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Calorimetric studies on stress-induced crystallization of pre-oriented poly(ethylene terephthalate) glasses

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ABSTRACT

The crystallization thermodynamics and kinetics of amorphous poly(ethylene terephthalate) (PET) fibres subjected to simultaneously thermal and mechanical treatments has been studied. A thermo-conductive calorimeter–dilatometer was constructed in the author's laboratories with that purpose. The obtained results interpretation was based on the Ozawa's equation. Relationships between the applied to filaments mechanical stress and the running of their crystallization process were established.

1. Introduction

It is well known that the final properties of the oriented polymeric materials strongly depend on their super molecular structure. In the case of undrawn filaments, the final structure is mainly a result of the melt spinning conditions and of the subsequent thermomechanical treatments, too. As a result of the formation in the fibres arise entities with higher arrangement, which at suitable conditions should be a crystalline nucleus and they are the so-called quasi-crystalline nucleus. Other consequence of the filaments formation is the rise of areas with frozen stresses in the fibres.

The mechanical stress applied to polymers during the crystallization process significantly changes the crystallization kinetics. The influence of a mechanical stress on the crystallization of poly(ethylene terephthalate) (PET) filaments is discussed by a number of authors [1–8]. Some of the experimental research has been conducted at constant temperatures and stresses [1,3] and with constant samples length [1,4,8]. In other of them the structural development of PET fibres has been studied in non-isothermal conditions [6–8]. Nevertheless, the question pertaining to the combined effect of stress and thermal treatments on the crystallization of PET yarns is not still clarified.

The paper presents results from calorimetric studies about the role of the simultaneous thermal and mechanical influence on the crystallization of as-spun PET filaments with saved preliminary orientation.

2. Experimental details

2.1. Materials

PET amorphous as-spun yarns were used as precursor samples. The filaments were produced on the industrial spinning machine under technological conditions as follows:

- melting temperature of 568 K;
- melt output of 50 g/min;
- spinning speed 1100 m/min;
- yarn linear density of 600 dtex
- number of spinnerets in yarn 32;
- single filament diameter 44 μm.

Initial basic characteristics of the studied fibres are:

- density $\rho = 1338.0\,\mathrm{kg/m^3}$;
- degree of crystallinity $\alpha = 1.7\%$;

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- birefringence $\Delta n = 0.008$;
- coefficient of amorphous orientation $f_a = 0.02959$.

It can be concluded that the investigated specimens were in practice amorphous and orientated.

2.2. Methods for samples characterization

Sample density was estimated by a densitometer "Mettler–Toledo" using the relation:

$$\rho = \frac{m_a}{m_a - m_f}\rho_0 \quad (1)$$

where ρ is the sample density; m_a is the fibber mass in air; m_f is the fibber mass in water; ρ_0 is the water density at the measurement temperature.

The degree of crystallinity was determined from the received density data, using the known equation:

$$\alpha = \frac{\rho - \rho_a}{\rho_c - \rho_a} \quad (2)$$

where α is the mass fraction of crystallinity; ρ is the sample density; ρ_a is the density of amorphous phase PET; ρ_c is the density of crystalline phase PET. The values of $\rho_c = 1515\,\text{kg/m}^3$ and $\rho_a = 1335\,\text{kg/m}^3$ were taken from the literature [9].

Birefringence of the investigated fibres was measured by a polarizing microscope "Amplival–pol. D" equipped with Bereck compensators.

The coefficient of amorphous orientation was determinated in accordance with Stein's equation [10]. The thermodynamics and kinetics of the fibres crystallization and their deformation behaviour were studied by a thermo conductive calorimeter–dilatometer [11].

3. Thermoconductive calorimeter–dilatometer for thermal behaviour investigation

The examination of the polymer filaments by the existing industrial DSC technique proposes samples preparation as a powder [12]. That is why it is not possible to investigate the effect of the preliminary fibres orientation on the structure development of the studied sample as well as to apply a mechanical stress on the specimen during the calorimetric experiment. At the same time, the existing different deformation calorimeters [13,14] measure only the heat generation as a consequence of samples mechanical treatment.

Because of the above mentioned reasons, in our laboratories was constructed and produced a calorimeter–dilatometer designed for investigation of the simultaneous thermal and mechanical effect on the phase transitions and deformation behaviour of oriented polymer materials [11]. The device represents a differential thermo conductive calorimeter that consists of two identical cells with "diathermic shells" and thermo battery, located in a general thermal container and supplied with a stretcher. The calorimetric equipment has a temperature range of reliable work from 270 K to 440 K with heating rates from 0.3 K/min to 12 K/min. The necessary tensile force has been applied to the investigated fibres by the stretcher.

