Changes of crystalline structure of poly(ethylene terephthalate) fibers in flame retardant finishing process*)

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Abstract: The poly(ethylene terephthalate) (PET) fibers of improved flammability were investigated. The modification applied to classic PET fibers consisted in a wet flame-retardant treatment of the fabrics during the dyeing process. In this study we took an attempt to describe the supermolecular structure of the flame retardant PET fibers with different content of the modifier as a function of a temperature of the flame retardant finishing process and additionally the structure transformation during the ageing process. To evaluate the crystalline structure of fibers differential scanning calorimetry (DSC) and wide angle X-ray scattering measurements (WAXS) were used.

Keywords: PET fibers, flame retardant finishing, supermolecular structure, DSC, WAXS.

Zmiany struktury krystalicznej włókien poli(tereftalanu etylenu) poddanych wykańczalniczej obróbce uniepalniającej

Streszczenie: Przedmiotem badań były włókna z poli(tereftalanu etylenu) (PET) poddane uniepalniającej modyfikacji. Polegała ona na wykańczalniczej kąpieli barwiącej z udziałem określonej ilości substancji ograniczających palność. Opisano wpływ ilości zastosowanego modyfikatora oraz temperatury obróbki na strukturę nadcząsteczkową badanych włókien. Oceniano też zmiany tej struktury w toku starzenia modyfikowanych włókien w warunkach atmosferycznych, w okresie 5 lat. Strukturę krystaliczną uniepalnionych włókien PET charakteryzowano z zastosowaniem metod różnicowej kalorymetrii skaningowej (DSC) oraz szerokokątowej dyfraktometrii rentgenowskiej (WAXS).

Słowa kluczowe: włókna PET, uniepalnianie, struktura nadcząsteczkowa, DSC, WAXS.

For many applications, due to legal regulations and consumer demands, an enhanced level of the flame retardancy of textiles is required [1]. Protection of consumers from unsafe apparel is only one area where flame retardancy is needed. Firefighters and emergency personnel require protection from flames as they go about their duties. Floor coverings, upholstery and drapery also need protection, especially when used in public buildings. The military and airline industry have multiple needs for flame-retardant textiles. For the production of technical textiles poly(ethylene terephthalate) (PET) fibers are mostly used.

Higher level of polyester fibers flame retardancy is usually achieved by organophosphorus or bromine-containing compounds, which are incorporated into polyester molecules during polycondensation [2–7] or are physically mixed with polymer in the fiber formation process [8–14].

The alternative method to reduce the flammability of polyester fabrics consists in applying of flame retardant treatments during finishing or coating processes [15–18]. The aim of the paper is to propose uncomplicated and inexpensive method of improving the flame retardant properties of PET fabrics. We used the flame retardant which was transferred on fabrics from the water bath in the pad-dry-heat set process [19]. An organophosphorus flame retardant together with a dispersed dye was used.

EXPERIMENTAL PART

Materials

The materials used in this work were all commercially available technical products. The poly(ethylene terephthalate) (PET) fibers supplied by Elana S.A. Toruń (Poland) were used and a commercial flame retardant modifier Roflam E [tris(2-chloro-ethyl) phosphate] — CAS 115-96-8 [Formula (I)] supplied by Rokita S.A. (Poland) was applied.

In the investigations, the uncolored and thermally spun polyester plain weave fabric, made from standard PET fibers was used. The finishing treatment was carried out in the laboratory dyeing device (Ahiba Turbomat —

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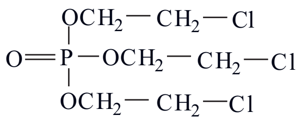

$$O{=}P(OCH_2{-}CH_2{-}Cl)_3 \qquad (I)$$

Switzerland). The applied conditions were as follows: temperature — 100 °C, 110 °C, 120 °C, 130 °C, treatment time — 1 h and heating rate — 1.5 °C/min. The flame retardant was added in the amount of 5 %, 10 % and 1 % to the fiber mass.

Methods of testing

— The examinations of the fiber flammability were carried out with the limited oxygen index (*LOI*) method in accordance with Polish Standard PN-ISO 4589.

