We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

4,800
Open access books available

122,000
International authors and editors

135M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities

CLARIVATE ANALYTICS BOOK CITATION INDEX INDEXED

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

5

Heat – Mechanically Induced Structure Development in Undrawn Polyester Fibers

Valentin Velev[1], Anton Popov[2] and Bogdan Bogdanov[2]
[1]*Konstantin Preslavsky University, 9712, Shumen,*
[2]*University "Prof. Dr. Assen Zlatarov", 8000, Burgas,*
Bulgaria

1. Introduction

The performances of the non-isotropic polymer systems strongly depend on their super molecular structure (Wu et al., 2001; Shabana, 2004; Keum & Song, 2005; Ziabicki & Jarecki, 2007; Sulong et al., 2011).

The wide application and consequently higher production of flexible chain fiber forming polymers, in particular poly (ethylene terephthalate) (PET) is due to the possibility of the heat mechanical modification to obtain highly modular and high strength materials from them (Llana & Boyce, 1999; Bai et al., 2000; Dupaix & Boyce, 2005; Guzzato et al., 2009). PET is an essential engineering polymer with properties strongly depending of the degree of crystallinity and the perfection of crystal phase, too**.** The effects of some basic parameters of the heat mechanically treatment such as strain force extension rate and temperature on the structure development of PET have been studied using different methods as differential scanning calorimetry (DSC), wide angle X-ray scattering (WAXS) (Kong & Hay, 2003; Zhang et al., 2004; Karagiannidis et al., 2008; Raabe et al. 2004), dynamic mechanical analysis (Ma et al., 2003), laser irradiation (Wijayathunga et al., 2007) and other.

The optimal performance of the high-temperature orientation modification is a complicated and still not sufficiently well studied process. The simultaneous mechanical and thermal modification however is extremely complex phenomenon occurring on the basis of statistical probabilistic processes, as are also the possible results from it. In this sense the results from variations of heat mechanical modification are unpredictable not unique and often very different, contradictory and unexpected. Moreover for each specific object and purpose exist additional conditions, and therefore needed special study of orientation thermal treatment for the obtaining of best mechanical performance. If the samples simultaneous heat mechanical modification (SHMM) is carried out without accounting and control of a number of events, processes and parameters the results can easily prove contrary to the expectations. And to make the results from STMM easily predictable, susceptible to control and allowing obtaining of materials with improved predefined wanted properties it is necessary in depth study on the nature, mechanism and kinetics of the justifying processes and the relationship between them. Therefore the study of these processes is a permanent "ever green" interest in the polymer physics. One of the most interesting from this point of view objects are polyethylene terephthalate fibers. There are varieties of investigations of the affects of the thermal and mechanical treatments on the

relaxation and phase transitions in PET fibers. In some of them as-spun filaments are subjected to thermal treatment at constant temperatures without stress (Betchev, 1995; Bai et al., 2000) as well with application of tensile force (Zhang et al., 2004; Sharma et al., 1997).
Important is the answer of the question on what schemes and under what conditions should be conducted SHMM to maximize the orientation effect at the expense of minimal object destruction at high temperature uni-axial deformation. To obtain definite answer to a similar question is necessary a multifactorial planning and carrying out of massive diverse experiment. The preliminary suggestive for a range of the possible conditions of withdrawal experiments are impressive much.
For initial approbation of the behavior of the specific object to the complex SHMM we accepted the technologically real (and maximum possible) temperature interval from 20 ^0C to 200 ^0C and sufficient as a beginning, a range of orientation tensions from 0 *MPa* to 1.7 *MPa* with enough good resolution of 0.1 *MPa.* The experiment was carried out in combination of gravitational loading of the samples at a linear heating in line with the coefficient of fibers thermal conductivity average heating rate of 3.5 $^0C/min$.
The dependence of the relative deformation from the tensile load values showed an initial intensive growth of the gradient of its increase up to strain stress value of 0.7 *MPa*, probably because of intensive destruction of macromolecular segments in the studied samples. A similar information was emitted and from the other performed structural analyses. The results led us to include new elements into the idea of the experiment and in particular to eliminate the adverse action of destructive tensions above those causing bundle deformation 290 %. Results showed that above loading of 1.2 *MPa* the relative samples elongation falls below the above mentioned value of the bundle reletive elongation and is no need to limit it.
In the new version the thermal deformation experiment was carried out without limitation of the bundle extension at combination of the samples gravitational loading in the range from 0 *MPa* to 3.0 *MPa* with a good resolution of 0.12 *MPa* at a linear heating with the same heating rate (3.5 $^0C/min$) and again in the temperature range from 20 ^0C to 200 ^0C. The structural tests of the SHMM samples in this preliminary experiment showed the disadvantages of the wide temperature range. Therefore, were tested modifications of PET fibers at well defined temperatures of 80 ^0C, 85 ^0C, 90 ^0C and 95 ^0C in the temperature range just above the glass transition temperature of the objects defined in our other investigations of 74 ^0C. The samples were loaded gravitationally (with different orientation tensions with initial values of 40 *MPa*, 80 *MPa* and 120 *MPa*, varying during the deformation downloading) as well as with constant rate of loading 0.1 *m /min* up to various relative elongations of 20 %, 40 % and 60 %.

2. Experimental

2.1 Materials

PET undrawn multifilament yarns produced by melt spinning on the industrial spinning installation Furnet (France) have been selected as a precursor samples. The technological parameters and basic characteristics of the original filaments are shown in Table 1.
It can be seen from the Table 1 that within the group of the selected samples have both amorphous and partially crystalline filaments. 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.

Sample	V_L, *m/min*	d, *μm*	Δn	α, %
A	1100	44.0	0.006	0.8
B	1150	44.0	0.008	1.7
S1	2280	14.5	4.32	23.7
S2	2805	13.0	5.35	28.8
S3	4110	11.0	5.82	36.9

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

2.2 Methods

2.2.1 Simultaneous heat-mechanically modification (SHMM)

Different versions of simultaneous thermal and mechanical treatments of the studied yarns were performed using devices constructed and produced in our laboratory.

The first version of SHMM includes linear samples heating from room temperature up to 200 ^0C accompanied by applied to the fiber bundle strain stress. The heating rate was 3.5 ^0C/min. The used gear consists of a vertically located cylindrical furnace, which moves around a rolled up PET bundle fixed by special holders and subjected to needed tensile stress. The temperature reaching of 200 ^0C was followed by a simultaneous termination of the tensile stress and the yarn remove from the oven at room temperature. Highly supercooled i.e. deep tempered and isothermally crystallized at temperatures close to the melting temperature thin films PET, used for forming of the investigated fibers are shown in Fig. 1a, b, c and d respectively.

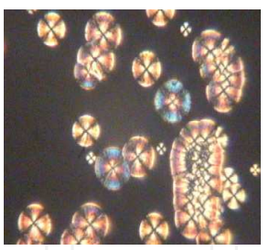


Fig. 1. a.

Fig. 1. b.

Fig. 1. c.

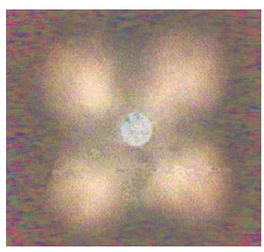


Fig. 1.d.

Fig. 1. a, b - polarization microphotography; Fig.1. c, d - diffraction pictures.

In the second variant of SHMM the investigated filaments were subjected to tensile stresses with different values under certain constant temperatures. 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 four different temperatures in a narrow temperature range from 80 ^0C to 95 ^0C closely above its glass transition temperature while they are subjected to a well-defined tensile stress.

In the next version of SHMM the studied PET filaments were subjected to extension at a constant speed and constant temperatures in the same temperature range from 80 ^0C to 95 ^0C. The structural characterizations of the studied fibers after the above described heat-mechanical treatments were realized using differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS) measurements.

2.2.2 Differential scanning calorimetry (DSC)

Part from the calorimetric studies was performed on a Mettler-Toledo heat-flux calorimeter DSC 820 with liquid nitrogen accessory. The furnace was purged with nitrogen at a flow rate of 80 *ml/min*. 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 μl aluminum pans.
Another part of the calorimetric analysis 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.

2.2.3 Wide-angle X-ray scattering (WAXS)

The fiber structure was studied by wide-angle X-ray scattering (WAXS), too using two different apparatus namely:

1. Diffractometer HZG 4 (Freiberger Präzisionsmechanik, Germany) and Ni-filtered Cu K_α radiation with wavelength λ = 1.5418 Å. Equatorial scattering was monitored in transmission mode. The fiber samples were prepared as a layer with 2 *mm* thickness and 10 *mm* width, and mounted on the sample holder of the diffractometer;
2. Diffractometer URD - 6 (under license of SIEMES) of the company "Freiberger Präzisionsmechanik" (Freiburg im Breisgau, Baden-Württemberg, Germany). Used is β-filtered with Ni-filter *Cu* K_α radiation with a wavelength λ = 1.5418 Å.