4. Results and discussion

The influence of mechanical stress on the samples' crystallization from rubbery state and their deformation behaviour was investigated by the above described calorimeter–dilatometer. Number of simultaneously calorimetric and dilatometric researches was performed at dynamic conditions with applied to fibres tensile stress as well as without stress.

4.1. Investigation of the crystallization thermodynamics

The thermodynamic parameters of the "cold" crystallization were studied at pseudo stationary samples heating conditions in the calorimeter–dilatometer with heating rate of 3.5 K/min in the range from 290 K to 440 K. In the next stage of the experiment the filaments were removed from the calorimetric device at a temperature of 290 K and with the length obtained during the treatment.

With a purpose to determine the strain stress influence on the fibres' crystallization enthalpy, two versions of calorimetric experiments were realized:

- crystallization of PET filaments from rubbery state without applied to samples strain stress;
- crystallization of PET filaments from rubbery state with applied to samples strain stress of 1.2 MPa.

Thermograms obtained from the calorimetric experiments without application to fibres strain stress (curve 1) and with application to PET bundle strain stress of 1.2 MPa (curve 2) are shown in Fig. 1. It can be seen that the applied mechanical stress strongly affects the crystallization process from rubbery state of the studied samples. With the purpose of more detailed investigation of the strain stress effect on the thermodynamic parameters of the "cold" crystallization of the studied samples, a number of calorimetrical experiments were performed at the above-mentioned heating conditions. In each of them the bundle was subjected to well-defined strain stress with values from 0.025 MPa to 1.2 MPa and with an increased step of 0.1 MPa.

The change of the crystallization enthalpy of the investigated fibres depending on the applied stress value is presented in Table 1. The obtained data shows an increment of the crystallization enthalpy with the increasing strain stress. From this can be assumed that the applied mechanical stress prevents the destruction in the filaments of the entities with higher degree of arrangement, during the samples transition from glassy to rubbery state. Thus the crystallization of the examined PET fibres realizes at more quasi-crystalline nucleus and leads to an increasing of the crystallization enthalpy.

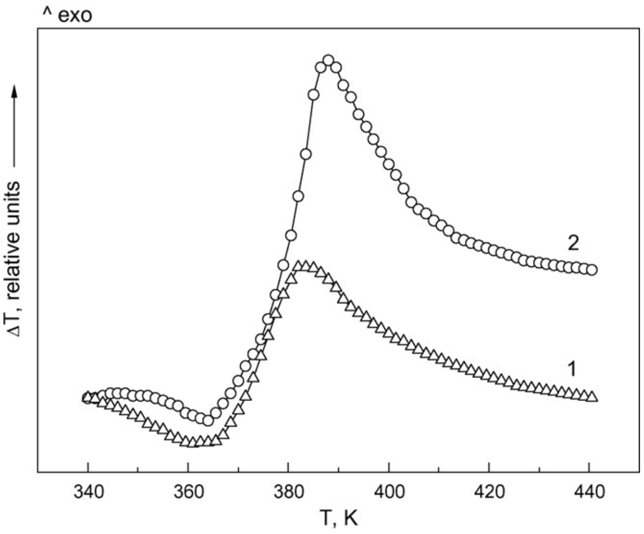

Fig. 1. Thermograms of crystallization of PET fibres without applied mechanical stress (curve 1) and under strain stress of 1.2 MPa (curve 2).

Table 1
Crystallization enthalpy $\Delta H/\Delta H_1$ of PET fibres depending on the values of the applied strain stress (ΔH_1 is the crystallization enthalpy at σ = 0.025 MPa)

No.	σ (MPa)	$\Delta H/\Delta H_1$
1	0.025	1.0
2	0.1	1.0
3	0.2	1.1
4	0.3	1.3
5	0.4	1.4
6	0.5	1.6
7	0.6	1.7
8	0.7	1.7
9	0.8	1.8
10	0.9	1.8
11	1.0	1.9
12	1.1	2.0
13	1.2	2.1
14	1.3	2.2

(1) No.: sample number; (2) σ (MPa): value of the applied strain stress; (3) $\Delta H/\Delta H_1$: change of the crystallization enthalpy.

