Flame retardant modification of partially oriented poly(ethylene terephthalate) fibers – structural conditions of application*)

Andrzej Gawłowski[1), **]**, Janusz Fabia**[1)]**, Czesław Ślusarczyk**[1)]**, Tadeusz Graczyk**[1)]**, Anna Pielesz**[1)]

Abstract: In this study, flame retardant modification of partially oriented (POY, partially oriented yarn) poly(ethylene terephthalate) (PET POY) fibers were applied using a high temperature bath method similar to dyeing fibers with disperse dyes. The flame retardant modifier used in this work – water-glass (WG) – was commercially available technical product. The flammability of fibers was evaluated by limiting oxygen index (*LOI*) method. Samples of the modified fibers were examined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Effect of the flame retardant on change in the supermolecular structure of PET POY fibers was evaluated using wide- and small-angle X-ray diffraction (WAXS and SAXS). As a result of the applied modification, PET POY fibers were provided with effective and durable flame retardant properties. Also noteworthy is the relatively low cost and simplicity of applying the proposed technology.

Keywords: partially oriented poly(ethylene terephthalate) fibers, limiting oxygen index, wide- and small-angle X-ray diffraction, differential scanning calorimetry, thermogravimetric analysis.

Modyfikacja trudnozapalna częściowo zorientowanych włókien z poli(tereftalanu etylenu) – strukturalne uwarunkowania aplikacji

Streszczenie: Do modyfikacji trudnozapalnej częściowo zorientowanych włókien z poli(tereftalanu etylenu) (PET POY) zastosowano, podobnie jak w wypadku procesu barwienia włókien PET barwnikami zawiesinowymi, wysokotemperaturową metodę kąpielową. W charakterze modyfikatora użyto technicznego produktu handlowego – szkła wodnego (WG). Palność włókien oceniano metodą wskaźnika tlenowego (*LOI*). Próbki zmodyfikowanych włókien badano za pomocą różnicowej kalorymetrii skaningowej (DSC) i analizy termograwimetrycznej (TGA). Wpływ dodatku WG na zmianę struktury nadcząsteczkowej włókien PET POY oceniano na podstawie wyników szeroko- i małokątowej dyfraktometrii rentgenowskiej (WAXS i SAXS). Otrzymane modyfikowane włókna PET POY wykazywały trwale zmniejszoną palność. Dodatkową zaletą zastosowanej metody modyfikacji jest jej stosunkowo niski koszt oraz prostota aplikacji.

Słowa kluczowe: włókna z poli(tereftalanu etylenu) częściowo zorientowane, wskaźnik tlenowy, szeroko- i małokątowa dyfraktometria rentgenowska, różnicowa kalorymetria skaningowa, analiza termograwimetryczna.

Poly(ethylene terephthalate) (PET) fibers are produced in very large quantities worldwide, due to their relatively low cost. Moreover, the fibers are characterized by very good mechanical properties, high resistance to physical and chemical agents. Therefore, they are very widely used as fibers for textiles, technical products (*e.g.*, cords for tires, safety belts)

and for the production of articles intended for interior furnishings of public facilities and means of transport. Due to such a wide range of applications, products from PET fibers are facing very strict requirements in terms of fire safety. PET fibers modified to be non-flammable may be obtained:

– by the addition of a flame retardant during the polymerization process [1],

– by the addition of a flame retardant during the spinning process [2–9],

– in the process of finishing the standard PET fibers with dyeing methods [10–14].

The first two ways pose technological difficulties and require high expenses. The third method, however, is characterized by simplicity and relatively low cost. Nev-

[1) University of Bielsko-Biala, Institute of Textile Engineering and Polymer Materials, Willowa 2, 43-309 Bielsko-Biała, Poland.

**) Author for correspondence; e-mail: agawlowski@ath.bielsko.pl]

ertheless, it requires the optimal technology to be developed, *i.e.*, the modification or selection of process parameters and the type and amount of additives.

During the application of flame retardants in the finishing process, the key problem is the accessibility of the fiber material to be penetrated by flame retardant particles. In case of standard PET fibers, this is accomplished by raising the temperature of modifying bath by 40 °C or more above the glass transition temperature of these fibers (in practice, a temperature of 120–135 °C). At these temperatures, there is a sufficient amount of so-called free volume that provide for optimal sorption of flame retardant particles [15].

In our previous works the method described above was used to modify the conventionally molded PET fibers [16, 17]. Due to the possibility to increase the accessibility of fiber material structure to be penetrated by flame retardant particles, replacing the standard PET fibers with PET partially oriented yarn (POY), it seems to be an interesting experiment.

Partially oriented fibers are obtained by increasing the forming rate several times as compared to the classic technology of manufacturing of PET filament fibers. The increasing of take-up velocity of the fibers makes it possible to eliminate the separate stretching operation. The take-up velocity of the fibers in POY technology is selected so that the final product has the specific tear strength equivalent to the one achieved for the fibers produced using the classic method. Despite the corresponding mechanical properties, the supermolecular structure of the POY fibers is different. PET POY fibers are characterized by low crystallinity and relatively small overall orientation, thus a supermolecular structure of the fibers is extremely sensitive to any kind of heat treatments [18–23]. These characteristics have an important influence on the sorption of the flame retardant particles by the fiber.

