

Calorimetric Studies of Poly(Ethylene Terephthalate) (PET) Fibers. Cold Crystallization Kinetics

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Abstract — Using Tian - Calvet differential calorimetry the cold crystallization kinetics at isothermal conditions of amorphous as-spun poly (ethylene terephthalate) (PET) filaments has been investigated. The Avrami's equation was applied for analysis of the obtained experimental data. It has been shown that the mechanical impact significantly influences the process of the samples crystallization. Has been studied and the influence of linear density on the objects crystallization kinetics. It was suggested that poly (ethylene terephthalate) fibers crystallizes one-, and two-dimensionally from preexisting nuclei. These results are in accordance with the assumption of the quasi-crystallization centers existing in the amorphous PET, formed during the fibers spinning.

Keywords: poly (ethylene terephthalate), filaments, Tian - Calvet calorimetry, crystallization kinetics, Avrami's equation.

I. INTRODUCTION

The flexible chain polymers are widely used in different areas of technology, but most frequently in the production of fibers, films, etc. The final structure of the polymeric filaments depends primarily on the melt spinning conditions as well as from the next technological processes. Established as a result of the forming conditions super molecular structure in the amorphous polymeric fibers influences the process of their crystallization [1-3]. During the fibrillate process in the fibers are formed zones with an increased degree of orderliness of the macromolecular segments, meso- and crystalline phases with different perfection. Under appropriate conditions the above mentioned entities can be converted into crystal nucleus, and they are the so called semi- or quasi-crystalline nuclei [4]. The object of the present work is poly (ethylene terephthalate) (PET) that is a crystallizable thermoplastic polymer of wide application often in the form of fibers and films [5]. The great importance from scientific point of view and the significant technological interest are the basic reasons to study the phase behavior of PET fibers. The relatively low crystallization rate allows depending on the cooling conditions the molten PET to be converted to almost completely amorphous as well as to semi crystalline filaments.

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Processes accompanying the fiber forming and orientation download of polyethylene terephthalate (PET) have been extensively studied in the recent years [6-8]. For the evaluation of the crystallization ability of the fiber forming polymers and in particular of the undrawn PET fiber, it is not sufficient knowledge of the basic thermodynamic characteristics of the phase transition. Complete characterization of the amorphous PET fibers crystallization requires the availability of data concerning the influence of the applied at their formation mechanical influence on the kinetics of crystallization, as well as the role of tensile stress in the additional thermo mechanical modification (TMM) which is not sufficiently studied. Obtaining of more information concerning the effect of the experimental conditions and the influence of the strain stress on the crystallization kinetics of amorphous PET fibers would contribute for more clarification to the role of the applied mechanical impact on their structure and physical properties.

II. MATERIALS

The experiments were performed with undrawn PET filaments produced from industrial installation of the company "Furnet" (France). Basic fibrillate conditions and the initial physical characteristics of the studied PET fibers are given in Tabl. 1. Using the data for the studied fibers density it was determined and their degree of crystallinity.

Table 1. Basic fibrillate parameters and initial physical characteristics of the studied PET fibers.

N	V_f , m/min	v , m/s	ρ_l , $dtex$	ρ , kg/m^3	α , %	$\Delta n \cdot 10^3$	$f_a \cdot 10^3$
1	1950	0,7	400	1342,0	3,9	16,1	58,54
2	1100	0,7	600	1336,0	0,6	6,1	22,18
3	1950	0,7	180	1344,0	5,0	17,8	64,72
4	1950	0,7	267	1342,0	3,9	17,9	65,09
5	1950	0,7	365	1342,0	3,9	15,6	56,72
6	1950	0,0	110	1344,5	5,3	20,0	72,72
7	1950	0,9	110	1340,0	2,8	18,40	66,90

, where: N – sample number;
 V_f m/min - speed of fibrillate;
 v , m/s - speed of the cooling air;
 ρ_l , $dtex$ - linear density;
 ρ , kg/m^3 – density;
 α , % - degree of crystallinity;
 Δn - birefringence;

f_a - coefficient of amorphous orientation.

