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THERMAL RESISTANCE OF POLYETHYLENE TEREPHTHALATE FIBRES

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ABSTRACT: *The thermal resistance of isotropic and orientated poly(ethylene terephthalate) (PET) samples was studied. Part of the oriented PET specimens was heat mechanically modified under different conditions. Using differential thermal analysis (DTA), thermal gravimetric analysis (TGA) and differential thermal gravimetric analysis (DTGA) it was investigated the influence of the forming methods and the modes of heat mechanically treatment on the relative samples thermal oxidation stability. It was determined basic thermodynamic and kinetic parameters, as well as the limiting mechanisms of the basic destruction of the PET objects.*

KEY WORDS: *poly (ethylene terephthalate), fibers, thermal resistance, destruction, differential thermal analysis (DTA), thermal gravimetric analysis (TGA*

Introduction

The main purpose of the heat mechanical modification of polyethylene terephthalate (PET) fibers is an improvement of their strength-strain properties. The improvement of the modular and strength characteristics of the polymer fibers can be realized primarily through the optimization of the manner and the packing density of the macromolecular chain segments (MMCS) in the process of uniaxial orientation drawing.

The final result from the uniaxial download is a consequence of the complex temperature-temporal superposition of the filaments deformation process. Depending on the drawing speed and temperature, the results of the non-destructive fibers deformation also depend from the optimal for the corresponding temperature and starting structure applied to the objects tensile stress. The orientation download is a complex combination from the mutually rival alternative processes of orientation and destruction of the MMCS. Both processes are strongly temperature dependent due to the thermal fluctuation nature, of both the orientation and untangling of the knots in the amorphous regions and the destruction of the overstretched segments. Therefore, it is necessary the fibers heat mechanical modification to be realized at an elevated temperature, but insufficient for carrying of intensive destruction of the polymer system. On the other hand, the external mechanical impact creates conditions for structurally determined micro local overloads and overheatings in the polymer volume.

For this reason the temperature prehistory of the objects is difficult predictable and controllable. Thus especially important for the optimum carrying out of the thermal mechanical modification is the detailed study of the heat-physical properties and thermal stability of the polymer fibers. This requires research on different starting structures with various temperature and mechanical background.

To identify the changes in the chemical composition under different temperature and mechanical modifications defining the initiation of the thermal oxidation destruction (TOD), except heat-physical and thermal analysis are necessary and various spectroscopic and other structural studies. For the selection of optimal conditions for thermo mechanical modification (TMM) most important and chronologically first are the thermo-gravimetric studies.

These initial studies are needed to clarify the temperature range, mechanism and the kinetics of TOD for the various tested objects as well as for planning of an experiment for a comprehensive study of the TOD of PET fibers.

2. Experimental

Temperature, mechanical and other physical impacts affect the qualitative and quantitative composition on the contained in the polymer materials low molecular and oligomeric compounds which can act as initiators and accelerators of TOD. Simultaneous administration of more than one similar influence strongly impedes the prediction of their combined effect on the strength-strain behavior of the objects. This is due to the emerging micro local overheating caused by mechanical super stresses in structural not homogeneity in the fibers.

Therefore often such modifications polymeric fibers lead to difficult to interpret and forecast results. In such cases, most reliable way to evaluate the results is the real specific experiment. To study the influence of the technological background and the additional TMM on the thermo physical properties and thermal stability of the studied objects were tested starting PET - granulate (sample № 1) and fibers formed and downloaded under different conditions on its basis. The granules possess close to the nascent structure of PET and it is not affected by multiple recrystallizations from different primary and secondary processing.

Some key parameters of the fiber forming and characteristics of the tested specimens are given in Table 1. In order to establish the role of the additional TMM on thermo-physical properties and thermal stability except PET granules and fibers were studied and thermo mechanically modified PET fibers, too.

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

Sample №	$V_{L,}$ *m/min*	n	d, *μm*	$\Delta n.\ 10^3$	α, %
2	1150	32	44,0	8	1,7
3	2280	32	14,5	4,32	23,7
4	4110	32	11,0	5,82	37,0

1. Sample; 2. V_L, *m/min* – fiber forming speed; 3. n – number of the single fibers in the filament yarn; 4. d,*μm* – single fiber diameter; 5. Δn – birefringence; 6. α, % - degree of crystallinity.

