

Complex influence of the preliminary orientation strain stress and annealing temperature on the structure development of poly (ethylene terephthalate) fibers

V. VELEV^{*}, R. ANDROSCH^a, T. DIMOV, A. POPOV^b, H.-J. RADUSCH^a

Konstantin Preslavsky University - Shumen, Shumen, 9712, Bulgaria

^aMLU, Halle-Wittenberg, Center of Engineering Sciences, 06217, Merseburg, Germany

^bUniversity "Prof. Dr. Assen Zlatarov" - Bourgas, Bourgas, 8000, Bulgaria

In the present work the structural development of freshly moulded poly (ethylene terephthalate) fibers with different preliminary orientation subjected to simultaneously thermal and mechanical treatments was studied. Uniaxially strain-loading experiments are conducted with partially crystalline PET yarns in a narrow temperature range from 80 °C to 95 °C and strain stress values of 40 MPa, 80 MPa, and 120 MPa. Differential scanning calorimetry and birefringence measurements were used to investigate the effects of the preliminary orientation, annealing temperatures and strain stress on the structure development of the studied samples. There are established relationships between the fibres preorientation, experimental parameters and the structural rearrangements running in the investigated yarns.

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1. Introduction

Poly (ethylene terephthalate) (PET) is a crystallizable thermoplastic polymer with large practical usages very often in the form of filaments and folios. The applications of PET are based on its relatively high glass transition temperature and low crystallization rate.

At the same time PET possess the property to crystallize in consequence of the deformation at the temperatures and strain rates used during processing. Strain induced crystallization increases the material density and resistance, and imparts anisotropy to the final product. The polymeric anisotropy leads to the increasing of the product stiffness and strength in given preferential directions.

As is well known the ultimate properties of the polymeric system with inherent anisotropy strongly depend on their super molecular structure [1-3]. In the case of the polymeric filaments, the end structure is mainly a result of the melt spinning conditions and of the subsequent heat mechanical treatments, too. By controlling of the running of the forming process and subsequent treatments the polymer fibers can take the desired super molecular structure that allows the obtaining of products with the needed final morphologies and properties [2, 3].

The effects of the strain force, strain rate and temperature on the phase development on amorphous PET have been well studied and reported. There are articles regarding uniaxially oriented PET subjected to isothermal treatment without application of stress [1, 4-6], isothermal treatment with application of stress [7, 8] and to non-isothermal treatments under stress [8, 9 - 11]. Regardless

of the great number of carried out investigations PET remains a popular research subject, intensively studied in the recent years.

At the same time, many aspects of the mechanical behaviour of PET fibers continue to be indistinct and rather the effects of strain-induced crystallization on the stress-strain behaviour. There is not a clear answer if the final filament structure depends mainly on the applied stress or on the heat treatment itself. The influence of the preliminary molecular orientation and combined loading and thermal treatments in the temperature region from 80 °C to 95 °C on the structural development of PET yarns is not still clarified. The aim of the present experiment is to study the structural changes in PET fibers with different preliminary orientation, occurring at a constant strain stress levels and at isothermal conditions in the temperature region close above the glass transition temperature from 80 °C to 95 °C.

2. Experimental

2.1. Materials

Three PET fibers named S1, S2 and S3 were used as precursor samples. PET yarns were prepared by melt spinning on the industrial spinning machine Furnet (France) using variable take-up velocities and under production conditions as follows:

- melt output of 10.8 g/min;
- number of the fibers in yarn 32;

- yarn linear density $\rho_1 = 48 \text{ dtex}$.

The basic characteristics of the original filaments are shown in Table 1.

Table 1. Basic characteristics of the investigated filaments. 1. Sample; 2. V_L , m/min – take-up velocity; 3. d , μm – diameter of the single fiber; 4. Δn – birefringence; 5. α , % - degree of the sample crystallinity.

Sample	V_L , m/min	d , μm	$\Delta n \cdot 10^3$	α , %
S1	2280	14,5	4,32	23.7
S2	2805	13,0	5,35	28.8
S3	4110	11,0	5,82	36.9

It can be seen from the Table 1 that the selected specimens are spun at different spinning speeds and thus with different preliminary orientation. So they are suitable for the achievement of the above-defined purpose of the present study.