From Tabl. 1 can be seen that the values of the linear density of the individual samples have large differences. At the same time the samples degree of crystallinity determined by the density is less than 5,3 %.

Therefore, the selected samples are suitable for testing of the effect of linear density and mechanical impact on the crystallization kinetics from rubbery state.

On TMM at isothermal conditions was subjected sample numbered 8, with the following main characteristics:

- spinning speed 1150 *m/min*;
- diameter of the single fiber 44 μm ;
- birefringence $\Delta n \cdot 10^3 = 8$;
- degree of the sample crystallinity 1,7 %

Calorimetric analysis of the heat mechanically modified samples was carried out using a NETZSCH heat-flux calorimeter STA 449 F3 Jupiter (TG/DSC) in static air atmosphere. Temperature calibration was done using the onset melting temperatures of indium, tin, bismuth and zinc, and the energy calibration was based on the heat of fusion of the same metals. Fibers were cut in pieces of less than 1 *mm* and sealed in standard 85 μl platinum pans.

III. METHODS

Birefringence of the studied fibers was measured using a polarizing microscope "Amplival-Pol. D" (Karl-Zeiss Jena), by using of rotatable compensators with a range (0 ÷ 130) λ . The coefficient of the amorphous fiber orientation (f_a) had been established using the Stein's equation [9]. Birefringence due to non uniformity in the fiber form (the so-called effect of Wiener) Δn , usually have values from 0,01 to 0,03 so that in the application of equation (1) it is most often neglected. The value of $\Delta n_a = 0,275$ is taken from the literature [10].

Kinetic studies on the fibers crystallization were carried out using a heat conductive calorimeter type Calvet [11] at isothermal conditions. Interpretation of the results can be performed on the basis of the equation of Avrami [12], which in logarithmic form looks as follows:

$$\lg[-\lg(1-\alpha)] = \lg k_n + n \lg \tau \quad (1)$$

, where:

α - the portion of the substance that is crystallized up to the time τ ;

k_n - constant contained parameters of the nuclei formation and the crystals growth;

n - constant dependent on the type of nuclei formation and the crystals growth.

If the relationship (1) is presented in coordinates: $\lg[-\lg(1-\alpha)]$, $\lg \tau$, graphically can be determined the crystallization parameters k_n and n .

The simultaneous heat mechanical samples modification was carried out using an apparatus created in our laboratory. The device involves a movable cylindrical oven located on the horizontal rails and a setup for the sample deformation reading. The heat-mechanical treatment begins when the

preheated oven was rapidly shifted around the studied PET bundle that was simultaneously stretched with the needed strain stress. The experiment involves annealing of an as-spun PET yarns at temperature of 85^oC closely above its glass transition temperature, without applied stress (0 *MPa*) as well as under well-defined tensile stress of 3 *MPa*.

IV. RESULTS AND DISCUSS

In order to establish the influence of the applied in the fibrillate process mechanical impact on the "cold" crystallization, it was necessary during the calorimetric experiments to preserve the obtained during the fibers formation orientation. With this purpose, the fibers were prepared in two different ways:

- into parts with length of about one millimeter;
- rigidly attached at both ends using special device.

Samples prepared under the first method are able to relax at temperatures lower than the crystallization temperature and at temperatures higher than the glass transition temperature. For the fibers prepared by the second way this option is turned off. Kinetic dependences of the crystallization of fibers prepared under both described above methods are presented in Fig. 1 and Fig.2.

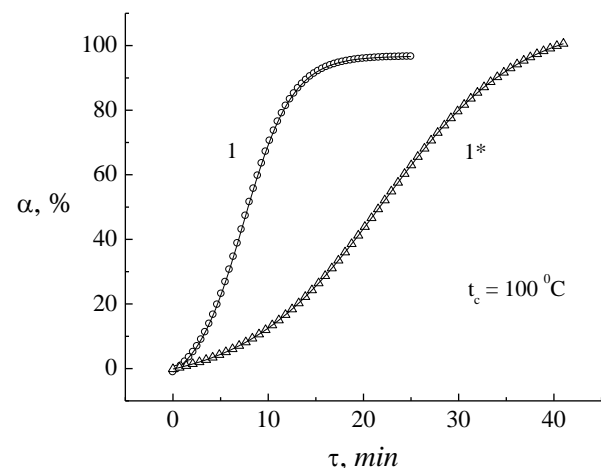


Fig. 1. Kinetic dependencies of crystallization of PET fibers prepared in two different ways: 1 - rigidly attached at both ends, 1* - into parts with length of about one millimeter.