Conditions on TMM of the analyzed samples are shown in Table 2. Thermo mechanical modification of the studied PET fibers was performed using the designed and manufactured in the Laboratory
“Physics of the polymers” in University of Shumen "Bishop K. Preslavski" setup for heat mechanical treatment of oriented polymer materials.

Table 2. TMM parameters of the studied PET fibers.

Sample №	V, *m/min*	T_{dr}, *^0C*	$V_{изт.,}$ *m/min*	ε, %
5	2280	80	0,1	60
6	4110	80	0,1	60
7	2280	95	0,1	60
8	4110	95	0,1	60

1. Sample; 2. V, *m/min* – fiber forming speed; 3. T_{dr}, *^0C* – drawing temperature; 4. $V_{dr,}$ *m/min* – drawing speed; 5. ε, % - relative fibers elongation.

The thermal analyses on the treated objects are carried out by using an apparatus for combined dynamic thermal analysis Derivatograf OD - 102 (MOM - Hungary). Registered are: TG - thermogravimetric curve, DTG - differential thermogravimetric curve and DTA - differential thermo-analytical curves under the following experimental conditions: temperature range 20 – 600 ^0C, heating rate of 6 *deg/min*; sample mass of 50 ± 1 *mg*; pot - metal-ceramic; environment - air (static).

From the obtained thermal curves are determined a number heat-physical and thermal characteristics of the tested samples, some of which are presented in Table 3.1 and 3.2. The associated with structural phase reorganization heat-physical effects before the beginning of the thermal oxidation destruction were confirmed and with the method of differential scanning calorimetry whose results will be reported in our future work.

Table 3.1. Thermal, thermodynamic and kinetic parameters of PET objects obtained and modified under different conditions.

№	VP, %	$T_{em.}$, ^0C	T_{onset}, ^0C	T_{max}, ^0C	T_{end} , ^0C
1	1,02	232-254	342	422	451
2	1,71	219-250	341	421	451
3	1,76	212-249	340	420	450
4	3,05	195-259	338	419	442
5	1,47	214-251	330	410	441
6	1,40	191-250	321	411	434
7	1,42	221-251	328	409	444
8	2,02	110-165	328	410	449

№ - *sample number;*

VP, % - quantity of the volatile products emitted prior to the main mass destruction;

$T_{em.}$ *VP,* ^0C *- temperature ranges of emission of VP;*

T_{onset}, ^0C *– onset temperature of the main TOD;*

T_{max}, ^0C *– temperature of maximum TOD speed;*

T_{end}, ^0C *- temperature of the end of major TOD.*

The mechanism and kinetics of TOD are determined on the basis of thermo gravimetric data using a methodology as well as the authors made computer program whose theoretical foundations are contained in the works [1-15].

In general the kinetics of solid-phase processes, in the present case, can be described analytically through the conversion α [1]:

$$\int_0^{\alpha} \frac{d\alpha}{\alpha^m (1-\alpha)^n \left[-\ln(1-\alpha)\right]^p} = \frac{A}{q} \int_0^{T} \exp(-\frac{E}{RT}) dT \qquad (1)$$

where: A – before exponential (frequency) multiplier;

q – speed of linearly temperature change ($q = dT/d\tau = const$);

E – seeming activation energy;

R – the universal gas constant;

T – absolute temperature.

Table 3.2. Thermal, thermodynamic and kinetic parameters of PET objects obtained and modified under different conditions.

№	Limiting mechanism, Lit. [8]	A, *s*$^{-1}$	E$_a$, *kJ/mol*	ΔS$^{\#}$, J/mol.K	ΔH$^{\#}$, *kJ/mol*	ΔG$^{\#}$, *kJ/mol*
1	2**	3,6.10^{12}	198	-56,9	191,5	230,2
2	2	4,6.10^{11}	193	-71,1	183,3	236,1
3	2	3,7.10^{12}	201	-53,1	189,0	235,2
4	2	1,43.10^{9}	163	-119,3	154,2	240,1
5	1*	5,3.10^{15}	235	6,92	229,0	223,1
6	2	8,21.10^{9}	167	-104,1	159,4	230,0
7	1	2,7.10^{14}	217	-18,8	213,9	226,2
8	1	2,1.10^{13}	201	-40,01	196,2	226,1

№ - *sample number;*
limiting mechanism;
A, s^{-1} *- before exponential (frequency) multiplier;*
E$_a$*, kJ/mol – seeming activation energy;*
ΔS$^{\#}$*, J/mol.K – the entropy at* $T = T_{max}$*;*
ΔH$^{\#}$*, kJ/mol – the enthalpy at* $T = T_{max.}$*;*
ΔG$^{\#}$*, kJ/mol - the free energy at* $T = T_{max.}$.

