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THERMO - MECHANICAL MODIFICATION OF AMORPHOUS POLYESTER FIBRES: I. DEFORMATION BEHAVIOUR

Valentin Velev

KONSTANTIN PRESLAVSKI UNIVERSITY OF SHUMEN, SHUMEN 9712, 115, UNIVERSITETSKA STR.

e-mail: v.velev@shu-bg.net

Abstract: *The deformation behaviour of as-spun amorphous poly (ethylene terephthalate) (PET) yarns subjected to simultaneous thermal and mechanical treatments has been studied. The samples heat mechanical treatments were realized using constructed and produced in the author's laboratory device. Thermal deformation experiments were carried out on conditions of linear samples heating from room temperature up to 200 ^{0}C while they were subjected to a well-defined constant tensile force. It was observed very interesting and seemingly strange dependence of the final fibre length from the values of the applied tensile stress. The results obtained show the role of the strain stress on the causing samples deformation and in the control of the rival processes of the fluid like deformation and stress-induced crystallization.*

Key words*: poly(ethylene terephthalate), amorphous filaments, heat - mechanical treatment, tensile stress, deformation behaviour.*

1. INTRODUCTION

As is known the characteristics and the final properties of the non-isotropic polymer materials (fibers and films) are highly dependent on their super molecular structure, which is a result on its heat mechanical prehistory [1, 2]. By selecting of the formation process parameters and subsequent treatments the polymer filaments can acquire the desired super molecular structure that allows the obtaining of products with the wanted structure and properties [3].

The analysis of the deformation behaviour of oriented amorphous but able to crystallize polymers subjected to mechanical treatment in a wide temperature range is one of the important challenges in the field of the polymer physics.

Suchlike an analysis requires to take into account as the transition of the material from solid like to rubbery state as well as the possible phase transitions of the amorphous component in the polymer system.

The present investigation is devoted to Poly(ethylene terephthalate) (PET) as a crystallizable thermoplastic polymer with the extensive application including in the form of fibers and films. Because of its low crystallization rate and depending on the cooling conditions the molten PET can be obtained as almost fully

amorphous as well as semi crystalline filaments. Optimal realized high-temperature orientation modification of polymer fibers is complex and not yet sufficiently studied process. Simultaneous mechanical and thermal treatment of oriented polymer systems is an extremely complex phenomenon based on statistical and probabilistic processes.

The effects of some basic parameters of the heat mechanically treatment such as strain force extension rate and temperature on the structure and phase development and respectively on the mechanical behaviour of oriented PET has been extensively investigated during the past years. Some of the experiments are carried out at isothermal conditions without mechanical loading of the oriented PET samples [4-6] and with application of constant strain force [7] or constant extension rate. In other of them the preoriented PET specimens are subjected to thermo-mechanical modification at non-isothermal conditions.

Despite of the realized studies some of the important questions pertaining to the role of the thermo-mechanical treatment parameters on the deformation behaviour and structural development of uncrystallized PET fibers remain without satisfactory answer. In an attempt to clarify the aforementioned questions the deformation behaviour of amorphous PET filaments subjected to heat mechanical treatment was studied in our laboratories.

Here we present results of an experiment in which amorphous PET yarns were subjected to simultaneously linear heating and to precisely defined tensile stress.

For initial approbation of the behavior of the investigated amorphous PET fiber at conditions of SHMM we accepted the technologically real (and close to the maximum possible) temperature interval from 20^0C to 200^0C and sufficient as a beginning, a range of tensile strain from 0 *MPa* to 1.7 *MPa* with enough good resolution of 0.1 *MPa*. The experiment was carried out in combination of gravitational loading of the samples at a linear heating with heating rate of $3.5^0C/min$. The results obtained at the specific experimental conditions were very interesting and showed that depending on the mechanical treatment the obtained structures could be semicrystalline or fully amorphous [8].

Therefore, it was interesting to follow the behavior of the same PET samples in the same mode of thermal influence but under a wider range of tensile stress values.

In the new version the thermal deformation experiment was carried out without limitation of the bundle extension at combination of the samples gravitational loading in the range from 0 *MPa* to 3.0 *MPa* with a good resolution of 0.12 *MPa* at a linear heating with the same heating rate ($3.5^0C/min$) and again in the temperature range from 20^0C to 200^0C.

