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Birefringence in heat-mechanical modified freshly moulded polyester fibers

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Abstract. The article submits new experimental data concerning to the role of combined thermo-mechanical treatments on the structural development of freshly moulded uncrystallized but crystallizable poly (ethylene terephthalate) (PET) fibers. The object of the present work is PET as a thermoplastic polymer with a large practical application. The report is devoted to the influence of the heat-mechanical modification temperature on the structure rearrangement in uniaxially orientated amorphous PET. The heat-mechanical modification of the investigated yarns and the optical measurements were realized by specialized gears constructed and built in the author’s laboratories. The fibers heat-mechanical modification includes samples annealing at constant temperature above their glass transition temperature ($T_g$) without strain stress. The yarn annealing has been followed from well defined uniaxially strain-loading with values from 0 MPa up to 30 MPa during two minutes. The optical measurements were carried out by an optical system using a polarization microscope and a CCD camera. The obtained experimental data has been analyzed by Mocha-1.2 (Jandel Scientific) software. There are established dependences between the heat-mechanical modification mode and the structural rearrangements running in the studied PET samples.

1. Introduction

Poly (ethylene terephthalate) (PET) is a crystallizable thermoplastic polymer, which is widespread in many high-volume usages very often in orientated forms such as filaments and folios. The widely applications of PET are founded on its crystallization ability, relatively low crystallization velocity and comparatively high glass transition temperature. It is known that the end properties of the orientated polymeric systems are direct consequence of their super molecular structure [1-3]. The final structure of the polymeric filaments depends mainly by the melt spinning conditions and by the subsequent heat-mechanical modifications, too. The desirable super molecular structure and the needed final morphologies and properties of the polymer fibers can be obtained by controlling of the forming process parameters as well as the subsequent treatments [4-6]. Several experimental aspects of the deformation behavior and super molecular structure rearrangement in PET fibers caused by heat and mechanical treatments have been investigated in the recent years including participation of the authors of this article. Part of the experiments have been carried out in non-isothermal conditions [7,8] while
in other of them the structural development of PET fibers are investigated at constant temperatures without application of stress [9] and with application of strain stress [10].

The objective of the ongoing experiments with polymer filaments in our laboratories is to establish links between the results collected at different experimental conditions and the basic parameters of the thermal deformation experiments and namely:

- regime of the specimens heat treatment;
- heating (cooling) rate in non-isothermal conditions;
- temperature of the samples thermal treatment in isothermal conditions;
- method of the mechanical treatment;
- degree and speed of fibers withdrawal;
- value of the applied tension stress.

Nevertheless the effects of the combined tension stress and thermal treatments on the structure development, relaxation process and phase transitions of the amorphous PET yarns remains unclear.

With purpose to clarify the role of the temperature and tension stress values on the structure development in uniaxially oriented PET in our labs were carried out thermal deformation experiments with amorphous PET filaments at constant temperature of 80 °C and under precisely defined strain stresses from 0 MPa to 30 MPa with increment step of 3 MPa [11]. The structural investigations of the heat mechanically modified specimens show very important results concerning the role of the temperature and the applied stress and in particular:

- appearance of "resonance" filaments birefringence with a pronounced maximum at tension stress value of 6 MPa;
- significant increase of more than 30 % of the fibers degree of crystallinity with the strain stress increasing from 3 MPa to 6 MPa [11].

Therefore it was very interesting for us to continue the investigations of the same PET specimens at enhanced temperature of 85 °C. In the present work we submit new experimental data pertaining to the part of the simultaneous thermal and mechanical modification on the deformation behaviour and structure development of amorphous PET fibers. The experiment includes annealing of an as-spun PET yarns at temperature 85 °C above its glass transition temperature defined in our other work at 74 °C [9] while the fiber bundle is subjected to a well defined strain stress from 0 MPa to 30 MPa with step of growth 3 MPa.

2. Experimental

2.1. Materials

Amorphous PET as-spun multifilament yarns prepared on the industrial spinning installation Furnet (France) have been selected as a precursor samples. The original filament features and formation conditions were as follows:

- spinning speed 1150 m/min;
- number of spinnerets in yarn 32;
- single filament diameter 44 μm.
- density \( \rho = 1338 \text{ kg/m}^3 \);
- degree of crystallinity \( \alpha = 1.7 \% \);
- birefringence \( \Delta n = 0.008 \);
- coefficient of amorphous orientation \( f_a = 0.029 \).