As can be seen from Figs. 1 and 2, the fibers with fixed ends crystallize faster, which was expected because in the fibers with fixed ends are preserved the quasi-crystalline nuclei formed during the fibrillate process. In the fibers prepared on the first way take place simultaneously the processes of crystallization and relaxation of the internal stresses, that affects the crystallization course - compare curves 1 with 1* (Fig.1.) and curves 2 with 2* (Fig.2). In the initial stages of the crystallization process ($\alpha < 0,5$), the rate of this process in the fibers with fixed ends (1 and 2) is larger than the rate at the samples in the free state - comparing curves 1 with 1* and curves 2 with 2*. It is known that during the polymer transition from glassy to rubbery state is defrosted the segment mobility of macromolecules, which allows them to relax and

take more advantageous conformational states. Moreover, arises meta-stability of the existing in the amorphous phase, areas with increased orderliness – begins destruction of these entities that leads to reduction in the amount of the polymer crystallization nuclei. In the fibers with fixed ends the possibility of the frozen stresses relaxation is eliminated. This allows the preservation of the ordered structure formations arising as a result of the applied tensile stress during the fiber forming. The absence of relaxation in the filaments with fixed ends prevents the processes of disorientation in them and thus the destruction of the existing quasi nuclei.

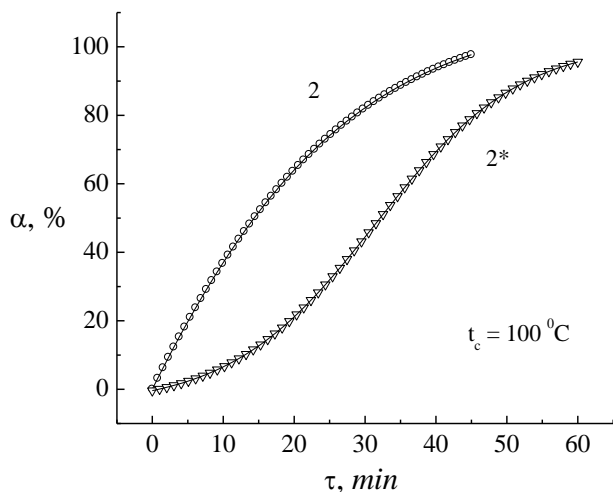


Fig. 2. Kinetic dependencies of crystallization of PET fibers prepared in two different ways: 2 - rigidly attached at both ends, 2* - into parts with length of about one millimeter.

As a result the volume concentration of the crystallization nuclei in the fibers with fixed ends will be greater from that in the objects in a free state, which explains the faster running of the initial phase of crystallization in them. At the end of the crystallization process ($\alpha > 0,8$) we can see (Fig. 1, 2) delay of the crystallization in the samples with fixed ends which leads to reduce in the slope of the kinetic dependencies in comparison with the fibers in a free state. The probable reason for the observed fact is that in the amorphous fibers are kept the frozen stresses occurring during the filaments formation.

The preservation of the fibers length during the crystallization prevents the accompanying process of rearrangement of the macromolecular chain segments at the transition from glassy to rubbery state. For that reason in these samples the volume areas in which the crystallization is hampered is larger.

The energy needed for transferring of a macromolecular segment from the amorphous phase on the surface of the growing crystal will be larger for the fibers with fixed ends. As a result the growth of the crystal formations in these areas is slowed or completely stopped.

In the following experiments were tested only fibers with fixed lengths. In Fig. 3 are shown kinetic dependencies of the crystallization of fibers with different linear densities.

Samples are produced at one and the same speed of fibrillate and cooling air but with different linear densities (Tabl. 1).

As can be seen from Fig. 3 the relationship between the crystallization rate and the fibers linear density is complex. Possible reason for the observed effect is the influence of the downtime in the fibrillate container as well as the applied during the fibers formation mechanical stress.

