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HEAT – MECHANICALLY INDUCED STRUCTURE DEVELOPMENT IN PARTIALLY CRYSTALLINE POLYESTER FIBERS. INFLUENCE OF THE MECHANICAL STRESS

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***ABSTRACT**: There are present results from high temperature uniaxial extension of partially crystalline poly (ethylene terephthalate) (PET) yarns. Effect of the applied to the samples tensile stress at isothermal conditions on the structural changes in the studied objects have been investigated. The structural analyses of the processed fibers were realized using differential scanning calorimetry (DSC).*

***KEYWORDS:** polyester fibers, orientation extension, isothermal conditions, tensile stress, differential scanning calorimetry.*

1. Introduction

As it is known the mechanical properties of the non-isotropic polymer systems strongly depend on their super molecular structure. Flexible chain polymer products are typically used in one- and two-axis oriented states in which they acquire improved deformation-strength performance. The wide application and consequently higher production of fiber forming polymers, in particular poly (ethylene terephthalate) (PET), is due to the possibility for additional treatments with purpose to obtain highly modular and high strength materials from them.

One of the main methods for improving of the mechanical properties of the oriented polymer materials is the heat-mechanical modification (HMM) in its various varieties [1-5]. A frequently used variant of HMM is the orientational high-temperature extension, which results in repackaging and in mutual parallel alignment of the macromolecular chain segments and improvement of the deformation-strength characteristics of the polymer system. The effectiveness of such a structural reorganization depends mainly on the properties of the primary polymer structure, and of the conditions of the non-destructive orienting download.

Therefore the necessary and sufficient condition for optimizing of the orienting extension is to find a science-based options to improve the mechanical properties on the flexible chain polymers in oriented state is the finding of a mutually suitable structures and conditions for their orientation downloading. On one side, finding of suitable of appropriate starting structure with a good deformability to achieve of maximum possible for a given polymer, non-destructive levels of orientational extension. On the other hand, finding of suitable conditions for achievement of maximum possible non-destructive levels of orientation download. Each structure requires the appropriate conditions for optimal downloading and specified downloading conditions are optimally suitable only for a single corresponding structure.

All of the above noted is particularly important for polyethylene terephthalate because of its great industrial production and wide application, mainly in oriented state. The crystallising PET is a model fiber forming complex two-phase (from a strictly physical point of view - multiphase) amorphous-partially crystalline system. The PET properties are strongly dependent on its degree of crystallinity as well as on the crystalline phase perfection. Therefore the studying actuality of the possibility for optimizing of its orientation download is indisputable.

2. Experimental

2.1. Materials and Methods

Partially crystalline PET as-spun multifilament yarn named S_2, have been selected as a precursor sample.

The initial characteristics of the studied PET fibers were as follows:

- ✓ speed of fibrillate 2805 *m/min;*
- ✓ number of single filaments in the complex thread 32;
- ✓ diameter of a single fibre 13,0 μm;
- ✓ degree of crystallinity α = 28,8 %;
- ✓ birefringence $\Delta n.10^3 = 5,35$.

Heat-mechanical treatment of the samples was carried out using a device for thermo-mechanical modification of orientated polymer materials, designed and made in the author's laboratory. The studied PET yarns were performed under isothermal conditions at temperatures of 80^0C and 85^0C, in a narrow temperature range closely above their glass transition temperature [6].

The sample HMM includes annealing of PET fibers for ten minutes at the appropriate temperature, after that they are subjected for 120 seconds at the same temperature, to a well-defined tensile stress with values 40 *MPa*, 80 *MPa* and 120 *MPa*. The effects of some basic parameters of the HMM such as strain force, extension rate and temperature on the structure development of PET have been studied using different methods but most often differential scanning calorimetry (DSC).

Structural changes in the treated samples were examined using a differential scanning calorimeter DSC "Mettler Toledo" – 820. In accordance with the requirements of the DSC analyzes [7], the studied fibers were cut into parts less than one millimeter in length.

2.2. Results and discussion

The obtained DSC thermograms of the untreated sample S_2 as well as of the high temperature modified at a temperature of 80^0C and under applied strain stress of 40 *MPa*, 80 *MPa* and 120 *MPa* are shown in Fig. 1.

As can be seen from Fig. 1, the effect of the tensile stress of 40 *MPa* is expressed in the narrowing of the multiple melting peak and the disappearance of the low temperature asymmetry in the melting peak of the untreated sample.

The most likely causes of the observed effect are as follows:

- ✓ homogenization of the fiber structure as a degree of orientation;
- ✓ unification of the packing density of the macromolecular chain segments.

As proof of this is the appearance of low-temperature melting phase, instead of the wide spectrum of fractions, that are responsible for the observed left asymmetry in the melting peak.

In combination with the observed fraction which melts at medium temperatures (Fig. 1), and with which overlaps strongly, the low temperature melting phases include within themselves the major amount of the polymeric material. Together with the fraction that melts at medium temperatures (Fig. 1), the phases that melt at lower temperatures include themselves the major amount of the polymeric material. At the same time, the quantitative reduction of the highest temperature-melting phase, indicates that the modification of the fiber under these conditions somewhat defects the polymer. Perhaps partial destructive processes affect this most ordered and pre-stressed structural part of the material.

At a strain stress of 80 *MPa* (Fig. 1) the high temperature melting phase recovers and even significantly exceeds quantitatively the high temperature melting phases of the untreated and less-oriented samples.

DSK curve obtained under strain stress of 120 *MPa* (Fig. 1) shows that the melting peak visible almost lost its multiple character. This may be a result of maximum compaction of the substance or overlapping of the phases and their reorganization in a single phase.