3. Results and discuss

3.1 Investigation of amorphous PET fibers simultaneous heat - mechanically modified at linear heating and constant strain stress values

The study of the relationships between the SHMM modes and subsequent structural development in the PET filaments includes different versions of experiments.
In the first one amorphous fibers marked as sample A (Table 1) were subjected to SHMM at conditions as follows: Heating with linear increasing of the temperature in a wide range from 20 ^0C to 200 ^0C with heating rate of 3.5 $^0C/min$ under constant strain stress from 0 *MPa* to 1.7 *MPa* (increasing step of 0.1 *MPa*). It should be noted the additional experimantal conditions for some of the samples. The extension of the yarns loaded with tensile stress from 0.7 *MPa* to 1.2 *MPa* was limited up to 290 %. Moreover after the reaching of the limited bundle length the sample continues to be heated up to 200 ^0C.
The length changes of the investigated yarns were registered during their combined heat mechanical treatment. As expected the filaments retain initial dimensions in the temperature range from room temperature up to 75 ^0C. In this temperature interval samples remain in glassy state and the structural changes are negligible.

The changes of the bundle dimensions depend on the applied strain stress level considerably and strongly at temperatures between 80 ^0C and 130 ^0C. The observed dependence can be explained with the sample transition from glassy to rubbery state. The deformation behaviour demonstrated by the samples at a level of applied tensile stress up to 0.7 *MPa* is expectable. Experiments showed a decrease of the final bundle length at small stress values. The filaments shrinkage can be logically explained with the process of frozen internal stresses relaxation in the samples at the temperature range of the transition from glassy to rubbery state.

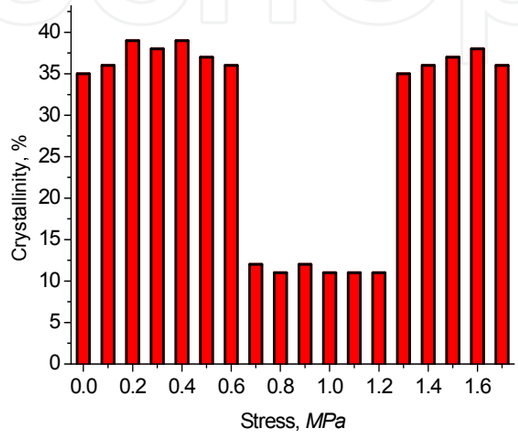


Fig. 2. Degree of crystallinity of PET fibers (sample A) depending on the SHMM conditions.

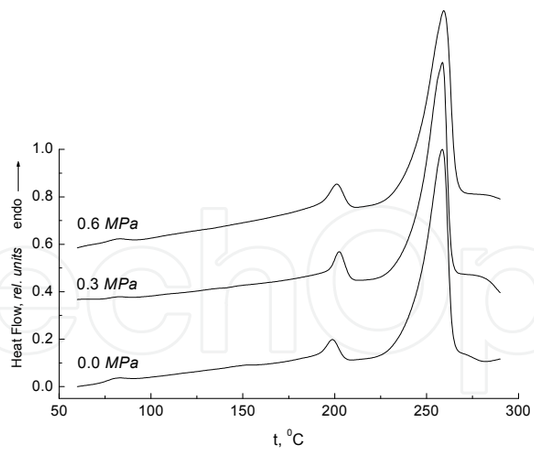


Fig. 3. Representative DSC curves of partially crystalline PET fibers (the curves are shifted vertically for clarity).

Unexpected and quite interesting was the deformation behavior of the bundles subjected to stresses in the range from 0.7 *MPa* to 1.2 *MPa*. As it was mentioned above the extension of the samples tested with tensile stress from 0.7 *MPa* to 1.2 *MPa* was limited up to 290 %. The observed deformation behavior strongly corresponds to the so-called fluid-like deformation. The bundle length was kept constant when the extension reached 290 %.

It is important to underline that such an intensive fluid-like deformation process was not observed for the samples subjected to strain stresses above 1.2 *MPa*. The received experimental data showed a decrease of the elongation with the stress values increasing.
Structural changes in the PET fibers as a consequence of the simultaneous thermal and mechanical treatments were studied using DSC, wide angle X-ray scattering (WAXS) and density measurements. The changes of the samples degree of crystallinity estimated on the basis of the DSC data depending of the strain stress values are presented in Figure 2. As it can be seen from Figure 2, some of the studied specimens are semi-crystalline while others are practically amorphous. The comparison with the SHMM conditions shows that the samples subjected to tensile stresses in the intervals from 0 *MPa* to 0.6 *MPa* and from 1.3 *MPa* to 1.7 *MPa* posses semi-crystalline structure. At the same time, the filaments with limited ability for extension treated in the stress interval from 0.7 *MPa* to 1.2 *MPa* are practically amorphous. Density measurements and WAXS diagrams proved the same crystallization properties of the studied PET specimens, too.

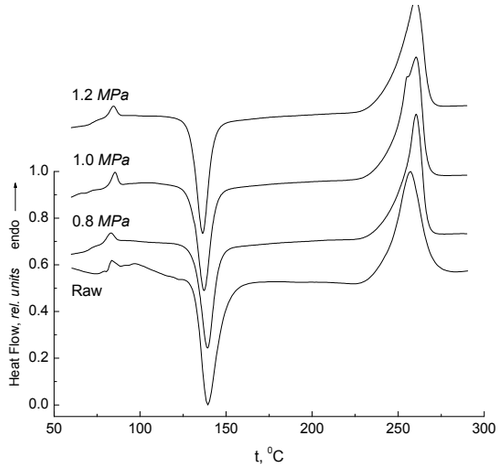


Fig. 4. Representative DSC curves of untreated and amorphous PET fibers (the curves are shifted vertically for clarity).

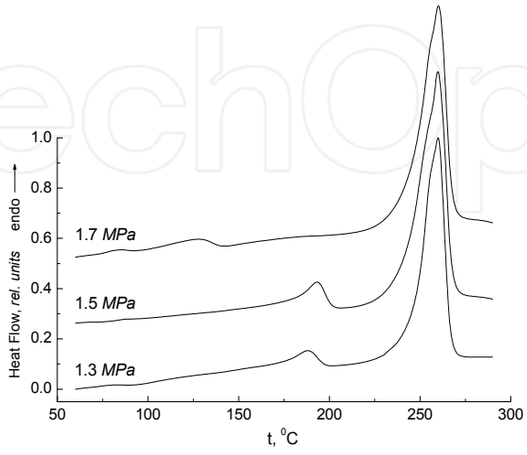


Fig. 5. Representative DSC curves of partially crystalline PET fibers (the curves are shifted vertically for clarity).

Representative DSC thermograms of partially crystalline and amorphous PET fibers subjected on heat mechanically treatments under the above decriebed conditions are present on Fig. 3, 5 and 4 respectively. As expected the DSC curve of the raw amorphous sample show pronounced cold crystallization and melting peaks. Unlike the untreated fibers, DSC thermograms in Fig. 3 and Fig. 5 show only preliminary melting and melting endotherms without cold crystallization peaks. Moreover the peak temperature of the premelting and melting endotherms in Fig. 3 smoothly shifts to higher temperatures with stress increasing. Multiple melting peaks in PET pellets (Kong & Hay, 2003) and filaments are observed and studied in earlier investigations. Similar to the raw PET filaments the DSC curves presented on Fig. 5, of the bundles subjected to SHMM at limited extension show glass – rubber transition, cold crystallization and melting peaks. Also it can be seen from Fig. 5 that the tensile stress increasing leads to fluently displacement of the cold crystallization peak to lower temperatures and to sliding to higher temperatures of the melting peak.

In conclusion it can be said that the heating with linear temperature rise, accompanied by application of external strain stresses strongly influences the nature of structural rearrangements in the investigated uncrystallized PET filaments. The observed fibers net deformation at tensile stress values less than 0.7 *MPa* and more than 1.2 *MPa* can be explained with a faster crystallization of the amorphous PET bundle from rubbery state, as a consequence of the influence of the applied tensile stress. The fluid-like deformation process predominates when the applied stresses are from 0.7 *MPa* to 1.2 *MPa*. It was found that after heating up to 200 ^{0}C amorphous PET filaments could preserve the amorphous state when the applied external strain stresses are in the same range.

At the same time questions having fundamental and practical aspects remain without clear answer and namely: What is the role of the restrictions and mechanical stress in obtaining of such qualitative different results? What would be the bundle deformation behaviour if there were no restrictions? What is the influence of the regime of heat treatment?

With purpose to clarify the role of the applied strain stress on the fibers structure development it was interesting to realize the above-described experiment without the mentioned limitations.

№	σ, *MPa*	№	σ, *MPa*
1	0.00	14	1.56
2	0.12	15	1.68
3	0.24	16	1.80
4	0.36	17	1.92
5	0.48	18	2.04
6	0.60	19	2.16
7	0.72	20	2.28
8	0.84	21	2.40
9	0.96	22	2.52
10	1.08	23	2.64
11	1.20	24	2.76
12	1.32	25	2.88
13	1.44	26	3.00

Table 2. Values of the applied strain stress during the SHMM.