* mechanism of accidentally formation and consequent nuclei increase with $n = 1$,
marked with A1F1, $g(\alpha) = -\ln(1-\alpha)$ [1, 9-11];
** mechanism of a chemical reaction, with $n = 3/4$, marked with F$_{3/4}$, $g(\alpha) = 1-(1-\alpha)^{1/4}$ [1, 9-11].

Perhaps these are mechanisms that determine and the active participation of the oxygen from the air in the system.
From the observable form of the integrand function:

$$f(\alpha) = \alpha^m (1-\alpha)^n [-\ln(1-\alpha)]^p \qquad (2)$$

determined in the case from the limiting the speed of the destruction phase, depends on the algebraic form of the decision g (α) of the conversion (the left in the equation 1) integral (table 3 in a note), and the temperature [2,3,5]:

$$\int_0^T \exp\left(-\frac{E}{RT}\right)dT = \frac{E}{R}\frac{\exp(-x)}{x^2}h(x) \qquad (3)$$

- by an emerging form of h(x), whose value for not especially precise calculations is assumed per unit [6]:

$$h(x) = \frac{x^4 + 18x^3 + 88x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \qquad (4)$$

, where x is the reduced activation energy (E/RT).

These solutions are applicable to the iso conversion method, and for the data from the individual a thermogravimetric (TG) curve.

Using information from the TG and DTG curves of the objects, the calculation method of Cats and Redfern [3] and with 35 known in the literature reference functions [4, 9] through the above-mentioned software are defined the effective kinetic parameters - the activation energy E_a [5, 8], before the exponent in the known Arrhenius equation for the rate constant of the chemical reaction - A [5] and the most likely mechanisms [8] of the basic thermal oxidation destruction of the samples (340^0C - 450^0C).

From the known thermodynamic equations for the Gibbs free energy and the theory of the activated complex (transition state) of Eyring [7, 12-15] are defined the enthalpy $\Delta H^{\#}$, the entropy $\Delta S^{\#}$ and the free energy $\Delta G^{\#}$ at T_{max}. As an additional criterion for assessing of the reliability of the destruction mechanism are determined and the coefficients of the linear regression in the calculation of E_a.

4. Discussion

The main idea and the logic of the experiment and discussion aimed to clarify optimal in respect of TOD processing conditions, or various types of thermal modification of PET fibers. Even when working away from the temperature range of main TOD, following multiple cyclic thermal loads are creating conditions for additive increase of the chemical pollution of the polymer with degradation products, which are the initiators and accelerators of the destruction. Due to the possibility for strong micro local overheating, the combined thermo mechanical impact increases the probability of such effects. Aging in real conditions under permanent or periodic load over time complicates considerably the uncertainty of such processes.

Their elucidation requires extensive thermal, calorimetric, spectroscopic, mechanical, microscopic and others research. This work aims initial determination of some basic thermal, thermodynamic and kinetic characteristics of the destruction of thermo mechanical modified under different conditions PET fibers, together with methodological approbation of the possibility to determine the mechanism of their destruction.

The ability for correctly identify of unambiguous differences in the thermal stability of a similar in composition and physical structure polymer fibers, in particular PET could help to clarify the mechanisms and kinetics of the structural reorganization and destruction under heating, and would allow reliable prediction of optimal conditions for their processing.

In the present initial experiments were investigated only granules of the starting PET, virgin fibers molded at three different speeds of fibrillate (Table 1) as well as further withdrawal (Table 2) at various temperatures.

Were examined the thermo physical behavior and destruction, in terms of the initial filaments structure (degree of crystallinity and orientation) and the temperature - temporal background - unmodified and thermo mechanically modified at different temperatures.

At the same download speed on the same objects the different temperatures determine different loads. The oriented stresses in micro areas of different sections of the objects volume fluctuate reciprocal of the respective fluctuations of the physical density. The specimen density depends ambiguous from the starting morphology and the degree of orientation of the sample. These are some of the factors that determine the complex course of the thermal curves on the studied fibers.