2.2. Methods

All fibers characterizations given in Table 1 were carried out before the heat mechanical treatments.

The birefringence measurements of the studied PET fibers were performed using a polarizing interference microscope equipped with a CCD camera [9]. The main element of the experimental set-up is the system of a polarizer (P), analyzer (A) and birefringent fiber (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.

The degree of crystallinity α was calculated using the data obtained by differential scanning calorimetry (DSC). A Mettler-Toledo DSC-820 heat-flux module equipped with liquid nitrogen accessory was used for the calorimetric studies. The furnace was purged with nitrogen at a flow rate of $80 \text{ ml} \cdot \text{min}^{-1}$. Temperature calibration was done using the onset melting temperatures of indium and zinc, and the energy calibration was based on the heat of fusion of indium. Fibers were cut in pieces of less than 1 mm and sealed in standard $40 \mu\text{l}$ aluminium pans. The value of the bulk heat of fusion of crystalline PET was taken from the literature [12].

The thermal and mechanical treatments were carried out using an apparatus constructed and produced in our laboratory. The gear involves a horizontal stand with rails, a movable cylindrical oven located on the rails and a device for the sample deformation reading. One of the ends of the studied fiber bundle with initial length of 0.1 m was attached to the stand while the other one was connected by an inextensible tread to the well defined strain stress forming weight (Table 2). The heat-mechanical treatment begins when the preheated oven was rapidly shifted around the studied PET bundle that was

simultaneously stretched with the needed tension (Table 2).

Table 2. Temperatures and strain stresses of the heat mechanical fibers treatments.

t , $^{\circ}\text{C}$	σ , MPa		
	40	80	120
80	40	80	120
85	40	80	120
90	40	80	120
95	40	80	120

The bundle was held in the oven under loading during 120 seconds while the furnace temperature maintains constant and is then removed from the oven and cooled to a room temperature.

The structural characterizations of the studied fibers are realized after the above described heat-mechanical treatment experiments, using DSC and birefringence measurements.

3. Results and discussion

The obtained experimental data allows tracking the following dependencies:

The influence of the annealing temperature at constant stress on the samples degree of crystallinity and orientation;

The influence of the applied strain/stress at constant temperatures on the samples degree of crystallinity and orientation;

The influence of the preliminary filament orientation on the structure development during simultaneous thermal and mechanical treatment:

Influence of the preliminary fiber orientation at constant stress;

Influence of the preliminary fiber orientation at constant annealing temperatures.

The changes of the degree of crystallinity and birefringence with enhancement of the annealing temperature at constant strain stress values of 40, 80 and 120 MPa are presented in Tables 3, 4 and 5, respectively.

Table 3. Degree of crystallinity and birefringence of the studied samples annealed under stress of 40 MPa at constant temperatures. t , $^{\circ}\text{C}$ – temperature; α , % - degree of crystallinity; Δn – birefringence.

t , $^{\circ}\text{C}$	Sample S1		Sample S2		Sample S3	
	α , %	$\Delta n \cdot 10^3$	α , %	$\Delta n \cdot 10^3$	α , %	$\Delta n \cdot 10^3$
80	34.2	4.27	34.7	6.22	36.0	4.96
85	34.2	3.70	36.0	6.70	37.1	6.87
90	38.9	3.83	37.4	5.89	34.7	7.18
95	37.4	3.23	39.8	5.03	37.0	6.23

The data in Table 3 show that the degree of crystallinity of the samples S1 and S2 subjected to strain loading of 40 MPa increases with the temperature enhancement from 80°C to 95°C while filaments birefringence marks lowering. At the same time in contrast to the samples S1 and S2 the temperature variance almost does not affect the degree of crystallinity of the specimen S3. The birefringence of the sample S3 increases with the temperature rise, passes over a maximum at 90 °C and reaches to value of 6.23×10^{-3} at temperature of 95 °C (Table 3).

As it can be seen from Table 4 the strain stress of 80 MPa leads to slightly growth and diminution of the degree of crystallinity of the specimens S1 and S2 correspondingly whereas the degree of crystallinity of the sample S3 practically does not alters.

The birefringence measurements show that at specific conditions occurs considerable birefringence alteration. The variance of the annealing temperature from 90°C to 95°C causes essentially rising and diminution of the birefringence of the specimens S1 and S2, respectively.