— Calorimetric (DSC) investigations were carried out with a TA Instruments equipped with a MDSC Calorimeter 2920 and RCS cooling system. The samples of powdered fibers were heated at the rate of 10 °C/min from 30 °C to 290 °C (atmosphere N_2, flow 40 cm^3/min; standard aluminum pans). The weight of the examined samples amounted to about 5 mg. Registration sensitivity was above 0.2 μW. The enthalpies and characteristic temperatures of transitions were calculated by means of the Universal V2.6D TA Instruments software.

In order to estimate the influence of ageing on the structure, calorimetric investigations were carried out both directly after applying flame retardant modification and after 5 years period.

— The wide angle X-ray scattering measurements (WAXS) were carried out on a Seifert URD6 diffractometer, equipped with ISO-DEBYEFLEX 3003 high voltage generator and a graphite monochromator. CuK_α radiation was used at 40 kV and 30 mA. The step scanning measurement mode was employed over a 2θ scattering angle ranging from 5° to 60°, with a step-size of 0.05°. Before calorimetric and diffraction experiments samples of fibers were powdered using Hardy's microtome.

It was estimated that the error in determining of the *LOI* index was circa 0.2 %, while the error of designation of the degree of crystallinity, both for DSC and WAXS methods, was circa 1 %.

RESULTS AND DISCUSSION

Flammability

The most important parameter for the modified fibers is, from a practical point of view, the parameter characterizing flammability of studied fibers — limited oxygen index (*LOI*). The *LOI* index measured for unmodified PET fibers equals to 21.4 %. The values of this parameter determined for fibers modified with Roflam E compound are presented in Table 1.

The increase of the bath temperature from 100 °C to 130 °C results in the increase of the oxygen concentration required for burning (*LOI*). As well by the increment of the flame retardant content in the bath, the distinct monotonical increase of the *LOI* index is observed.

T a b l e 1. Limited oxygen index of modified PET fibers

Temperature of treatment, °C	*LOI*, %		
	5 % Roflam E	10 % Roflam E	15 % Roflam E
100	22.1	22.7	22.7
110	23.4	24.6	24.6
120	24.6	25.8	26.6
130	26.6	27.2	28.4

Supermolecular structure

Simultaneously, in our study, it was interesting to define an influence of the presence of the flame retardant compound Roflam E on the fiber nanostructure order level. To evaluate the enthalpy based mass fraction of crystalline phase the DSC measurements were performed.

The setting-up of DSC curves obtained for fibers modified in established conditions (100, 110, 120, 130 °C and 5, 10, 15 % of Roflam E content, respectively) are shown in Fig. 1.

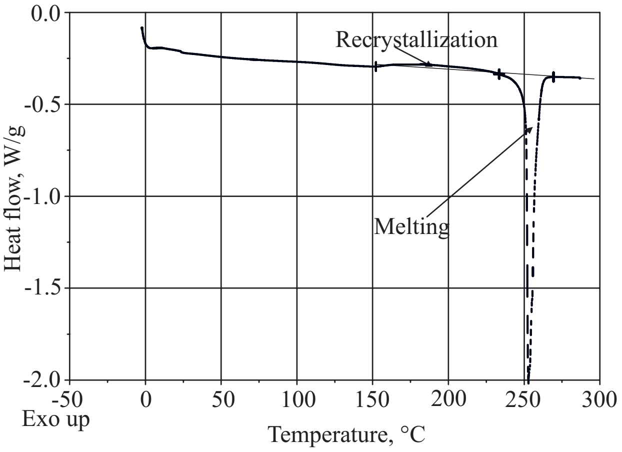

Fig. 1. Shape of exemplary DSC curve (sample modified in 130 °C, Roflam E content 5 %) of studied PET flame retardant fibers during the heating (10 deg/min) in nitrogen (flow 40 cm^3/min) from 0 to 280 °C

All registered DSC curves, irrespective of the heat treatment temperature and the content of the flame retardant compound have the same character. They reveal the analogical thermal effects of recrystallization and melting processes and the third endothermic effect in the temperature range of 130—160 °C. It reflects transformation of supermolecular structure of fibers connected with the applied heat treatment. It is important to mention that when the heat treatment temperature increases, a minimum of peak corresponding to that effect is shifted towards higher temperatures.