On the other hand, the thermal effects on the registered DTA, DTG and DSC curves, with temperature increasing, show (more clearly or slightly, and with different temperature deviation) several areas: 1 - of glass transition temperature, 2 - low temperature ("cold") crystallization; 3 - release of volatile products (LP); 4 - before crystallization; 5 – melting; 6 - destruction.

Glass transition is less marked, with different intensity and distribution profile with a maximum in the temperature range 70^0C - 80^0C. At the oriented samples are observed effects of asymmetry and excess, and possibly with a poly modality but due to the low intensity of the processes even at the DSC-curves is not possible decomposition or any other processing of the peaks profile.

"Cold" crystallization occurs with a maximum in the range 110^0C -130^0C. At the granules, it is very poorly marked about 115 ^0C and in the fibers produced at a low speed of fiber forming (sample 2) the "cold" crystallization exhibits a distinct right asymmetry corresponding to the higher temperature relaxation as a result of the orientation. The separating of volatiles products is possible in the temperature range 100^0C - 250^0C. These products could be moisture or other low molecular weight oligomeric products associated with the production and modification of the polymer and fibers. Their content in the studied objects is 1-3 %. Lowest one is the content of volatiles in the granules, and highest in the molded at a high speed and drawn at high temperature samples. For the samples that are not additionally heated (1-4) the basal amount of volatile products are removed immediately before the melting at temperatures 190^0C - 250^0C, while at the thermo mechanically processed samples (5-8) the separation starts at 100^0C -150^0C.

For the treated at the highest temperature sample 8 the volatiles are fully removed up to 150^0C. If all this is connected with the earlier and increased destruction (Table 3) can be assumed that the process is due to the increased fragmentation at high-temperature thermo mechanical modification.

Prior crystallization in the range of 210^0C - 250^0C is observed only for the molded at high speed samples 3 and 4. Probably the process is due to crystallization of highly oriented regions at temperatures near the melting temperatures of the most imperfect crystalline formations.

Thermo mechanically processed samples 5-8 do not show noticeable "cold" crystallization and before crystallization, which suggests depletion of the adequate resources for the realization of the process in the conditions of thermo mechanical modification.

The melting of primary and secondary crystalline phases is registered most often in the range 240-260^0C. The highest degree of crystallinity shows the modified at 95^0C PET fibers. Multiple melting peaks indicate samples 1, 3, 4, which is an indication of very different in size and perfection crystallites or regions of coherent scattering of the PET crystal phase.

The existence of two separate melting peaks for samples 6 at 270 ^0C and 8 at 300^0C is perhaps testimony to the presence of polymorphisms in PET or formation of crystals with stretched chains, which is possible under effects of major orientation stresses typical for these samples. The clarification of these issues requires detailed X-ray structural studies.

Analyzing the results for the different thermal characteristics of the studied objects is observed a trend of slightly decrease of the temperatures determining the relative thermal oxidation stability of PET with increasing the fiber forming speed and the temperature of TMM. The effective activation energy of the reactions of the total destruction also decreases.

This means that the heat treatment, and especially the combined TMM, reduces the initial thermal stability of PET. More significant are the changes in samples 4, 6, 8, at the expense of much weaker ones at 3, 5, 7, which is quite logical in terms of the above reached conclusion.

The formed radicals under the analysis conditions form hydro peroxides structures which are initiators of TOD. The found main limiting mechanisms of thermal oxidation destruction are not changed as a result of the processing. These are basically two competing mechanisms:

1) mechanism of accidental formation and subsequent growth of germ nuclei of the destruction, with n = 1, which is typical for the chain processes in polymers, indicated in the cited literature as A1F1 (describing with the equation of Avrami-Erofeev, $g(\alpha) = -\ln(1-\alpha)$);

2) mechanism of chemical reaction with n = ¾, indicated with $F_{3/4}$ ($g(\alpha) = 1-(1-\alpha)^{1/4}$) [1]. Perhaps these are mechanisms determining and from the active participation of oxygen from the air in the system.

The entropy change in most cases have a negative sign (Table 3), which is an indication of the higher organization degree of the system in "the transition state" compared to the baseline one. I.e. increases the negentropy, the order in the system which requires energy.