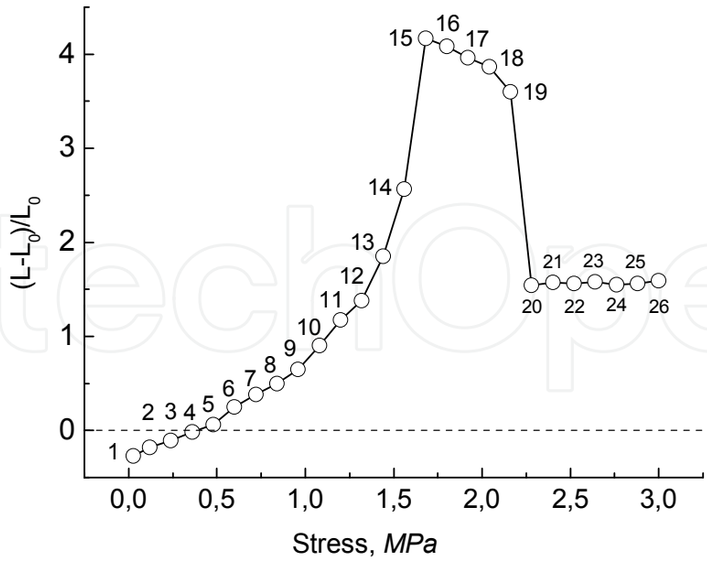


Fig. 6. Relative change of the bundle length (sample B) depending on the tensile stress values (here L_0 and L are the initial and final fibers length respectively).

In the next thermal deformation experiment amorphous PET fibers named sample B (Table 1), were linearly heated with rate of 3.5 $^0C/min$ from 20 ^0C to 200 ^0C. During the filaments heating they were subjected to constant tensile stress in a wider range from 0 *MPa* to 3.0 *MPa* (increasing step of 0.12 *MPa*, Table 2) without restrictions of the bundle deformation. The bundle length obtained after the heat mechanical treatment as a function of the applied strain stress is presented in Figure 6, where the dashed line marks the initial sample length.

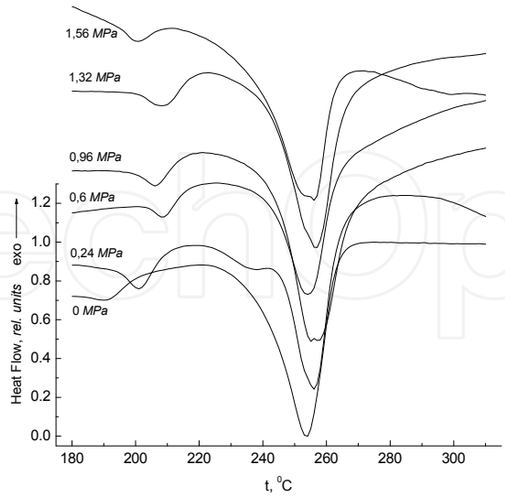


Fig. 7. Representative DSC curves of melting peaks of SHMM PET fibers from the first group (the curves are shifted vertically for clarity).

The deformation behaviour demonstrated by the samples at a level of applied stress up to 1.68 *MPa* is expectable. Experiments showed entropy shrinkage of the first four samples at

small stress values up to the level of 0.36 *MPa*. The filaments shrinkage is a consequence of the frozen internal stresses relaxation at the temperature range of the sample glass transition. It could be supposed that the applied (external) stresses in our experiments up to value of 0.36 *MPa* do not compensate the emerging shrinkage forces.
Significant sample extension is stimulated by the stress increasing from 0.36 *MPa* up to 1.68 *MPa*. As it can be seen from the results presented in Figure 6 only increment of the final bundle length can be observed in this case. Obviously such of dependence can be detected when the applied strain stress is higher than the potential entropy shrinkage forces in an amorphous uniaxially oriented sample within the temperature range of glass transition. The received experimental data strongly corresponds to the so-called fluid-like deformation. At stress value of 1.68 *MPa* is reached more than fivefold bundle monotonic download. This is the maximum achievable prolongation by used method and conditions of SHMM.

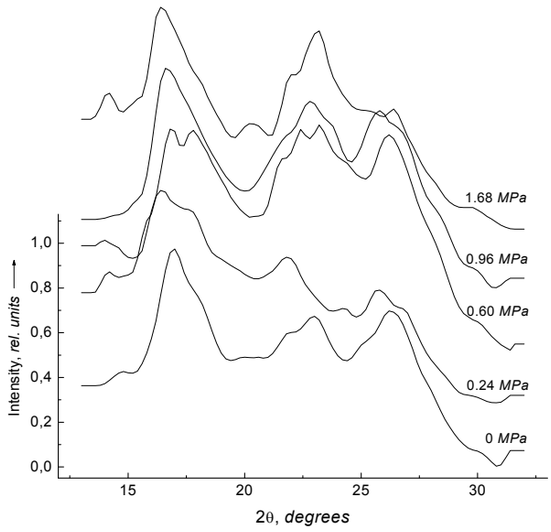


Fig. 8. Representative wide-angle X-ray scattering curves of SHMM PET fibers from the first group (the curves are shifted vertically for clarity).

Much more interesting and non-expectable is the deformation behaviour of the samples subjected to stresses in the range from 1.8 *MPa* up to 3.0 *MPa*. As it is illustrated on the Figure 6 the increasing of the tensile stress values from 1.68 *MPa* to 2.16 *MPa* leads to gradually decrement of the final bundle length. A significant reduction of the net deformation occurs at the stress levels of 2.28 *MPa* and more. Despite of the rise of the applied stress values the samples extension decreases considerably. Moreover the change of the tensile stress does not affect the deformation behaviour of the last seven yarns. Their ultimate length is more than twice less than the maximum achieved nder stress value of 1.68 *MPa.* Depending on the deformation behavior the investigated samples can be conditionally divided into three groups as follws. First one includes the bundles with numbers from one to fifteen. In the second one are the yarns from sixteen to twenty, and the third group includes the last six specimens which despite of the stress values increasing are extended less. Structural rearrangements occurred in the PET fibers as a result of the SHMM were studied using DSC and WAXS. It should be underlined that in contrast to the previous experiment the performed structural analysis show that all of the heat mechanically modified PET filaments are partially crystalline. Representative DSC curves of melting

peaks of the above defined three groups of samples are present in Figures 7, 9 and 11. As it is visible from Figure 7 during the SHMM are formed three types of structures with three different types of perfection and stability. Depending on the melting temperature can be distinguished entities with a higher level of order forming an easy fusible mesophase, middle crystalline phase with lower perfection and main crystalline phase. Samples heating whether without load, forms easy fusible structure, which melts at about 190 ^0C. Just small increasing of the stress values leads to the structure improvement and stabilization and to the moving of the mesophase melting temperature to higher temperatures up to around 210 ^0C - 215 ^0C. The intermediate crystalline phase with lower perfection is observed as splitting of the main melting peak which visible migrate to the higher temperatures. With the tensile stress increasing the first melting peak as well as the main melting peaks are deformed with a tendency to split. The melting peaks also fluctuate around an average melting temperature significantly higher in comparison with the obtained without load. The observed shifting of the endo effects at higher temperatures possibly is a consequence of more organized structure formation due to the applied orientated pulling load. Only the sample from this group loaded with stress of 1.68 *MPa* show a slightly different melting behavior.

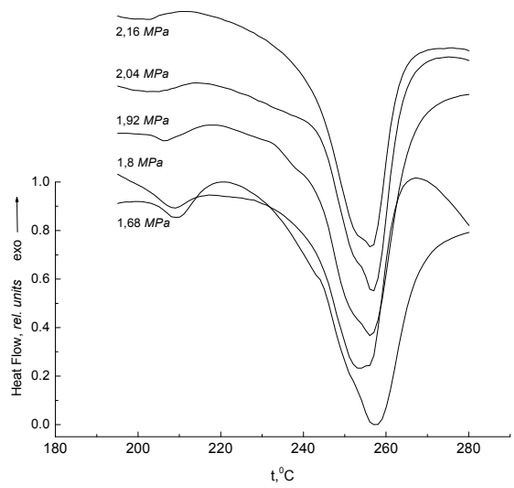


Fig. 9. Representative DSC curves of melting peaks of SHMM PET fibers from the second group (the curves are shifted vertically for clarity).

Representative wide-angle X-ray scattering curves of SHMM PET fibers from the above defined three groups of samples are present in Figures 8, 10 and 12. The diffraction curves are presented to illustrate the change in the fibers degree of crystallinity and orientation with the samples load increasing as well as their compliance with the DSC curves of the same objects for comparison of the structural information from the both methods wich are respectively geometric and energetically-structural sensitive. The first group of samples is characterized by a monotonic, although nonlinear elongation increase with the strain stress increasing up to the specimen with number 15 (Fig. 6). As is evident from Fig. 8, with the load increasing within this group the intensity distribution in the diffraction pattern shows noticeable changes with the stress increase, which is evidence for the significant structural reorganization without strict consistent trend observed in a specific type of amendment.

