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Deformation and Phase Behavior of Thermo-Mechanically Modified As-Spun Polyester Fibers

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Abstract* — *Thermo mechanically induced dimensional changes, birefringence and degree of crystallinity in amorphous poly (ethylene terephthalate) PET fibers were investigated. The heat mechanical treatments and optical measurements of the investigated filaments were performed by specialized devices constructed and made in the author's laboratories. Undrawn PET yarns were subjected on heat mechanical modification at constant temperature of 95^{0}C above their glass transition temperature 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 structural changes. Was established the effect of the superposition "annealing temperature/tensile stress" on the filaments birefringence as well as the dominant role of the strain stress on the fibers degree of crystallinity. It was found correlation between the filaments deformation behavior and the crystallization process in the studied PET objects.

Keywords* — *birefringence, deformation behavior, degree of crystallinity, fibers, strain stress.

I. INTRODUCTION

Object of the present work is poly (ethylene terephthalate) (PET) as a crystallizable thermoplastic polymer, which is widely used in many areas and very often in oriented forms such as filaments and folios. The wide application of PET is due to the its crystallization ability, relatively low crystallization rate and high glass transition temperature. There are two main reasons to study the deformation and phase behavior of PET fibers. The first one is a significant technological interest.

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As it is known the as-spun fibers and especially the obtained at low-speed spinning rate are primarily non-crystalline and the crystallization and additional orientation needs of different subsequent processing such as annealing and drawing. The second reason is the great importance from a scientific point of view since under certain technological conditions PET can be easily obtained in an amorphous oriented state. Therefore in order to obtain materials with the desired properties it is necessary to seek mechanisms for subsequent crystallization and structure development. The desired properties of the final polymeric products are directly related to their super molecular structure [1-3]. In the case of the polymer fibers the final structure formation is a direct consequence of the melt spinning conditions as well as of the subsequent heat-mechanical modifications, too [4-6]. Many studies on the deformation behavior and the super molecular structure reorganization in PET fibers caused by thermal and mechanical treatments have been made over recent years. Some of the experiments were performed under non-isothermal conditions [3, 6, 7] while in others of them are investigated the structure development of PET filaments at constant temperatures without application of stress [8, 9] and under tensile stress [10]. Despite of all the effect of the combined mechanical and thermal treatments on the structural changes, phase and relaxation transitions of the amorphous PET yarns remains insufficiently clarified. The aim of this work is to present new experimental data on the deformation and orientation behavior as well as the structure development of amorphous PET filaments caused by simultaneous thermal and mechanical treatments. The study includes three main topics namely: 1. the changes in the samples dimensions; 2. determination of the filaments orientation; 3. crystallization from rubbery state under tensile stress. The glass transition temperature of the studied amorphous sample was determined of 74 ^0C in our previous work [8]. With purpose to clarify the role of the temperature and strain stress values on the structure development in amorphous PET filaments were performed thermal deformation experiments at three constant temperatures of 80 ^0C, 85 ^0C and 90 ^0C above the glass transition temperature and under precisely defined tensile stresses from 0 *MPa* to 30 *MPa* with increment step of 3 *MPa*. The structural investigations of the heat mechanically modified PET objects showed very important results concerning the role of the temperature and applied stress on the deformation behavior, specimens orientation and degree of crystallinity. Interesting for us was to continue our research of the same PET filaments but at enhanced temperature of 95 ^0C.

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

To determine the samples density was used gradient column filled with a tetra chloromethane and *n*-heptane mixture. Degree of crystallinity of the precursor specimens was calculated on the basis of 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. Using the obtained birefringence data and the Stein's equation [11] was calculated the coefficient of amorphous orientation. Filaments heat-mechanical modifications have been performed by a specialized device designed and manufactured in our laboratory. The thermal deformation experiment includes quick sample heating from room temperature up to temperature of 95^0C with subsequent annealing for ten minutes. After annealing time the studied PET bundle was loaded with well-defined tension stress from 0 *MPa* to 30 *MPa* with increment step of 3 *MPa* with keeping the temperature during two minutes. The heat mechanical yarns treatment was followed by a simultaneously removal of the applied strain stress and yarn moving from the oven to room temperature.

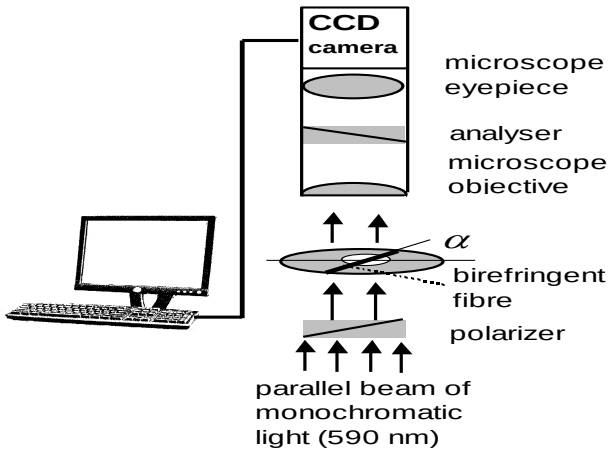

Figure 1. Scheme of the device for birefringence measurements.