2.2. Methods

The density of the raw fibers was determined using a density gradient column filled with a tetra chloromethane and n-heptane mixture. The samples degree of crystallinity was calculated on the basis of the obtained filaments density data. The birefringence of the untreated fibers was measured using an Amplival POL D (Karl-Zeiss Jena) polarizing microscope, provided with Bercek compensators. The coefficient of amorphous orientation of the rough filaments was calculated using the obtained birefringence data and the Stein’s equation [12].
The samples heat-mechanical modification was carried out using a specialized device designed and produced in our laboratory. The thermal deformation experiment includes rapidly sample heating from a room temperature up to temperature of \(85^\circ\text{C}\) with subsequent annealing for ten minutes. After annealing time the studied yarn was loaded during two minutes with well-defined tension stress from 0 MPa to 30 MPa with increment step of 3 MPa. The heat mechanical filaments treatment was followed by a simultaneously taking down of the applied strain stress and yarn moving from the oven to room temperature.

The birefringence measurements of the heat mechanically treated PET fibers were performed using a specialized set-up developed and made in the author’s laboratory. The gear involves polarizing interference microscope with a CCD camera attached [9]. The keystone of the experimental device is the system of a polarizer (P), analyzer (A) and birefringent filament (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.

3. Results and discussion
With purpose to specify the occurred in the fibers structure developments the transmission of linearly polarized monochromatic light with wavelength \(\lambda = 590\ \text{nm}\) across the P-F-A system has been investigated. The obtained birefringence data of the heat mechanical treated PET samples depending on the applied to the yarn tension stress are present in figure 1.

![Figure 1. Birefringence of the heat mechanical treated PET filaments depending on the applied strain stress.](image)

The experimental results shown on the figure 1 allow to see the role of the temperature of the heat mechanically treatments of the same PET filaments. In contrast to the birefringence received at temperature \(80^\circ\text{C}\) where exist “resonance” dependence with pronounced peak at 6 MPa [11] here we can see a wide basic peak at stresses of 12 MPa, 15 MPa and 18 MPa with two attendant smaller peaks at stresses of 3 MPa and 27 MPa correspondingly.

The specimen’s deformation behaviour during the thermal deformation experiments and more specifically the fibers diameter changes are shown in figure 2.

The alterations of the treated filaments length \((L - L_0)\) are present in the “stress-deformation” diagram in figure 3, where \(L_0\) is the initial length of the fibers bundle. Here we detect the affect of the temperature on the PET filaments extension. The relatively few temperature increasing from \(80^\circ\text{C}\) in our previous experiments [11] to \(85^\circ\text{C}\) in the present heat mechanical fibers treatments leads to a
tenfold yarns elongation growth (figure 3). As it can be seen from the figures 1, 2 and 3 the filaments’ birefringence changes are in a good agreement with the samples’ deformation behaviour.

![Graph showing diameter vs stress](image)

**Figure 2.** Fibers diameter.

The increasing of the amorphous orientation function and respectively the fibers birefringence at the applied strain stress from 0 MPa up to 3 MPa (figure 1) is in accordance with the collapse of the samples diameter (figure 2) and with the degree of withdrawal (figure 3).

![Graph showing stress vs extension](image)

**Figure 3.** Tensile stress – extension diagram.

The specimens’ birefringence reduction in the interval of the tension stress from 3 MPa to 6 MPa (figure 1) and the appropriate deformation behaviour (figures 2, 3) can be explained with the additional segments stretching and with the rupture of the pre-stressed segments, too. The strain stress values increasing from 9 MPa up to 27 MPa leads to the smooth filaments diameter (figure 2) reduction and to the gradually yarns length increase (figure 3). The possible reason for the observed
deformation behaviour and the accompanying changes of the birefringence (figure 1) are the further fibrils withdrawal and slip accompanied from destructions and subsequent drop of the segments orientation. It should be mentioned the deformation behaviour of the studied filaments subjected to tension stress of 30 MPa (figures 2, 3) where in contrast to the bearing of the previous samples the increasing of the strain stress value leads to fibers diameter increasing and to yarns length decrease.

4. Conclusions
Correlations between the heat-mechanical modification parameters and the occurred structure rearrangement in the investigated uniaxially orientated amorphous PET have been established.

The temperature increase of the heat-mechanical treatment from 80 °C to 85 °C causes a tenfold PET filaments elongation increment.

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

The experiments realized at temperature of 85 °C are the next step of the planned structural studies in amorphous PET filaments in the temperature range from 80 °C to 95 °C caused by combined heat-mechanical treatments.

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