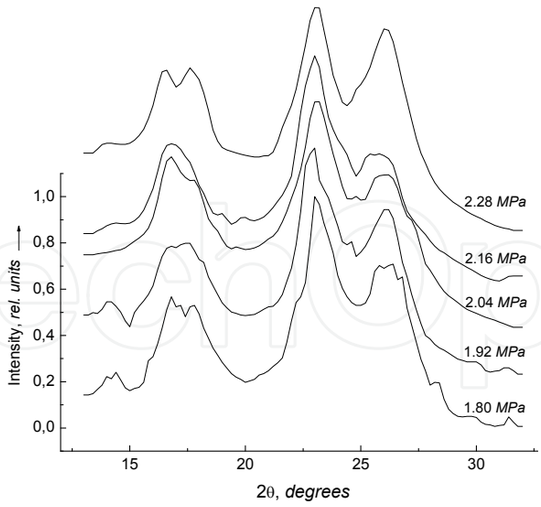


Fig. 10. Representative wide-angle X-ray scattering curves of SHMM PET fibers from the second group (the curves are shifted vertically for clarity).

Representative DSC curves of melting peaks from the second group of samples are given in Figure 9, where is observed a tendency on clearing of any thermo-effects with increasing of the strain stress values. That could be explained reasonably from viewpoint of the model for the homogenization of the structure at medium load values and respectively maximum deformation (Fig. 6). The samples deformation behavior corresponds to heat mechanicaly modified fibers stretched up to position in which the carrying are the most widespread fractions in the amorphous regions according to the normal Gaussian distribution. It is logically that the orientation processes at this group to be most effective with predominance of the orientation processes over destructive.

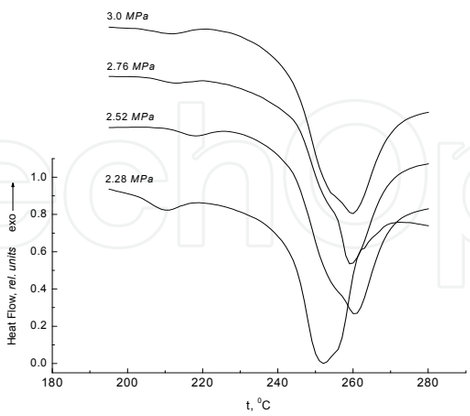


Fig. 11. Representative DSC curves of melting peaks of SHMM PET fibers from third group (the curves are shifted vertically for clarity).

In the second group of WAXS curves (Fig. 10) occurred more stable trend of increase in the intensity of the difraction radiation from improved crystalline and oriented regions in the

samples. The DSC curves from the same group (Fig. 9) also showed a stable trend of deviation of the melting process to higher temperatures which confirms the suggestion for improvement of the crystalline phase. The same is valid and for the oriented amorphous regions. As from the diffraction and DSC curves, as well as from the stress - deformation dependence is confirmed the assumption for additional objects orientation allowing improvement of the crystalline phase and the supporting fraction in amorphous sections, which leads up to decrease in the total relative fibers deformation.

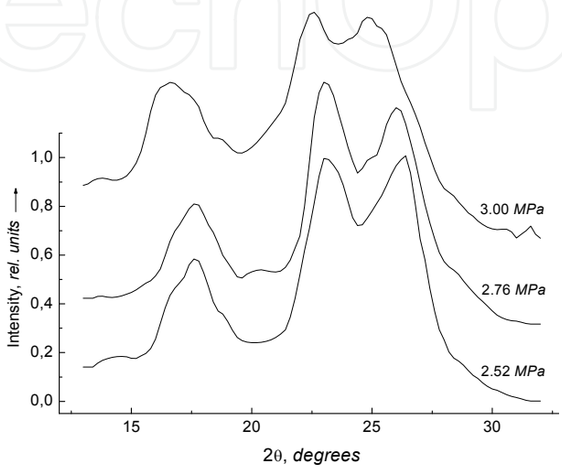


Fig. 12. Representative wide-angle X-ray scattering curves of SHMM PET fibers from third group (the curves are shifted vertically for clarity).

The DSC thermograms of the samples from the third group are present in Figure 11. It can be seen that with the tensile stress increasing endo peaks shift to lower temperatures. And it is valid for both before melting and the main melting processes. The most likely reason for the observed effect is that this third group of samples was withdrawn most suboptimal, with a predominance of destructive processes over the orientation. As a result, the obtained structure is mechanically and thermodynamically unstable, with the lowest density and perfection and therefore melts most easily at lower temperatures. As in Figure 9 as well as in Figure 11 are seen beginnings of split of the main melting peaks. The reasons for the splitting of the melting peaks may be different. In this case, at this type of heat mechanically fibers modification, the splitting occurs most probably due to structural reorganization during the melting process.

With the strain stress increasing at the samples with numbers from 20 up to 26 in which the relative fibers deformation almost does not change (Fig. 6) the intensity of the diffraction reflections significantly increase (Fig. 12). Probably for the account of low elastic deformation is realized a significant improvement of the crystalline phase on the surface of the lamellae or in the newly oriented regions. The exception occurs only in the sample subjected of the biggest tension stress of 3.0 *MPa*, where the intensity of the diffraction pattern falls strongly. Perhaps the increased destruction of separate fractions of macromolecular segments partially distorts the degree of the orderliness in the polymer system. At the same time the indestructable part of additional downloaded segments further improves their arrangement so that is realized more detailed infrastructure of

distribution of the intensity of the powder diffraction pattern. The thermal curves (Fig. 11) show logically enhancement of the high temperature melting fractions with the tension stress increasing, as well their visible split.

On the basis on the carried out structural investigations of amorphous PET fibers simultaneous heat - mechanically modified at isothermal conditions and constant strain stress values it can be make the following conclusions: The mechanical strain force applied simultaneously with the linear heating of the studied PET yarns affects significantly the deformation behaviour and samples crystallization kinetics. Moreover in contrast to the results obtained in the first experiment, all of the so treated specimens are partially crystalline. The role of the tensile stress in the adjustment of the interacting processes of the fluid like deformation and stress-induced crystallization clearly reveals in the ultimate samples deformation. At stress values from 1.56 *MPa* to 2.16 *MPa* predominates the fluid like fibers extension, while the further stress increasing leads to the earlier crystallization start and thereby to decrease of the final fibers length.

3.2 Investigation of amorphous PET fibers simultaneous heat - mechanically modified at isothermal conditions and constant strain stress values

The glass transition temperature of the amorphous sample B (Table 1) was determined of 74 ^0C in our previous work. It was very interesting to follow the influence of SHMM on the structural development of studied samples in the transition temperature range between the glassy and rubbery fibers state.

With purpose to clarify the role of the temperature and tension stress values on the structure development in amorphous PET yarns, were carried out thermal deformation experiments at constant temperatures in a narrow temperature range from 80 ^0C to 95 ^0C. The experiment involves annealing of an as-spun PET bundles at temperatures of 80 ^0C, 85 ^0C, 90 ^0C and 95 ^0C accompanied by precisely defined tensile stresses from 0 *MPa* to 30 *MPa* with increment step of 3 *MPa*. The samples were loaded during two minutes with tensile stress after ten minutes annealing.

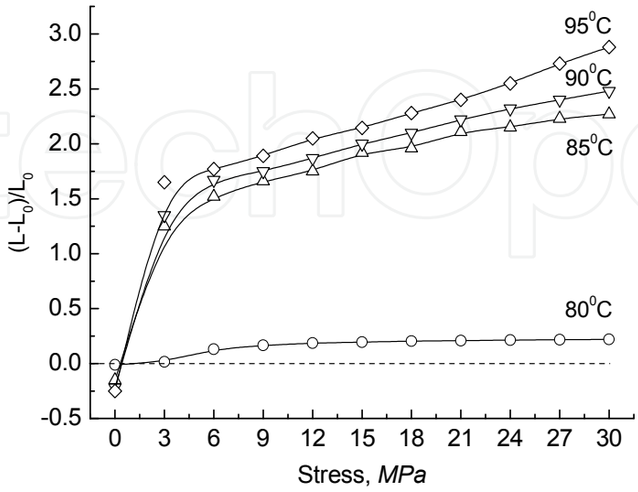


Fig. 13. Relative change of the bundle length annealed at different temperatures, depending on the tensile stress values (here L_0 and L are the initial and final fibers length respectively).

The yarn length obtained after the above described heat mechanical treatment as a function of the applied strain stress is presented in Figure 13 where the dashed line shows the initial sample length. As is apparent from Table 1 the sample B is almost completely amorphous, possess relatively low birefringence value and therefore weak pre-orientation of the amorphous phase. Specimen B is subjected to SHMM with a good resolution in the particularly effective temperature range above the glass transition. The curve obtained at temperature of 80 ^0C shows the initial level of the material deformation at selected conditions. The bundle deformation behavior (at 80 ^0C) is probably due to a slight stretch, uncoupling and disentangle of the free and slightly folded segments in the amorphous areas. Similar effects are observed up to stress value of 9 *MPa*, but mainly at stress levels between 3 *MPa* and 6 *MPa.* At loading above 9 *MPa* the curve comes to the a plateau and up to normal load of 30 *MPa* the structure is stable.

The temperature raising to 85 ^0C and 90 ^0C shows a common way of the obtained curves where can be seen an initially entropy contraction for the unladen samples and a significant increasing of the relative residual deformation at stress level of 3 *MPa*. After the initial sharply increase of the ultimate bundle length both curves indicate only small increments of the deformation and orientation with load increasing. Behavior of the curve at 95 ^0C displays much higher values of the sample deformation, which growing with the load values rising. The observed trend can be result from reinforced destruction and slip the segments instead of unfolding and orientation, i.e. from sub-optimal fibers straining. The differences in the bundles deformation behavior, depending on the load values and temperature show that the selected interval of the complex stress - temperature conditions is a suitable to realize the objectives of the thermal deformation experiment.