The birefringence measurements of the modified 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 [8]. 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 (Fig. 1). The transmitting directions of the polarizers P and A are mutually perpendicular (crossed polarizers). The studied Calorimetric analyzes were performed by means of 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

During the thermal deformation experiments was registered and the specimen's deformation behaviour. The fibers diameter changes depending on the applied stress values are shown in Fig. 2.

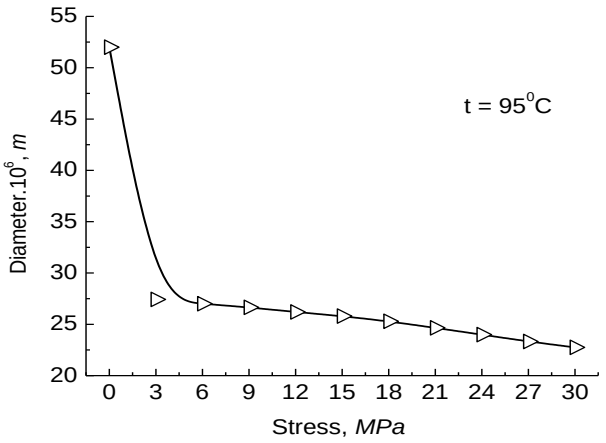

Figure 2. Fibers diameter.

On the "stress-deformation" diagram (Fig. 3) are present the dependency of the relative change of the yarns length $(L-L_0)/L_0$ from the tensile loading, where L_0 is the initial length of the fibers bundle.

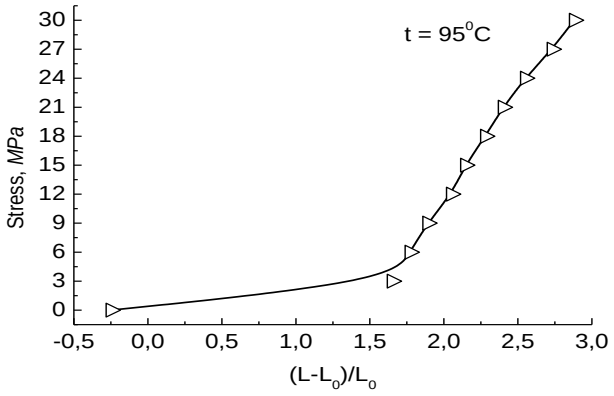

Figure 3. Tensile stress – relative elongation diagram.

The structural analyses of the heat-mechanically modified at the above-described conditions PET yarns were performed using birefringence measurements and differential scanning

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calorimetry. Birefringence determination is convenient, effective and preferred method for investigating of the orientation effects in the amorphous areas of the flexible chain polymers. Fibers birefringence as a criterion for the degree of orientation was measured by transmission of linearly polarized monochromatic light with wavelength $\lambda = 590$ *nm* across the P-F-A system. The obtained birefringence data depending on the applied to the yarn tensile stress are present in Fig. 4.

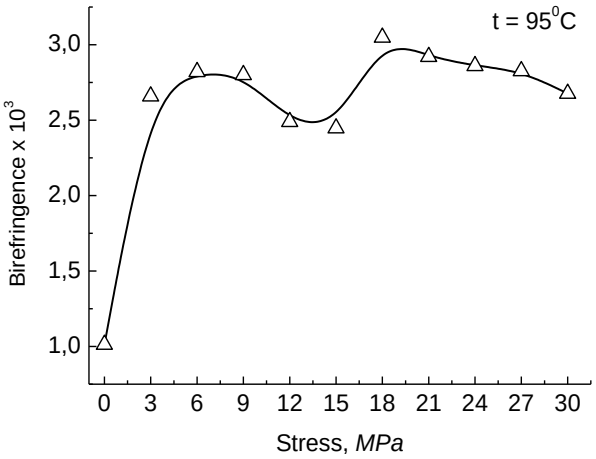

Figure 4. Birefringence of the heat mechanical treated PET filaments depending on the applied strain stress.

In our previous experiments the samples birefringence was measured at the same values of the applied stress but at temperatures of 80^0C, 85^0C and 90^0C. Obtained together with the results at 95^0C experimental data allow trace the role of the temperature in a narrow temperature range from 80 ^0C to 95 ^0C on the filaments orientation. The birefringence obtained at temperature 80^0C is characterized by the presence of "resonance" dependence with pronounced peak [12]. Filaments birefringence received at 85^0C show a wide basic peak with two attendant smaller peaks. Similar to the filaments birefringence at temperature 90^0C, the overall birefringence picture at 95^0C (Fig. 4) shows a steady state mode of increased orientation in the entire range of gravimetric load with the exception in the range 12-15 *MPa*. The increasing of the amorphous orientation function and respectively the fibers birefringence at the applied strain stress from 0 *MPa* to 3 *MPa* is in accordance with the collapse of the samples diameter (Fig. 2) and with the degree of elongation (Fig. 3). The specimens' birefringence reduction in the interval of the tension stress from 0 *MPa* to 3 *MPa* 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 further growth of the strain stress values from 9 *MPa* up to 30 *MPa* is characterized by a permanent decrease in the fibers diameter (Fig. 2) and with gradually yarns length increase (Fig. 3). As it can be seen from the Fig. 2, 3 and 4, the filaments birefringence changes are in a good agreement with the samples' deformation behaviour. Possible reason for the observed deformation behavior and the accompanying changes in the birefringence is additional download and slippage of the fibrils together with destruction and fall of the orientation of the macromolecular segments. Except the birefringence measurements the heat – mechanically treated objects were tested and by differential scanning calorimetry. Representative DSC curves obtained for the untreated and for the heated without mechanical loading (0 *MPa*) and under strain stress of 3 *MPa* are shown on Fig. 5.