Positive values of the enthalpy change and the Gibbs free energy also show that the investigated processes are not spontaneous and are characterized by the corresponding potential barriers and activation energies.

From the studies carried out it can be concluded that the precise qualitative and quantitative assessment of the destruction and its modification can serve as a good criterion for the effectiveness of carrying out of TMM.

The reliability of the assessment could be increased in combination with other physical methods of examination as spectroscopic, mechanical, microscope, etc. Unambiguous tying of the full range of the possible mechanisms of destruction of any object, with the terms of modification and the initial structure (crystallographic and morphological) with all its prehistory would ensure the objectivity of the assessment and allow prediction of the results of TMM, as well as the thermal stability and kinetics of realization of TOD.

The use of the iso conversion method and its modified versions for collecting and processing of large databases thermal and thermo gravimetric information would allow not only increasing of the estimates accuracy but also the qualitative enrichment of the spectrum of possible mechanisms and their individual details. This will open new horizons for improving the accuracy and reliability. A similar optimistic prognosis s not fiction, taking into account that any larger plurality of more precisely obtained reliable data enables more accurate functional description, by means of well defined regression analysis.

A good idea is to investigate the destruction kinetics of various modified PET films and fibers by iso-conversion method, employing a statistics of thermo gravimetric data at various values of the experimental parameters.

Thermo gravimetric data could be obtained under various heating rates, various masses of the studied objects, different preliminary chemical composition (by drying and extraction of low molecular compounds), various strictly-defined and accurately determined highly distinct starting structure with different thermal, etc. physical background, followed by a complex joint interpretation.

A similar approbation of the idea for conversion of the thermal destruction and its change in a convenient criterion for evaluation of the conditions for TMM very likely would help to obtain better results and ideas for a better experiment.

5. Conclusions

1. Using differential thermal analysis (DTA) was studied isotropic PET, fibers obtained therefrom at various fiber forming speeds, as well as thermo mechanical modified fibers at different temperatures. In PET-fibers obtained at low fibrillate speeds of 1150 *m/min* were observed exothermic effects of "cold" crystallization at temperatures around 115^0C - 120^0C.

At fiber forming speed of 4100 *m/*min, the phenomenon of "cold" crystallization at the above mentioned temperatures gradually fades, but appears the effect of the so-called before crystallization or crystallization at temperatures immediately before the melting of the main crystalline phase in the range 220^0C -250^0C. It can be assumed that the fiber forming at high-speed impedes the spontaneous crystallization at lower temperatures.

2. At heat mechanical modified PET fibers noticeable thermal effects of "cold crystallization" missing, which implies depletion of the objects relaxation possibilities in terms of its realization. Proof of this are the higher degree of crystallinity determined in our other studies, and the observed multiplicities of the melting endothermic effects due to differences in size, perfection and stability crystallites formed under different conditions of disequilibrium crystallization. The fibers drawn at 95^0C show also effects of fusion of new crystalline phases or crystallites with stretched chains at temperatures higher than 260^0C.

3. Applying the methods of TG, DTG and DTA was studied the influence of different ways for obtaining and heat mechanical objects treatment on the relative samples thermal oxidation stability. Are determined the effective kinetic parameters, the most likely summary mechanisms of the main thermal oxidation destruction as well as the enthalpy change, entropy and the free energy at the temperature of maximum destruction rate.

It was found that any additional processing of PET, leads to an increase of the amount and decrease of the temperature range of removal of the volatile products in the system. There is a tendency of a slight decrease of the relative thermal stability of the treated samples, except samples 5 and 7 obtained at fiber forming speed of 2280 *m/min*.

4. The specified limiting mechanisms of the base destruction of the PET objects are two competing mechanisms (1 - accidental formation and subsequent

growth of the nuclei with n = 1 and 2 - a mechanism of a chemical reaction with n = ¾), whose priority at the different objects do not shows visible depending from the used so far modification conditions.

This determines the need to extend the experimental conditions to the maximum possible for realization differences in regard to starting structures, objects background, speed, temperature and variants of stretching, ensuring the realization of very different orientation stresses.

5. Established is the possibility of using the evaluation of the thermal stability, its modification as well as the TOD kinetics for determining the suitability and effectiveness of the conditions for TMM of PET fibers. On this basis, is shown the need to develop such studies with application of new schemes for planning and realization of the experiment.

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