It is worth to notice that the value of melting peak minimum temperature, referring to the fastest melting of crystallites does not change considerably for all studied fibers. The same conclusion refers to the temperatures of the so-called extrapolated beginning and the end of the melting process. It may indicate that the addition of flame retardant compound changes the contents of crystallite fraction in the modified structure of PET fibers without causing the change in the mean size of crystallites.

We can therefore state that the flame retardant modifier Roflam E affects also the shape of fibers crystalline fraction, although it is done in a limited and specific way.

For a quantitative consideration the crystallinity index as a main parameter of investigated fibers nanostructure, corrected for the sake of recrystallization process (perfection of existing crystallites), was calculated as follows:

$$\kappa = \frac{\Delta H_m - \Delta H_r}{\Delta H^0} \cdot 100\ \% \tag{1}$$

where: ΔH_m — enthalpy of sample melting (measured value), ΔH_r — enthalpy of recrystallization which appears in sample during the DSC measurement, ΔH^0 — enthalpy of melting of pure PET fully crystalline standard sample (calculated value, in our study 140.1 J/g was taken [20]).

Values of the corrected crystallinity index calculated for fibers treated in the bath of extremely high temperature 130 °C are submitted in Table 2.

Values of the crystallinity index calculated for all investigated fibers as a function of the modifier Roflam E content and temperature of the heat treatment are presented in Fig. 2. The character of revealed dependencies is quite obvious and compatible with the expectations. Noteworthy change of the crystallinity is especially significant with the increase of temperature from 110 to 120 °C.

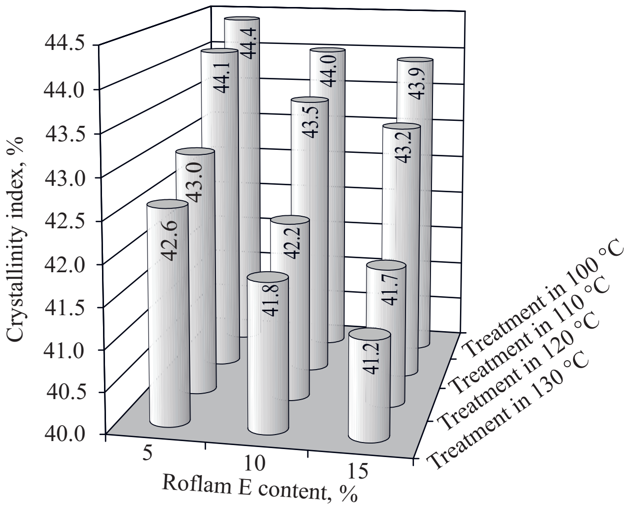

Fig. 2. Changes of crystallinity index of modified flame retardant PET fibers, evaluated on the basis of DSC measurements, as a function of Roflam E content and the temperature of modifying bath

T a b l e 2. Values of: a temperature of melting (T_m), enthalpies of melting (ΔH_m) and recrystallization (ΔH_r) evaluated on the basis of DSC curves and values of the crystallinity index calculated according to eq. (1). Temperature of the heat treatment = 130 °C

Sample	Roflam E content, %	T_m, °C	ΔH_m, J/g	ΔH_r, J/g	κ, %
PET+Roflam E	5	258.5	59.70	0.44	42.3
PET+Roflam E	10	258.2	58.51	0.53	41.4
PET+Roflam E	15	258.2	57.66	0.57	40.7

Crystalline structure of fibers

The wide angle X-ray diffraction patterns obtained for investigated fibers (Fig. 3) unequivocally show the lack of any distinct qualitative differences of the supermolecular structure of fibers flame retardant modified in different temperatures of finishing bath.

PET crystallizes in a triclinic system and the edges of the elementary cell are single monomeric unit of PET homopolymer. PET chains assume an approximately planar configuration. The chain plain is almost parallel to the (100) lattice plane. The mean crystallite sizes in the direction perpendicular to the (100) plane have been calculated by means of the familiar Scherrer equation.

For the separation of an experimental diffraction pattern into two components connected with the scattering from crystalline and amorphous regions, respectively, the curve-fitting computer package OptiFit [21] was used (Fig. 4).