2. EXPERIMENTAL

2.1. MATERIALS

Poly (ethylene terephthalate) (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 SIMULTANEOUS HEAT-MECHANICALLY MODIFICATION (SHMM)

Simultaneous thermal and mechanical treatments of the studied yarns were performed using device constructed and produced in our laboratory [8]. It involves a vertically located tubular heater, which can be moved to enclose the loop of the studied PET- bundle. The fibers SHMM 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.

The structural characterizations of the studied fibers after the above described heat-mechanical treatments were realized using Differential scanning calorimetry (DSC) and Wide-angle X-ray scattering (WAXS) measurements.

3. RESULTS AND DISCUSS

The study of the relationships between the SHMM modes and subsequent structural development in the PET filaments includes different versions of experiments.

Table 1. Values of the applied tensile stress during the SHMM.

№	1	2	3	4	5	6	7	8	9	10	11	12	13
σ, *MPa*	0.00	0.12	0.24	0.36	0.48	0.60	0.72	0.84	0.96	1.08	1.20	1.32	1.44
№	14	15	16	17	18	19	20	21	22	23	24	25	26
σ, *MPa*	1.56	1.68	1.80	1.92	2.04	2.16	2.28	2.40	2.52	2.64	2.76	2.88	3.00

In the performed thermal deformation experiment the investigated amorphous PET fibers were linearly heated with rate of $3.5^0C/min$ from 20^0C to 200^0C. During the filaments heating they were subjected to constant tensile stress in a wider range from 0 *MPa* to 3.0 *MPa* with an increasing step of 0.12 *MPa* (Table 1). The bundle length obtained after the heat mechanical treatment as a function of the applied strain stress is presented in Fig. 1, where the dashed line marks the initial sample length.

The deformation behaviour demonstrated by the samples at a level of applied stress up to 1.68 *MPa* is expectable. Experiments showed entropy shrinkage of the first four samples at small stress values up to the level of 0.36 *MPa*. The filaments shrinkage is a consequence of the frozen internal stresses relaxation at the temperature range of the sample glass transition. It could be supposed that the applied (external) stresses in our experiments up to value of 0.36 *MPa* do not compensate the emerging shrinkage forces.

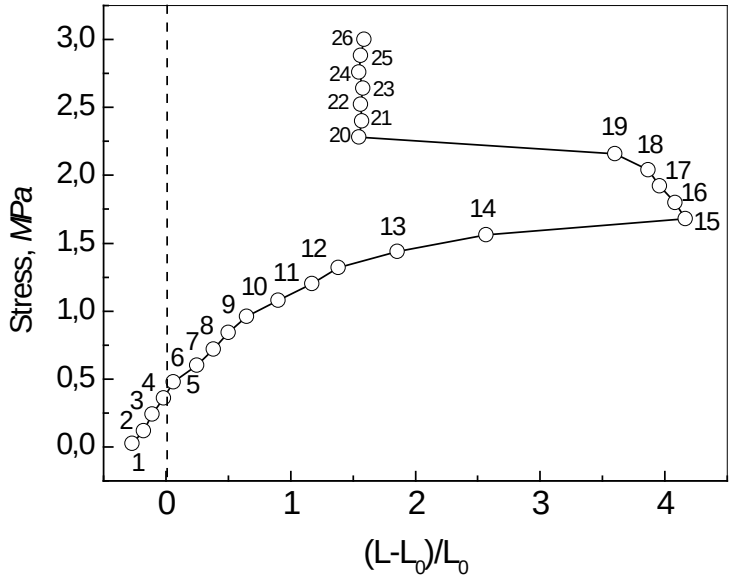

Fig. 1. Relative change of the bundle length (sample B) depending on the tensile stress values (here L_0 and L are the initial and the final fibers length respectively).

Significant sample extension is stimulated by the stress increasing from 0.36 *MPa* up to 1.68 *MPa*. As it can be seen from the results presented in Fig. 1 only increment of the final bundle length can be observed in this case. Obviously such of dependence can be detected when the applied strain stress is higher than the potential entropy shrinkage forces in an amorphous uniaxially oriented sample in rubbery state. The received

experimental data strongly corresponds to the so-called fluid-like deformation. At stress value of 1.68 *MPa* is reached more than fivefold bundle monotonic download. This is the maximum achievable prolongation by used method and conditions of SHMM.