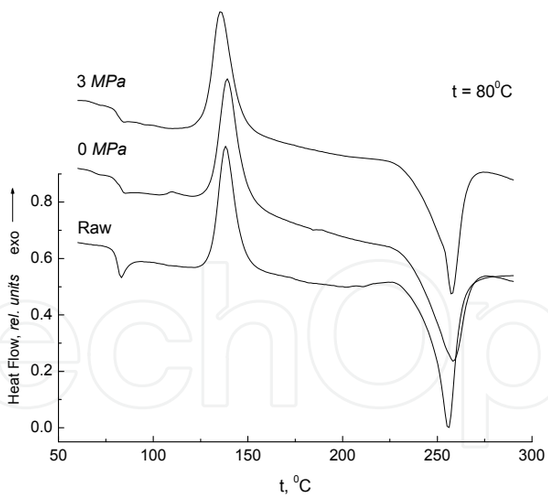


Fig. 14. DSC curves of untreated sample B and heat mechanically modified under different strain stresses at temperature of 80 ^0C (the curves are shifted vertically for clarity).

The structural analyses of the amorphous PET yarns heat-mechanically treated at the above-described conditions were carried out using differential scanning calorimetry and birefringence measurements. The clearly expressed cold crystallization (Fig. 14) of the samples modified at 80 ^0C is due to the presence of disordered and unstable structure in the unorientated amorphous fibers. In such structures, heated up to temperatures around 130 -

140 ^0C in the absence of external stress (0 *MPa*) is released the segment mobility in macromolecules, which is a precondition for the cold crystallization. For similar structures the applied stress of 3 *MPa* at temperature of 80 ^0C is not enough to cause noticeable fibers orientation and structure stabilization. The melting peaks of these samples are broader and imperfect because the melting polymer system is imperfect, contains less and more defective crystalline phase.

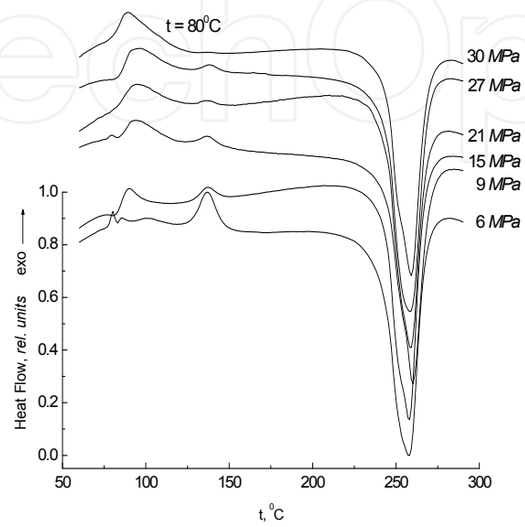


Fig. 15. DSC curves of sample B heat mechanically modified under different strain stresses at temperature of 80 ^0C (the curves are shifted vertically for clarity).

With increasing of the tensile stress values from 6 *MPa* and more (Fig. 15) the cold crystallization peak at about 140 ^0C gradually disappears but appears a new similar peak at much lower temperatures, immediately after the transition from glassy to rubbery state. Probably the higher stress further destabilize the structure and facilitates the glass transition proces. Furthermore it is observed an increase of the melting enthalpy and monotonous proportional dependence of the melting temperature increasing with the load growth and respectively the quality and quantity of the crystalline phase. And more essential, in accordance with the crystalline phase and structure improvement the low temperature cold crystallization moves to the lower temperatures. Consequently the more improved and arranged structure crystallizes at lower temperatures in the amorphous phase, while more difficult at higher temperatures melts the more perfect crystal phase.

Except the study by differential scanning calorimetry was measured and the birefringence as a function on the stress of the heat – mechanically treated at 80 ^0C fibers. It is interesting to note the appearance of "resonance" filaments birefringence with a pronounced maximum at tension stress value of 6 *MPa* which is an additional evidence for the role of the applied stress in the filaments structure rearrangement. With increasing of the SHMM temperature from 80 ^0C to 85 ^0C (Fig. 16) and under minimum load of 3 *MPa* losing the effect of the samples cold crystallization at temperatures around 130 - 140 ^0C. Instead appears the above described cold crystallization at lower temperatures around 110 ^0C. It is observed an increasing of the melting temperature and enthalpy as well as the perfection of the melting crystalline phase. At middle and higher loads a cold crystallization at 130 - 140 ^0C does not

happen. It is observed the same effect of lowering of the temperature and intensity of the earlier cold crystallization. With the loads increasing is enhanced the tendency for splitting of the melting peaks as well as homogeneous proportional increases of the melting temperature. An interesting fact is that at load of 6 *MPa* has spilled, extended over a wide temperature range endo effect of enhanced segmental mobility and entropy and at stress of 12 *MPa* has rudiment of one.

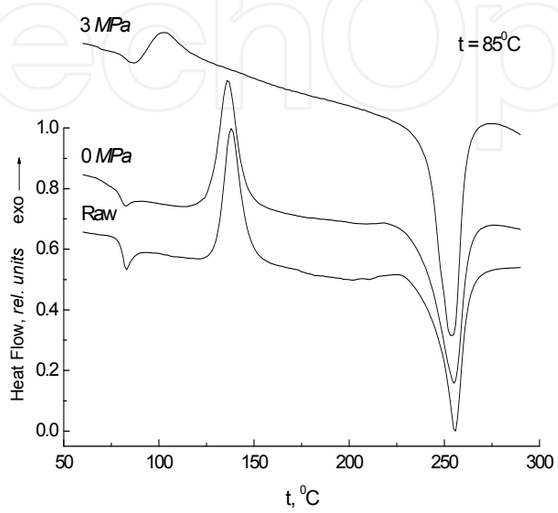


Fig. 16. DSC curves of untreated sample B and heat mechanically modified under different strain stresses at temperature of 85^0C (the curves are shifted vertically for clarity).

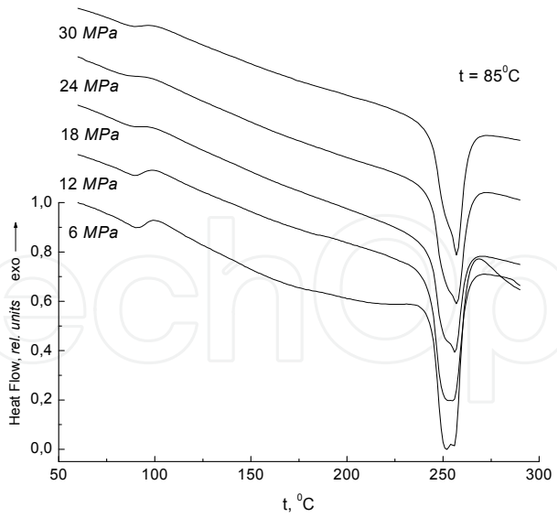


Fig. 17. DSC curves of sample B heat mechanically modified under different strain stresses at temperature of 85^0C (the curves are shifted vertically for clarity).

With purpose to specify the occurred in the samples structure developments caused by the SHMM at temperature 85 ^0C has been measured and the fibers birefringence. The obtained results pertaining to the birefringence values depending of the applied load show 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.

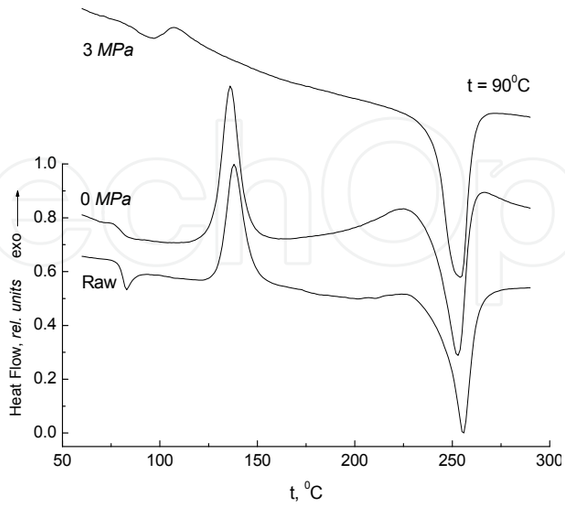


Fig. 18. DSC curves of untreated sample B and heat-mechanically modified under different strain stresses at temperature of 90 ^{0}C.

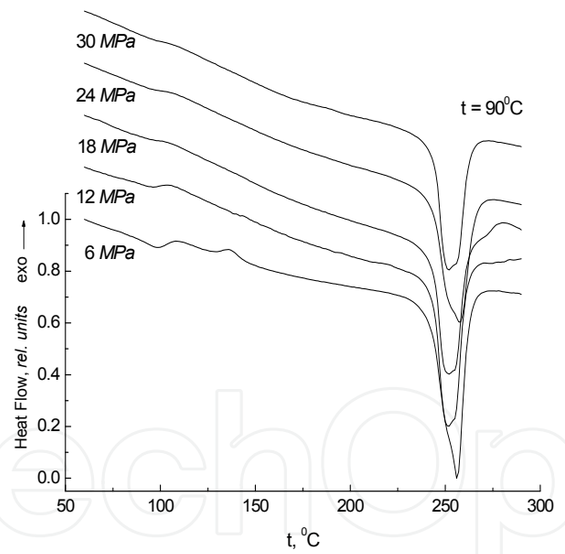


Fig. 19. DSC curves of sample B heat -mechanically modified under different strain stresses at temperature of 90 ^{0}C.