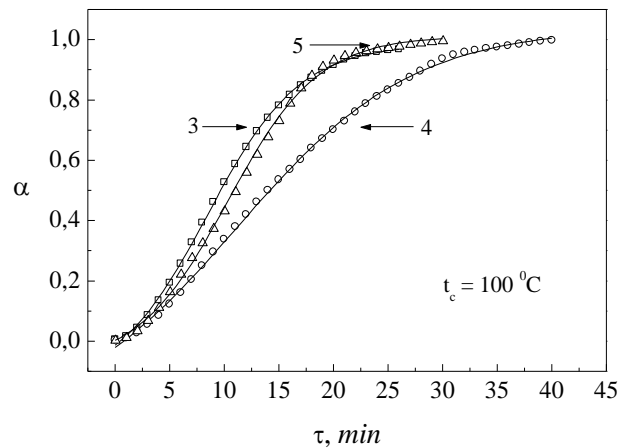


Fig. 3. Kinetic dependencies of crystallization of samples 3, 4 and 5 produced at one and the same speeds of fibrillate and the cooling air but with different linear densities: 3) $\rho_l = 180 dtex$, 4) $\rho_l = 267 dtex$, 5) $\rho_l = 365 dtex$.

Role of the mechanical stress consists in storing of the existing quasi crystallization nuclei and the residual (frozen) internal stresses, usually existing in the filaments close to various defects in them. If these tensions no relax at α -transition, the crystallization process in the areas of frozen tensions can be hampered and even completely stopped. The processing of the kinetic curves using the Avrami's equation is given in Fig. 4 and it allows establishing of some basic dependencies about the parameters of the crystallization process.

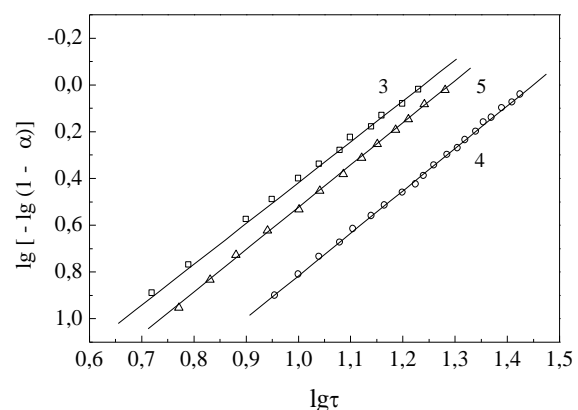


Fig. 4. Dependence of $lg [-lg (1 - \alpha)]$ from $lg \tau$ for crystallized PET fibers produced at one and the same velocity of fibrillate and the cooling air but with different linear densities.

Were obtained parameters of the crystallization process (Table 2) as well as some basic relations. As follows from Tabl. 2, the parameter n in the Avrami's equation ranged from 1,70 to 1,94. Considering the obtained values of the parameter n and in accordance with the formulated on the basis of theoretical and experimental analyze conceptions [13, 14], it can be assumed that the growth of the crystal formations is predominantly one-dimensional (cylinders) and two-dimensional (lamellas).

Table 2. Data from isothermal crystallization kinetics of PET fibers obtained by Avrami's equation.

N	$t_c, ^\circ C$	$\tau_{0,5}, min$	$\tau_{0,9}, min$	n	$-lg k_n$
3	100	9,8	18	1,79	1,73
4	100	15,0	29	1,79	1,87
5	100	10,0	18	1,94	1,87
6	100	10,5	20	1,79	1,77
7	100	11,3	23	1,70	1,88

where: N - sample number;
 $t_c, ^\circ C$ - crystallization temperature;
 $\tau_{0,5}, min$ - half time of crystallization;
 $\tau_{0,9}, min$ - time for realization of 0,9 of the crystallization;
 k_n - parameter in the Avrami's equation.