Much more interesting and non-expectable is the deformation behaviour of the samples subjected to stresses in the range from 1.8 *MPa* up to 3.0 *MPa*. As it is illustrated on the Fig. 1 the increasing of the tensile stress values from 1.68 *MPa* to 2.16 *MPa* leads to gradually decrement of the final bundle length. A significant reduction of the net deformation occurs at the stress levels of 2.28 *MPa* and more. Despite of the rise of the applied stress values the samples extension decreases considerably. Moreover the increasing of the tensile stress does not affect the deformation behaviour of the last seven yarns. Their ultimate length is more than twice less than the maximum achieved under stress value of 1.68 *MPa*. Depending on the deformation behavior the tested samples can be conditionally separated 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. The probable cause of the above-described deformation behavior of the treated fibers is the role of the tensile stress in the regulation of the interacting processes of the fluid like deformation and stress-induced crystallization clearly reveals in the ultimate samples deformation. At first the rate of the fluid like deformation increases with the tensile force increment up to value of 1.68 *MPa*. At the some time despite the affect of the higher tensile stress leads to an earlier hold back the fiber deformation by more quickly stimulation of the phase transition to crystalline state. Because of it the final samples extension decreases significantly and remained constant over the past seven samples regardless of the tensile stress increasing. Nevertheless the detailed explanation of the obtained experimental data needs of additional structural analyses. The structural rearrangements occurred in the PET fibers as a result of the SHMM were studied using Differential scanning calorimetry (DSC) and Wide-angle X-ray scattering (WAXS) .

4. CONCLUSIONS

Based on the realized experiments can formulate the following conclusions:

The applied tensile force simultaneously with the linear heating of the studied PET yarns strongly affects the samples deformation behaviour;

Depending on the values of the applied stress were observed three groups of samples with different types of deformation behaviour;

The values of the applied stress influences of the interacting processes of the fibber shrinkage, fluid like deformation and stress induced phase transitions;

Detailed explanation of the obtained experimental data needs of additional structural analyses.

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REFERENCES

[1] Clauss B., Salem. D. R., A Chain-Intrinsic Fluorescence Study of Orientation-Strain Behaviour in Uniaxially Drawn Poly(ethylene terephthalate) Film. *Macromolecules*, 28 (1995), 8328 – 8333;

[2] Gorlier E., Haudin J. M., Billon N., Strain-induced crystallization in bulk amorphous PET under uni-axial loading. *Polymer*, 42 (2001), 9541-9549;

[3] Kwon K., Isayev A. I., Kim K. H., Van Sweden C., Theoretical and experimental studies of anisotropic shrinkage in injection moldings of semicrystalline polymers. *Polym. Eng. Sci.*, 46 (2006), N6, 712 – 728;

[4] Betchev Ch., On the Characterization by Shrinkage Forces of As-spun Poly (ethyleneterephthalate) Filaments. *Polymer Testing*, 14 (1995), 163 – 172;

[5] Dimov T., Velev V., Iliev I., Betchev Ch., "Sigmoidal" Temperature Dependence of Mechanically Induced Birefringence in Polymers. *J. Optoelectr. Adv. Mater.*, 9 (2007), N2, 275 – 277;

[6] Velev V., T. Dimov, A. Popov, Y. Denev, H. Hristov, T. Angelov, K. Markova, M. Zagortcheva, N. Arhangelova, N. Uzunov, Birefringence in heat-mechanical modified freshly moulded polyester fibers, *Journal of Physics: Conference Series*, **253** 012026, 2010;

[7] Salem D.R., Microstructure Development During Constant-Force Drawing of Poly (ethyleneterephthalate) Film, *Polymer*, 39 (1998) No. 26, 7067 – 7077;

[8] Velev V., Popov A., Bogdanov B., Chapter № 5 titled *"Heat – mechanically induced structure development in undrawn polyester fibers"* in the book "Thermodynamics",ISBN978-953-307-283-8, pages 89-114, 2011

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