Very interesting is the DSC curve obtained without loading (strain stress value of 0 *MPa*) and temperature of 90 ^{0}C (Fig. 18). It is impressive much larger peak of cold crystallization in comparison with all other temperatures. This is probably the most suitable temperature for heat mechanical modification of the studied amorphous PET fibers, with the relevant background. At this temperature are released large resources for structural reorganization. From the same graph (Fig. 18) is seen that the effect of restoration of the segmental motion, known also as alpha-relaxation transition is practically suppressed. Perhaps during of the

SHMM directly achieves some effect of low-temperature arrangement in the free state of the object at load absence. The fact that only at this temperature takes place so intensive cold crystallization, with pronounced additional crystallization (or pre-crystallization), just before the samples melting is evidence for the optimal combination of the initial structure of the object with the selected temperature of SHMM. As at temperatures of 80 ^0C and 85 ^0C (Fig. 15 and 17) as well at 90 ^0C is observed a complex nature of the cold crystallization again under load of 6 *MPa*.

As is evident from Fig. 20 at temperature 95 ^0C the amorphous samples heat mechanically processed at lower loading values indicate a decreasing intensity of cold crystallization and

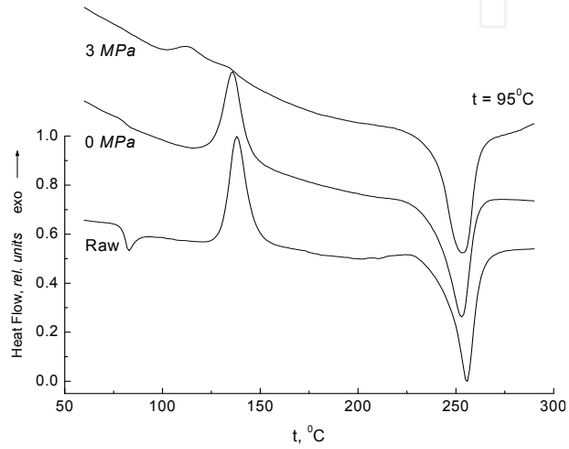


Fig. 20. DSC curves of untreated sample B and heat-mechanically modified under different strain stresses at temperature of 95 ^0C.

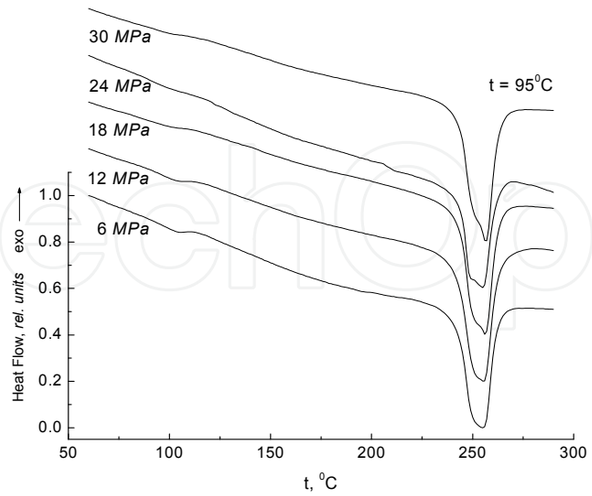


Fig. 21. DSC curves of sample B heat -mechanically modified under different strain stresses at temperature of 95 ^0C.

rising thermograms inclination. Possible reason for the observed tendencies are due to the overall increase of the entropy of the system with the samples heating, resulting in the

amend of the thermal conductivity and heat capacity of the objects. In the field of the medium and high loads (Fig. 21) appears the same effect of the lowering of the temperature and intensity of the cold crystallization and homogeneous proportional increasing of the melting temperature. With the loads increasing are monitored and enhanced split of the melting peaksp too. It is reasonable that with the stress values rising to differentiate two phases in the studied samples with structural differences between them and accordingly with different melting temperatures.

№	σ, *MPa*	α, % (80 ^0C)	α, % (85^0C)	α, % (90^0C)	α, % (95^0C)
1	Raw	1.7	1.7	1.7	1.7
2	0	2.0	11.8	4.0	13.7
3	3	2.9	39.5	36.1	40.7
4	6	34.7	38.5	39.2	42.1
5	9	34.9	39.3	41.3	43.3
6	12	35.0	41.6	42.5	45.0
7	15	34.0	42.5	43.3	44.7
8	18	33.3	41.8	42.6	44.5
9	21	33.7	41.5	41.5	44.4
10	24	34.0	39.7	40.6	44.6
11	27	35.8	40.5	40.0	44.9
12	30	34.2	40.7	40.9	43.8

Table 3. Degree of crystallinity of sample B subjected to SHMM at isothermal conditions and constant strain stresses.

On the basis of the data obtained by DSC was calculated and the degree of crystallinity of the studied PET fibers. The obtained results are presented in Table 3. If compare the data given in Table 3 with the relative change of the bundle length (Fig.22) will be seen certain similarity in the change the samples degree of crystallinity and fibers deformation behavior. The bundle deformation behavior observed at temperature of 80 ^0C (Fig. 22) shows a relatively large yarns extension with the stress level increasing from 3 *MPa* to 6 *MPa.* As it is visible from the Table 3 the samples degree of crystallinity at the same temperature (80 ^0C) and load levels (3 - 6 *MPa*) grows with more than thirty percents. Further more, at loadings above 9 *MPa* both the final bundle length and filaments crystallinity comes to a plateau up to load value of 30 *MPa.*

Very interesting are the changes of the filaments degree of crystallinity obtained with the temperature rising to 85 ^0C and 90 ^0C where a sharp increase of the samples crystallinity occurs even at stress value of 3 *MPa.* Like the bundle deformation behavior (Fig. 22) after the initial sharply increase of the filamemts crystallinity, both dependencies practically follow a common course. At loadings above 6 *MPa* they are coming to a plateau up to stress values of 30 *MPa.* Similar is the course and of the fibers degree of crystallinity at temperature 95 ^0C. It can be concluded that the samples degree of crystallinity reasonably good follows the bundle deformation, which is additional proof for the role of the strain stress in the crystallization of the studied PET fibers.

3.3 Investigation of partially crystalline PET fibers simultaneous heat - mechanically modified at isothermal conditions and constant strain stress values

The next stage from the the realized studies was to investigate the role of the SHMM conditions on the structure developments of partially crystalline PET filaments with different preliminary orientation.

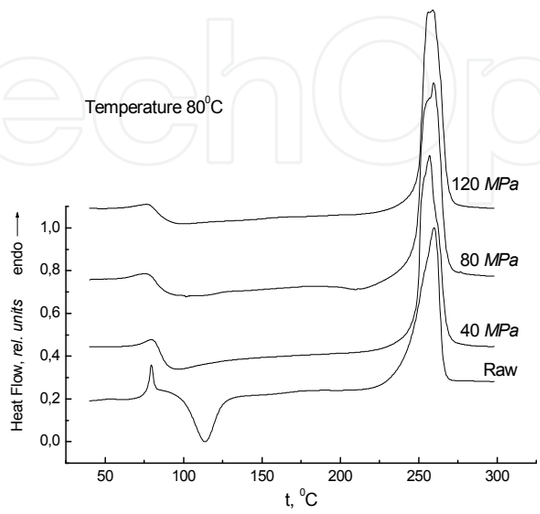


Fig. 22. DSC curves of untreated sample S1 and heat-mechanically modified under different strain stresses at temperature of 80^0C (the curves are shifted vertically for clarity).

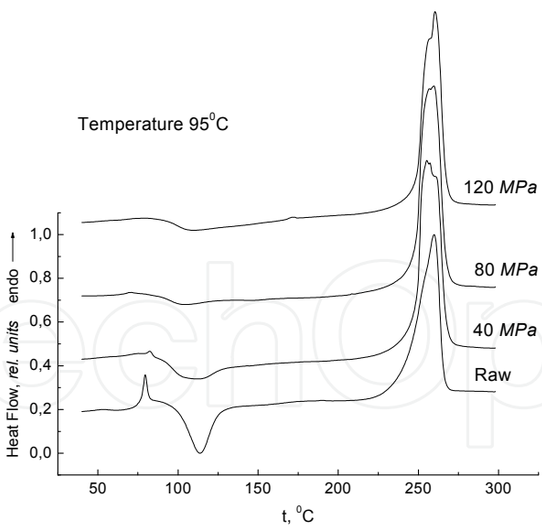


Fig. 23. DSC curves of untreated sample S1 and heat-mechanically modified under different strain stresses at temperature of 95^0C (the curves are shifted vertically for clarity).

