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THERMO-MECHANICALLY MODIFICATION OF AMORPHOUS POLYESTER FIBRES: II. CALORIMETRIC INVESTIGATIONS

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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) occurred* as a result of *heat mechanical treatments.*

The deformation behavior of as-spun amorphous poly (ethylene terephthalate) (PET) yarns subjected to simultaneous thermal and mechanical treatments has been studied. It was found that the applied tensile force simultaneously with the linear heating of the studied PET yarns strongly affects the samples deformation behaviour. Differential scanning calorimetry (DSC) has been used to study the structural rearrangements in the thermo-mechanically processed PET fibers occurred as a result of the treatment structural changes. Have been established dependencies between the parameters of the thermal deformation experiment and occurred in the samples structural changes.

Key words: *poly (ethylene terephthalate), filaments, heat - mechanical treatment, tensile stress, strain-induced crystallization, differential scanning calorimetry.*

1. INTRODUCTION

One of the most important from practical point of view characteristics of the oriented polymers is their structural anisotropy. The mechanical and other physical properties of anisotropic polymer systems are extremely dependent on the super-molecular structural organization in the polymer [1, 2].

As an object of the present investigation it was selected poly (ethylene terephthalate) (PET). PET is a polymer that because of their good mechanical properties and high heat resistance has a wide practical application.

There are known various methods for improving of the mechanical properties of the oriented polymers, but one of the frequently used is thermal -mechanical modification.

The influence of different variants of combined thermal and mechanical treatments of oriented polymers on the sample structure changes is intensively studied in the

recent years, including with the participation of the authors of the present message [3-5].

Despite the existing of many studies of PET, the question of the influence of the thermo-mechanical modification parameters on the course of the phase and relaxation transitions is not fully understood. The specific purpose of the realized heat-mechanical modification of the studied PET filaments was to provide additional clarifications regarding the influence of the applied to the samples tensile stress in combination with linear heating on the course of the structural reorganization in the PET fibers.

In the present work we submit results from large scale studies of the influence of the thermo-mechanical modification parameters on the structural changes in amorphous poly (ethylene terephthalate) fibers.

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 modification (STMM) of the studied PET yarns was performed using device constructed and produced in our laboratory [6]. It involves a vertically located tubular heater, which can be moved to enclose the loop of the studied PET-bundle. The fibers thermal and mechanical treatment includes linear heating from room temperature up to 200^0C accompanied by applied to the fiber bundle strain stress. 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.

2.2.2 DIFFERENTIAL SCANNING CALORIMETRY (DSC)

The calorimetric analysis was carried out using a NETZSCH heat-

flux calorimeter STA 449 F3 Jupiter (TG/DSC) in static air atmosphere. Temperature calibration was done using the onset melting temperatures of indium, tin, bismuth and zinc, and the energy calibration was based on the heat of fusion of the same metals. Fibers were cut in pieces of less than 1 *mm* and sealed in standard 85 μl platinum pans.

3. RESULTS AND DISCUSS

Depending on the deformation behavior the investigated samples can be 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. Structural rearrangements occurred in the PET fibers as a result of the STMM were studied using DSC and WAXS.

It should be underlined that the performed structural analyses show that all of the heat mechanically modified PET filaments are partially crystalline.

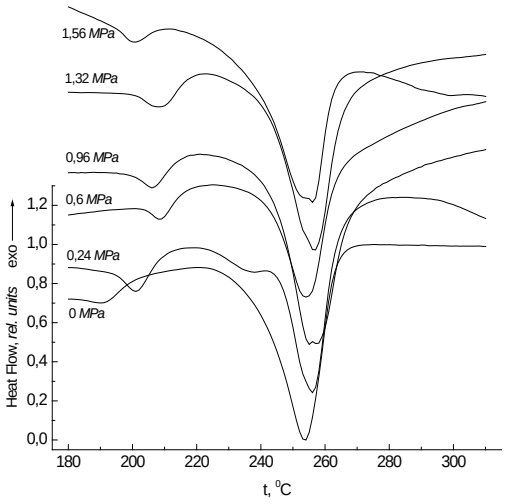

Fig. 1. Representative DSC curves of melting peaks of heat-mechanically treated PET fibers from the first group (the curves are shifted vertically for clarity).

Representative DSC curves of melting peaks of the above defined three groups of samples are present in Figures 1, 2 and 3. As it is visible from Figure 1 during the STMM are formed three types of structures with three different types of perfection and stability.