Fractional values of n can be explained by simultaneously realization of crystallization and improving the orderliness in the crystalline regions, i.e., process of secondary crystallization which for PET is highly expressed. It should be emphasized that the values of the parameter n depend on several factors such as the crystallization temperature, the shape and size of the sample, the heterogeneous influence of the cuvette walls, the examination method and others. Therefore, in order to draw clear conclusions about the morphology of the crystal formations is needed additional micro and macro information about the crystallization mechanism and the nature of the occurring in the crystallized PET fibers structural changes. Taking into account that the calorimetric technique is sensitive predominantly to the crystal growth [14], in the present case must be concluded that the crystallization is realized by a heterogeneous mechanism of nuclei formation. Therefore, the structure formation in the studied borders of variation of the fibrillate parameters is to such an extent developed that all the centers of crystallization arise on ready polymer nuclei.

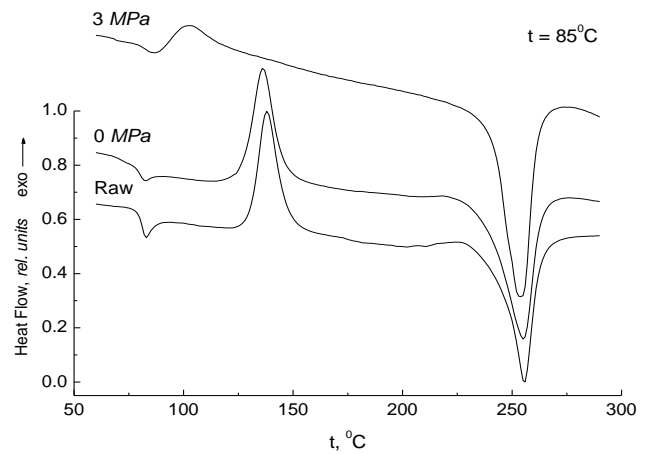


Fig. 5. DSC curves of untreated sample (number 8), heat mechanically modified without and under strain stress at temperature of 85°C (the curves are shifted vertically for clarity).

With purpose to clarify the role of the temperature and tension stress values on the structure development in amorphous PET yarns (sample number 8), were carried out thermal deformation experiments at constant temperature of 85°C.

The experiment involves the bundle annealing during twelve minutes at temperature of 85°C without loading. In the next experiment PET yarns were subjected to annealing during ten minutes without strain stress and then loaded during two minutes with tensile stress of 3 MPa at the same temperature.

The structural analyses of the amorphous PET yarns heat-mechanically treated at the above-described conditions were carried out using differential scanning calorimetry and the obtained results are present in Fig.5.

Clearly expressed cold crystallization (Fig. 5) of the untreated and samples modified at 85°C is due to the presence of disordered and unstable structure in the unoriented amorphous fibers. In such structures, heated up to temperatures around 130 °C - 140 °C in the absence of external stress (0 MPa) is released the segment mobility in macromolecules, which is a precondition for the running of cold crystallization. Very interesting is the DSC curve obtained under loading of 3 MPa and temperature of 85 °C (Fig. 5) where we can see losing of the effect of the samples cold crystallization at temperatures around 130 - 140 °C.

The cold crystallization peak at about 140°C disappears but appears a new smaller peak at much lower temperature around 110 °C, immediately after the transition from glassy to rubbery state. Probably the tensile stress further destabilizes the structure and facilitates the glass transition process.

V. CONCLUSIONS

The "cold" crystallization of amorphous PET fibers prepared in two different ways as well as with different linear densities was studied.

It was investigated the influence of the applied during heat mechanical modification tensile stress on the running of the "cold" crystallization of uniaxially oriented PET.

It was found that the applied upon formation mechanical impact has a significant influence on the crystallization kinetics from rubbery state.

Values of the parameter n in the Avrami's equation allow assuming that the growth of the crystal formations is predominantly one-dimensional (cylinders) and two-dimensional (lamellas).

The observed results can be explained by the role of mechanical stress in the processes of preservation in the fibers of quasi nuclei as well as areas with frozen internal stresses.