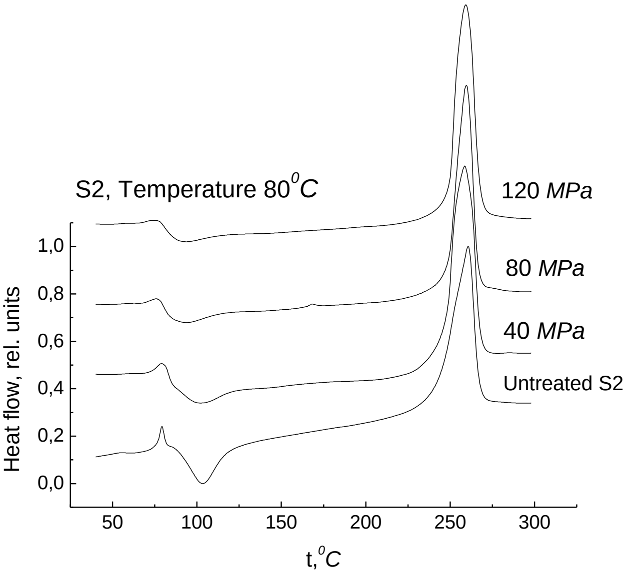

Fig. 1. DSC curves of PET fibers, heat mechanically modified at 80^0C and values of the applied tensile stress of 40 *MPa*, 80 *MPa* and 120 *MPa*.

Probably, this phase is characterized by a close enough distribution between the molecular contacts of interaction energy, which is related to a narrow distribution of the macromolecular segments in the amorphous regions by degree of tautness.

The results of the DSC analyzes of sample S_2 subjected to HMM under conditions described above and temperature 85^0C are shown in Fig. 2. As it can be seen from Fig. 2, with the increasing of HMM temperature up to 85^0C, immediately at a tensile stress of 40 *MPa* there is observed a marked reduction in the width and asymmetry of the multiple melting peak.

Typical here is that even at this first, lowest strain load at HMM, the multipurpose structure of the composite peak almost disappears. This shows a strong compaction and alignment of the packaging of the macromolecular chain segments with low presence of left asymmetry and the existence of a low temperature-melting fraction.

With increasing of the orientation strain stress up to 80 *MPa*, at the same temperature of the object elongation (Fig. 2), the observed trend of stacking, respectively sealing of the packaging segment is preserved. It is observed a further reduction of the half-width of the composite melting peak which looks almost symmetrical. Low temperature asymmetry has disappeared, and peak narrowing corresponds with its little deviation to the higher temperatures to the right on the temperature scale.

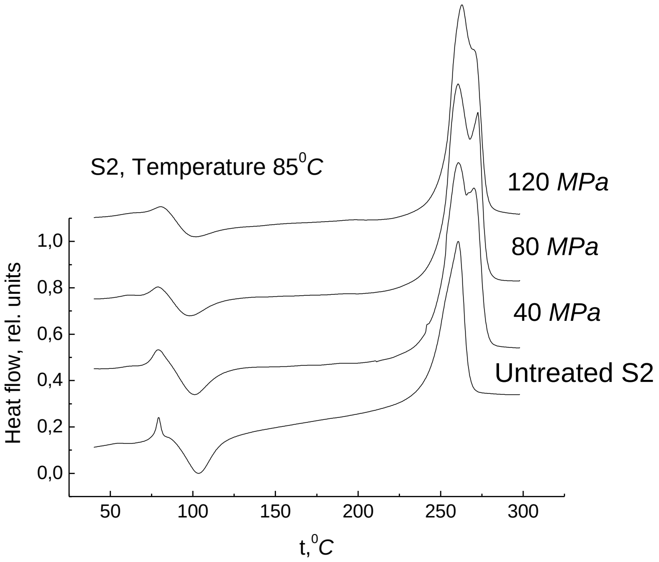

Fig. 2. DSC curves of PET fibers, heat mechanically modified at 85^0C and values of the applied tensile stress of 40 *MPa*, 80 *MPa* and 120 *MPa*.

It can easily be assumed that the packing of the macromolecular chain segments of PET into the amorphous areas requires more heat energy, at a higher temperature to break intermolecular contacts and melt the material.

Increasing of the load to the maximum experimental of 120 *MPa* orientation tensile stress (Fig. 2) confirms the same, but less noticeable trend. In addition, there is observed a very low reverse position deviation of the melting peak on the temperature scale. Probably also in this case the highest mechanical load values, along with the high temperature of the modification, cause destructions that breaks the packaging of the macromolecular chain segments.

In conclusion, it is possible to note the deterministic influence of the orientation mechanical stress on the structural reconstruction of PET fibers in the isothermal modification mode.

On the other hand makes an impression the ambiguous role of its growth on the order increasing, homogeneity and consolidation of the structural organization of the objects. The above is based on the observed change in the quantitation ratio between the phases with different melting temperatures in the multiple melting peaks.

The observed effects are a logical consequence of the complex superposition of the alternative and mutually dependent competitive processes of orientation and destruction, defining the mechanism of the high temperature orientation extension.

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Conclusion

Partially crystalline polyethylene terephthalate fibers were subjected to a high temperature orientation elongation. Samples were subjected to strain stresses of 40 *MPa*, 80 *MPa* and 120 *MPa* at temperatures of 80^0C and 85^0C.

Structural changes in the treated objects were studied using differential scanning calorimetry.

It was found that the orientation mechanical stress has a decisive influence on the structural changes of PET fibers in the isothermal mode of modification.

A satisfactory explanation of the obtained results needs of additional investigations and they are coming.

The planned next step of the studies, concerning the structural changes in PET filaments caused by heat-mechanical modification, includes fibers treatment at elevated temperatures of 90^0C and $95\ ^0C$.

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