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Effect of a mechanical stress on the crystallization of undrawn polyethylene terephtalate fibres

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It has been shown that the intensity of the mechanical field accelerates crystallization to a varying degree in the samples of undrawn polyethyleneterephthalate (PET) fibres investigated. The relation was non-linear. This phenomenon is explained by metastability of the texture in the amorphous PET formed during the spinning to undrawn fibres. The applied mechanical field impedes the destruction of the latter during the passage of the polymer from the glass to the rubber state up until beginning of crystallization.

1. Introduction

The mechanical stress applied to polymers in many technological processes and in particular in the production of man-made fibres considerably affects the crystallization processes in them [1]. The processes occurring in the orientational extension of polyethyleneterephthalate (PET) fibres has been studied by several authors [2–5], but the crystallization kinetics of PET under mechanical stress has not been sufficiently investigated.

This paper deals with the thermokinetics of crystallization in undrawn PET fibres which are in a strained state during the experiment.

2. Experimental procedure

Some more important characteristics of the samples of undrawn PET fibres investigated are shown in Table I. A differential calorimeter of the Kalvet type, similar to the one previously described [6], was used for the thermokinetic investigations. The calorimeter was placed in a vessel with double walls, between which silicon oil circulated.

The whole system was put in an ultra-thermostat, which made it possible to maintain the temperature throughout the experiment with a stability of not less than ± 0.5 K. The sample yarn, composed of 400 filaments, was loaded with a certain weight after threading through a coiled copper tube. The ends of the yarn were firmly fastened to the body of the coil, which was placed in the calorimetric cell. Thus the sample was held at constant length during the experiment. The inertia constant used, τ_k (the response time of the calorimeter) [7] amounted to 2 min. The small size of the copper tube did not lead to a change of τ_k, so that the inertia of the calorimeter was caused by the mass of the polymer sample. Care was taken to strictly observe the condition $\tau_{0.5} \geqslant \tau$, where τ is the crystallization time and $\tau_{0.5}$ is the half-crystallization time, at all temperatures in the range studied (366 to 378 K), so as to obtain a more reliable determination of $\tau_{0.5}$ [7].

3. Results and discussion

The crystallization kinetics were investigated both in the free and the strained state of the samples at different stretching tensions. The crystallization

TABLE I Some characteristics of the investigated samples

Characteristic	Value
Density (g cm^{-3})	1.348
Thickness of the fibres (μm)	57.9
Bi-refringence	0.003
Relative viscosity (0.5% m-cresol)	0.32

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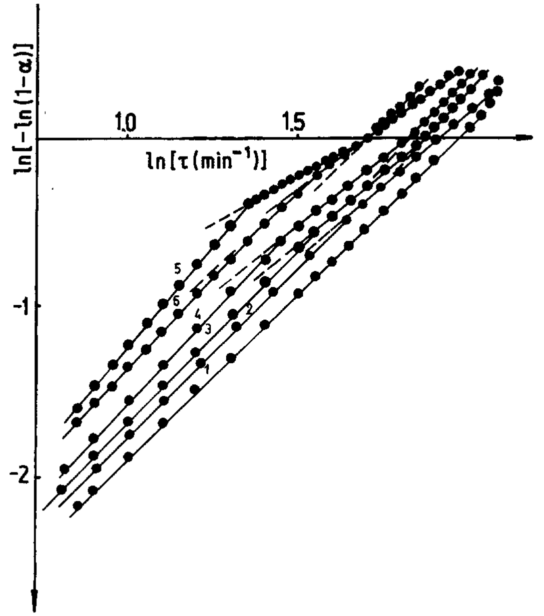

Figure 1 Crystallization isotherms for samples crystallized at different stretching tensions: 1, $\sigma = 0$; 2, $\sigma = 3.48$; 3, $\sigma = 6.25$; 4, $\sigma = 11.8$; 5, $\sigma = 17.4$; 6, $\sigma = 22.9$; where σ is measured in 10^5 kg m^{-2}.