Depending on the melting temperature can be distinguished entities with a higher level of order forming an easy fusible mesophase, middle crystalline phase with lower perfection and main crystalline phase. Samples heating whether without

load, forms easy fusible structure, which melts at about 190^0C. Just small increasing of the stress values leads to the structure improvement and stabilization and to the moving of the mesophase melting temperature to higher temperatures up to around 210^0C - 215^0C. The intermediate crystalline phase with lower perfection is observed as splitting of the main melting peak which visible migrates to the higher temperatures. With the tensile stress increasing the first melting peak as well as the main melting peaks are deformed with a tendency to split. The melting peaks also fluctuate around an average melting temperature significantly higher in comparison with the obtained without load. The observed shifting of the endo-effects at higher temperatures possibly is a consequence of more organized structure formation due to the applied orientated pulling load. Only the sample from this group loaded with stress of 1.68 *MPa* show a slightly different melting behavior.

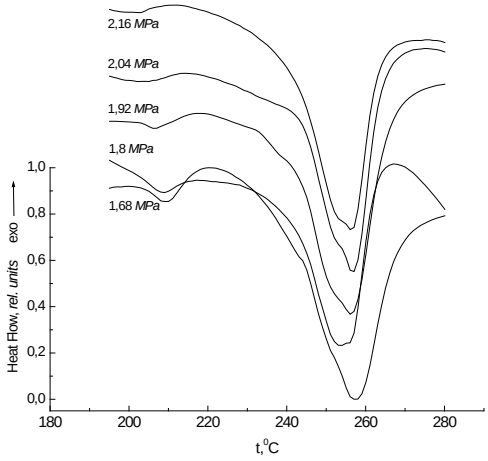

Fig. 2. Representative DSC curves of melting peaks of STMM PET fibers from the second group (the curves are shifted vertically for clarity).

Representative DSC curves of melting peaks from the second group of samples are given in Figure 2, where is observed a tendency on clearing of any thermo-effects with increasing of the strain stress values. That could be explained reasonably from viewpoint of the model for the homogenization of the structure at medium load values and respectively maximum deformation. The samples deformation behavior corresponds to heat mechanically modified fibers stretched up to

position in which the carrying are the most widespread fractions in the amorphous regions according to the normal Gaussian distribution. It is logically that the orientation processes at this group to be most effective with predominance of the orientation processes over destructive.

The DSC curves of the second group (Fig. 2) 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 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.

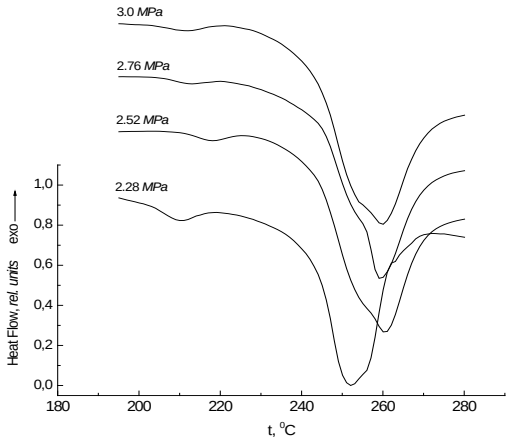

Fig. 3. Representative DSC curves of melting peaks of SHMM PET fibers from the third group (the curves are shifted vertically for clarity).

The DSC thermo grams of the samples from the third group are present in Figure 3. It can be seen that with the tensile stress increasing endo peaks shift to lower temperatures. And it is valid for both before melting and the main melting processes. The most likely reason for the observed effect is that this third group of samples was withdrawn most suboptimal, with a predominance of destructive processes over the orientation. As a result, the obtained structure is mechanically and thermodynamically unstable, with the lowest density and perfection and therefore melts most easily at lower temperatures. As in Figure 2 as well as in Figure 3 are seen beginnings of split of the main melting peaks. The reasons for the splitting of the melting peaks may be different. In this case, at this type of heat mechanically fibers modification, the splitting occurs

most probably due to structural reorganization during the melting process.

Likely for the account of low elastic deformation is realized a significant improvement of the crystalline phase on the lamellae surface or in the newly oriented regions. The thermal curves (Fig. 3) show logically enhancement of the high temperature melting fractions with the tension stress increasing, as well their visible split.

4. CONCLUSIONS

On the basis on the carried out structural investigations of amorphous PET fibers simultaneous heat - mechanically modified under linear heating and constant strain stress values it can be make the following conclusions:

The mechanical strain force applied simultaneously with the linear heating of the studied PET yarns affects significantly the samples deformation behaviour.

All of the so treated specimens are partially crystalline.

Calorimetric studies have shown that the deformation behavior of the samples is a direct consequence from the occurred as a result of the STMM phase transitions and especially of the strain-induced crystallization in the fibers.

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