Table 4. Degree of crystallinity and birefringence of the studied samples annealed under stress of 80 MPa at constant temperatures. t , °C – temperature; α , % - degree of crystallinity; Δn – birefringence.

t , °C	Sample S1		Sample S2		Sample S3	
	α , %	$\Delta n \cdot 10^3$	α , %	$\Delta n \cdot 10^3$	α , %	$\Delta n \cdot 10^3$
80	37.4	5.86	40.5	5.99	40.7	6.23
85	41.9	4.52	40.4	6.40	40.4	6.38
90	39.0	3.73	38.4	6.73	40.0	7.56
95	40.0	5.48	39.2	4.49	41.0	6.95

Very interesting variation of the samples degree of crystallinity and birefringence were obtained by the heat mechanical fibers treatments under stress of 120 MPa (Table 5). Table 5 displays that the degree of crystallinity of the samples S1 posses unexpected clearly marked minimum at temperature of 85°C, while the sample birefringence follows a light tendency of lessening without abrupt changes in the studied temperature interval. In contrast to the sample S1 it can be seen (Table 5) that the degree of crystallinity of the samples S2 and S3 gradually increments. At the same time the alterations of the specimens S2 and S3 birefringence show maximum and minimum respectively once again at temperature of 85°C.

Table 5. Degree of crystallinity and birefringence of the studied samples annealed under stress of 120 MPa at constant temperatures. t , °C – temperature; α , % - degree of crystallinity; Δn – birefringence.

t , °C	Sample S1		Sample S2		Sample S3	
	α , %	$\Delta n \cdot 10^3$	α , %	$\Delta n \cdot 10^3$	α , %	$\Delta n \cdot 10^3$
80	39.4	6.9	41.5	4.72	40.6	6.58
85	31.2	6.53	42.0	7.57	38.8	4.68
90	41.4	5.9	41.7	5.33	41.7	4.9

95	42.0	6.33	42.8	4.48	42.5	8.67
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Figs. 1, 2 and 3 present examples of the experimental scans of the annealing temperature and strain stress roles in the structure developments of the samples S1, S2 and S3 correspondingly.

Fig. 1 shows clearly that the glass transition region and the crystallization zone, which have shifted to the higher and to the lower temperatures respectively interfere for the highest temperatures whereas there is no merger for the untreated sample. Moreover, the melting region narrows and the melting process of the sample S1 subjected to strain stress of 120 MPa runs temperature independent. At the highest temperatures appear beginnings of the melting peak split.

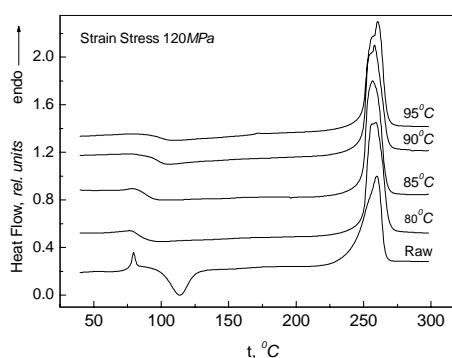


Fig.1. DSC curves of the sample S1 annealed at different temperatures under strain stress of 120 MPa.

As it can be seen from Fig. 2 the crystallization peak shifts towards the lower temperatures, while the glass transition (around 74°C [4]) does not interfere with the crystallization zone. Besides the crystallization peak area decreases with the increasing of the applied stress values.

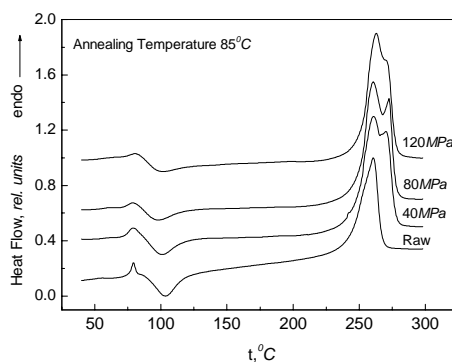


Fig.2. DSC curves of the sample S2 annealed under different strain stresses at constant temperature.