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REFERENCES

1. D. R. Salem, Structure Formation in Polymeric Fibers, Carl Hanser Verlag GmbH & Co. KG, 580, 2001. Available:<http://www.gettextbooks.com/bz/search/?isbn=David+A+Hanser&pg=2>.
2. H. H.A. Hergeth, Synthetic Fibers, Carl Hanser Verlag GmbH & Co. KG, 904, 1999. Available: <http://www.scribd.com/doc/47414580/Synthetic-Fibers#scribd>.
3. Van der Meer D.W., Structure-Property Relationships in Isotactic Polypropylene, Ph. D. thesis, Twente University Press, 2003; Available: <http://doc.utwente.nl/40660/1/t000004f.pdf>.
4. S Ran, Z Wang, C Burger, B Chu, BS Hsiao, Mesophase as the Precursor for Strain-Induced Crystallization in Amorphous Poly(ethylene terephthalate) Film, *Macromolecules*, 35 (27), pp 10102–10107, 2002; Available: <http://pubs.acs.org/doi/abs/10.1021/ma021252i>.
5. J. Scheirs, T. E. Long (Eds.), Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters, John Wiley & Sons, 784, 2005; Available:http://www.google.bg/books?hl=bg&lr=&id=ZgXgZ5vfxTkC&oi=fnd&pg=PR5&dq=Structure-Property+Relationships+poly+%2C+ethylene+terephthalate%29+%28PET%29+fibers+and+films&ots=DrEFewmbIo&sig=JVYkJTkWOT6XxRTOguFTT4gjPrM&redir_esc=y#v=onepage&q&f=false
6. V.B. Gupta, and Z. Bashir. (2002) PET Fibers, Films, and Bottles: Sections 5–7, in Handbook of Thermoplastic Polyesters: Homopolymers, Copolymers, Blends, and Composites (ed S. Fakirov), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, FRG. doi: 10.1002/3527601961.ch7b. Available:<http://onlinelibrary.wiley.com/doi/10.1002/3527601961.ch7b/summary>.
7. D. Kawakami, B. S. Hsiao, S. Ran, C. Burger, B. Fu, I. Sics, B. Chu, and T. Kikutani, Structural formation of amorphous poly(ethylene terephthalate) during uniaxial deformation above glass temperature, *Polymer*, Vol. 45(3), February 2004, Pages 905–918. Available:<http://www.sciencedirect.com/science/article/pii/S0032386103010747>.
8. V. Velev, A. Popov, P. Kyurkchiev, L. Veleva, and R. Mateva. Thermo - mechanically modification of amorphous polyester fibres: II. Calorimetric investigations, *Journal Scientific and Applied Research*, vol.4, 229-234, 2013. Available:<http://www.associationsar.com/journal-scientific-and-applied-research/>.
9. R. S. Stein, and G. L. Wilkes. (1975). Structure and properties of oriented polymers. I. M. Ward (ed.). Ch.3. Physico-chemical approaches to the measurement of anisotropy. Available:http://link.springer.com/chapter/10.1007/978-94-010-9803-8_3#page-1.
10. D. W. Van Krevelen, Properties of polymers: correlations with chemical structure, Elsevier Publ, p. 427, 1972. Available:<http://www.elsevier.com/books/properties-of-polymers/van-krevelen/978-0-08-054819-7>.
11. E. Calvet, H. Prat. Recent Progress in Microcalorimetry, MacMillan, New York, 1963. Available:http://www.google.bg/books?hl=en&lr=&id=ojUXBQAAQBAJ&oi=fnd&pg=PP1&dq=Calvet+E.,+Prat+H.,+Recent+Progress+in+Microcalorimetry,+MacMillan,+New%09York,+1963&ots=1QiIKHuyec&sig=WpwSVrwoXwWMn-kORH6XqzdyTdm&redir_esc=y#v=onepage&q=Calvet%20E.%2C%20Prat%20H.%2C%20Recent%20Progress%20in%20Microcalorimetry%2C%20MacMillan%2C%20New%09York%2C%201963&f=false.
12. M.J. Avrami. *Chem. Phys.*, 7, 1103-1118, 1939.
13. Wunderlich B., *Macromolecular Physics*, Vol. 2, Academic Press, p. 574, 1976. Available:<http://onlinelibrary.wiley.com/doi/10.1002/crat.19770120121/abstract>.
14. J.K. Godovskiy *Teplofizicheskie metody issledovaniya polimerov*, M., Himia, p. 216, 1976.