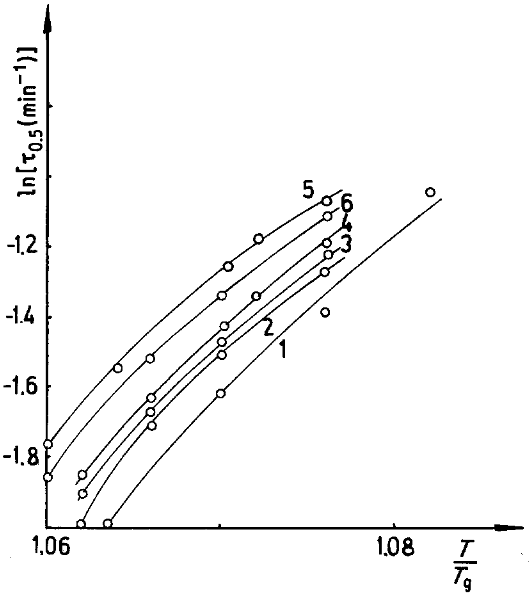

Figure 2 Dependence of $(\tau_{0.5})^{-1}$ on T/T_g, for samples crystallized at different stretching tensions: 1, $\sigma = 0$; 2, $\sigma = 3.48$; 3, $\sigma = 6.25$; 4, $\sigma = 11.8$; 5, $\sigma = 17.4$; 6, $\sigma = 22.9$; where σ is measured in 10^5 kg m^{-2}.

isotherms, at 375 K are plotted as $\ln[-\ln(1-\alpha)]$, where α is the rate of crystallization [8], against $\ln \tau$ for a range of applied tensions, in Fig. 1. As can be seen, the results cannot be described by the equation of Avrami [8], as the experimental points lie on two or more straight lines. In the initial crystallization stage ($\alpha < 0.5$) the higher the applied stress the greater the crystallization rate. At higher crystallization ($\alpha > 0.5$) the rate decreases, i.e., a reduction of the slope of the straight lines in Fig. 1. In the opinion of the authors, this is due to the following causes: (a) internal stresses in the undrawn PET fibres arising through, albeit minor, orientation of parts of the macromolecules during the spinning process; (b) additional stresses caused by the applied strain, concentrated at textural boundaries, existing in the amorphous polymer material [9]; and (c) inhibition of the thermally induced disorientation processes after the material becomes highly elastic by mechanical strain. Thus, the application of a mechanical stress to the samples impedes the destruction of the polymer nuclei during the transition of the material from a glass to a rubber state, which leads to a considerable acceleration of crystallization in the initial stages.

The crystallization kinetics in the undrawn PET fibres, when a mechanical stress acts on the samples at different temperatures in the 366 to 378 K range (limited by the time constant of the calorimetric apparatus) was investigated. As can be seen from Fig. 2, the crystallization rate increases smoothly with temperature, i.e. the classical dependence of $\ln(\tau_{0.5})^{-1} = f(T_{cr}/T_g)$ is observed [8]. The effect of the mechanical strain on the crystallization rate at just one temperature (373 K) will be examined since the analysis of results would be similar to any other temperature in the range (see the family of curves in Fig. 2). The effects of different time/temperature relaxation of any internal strains prior to crystallization under external stress are shown in Fig. 3. Significant differences can be seen. For example in Curve 3, the dependence $\ln(\tau_{0.5})^{-1} = f(\sigma)$, where σ is the applied strain, passes through a maximum. In the present experiments the possibilities of varying the applied strain were limited, owing to the development of a plastic deformation of the samples during their preparation at the start and during the calorimetric experiment. However, within these relatively narrow limits of change of applied tension, the crystallization rate increases non-linearly with an increase of the stretching tension. This behaviour can be explained by the metastability of the texture of the amorphous PET (in our case undrawn PET fibres). Indeed, if it is assumed that a certain part of the ordering of the

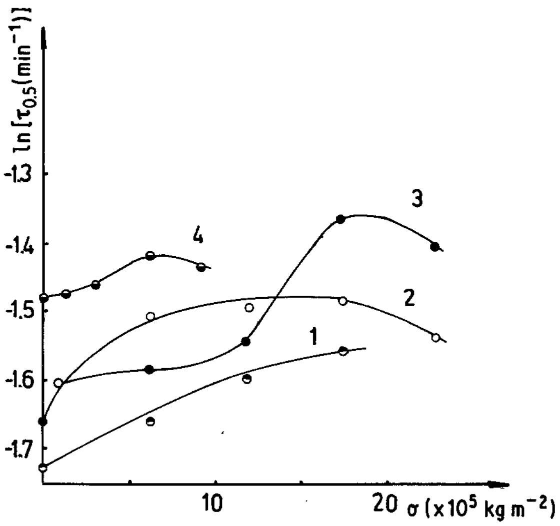

Figure 3 Dependence of $(\tau_{0.5})^{-1}$ at temperature 373 K on the appied stretching tension for samples with a different thermomechanical prehistory resp. curves: 1, 30 min relaxation in air at $T = 353$ K; 2, 30 min relaxation in H_2O at $T = 353$ K; 3, without previous treatment; 4, 10-day relaxation in air at $T = 293 \pm 3$ K.