The crystallinity index calculated as the ratio of the total area under the resolved crystalline peaks to the total area under the unresolved X-ray scattering curve for all measu-

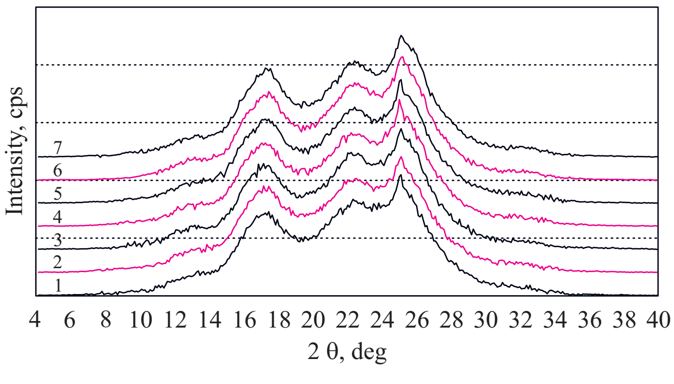

Fig. 3. WAXS patterns of PET fibers modified with different contents of Roflam E: 1 — PET + 5 % Roflam E/100 °C, 2 — PET + 15 % Roflam E/100 °C, 3 — PET + 5 % Roflam E/120 °C, 4 — PET + 15 % Roflam E/120 °C, 5 — PET + 5 % Roflam E/130 °C, 6 — PET + 15 % Roflam E/130 °C, 7 — PET + 30 % Roflam E/130 °C

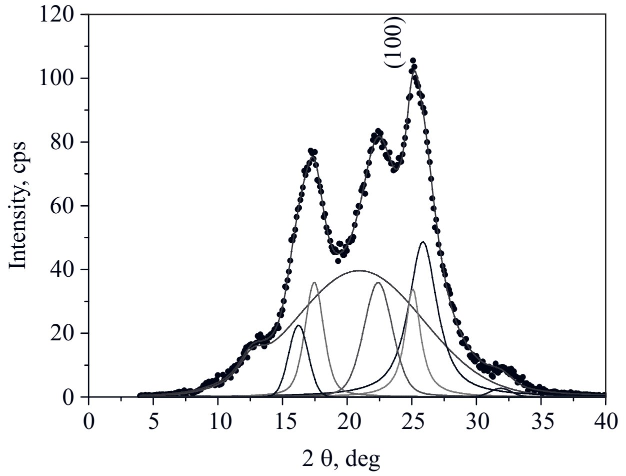

Fig. 4. Exemplary WAXS curve for a sample of fibers modified with Roflam E (15 %) in the temperature of 130 °C resolved for individual diffraction peaks

red samples comprised to a narrow range between 47 and 49 % with a little lowering tendency versus the flame retardant modifier content. The crystallite sizes estimated by means of the Scherrer equation varied from ca. 5 to above 6 nm without the distinct regularity of changes.

Ageing

The problem of the transformation of PET fibers supermolecular structure modified with Roflam E compound during the process of ageing in the atmospheric conditions (temperature of 20 °C, humidity ca. 60 %) was also considered. To reveal the discussed transformation, two series of DSC measurements were carried out. The measurements were performed within a time period of 5 years in a respectively broad temperature range. Results are presented in Figs 5 and 6.

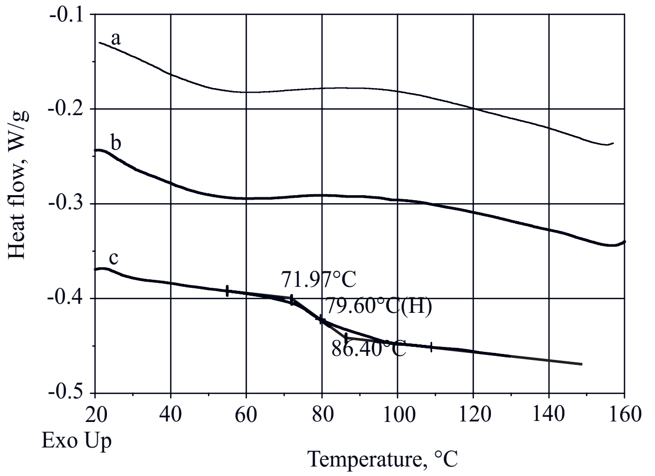

Fig. 5. An example of a setting-up of DSC curves registered for: a) modified flame retardant PET fibers (15 % Roflam E, in bath of temperature 130 °C) directly after the formation process, b) the same fibers after 5 years of natural ageing, c) the material of these fibers earlier quenched from the melt; heating rate 10 °C/min, atmosphere N_2, flow 40 cm^3/min; analysis of the glass transition region

