the samples' deformation behaviour.

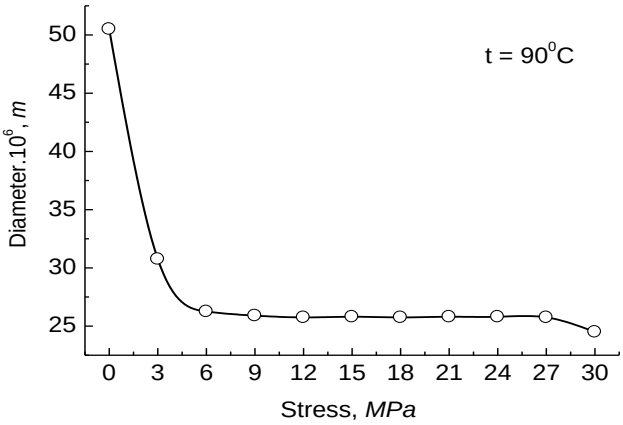

Figure 2. Fibers diameter.

The increasing of the amorphous orientation function and respectively the fibers birefringence at the applied strain stress from 0 *MPa* up to 3 *MPa* (Fig. 1) is in accordance with the collapse of the samples diameter (Fig. 2) and with the degree of withdrawal (Fig. 3). The specimens' birefringence reduction in the interval of the tension stress from 3 *MPa* to 6 *MPa* (Fig. 1) and the appropriate deformation behaviour (Fig. 2, 3) can be explained with the additional segments stretching and with the rupture of the pre-stressed segments, too. The strain stress values increasing from 9 *MPa* up to 27 *MPa* leads to the smooth filaments diameter (Fig. 2) reduction and to the gradually yarns length increase (Fig. 3). The possible reason for the observed deformation behaviour and the accompanying changes of the birefringence (Fig. 1) are the further fibrils withdrawal and slip accompanied from destructions and subsequent drop of the segments orientation.

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It should be mentioned the deformation behaviour of the studied filaments subjected to tension stress of 30 *MPa* (Fig. 2, 3) where in contrast to the bearing of the previous samples the increasing of the strain stress value leads to fibers diameter increasing and to yarns length decrease.

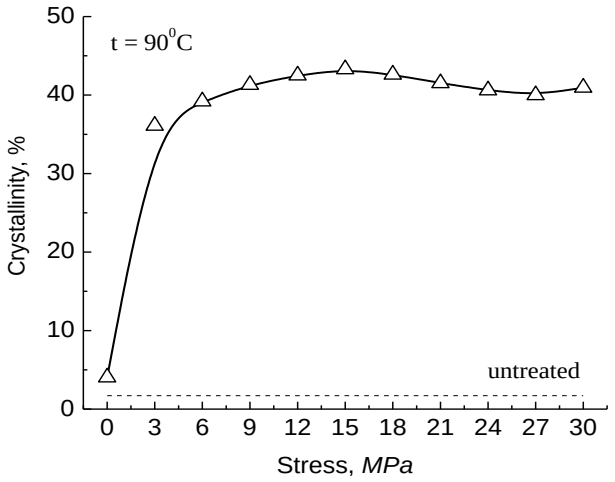

Figure 4. Degree of samples crystallinity depending of the tensile stress values.

Using DSC data was determined filaments degree of crystallinity, too. On Fig. 4 are present degree of crystallinity of untreated PET fibers and of the specimens crystallinity obtained as a result of heat mechanically treatments. As it can be seen from Fig. 4 the degree of crystallinity of the sample heated without stress (0 *MPa*) is negligible. But only *slight increase* of the tensile stress from 0 *MPa* to 3 *MPa* leads to impressively increase of the filaments crystallinity with more than 35% which is a powerful illustration of the role of the mechanical impact in the crystallization process. The further increasing of the tensile stress values does not lead to a significant increase in the degree of crystallinity. Moreover, as can be seen from Fig. 2, 3 and 4, there is a correlation between the deformation behavior and the crystallization process in the studied PET objects.

IV. CONCLUSIONS

The influences of the heat mechanical modification parameters on the occurred structure rearrangement in the investigated PET fibers have been established. Strain stress of 3 *MPa* applied simultaneously with fibers annealing leads to significant birefringence increasing. Has been confirmed the key role of the tensile stress on the samples crystallization process. It was found correlation between the filaments deformation behavior and the crystallization process in the studied PET objects. The experiments realized at temperature of 90^0C were the next step of the planned studies concerning the structural changes in amorphous PET filaments in the temperature range up to 95 ^0C caused by combined heat-mechanical treatments. A satisfactory explanation of the obtained results needs of additional investigations and they are coming.

V. ACKNOWLEDGMENT

Part of the present work has been supported by Grant-2015 from Fund for Scientific Research of Konstantin Preslavsky University, Shumen.

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