With that purpose the samples named S1, S2 and S3 (Table 1) were heat – mechanically treated at constant temperatures in the same transient range from glassy to rubbery state. The thermal deformation experiment involves bundles annealing at temperatures of 80 ^{0}C, 85 ^{0}C, 90 ^{0}C and 95 ^{0}C accompanied by constant gravimetric tensile loadings of 40 *MPa*, 80

MPa and 120 *MPa* during two minutes. In comparison with the above described experiments the applied strain stress values are significantly larger. The experimental conditions allow to trace the combined unfluence of the tensile stress, temperature and preliminary fibers orientation on the going in the samples structural changes.
The structural analyses of the PET filaments subjected to SHMM at the above-described conditions were carried out using differential scanning calorimetry and birefringence measurements.
Representative panels of DSC curves of sample S1 obtained at temperatures 80 ^0C and 95 ^0C are present in Figures 22 and 23. The DSC curves of the heat mechanicaly treated samples show very important differences due to the structural reorganization occurred as a result of the modification. There is a radical change of the objects behavior in the temperature regions of the segmental motions defrosting (glass transition) and an increase in the macromolecules mobility (melting). In the areas of the hardening (change of the thermodynamic, entropy mobility of the polymers) and liquefying (increased viscous-liquid mobility) are observed visible structural changes with a steady trend with increasing the load and temperature. Probably due to the regulating effect of the SHMM on the structural organization the glass transition disappears together with the cold crystallization relatively monotonous. After samples SHMM there are no large differences in conformation state of the frozen and with very high entropy segments or larger ensembles of them. With the load and temperature increasing there is a slight shift towards the higher temperatures and increased splitting of the melting peaks. With the load values increasing before everything is lost the low temperature component of the melting peak. It is difficult to define the contributions of the unidirectional influence of the heating and loading in the phases forming during the high temperature multiple melting proces. Sometimes these effects are slight and not quite as a regular visible trend but such is the nature of the processes of structural transformation, too. Much more impressive is the objects behavior in rubbery state in the whole temperature range of increasing segmental mobility and relaxation effects between the processes of glass transition and melting in comparison with the above discussed objects modified under linear heating.

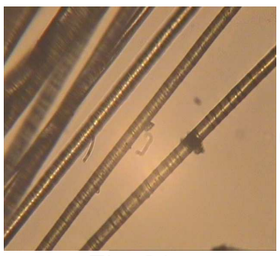


Fig. 24a.

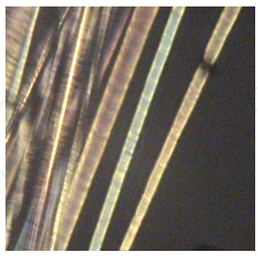


Fig. 24b.

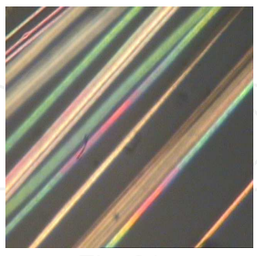


Fig. 24c.

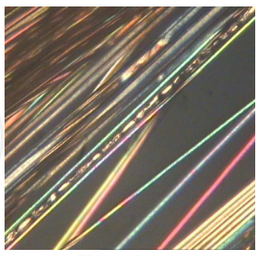


Fig. 24d.

Fig. 24. a) light microphotography of suboptimal drawn PET fibers with pronounced stripes due to enhanced destructive processes; b) polarization microphotography of similar objects; c) polarization microphotography of not homogeneous oriented sections; d) similar objects with filler defects.

Different types of defects and orientation inhomogeneity of PET fibers samples S1, S2 and S3 heat – mechanically treated at constant temperature of 95 ^0C and under constant gravimetric tensile loading of 120 MPa are present in Fig. 24.

In contrast to the rich on thermal effects relaxation area of the filaments rubbery state at the linear heated objects, here is observed fully stable samples behavior. The fibers modification under present conditions forms more homogeneous stable structure more compact (oriented) and poor of thermal effects during scanning proces.

3.4 Investigation of partially crystalline PET fibers simultaneous heat - mechanically modified at isothermal conditions and constant extension speed

After the examination of different variants of thermal treatment of PET fibers combined with different levels of constant gravimetric tensile loadings it was interesting to clarify the role of the mechanical treatment mode on the structure reorganization in the studied filaments. Therefore in the following variant of the thermal deformation experiment the studied partially crystalline PET yarns S1, S2 and S3 (Table 1) were subjected to extension at a constant speed under constant temperatures again in the same temperature range above the glass transition temperature from 80 ^0C to 95 ^0C. In the present investigation PET bundles were annealed during ten minutes at temperatures 80 ^0C, 85 ^0C, 90 ^0C and 95 ^0C then were withdrawn with a constant rate of 0.1 *m/min* up to relatively elongation (ε) of 20 %, 40 % and 60 %. Immediately after the treatment the sample was removed from the furnace at room temperature. The structural developments of the so heat mechanically modified filaments were investigated using differential scanning calorimetry.

Representative stacks of DSC curves of sample S1 subjected to SHMM at different levels of elongation and temperatures 80 ^0C and 95 ^0C are present in Figures 25 and 26.

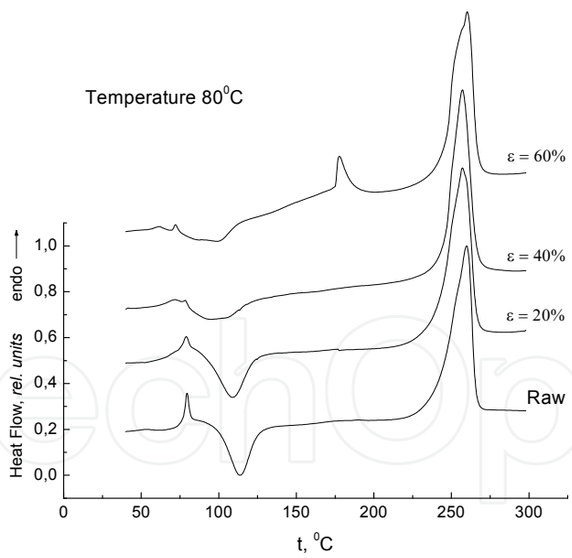


Fig. 25. DSC curves of untreated sample S1 and heat - mechanically modified at temperature of 80 ^0C and constant extension rate (the curves are shifted vertically for clarity).

Received by DSC results for the samples S1, S2 and S3 show that at the gravitational load of the fibers the attenuation and the practical disappearance of the effects of softening and cold crystallization follow monotonic trend with the temperature increasing, while for the drawn samples the temperature dependence is weaker, seems secondary. For these samples has a stronger dependence of the observed effects from the mechanical influence, respectively

from the withdrawal degree. In each panel of DSC curves is observed highly reduction of the intensity of the softening and cold crystallization running with increasing of the fibers elongation. At the highest temperature (95 ^0C), these processes are less pronounced even at the small degrees of withdrawal but here also is observed damping of the effects, proportional to the extension degree increasing.

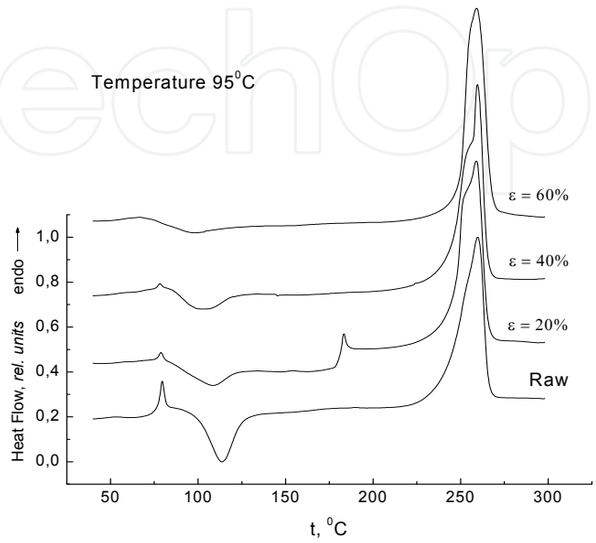


Fig. 26. DSC curves of untreated sample S1 and heat - mechanically modified at temperature of 95 ^0C and constant extension rate (the curves are shifted vertically for clarity).

The appearance on effects of pre-melting in relaxation area around 190 ^0C - 200 ^0C (Fig. 25 and 2) in the fibers subjected to extension at a constant rate is very interesting. It is observed at all temperatures but is less pronounced in the intermediate temperatures of 85 ^0C and 90 ^0C. At the lowest temperature (80 ^0C) the effect of pre-melting occurs at the largest deformation, respectively the largest structural reorganization. At the intermediate temperatures the effect is more slightly marked and is observed at the mean degree of the fibers elongation while at the highest temperature it occurs even at the smallest deformations. In addition all DSC curves with the observed pre-melting effects are steeper, with a larger gradient of the specific heat capacity increasing of the polymer structure with the temperature rise.