The observed experimental fact is a result of the raising of the fibers degree of crystallinity (Tables 3, 4, 5) and illustrates the strain-loading role in the structure development of the specimen S2 annealed at temperature of 85°C. Other peculiarity of the present DSC curves is the

melting zone widening and the appearance of second melting peak, which is most clearly pronounced at stress of 80 MPa.

The presence of second melting peak in the DSC curves of the sample S2 is an evidence for the existence in the filaments of micro zones with higher melting temperatures. The possible reason for that is the appearance of fractions with the relevant melting mechanisms and enthalpies, as a consequence of the influence of the strain loading on the polymer system.

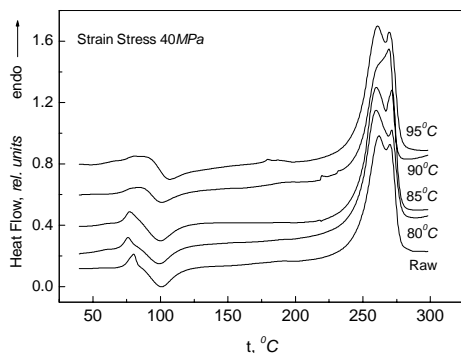


Fig.3. DSC curves of the sample S3 annealed at different temperatures under strain stress of 40 MPa.

The family of the DSC thermograms for the specimen S2, obtained under strain stress of 40 MPa and at different annealing temperatures is presented on Fig.3. It can be seen from the figure that the temperature growth essentially alters the enthalpic relaxation but almost does not affect as the cold crystallization temperature as well as the crystallization peaks areas and fibers degree of crystallinity respectively (Table 3). Typical for the represent DSC curves is the bifurcated melting peak that is most clearly shaped at temperature of 85°C. The alteration of the melting peak shape show the role of the annealing temperature on the forming in the polymer fibers of different entities with the relevant melting temperatures.

4. Conclusions

The complex influence of the preorientation, strain stress and temperature of uniaxially drawing on the degree of crystallinity and orientation in the amorphous regions of PET fibers is not simple.

The effect of the annealing temperature at a given constant stress on the crystallinity is minor. At best, there is observed only a small increase of the crystallinity with increasing of the annealing temperature.

In contrast, the applied strain stress exercises strongest affect on the structure development of the studied samples. There is observed a major increase of the crystallinity with increasing stress level.

The initial filament-orientation influences the structure rearrangements in the studied samples depending on the specific conditions of the heat-mechanical treatment.

The observed data can be explained with a strong effect of the combined stress and heat treatments on the structure evolution in oriented crystallizable PET. At the specific conditions, the deformation of the amorphous phase predominates and stops the fiber crystallization.

Precise final conclusions require additional structural investigations.

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References

- [1] K. Jong, H. Hyun, *Polymer*, **46**, 939 (2005).
- [2] H. M. Shabana, *Polymer Testing*, **23**, 291 (2004).
- [3] A. Ziabicki, L. Jarecki, *J. of Appl. Polym. Sci.*, **105**, 215 (2007).
- [4] T. Dimov, V. Velev, I. Iliev, Ch. Betchev, *J. Optoelectron. Adv. Mater.* **9**(2), 275, (2007).
- [5] R. Minqiao, Z. Zhiying, Wu Shizhen, W. Jia, X. Changfa, *J. Polym. Res.*, **13**, 9, (2006).
- [6] Ch. Betchev, *Polym. Test.*, **14**, 163 (1995).
- [7] P. Desai, A. S. Abhiraman, *J. Polym. Sci., Part B: Polym. Phys.*, **26**, 1657 (1988).
- [8] Y. Q. Rao, R. J. Farris, Univ. of Massachusetts Amherst, Annual Technical Conference - Society of Plastics Engineers, Amherst, USA, 64th, 1605 (2006).
- [9] V. Velev, R. Androsch, H.-J. Radosch, Ch. Betchev, *Macromol. Mater. and Eng.* **286**(12), 752 (2001).
- [10] V. Velev, Ch. Betchev, *Thermochim. Acta*, **473**, 50 (2008).
- [11] Ch. Betchev, V. Velev, R. Androsch, H.-J. Radosch, "Polymerwerkstoffe '2002", Merseburg, Germany, 195 (2002).
- [12] D. J. Blundell, B. N. Osborn, *Polymer* **24**, 953 (1983).

*Corresponding author: v.velev@shu-bg.net