TABLE II Density of samples after crystallization in a strained state at $T_{cr} = 372.8$ K

Treatment before calorimetrical experiment	Applied mechanical field σ (10^5 kg m^{-2})	Density* (g cm^{-3})
Without treatment	0	1.3755
	3.48	1.3700
	6.25	1.3640
	11.82	1.3710
	17.43	1.3695
	22.92	1.3655
Treatment with water for 30 min at $T = 353$ K	0	1.3725
	1.25	1.3635
	3.22	1.3580
	6.23	1.3730
	9.20	1.3700
Treatment in air for 30 min at $T = 353$ K, Relaxation of strained fibres	0	1.3650
	17.43	1.3720
	3.48	1.3740
	11.82	1.3730
	17.43	1.3695

*The density was determined by the method of gradient tubes with an accuracy of 0.0005 g cm^{-3} [9].

undrawn PET fibres is destroyed during the transition from a glass to a rubber state, as a result of the thermal vibrations of the macromolecular segments, then the volume concentration of the crystallization nuclei should decrease. Consequently, in the sample subjected to crystallization in a free state, there will be fewer crystallizations than in a strained state under tension. This will naturally lead to a certain increase in rate of crystallization in strained samples. On the other hand, the maximum crystallinity in them will be lower than in the samples crystallized in a free state. This assumption is borne out by the experimental results of the sample density after crystallization in a calorimeter (Table II).

The crystallization rate in samples of undrawn fibres with a different thermal prehistory was studied with a view to detailing and checking the proposed mechanism. The investigated samples were heated in air and in an aqueous medium at

TABLE III Kinetic parameters of crystallization in accordance with the Avrami equation $\alpha = I - \exp(-k\tau^n)$; $T_{cr} = 372.8$ K

Applied strain σ (10^5 kg m^{-2})	Half time of crystallization $\tau_{0.5}$ (min)	Kinetical parameters according to the equation of Avrami		
		n	$-\ln k$	α
0	47.5	1.91	3.80	0.05–0.90
3.48	41.0	1.95	3.68	0.05–0.88
		1.68	3.17	0.68–0.98
6.25	37.5	2.00	3.68	0.05–0.74
		1.65	3.08	0.74–0.90
11.8	33.0	2.00	3.64	0.05–0.70
		1.60	2.90	0.70–0.90
17.4	21.5	2.15	3.45	0.05–0.68
		1.13	1.88	0.68–0.78
		1.56	2.54	0.78–0.95
22.9	24.5	2.00	3.47	0.05–0.72
		1.74	3.04	0.72–0.90
		2.00	3.44	0.90–0.98

353 K for 30 min up to the start of the calorimetric experiment. The experimental results (Fig. 3) show that the crystallization rate of the samples treated in air (Curve 1) increases monotonically with an increase of the stretching tension but is lower than that of the non-treated samples (Curve 3). The effect of the mechanical field is less pronounced, probably owing to the relaxation of the applied tension up to the beginning of the experiment. In that case its action consists in a certain arrangement of the macromolecular segments along the axis of the fibres.

Crystallization of fibres treated in an aqueous medium is more rapid than in the initial samples, as is apparent from a comparison of Curves 3 and 4 of Fig. 3. Most probably this is connected with the fact that crystallization had already started during the aqueous treatment, i.e. at the beginning of the experiment.

The results obtained in studying samples relaxed for 10 days under tension in isometric conditions (wound on a copper tube) are, in the authors' opinion, most interesting. They reveal (Fig. 3, Curve 2) that the dependence $\ln(\tau_{0.5})^{-1} = f(\sigma)$ has a similar non-linear character as in the other cases examined. It is interesting to note, however, that at tensions less than 13×10^5 kg m^{-2} the crystallization rate in these samples is higher than that in the initial samples. Perhaps new crystallization nuclei are formed in samples in a strained state during their 10-day relaxation. Thus, the final degree of crystallinity should increase with an increase in magnitude of the applied initial tension, as confirmed by the data on the density of the crystallized samples (Table III). The passage of the dependence $\ln(\tau_{0.5})^{-1} = f(\sigma)$ through a maximum and a decrease of the crystallization rate for the region of tensions from 17 to 1×10^5 kg m^{-2} is probably connected with the development of irreversible deformations during the relaxation of the samples, as well as with the destruction of their initial structure.

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