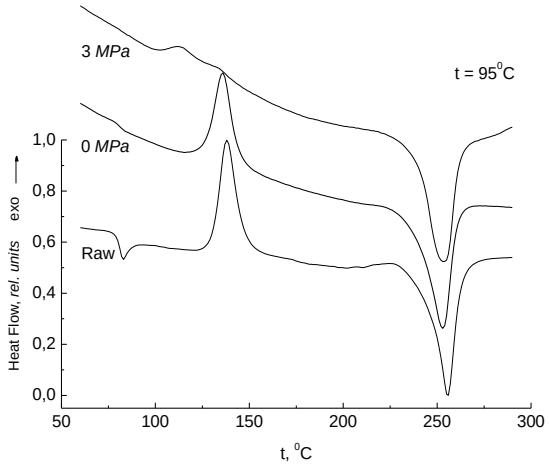

Figure 5. DSC curves of untreated sample and heat-mechanically modified without and under strain stresses at temperature of 95 ^0C.

As is apparent from Fig. 5, the DSC curve of untreated amorphous sample shows clearly expressed glass transition and cold crystallization. Similar is and the thermogram of the specimen processed without loading (0 *MPa*). At this sample, however, the glass transition is not so pronounced and the cold crystallization peak is slightly shifted to the lower temperatures. The observed effects are due to the presence of disordered and unstable structure in the unoriented amorphous fibers. In such structures heated up to temperatures around 130÷140 ^0C in the absence of external stress (0 *MPa*) is released the segment mobility in macromolecules and it is a precondition for the cold crystallization. The samples processed at loading value of 3 *MPa* indicate only anemic cold crystallization occurring at relatively low temperature. Possible reason for the observed tendencies is due to the overall increase of the entropy of the system resulting in change of the objects thermal conductivity and heat capacity. Based on DSC data it was determined objects degree of crystallinity, too. On Fig. 6 is present the specimens degree of crystallinity obtained as a result of heat mechanically treatments, where with dashed line is indicated the crystallinity of untreated PET fibers. As it can be seen from Fig. 6 the degree of crystallinity of the sample heated without stress (0 *MPa*) is slightly raised. But it is sufficient to apply to the fibers modification tensile stress of 3 *MPa* to increase the filaments crystallinity to more than 40% and this is definite proof to the role of the mechanical affect on the crystallization process.

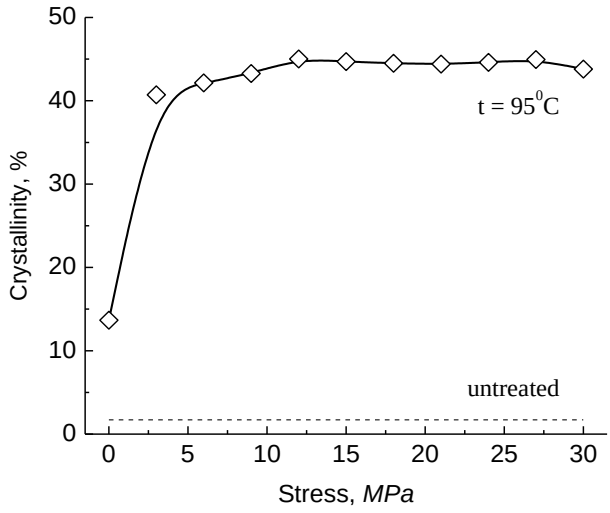

Figure 6. Degree of samples crystallinity depending of the tensile stress values.

It should be noted that the further increasing of the tensile stress values almost no influence on the degree of crystallinity. Moreover, as can be seen from Fig. 2, 3 and 6, there is observed a correlation between the deformation behavior and the crystallization process in the studied PET objects. It can be concluded that the samples degree of crystallinity reasonably good follows the bundle deformation, which is additional proof for the role of the strain stress in the crystallization of the studied PET fibers.

IV. Conclusions

Has been found the effect of the heat-mechanical modification parameters on the structure development in the investigated PET fibers. Strain stress of 3 *MPa* applied simultaneously with the objects annealing causes a significant birefringence increment as well as dimensional changes. It was confirmed the key role of the tensile stress under the specific experimental conditions on the samples crystallization process. Have been established correlation between the filaments deformation behavior and the crystallization process in the studied PET objects. The experiments performed at temperature of 95^0C were the last step of the planned studies concerning the structural changes in amorphous PET filaments in the temperature range from 80 ^0C to 95 ^0C caused by combined heat mechanical treatments.

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