4.2. Kinetics of crystallization

To clarify the strain stress influence on the samples crystallization kinetic two types of experiments were carried out using the above described calorimeter–dilatometer:

- At different heating rates as follows: 2 K/min; 3.5 K/min; 5 K/min; 6.5 K/min, without applied strain stress.
- At the same heating rates and with applied to the bundle strain stress of 1.2 MPa.

Respectively with the experimental no isothermal conditions, the obtained data from the fibres crystallization kinetics were interpreted using Ozawa's theory [15,16].

According to this theory the degree of the crystallization completeness (α) at temperature (T) is defined by the following equation:

$$-\ln(1-\alpha)=\frac{\chi_c(T)}{\theta^n} \qquad (3)$$

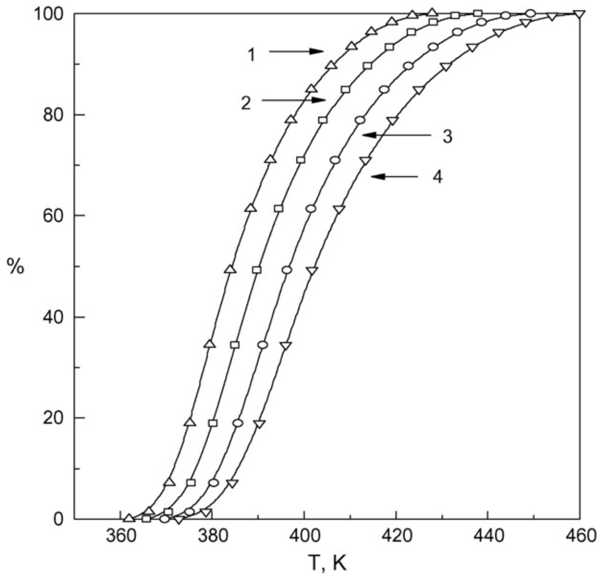

Fig. 2. Crystallization kinetics of PET fibres without mechanical loading at heating rates as follows: (1) 2 K/min; (2) 3.5 K/min; (3) 5 K/min; (4) 6.5 K/min.

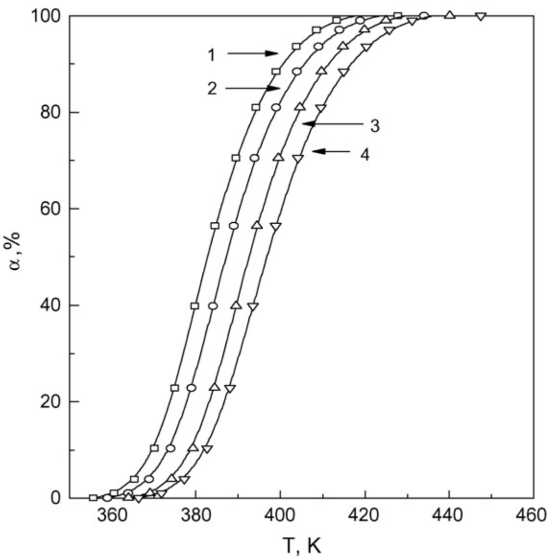

Fig. 3. Crystallization kinetics of PET fibres under strain stress of 1.2 MPa at heating rates as follows: (1) 2 K/min; (2) 3.5 K/min; (3) 5 K/min; (4) 6.5 K/min.

where θ is the heating rate; χ_c is the crystallization function; n is the number with values from 1 to 4.

The dependence of the samples crystallization kinetic at different heating rates, received without stress and under strain stress of 1.2 MPa are presented in Figs. 2 and 3.

As it can be seen the increasing heating rate leads to the fibbers crystallization at higher temperatures. The obtained results can be explained with the relationships between the polymer structure development and the heating rate. At higher heating rates the polymer glass transition realizes at higher temperatures that leads to the increase of the crystallization temperature.

The comparison of Figs. 2 and 3 shows an initial accelerated and a delayed in the final stage crystallization process. A likely reason for the observed fact is that the applied to the filaments during the calorimetrical experiments strain stress, impedes the quasi-crystalline nucleus destruction in the sample. As a result the crystallization process starts on the basis of more crystalline nucleus.