All this makes it possible to conclude that the forced modification of the studied PET fibers allows to form inhomogeneous and unstable stressed and overstressed structures which under certain conditions are thawed and melted during the DSC scanning. Similar entities could represent permanently stable in the time more stressed micro-localized areas, resulting in the observed during DSC measurement effects. For the gravitational loading similar effects are not monitored and this is reasonable. In the terms of this version of SHMM in the conditions of mutually coordinated influences and interactions of the mechanical affects the structural reorganization occurs more smoothly and slowly and turns off the formation and permanent freezing of overstressed regions. The DSC curves of both the filaments extended at a constant rate and filaments loaded at constant levels show beginnings of split of the melting peaks, which grow with the increase of the load and temperature.

It can be concluded that both the temperature and strain stress enable the structural reorganization and orientation of the polymer, but the forced withdrawal shows stronger orientation effects than the SHMM under constant loadings. Only concrete tests of the fibers strain-strength properties can arbitrate which samples are more optimally orientated and with less micro destructions.

4. Conclusion

Based on the analysis of the results obtained from the recent large-scale experiment it can draw the following conclusions:

There are studied PET fibers with different starting structure as amorphous as well partially crystalline samples with different pre-orientation;

Have been applied different regimes of thermal treatment as linear heating of the objects in a wide temperature range from 20 ^0C to 200 ^0C and annealing at constant temperatures in very important in terms of the structural changes temperature band from 80 ^0C to 95 ^0C, located close above the glass transition temperature;

The thermal treatments were accompanied from different levels of constant gravimetric tensile loadings and by withdrawal of the fibers to different levels at a constant extension rate;

The structural analyses of the investigated PET fibers subjected to SHMM show very important results concerning the role of the temperature and the applied strain stress and in particular:

the deformation behaviour of amorphous PET fibers subjected to linear heating from 20 ^0C to 200 ^0C show the role of the tensile loading in the management of the rival processes of fluid like deformation and strain induced crystallization;

significant increase of more than 30 % of the fibers degree of crystallinity in conditions of annealing in temperatures from 80 ^0C to 95 ^0C, with the strain stress increasing from 3 MPa to 6 MPa;

the received by DSC results for the partially crystalline samples S1, S2 and S3 show the role of the mechanical treatment mode on the running relaxation and phase transitions. At the gravitational fibers loading the attenuation and disappearance of the effects of the glass transition and cold crystallization follow monotonic trend with the temperature increasing, while for the drawn samples the temperature dependence is weaker, seems secondary. For these samples has a stronger dependence of the observed effects from the mechanical influence, respectively from the withdrawal degree.

The further steps are specific strain-strength tests that may arbitrate, which samples are optimally modified and such studies ahead.

The purpose of future research is by comparison between the gravitational load and different type of orientation drawing and thermal treatment to choose the optimal combination between them.

5. Acknowledgment

Part of the present work has been supported by Grant РД 07 - 340/15.03.2011 from Konstantin Preslavsky University, Shumen, as well as by Grants DO-02-61/08 and DDVU-02-106/2010 from University "Prof. Dr. Assen Zlatarov", Burgas.

6. List of the used symbols

α	degree of the sample crystallinity
d	diameter of the single fiber
ε	value of the relatively bundle elongation
λ	wavelength of the radiation in the WAXS apparatus
L_0	initial bundle length of the raw sample
L	final bundle length obtained after heat mechanically treatment
Δn	birefringence of single fiber
σ	applied to the objects tensile stress
V_L	speed of the filaments formation

7. References

Bai C., Spontak R. J., Koch C. C., Saw C. K., Balik C. M. (2000). Structural changes in poly (ethylene terephthalate) induced by mechanical milling. *Polymer*, Vol. 41, pp. 7147-7157, ISSN 0032-3861

Betchev Ch. (1995). On the Characterization by Shrinkage Forces of As-spun Poly (ethylene terephthalate) Filaments. *Polymer Testing*, Vol. 14, pp. 163–172, **ISSN** 0142-9418

Dupaix R. B., Boyce M. C. (2005). Finite strain behavior of poly(ethylene terephthalate) (PET) and poly(ethylene terephthalate)-glycol (PETG). *Polymer*, Vol. 46, Issue 13, pp. 4827 – 4837, ISSN 0032-3861

Guzatto R., Da Roza M. B., Denardin E. L. G., Samios D. (2009). Dynamical, morphological and mechanical properties of poly (ethylene terephthalate) deformed by plane strain compression. *Polymer Testing*, Vol. 28, pp. 24–29, ISSN 0142–9418

Karagiannidis P. G., Stergiou A. C., Karayannidis G. P. (2008). Study of crystallinity and thermomechanical analysis of annealed poly (ethylene terephthalate) films. *European Polymer Journal*, Vol. 44, pp. 1475-1486, ISSN 0014–3057

Keum J. K., Song H. H. (2005). Thermal deformations of oriented noncrystalline poly(ethylene terephthalate) fibers in the presence of mesophases structure. *Polymer*, 46, pp. 939–945, ISSN 0032-3861

Kong Y., Hay N. J. (2003). Multiple melting behaviour of poly (ethylene terephthalate). *Polymer*, Vol. 44, pp. 623-633, ISSN 0032-3861

Llana P. G., Boyce M.C. (1999). Finite strain behavior of poly(ethylene terephthalate) above the glass transition temperature. *Polymer,* Vol. 40, pp. 6729–6751, ISSN 0032-3861

Ma H., Zeng J., Realff M. L., Kumar S., Schiraldi D. A. (2003). Processing, structure, and properties of fibers from polyester/carbon nanofiber composites. *Composites Science and Technology*, Vol. 63, pp. 1617-1628, ISSN 0266-3538

Raabe D., Chen N., Chen L. (2004). Crystallographic texture, amorphization, and recrystallization in rolled and heat treated polyethyleneterephthalate (PET). *Polymer*, Vol. 45, pp. 8265-8277, ISSN 0032-3861

Safapour S., Seyed-Esfahani M., Auriemma F., Ruiz de Ballesteros O., Vollaro P., Di Girolamo R., De Rosa C., Khosroshahi A. (2010). Reactive blending as a tool for obtaining poly (ethylene terephthalate)-based engineering materials with tailored properties. *Polymer*, Vol. 51, pp. 4340-4350, ISSN 0032-3861

Shabana H. M. (2004). Refractive index-structure correlation in chemically treated polyethylene terephthalate fibers. *Polymer Testing*, Vol. 23, pp. 291-297, ISSN 0142-9418

Sharma V., Desai P., Abhiraman A. (1997). Crystallinity Vis-a-Vis Two – Phase Models of Oriented Polymers: Inferences from an Experimental Study of Poly (ethylene terephthalate). *Journal of Applied Polymer Science,* Vol. 65, pp. 2603-2612, ISSN 1097-4628

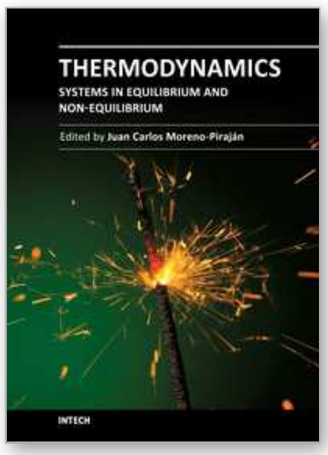
Sulong A. B., Park J., Azhari C. H., Jusoff K. (2011). Process optimization of melt spinning and mechanical strength enhancement of functionalized multi-walled carbon nanotubes reinforcing polyethylene fibers. *Composites: Part B*, Vol. 42, pp. 11-17

Wijayathunga N. V., Lawrence C. A., Blackburn R. S., Bandara M. P. U., Lewis E. L. V., El-Dessouky H. M., Cheung V. (2007). Influence of laser irradiation on the optical and structural properties of poly (ethylene terephthalate) fibres. *Optics & Laser Technology,* Vol. 39, pp. 1301–1309, ISSN 0030–3992

Wu J., Schultz J. M., Samon J. M., Pangelinan A. B., Chuah H. H. (2001). In situ study of structure development during continuous hot-drawing of poly (trimethylene terephthalate) fibers by simultaneous synchrotron small- and wide angle X-ray scattering. *Polymer*, Vol. 42, pp. 7161-7170, ISSN 0032-3861

Zhang Z., Wu Sh., Ren M., Xiao Ch. (2004). Model of cold crystallization of uniaxially oriented poly(ethylene terephthalate) fibers. *Polymer*, Vol. 45, pp. 4361-4365, ISSN 0032-3861

Ziabicki A., Jarecki L. (2007). Crystallization-controlled limitations of melt spinning. *Journal of Applied Polymer Science*, Vol. 105, pp. 215-223, ISSN 1097-4628



Thermodynamics - Systems in Equilibrium and Non-Equilibrium
Edited by Dr. Juan Carlos Moreno PirajÃ¡n

ISBN 978-953-307-283-8
Hard cover, 306 pages
Publisher InTech
Published online 10, October, 2011
Published in print edition October, 2011

Thermodynamics is one of the most exciting branches of physical chemistry which has greatly contributed to the modern science. Being concentrated on a wide range of applications of thermodynamics, this book gathers a series of contributions by the finest scientists in the world, gathered in an orderly manner. It can be used in post-graduate courses for students and as a reference book, as it is written in a language pleasing to the reader. It can also serve as a reference material for researchers to whom the thermodynamics is one of the area of interest.

InTech Europe
University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166
www.intechopen.com

InTech China
Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

IntechOpen