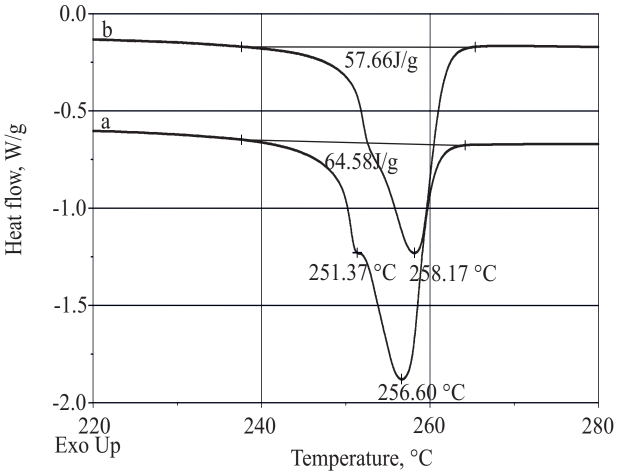

Fig. 6. DSC curves of flame retardant PET fibers modified with 15 % Roflam E in bath of temperature 130 °C: a) after 5 years of ageing in atmospheric conditions, b) directly after the fabrication; heating rate 10 °C/min, atmosphere N_2, flow 40 cm^3/min; analysis of the melting region

Unexpectedly, the shape of DSC curves did not change in the temperature region of glass transition corresponding to the transformation of the amorphous fraction of fibers material. Curves a) and b) in Fig. 5 are almost the same. The interpretation of their shape in the analyzed temperature region is rather ambiguous, as well as the value of T_g is practically undeterminable using the classic DSC method, because of the superposition of an energetically opposite effect of cold crystallization proceeding in fibers during the heating run. Only on the curve c), the unique distinct shift of the heat capacity occurred — enabling to determine the value of T_g. This was registered for the material of modified PET fibers, earlier quenched from the melt.

The only interesting changes of calorimetric signals registered for modified PET fibers after 5 years of ageing, appeared in the melting temperature range (Fig. 6). The differences of a course of DSC curve in the temperature range of the melting peak are particularly distinct in the case of fibers treated in the bath of extremely high temperature 130 °C during the simultaneous processes of dyeing and flame retardant modifying. For these fibers after 5 years of ageing, the value of the melting peak minimum temperature is shifted by ca. 1.6 °C towards lower temperatures and the characteristic shoulder relating to the recrystallization has appeared. In such a case ca. 12 % increase of the crystallinity index calculated from the equation (1) is observed.

CONCLUSIONS

The studies performed showed that:

— The flame retardant modification of classic PET fibers with the Roflam E compound by means of the bathing method really causes the lowering of their flammability. Lowering flammability obtained with this method is slightly lower than the effect caused by the incorporation of the flame retardants during polycondensation or physical mixing [22]. However, it should be noted that both of these methods are considerably more expensive than the method proposed in this paper.

— The influence of the flame retardant modification on the fiber thermal properties, demonstrated through the lowering of the recrystallization temperature T_r as well as the enthalpy of melting ΔH_m, together with the increase in the content of the flame retardant compound and the temperature of treatment has been found. However, an unambiguous tendency of changes of melting temperature T_m has not been demonstrated.

— It has been proven that the crystalline phase order level of the modified PET fibers allowed the recrystallization phenomenon to take place during the calorimetric measurement. The values of the recrystallization enthalpies ΔH_r increased with the temperature modification as well as the increase of Roflam E compound content. The increase of crystallinity was more considerable for higher temperature of flame retardant processing.

— The results of our calorimetric and diffraction investigations show that the applied modifier Roflam E affects the crystalline fraction shape of PET fibers, although in a limited and specific way. The use of alternative methods causes more pronounced changes in the sizes of crystallites and the degree of crystallinity. This is because both the incorporation of flame retardants during polycondensation and physical mixing significantly affect crystallization conditions of PET macromolecules.

— After 5 years of natural ageing of modified fibers distinct changes were observed only in the melting temperature region and they corresponded to the increase in the content of the crystalline phase. The crystallinity index increased most significantly as Roflam E modifier was used in temperature of 130 °C.

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