On the other hand, the mechanical stress prevents the glass transition in the existing areas with frozen stresses in the fibres

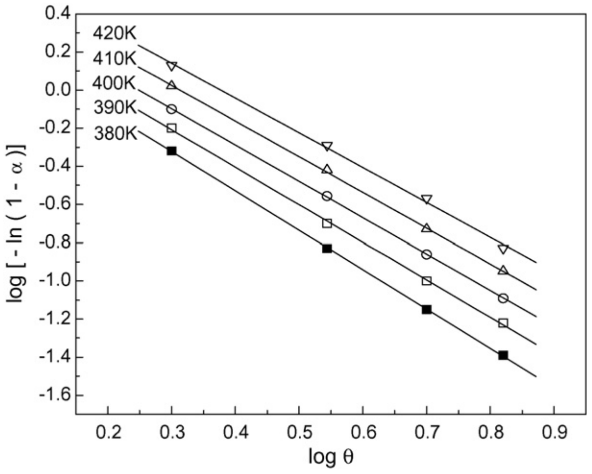

Fig. 4. Dependence of $\log[-\ln(1-\alpha)]$ on $\log\theta$ for PET fibres crystallized without applied mechanical stress.

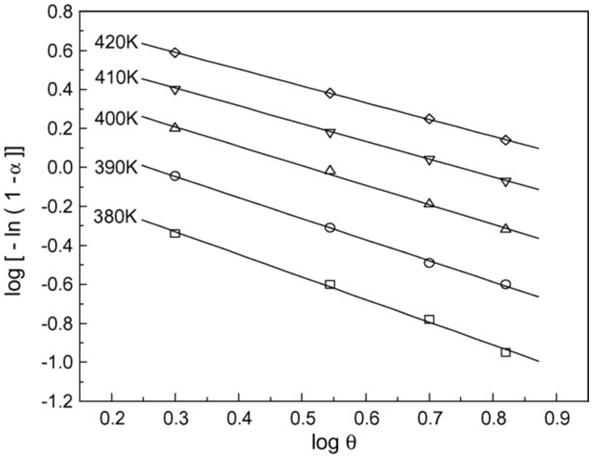

Fig. 5. Dependence of $\log[-\ln(1-\alpha)]$ on $\log\theta$ for PET fibres crystallized under strain stress of 1.2 MPa.

Table 2
The exponent (n) and correlation coefficient (R) values, obtained using the Ozawa's equation for crystallization kinetics without mechanical loading and under strain stress

T (K)	Without mechanical stress		Under mechanical stress	
	n	R	n	R
380	2.1	0.9999	1.2	0.9982
390	2.0	0.9997	1.1	0.9994
400	1.9	0.9999	1.0	0.9987
410	1.9	0.9998	0.9	0.9988
420	1.9	0.9988	0.9	0.9995

(1) T (K): temperature; (2) Exponent (n) and correlation coefficient (R) values, obtained for crystallization without mechanical loading; (3) exponent (n) and correlation coefficient (R) values, obtained for crystallization under strain stress of 1.2 MPa.

that leads to embarrassed or fully stopped crystallization in the last stages of the phase transition.

Eq. (3) can be presented as follows:

$$\log[-\ln(1-a)] = \log\chi_c(T) - n\log\theta \quad (4)$$

In Figs. 4 and 5 are shown the dependences of the left side of Eq. (4) from $\log\theta$ for the studied fibres crystallized without applied stress and crystallized under stress, respectively. According to Eq. (4) the lines slope allows to determinate the exponent n in Eq. (3) and the obtained data as well as the relevant correlation factors are presented in Table 2. As it can be seen the exponent values for the filaments crystallized without stress are around two (average value $\langle n\rangle = 1.97$) while for the samples crystallized under stress are roughly one (average value $\langle n\rangle = 1.02$). Considering of the heterogeneous nucleus formation in the undrawn PET fibres and Ozawa's theory conclusions, we can presume that the applied mechanical stress restricts the crystal entities growth in tubular form. The mechanical influence absence leads to the development of crystals in a lamellar shape.

The increase of parameter n can be interpreted as a change of the crystals geometry as a consequence of the fibres orientation increment. It should be noticed that an explicit conclusion about the crystallized samples morphology needs additional structural analyses.

5. Conclusions

Crystallization thermodynamics and kinetics of polyethylene terephthalate filaments subjected to simultaneously thermal and mechanical treatments has been investigated using self-constructed thermoconductive calorimeter–dilatometer.

The influence of the applied to fibres mechanical stress on their crystallization thermodynamics and kinetics was established.

The existence of quasi-crystalline nucleus in the amorphous PET filaments is supposed and this assumption was used in explanation of the obtained experimental data.

The obtained experimental results from the investigation of the crystallization kinetics show that the Ozawa's model can be used in the qualitative description of the amorphous PET fibres crystallization.

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