Currently, the flame retardant modification of PET fibers is mainly achieved by using organic phosphorus flame retardants which replaced previously used halogenated organic flame retardants [2, 3, 5, 10, 24–26]. Halogenated organic flame retardants, despite their high efficiency, have been withdrawn from use because of allergic and toxic effects on living organisms (among others, toxic hydrogen halide is formed while burning them) [27–31]. In addition to phosphorus derivatives, silicon derivatives are also used as flame retardant additives [2, 3, 9, 12, 26, 32]. In this study, the flame retardant modification of PET POY fibers has been successfully achieved by using aqueous sodium silicate solution – the so-called water-glass, a modifier that is inexpensive and, above all, 100 % ecological.

EXPERIMENTAL PART

Materials

The materials used in this work: PET POY fibers supplied by Torlen Sp. z o.o. Toruń (Poland), the flame re-

tardant modifier – water-glass (WG) – CAS 1344-09-8 supplied by Rudniki SA (Poland), were commercially available technical products.

Flame retardant modification process

The finishing treatment was carried out in the laboratory dyeing device Ahiba Turbomat (Switzerland) with a liquor ration of 1 : 50. The applied conditions were as follows: temperature – 115 °C, treatment time – 1 h and heating rate – 2.5 °C/min, respectively. The PET POY fibers were treated in the water-glass solution of: 0.3, 0.5, 1.0, 5.0 and 10.0 wt %. Dispersing agent: Dyspergator NNO (nonionic dispersing agent from Organika-Rokita, Poland) was added into the modification bath in the amount of 1.5 g/dm³. After the modification treatment, the investigated samples were washed in a solution of detergent Pretepon G (Organika-Rokita, Poland) in the amount of 5 g/dm³. The washing time was 30 min and the temperature 60 °C.

Methods of testing

– The resulting flame retardant effect of PET POY fibers was evaluated using the limiting oxygen index (*LOI*) method. A parameter that characterizes the method is the lowest percentage of oxygen in the mixture with nitrogen, at which the test specimen ignites and burns on its own. The measurements were performed in accordance with PN–ISO 4589 standard.

– Differential scanning calorimetry (DSC) measurements were performed using a TA Instruments Thermal Analysis System 5100 equipped with TA Instruments 2920 Calorimeter and RCS cooling system. The temperature was calibrated with the melting point of indium (156.6 °C) and the enthalpy was calibrated with indium (28.4 J/g). The measurements were registered in the temperature range 20–290 °C, using TA standard aluminum pans, under nitrogen atmosphere (flow 40 cm³/min) with a heating and cooling rate of $\beta_+ = \beta_- = 10$ deg/min. The data were evaluated by means of the Universal V4.5A (TA Instruments) software. For a quantitative consideration, the degree of crystallinity in our study 140.1 J/g was taken.

– TGA investigations were performed using Thermogravimetric Analyzer TA Instruments Q500. The measurements were done in a temperature range from 30 to 800 °C with the heating rate of 10 deg/min.

– Wide-angle X-ray scattering (WAXS) investigations were carried out with a URD-65 Seifert diffractometer. CuK_α radiation was used at 40 kV and 30 mA. Monochromatization of the beam was obtained by means of a nickel filter and a graphite crystal monochromator placed in the diffracted beam path. A scintillation counter was used as a detector. Investigations were performed in the range of the angle 1.2° to 7° with a step of 0.05° and 7° to 40° with a step 0.1°. For the separation of an experimental diffraction pattern into two components connected with the

scattering from crystalline and amorphous regions, the curve-fitting computer package WAXSFIT [33] was used.

– The small-angle X-ray scattering (SAXS) measurements were carried out with the compact Kratky camera, equipped with the SWAXS optical system of HECUS--MBRAUN (Austria). The Cu target X-ray tube, operated at: $U = 40$ kV, $I = 25$ mA was used as a radiation source ($\lambda = 0.154$ nm). Scattered radiation was recorded in acquisition time of 900 s by means of a MBRAUN linear position-sensitive detector, model PSD 50, which worked in a strictly defined range of energy spectrum. The detector had 1024 channels with a channel-to-channel distance of 52 µm. The SAXS data were collected as a function of the scattering vector $s = (2/\lambda)\sin\theta$, where 2θ is the scattering angle.

RESULTS AND DISCUSSION

The first question that has been tackled in this study was to determine the appropriate temperature of the flame retardant modification process. In our previous studies in this field conducted for conventional PET fibers [16, 17], the optimum temperature of the bath in which the modification was carried out was determined as 130 °C. The use of similar bath temperature in the case of PET POY fibers did not prove successful. After the modification process, the obtained fibers (multifilament) were strongly deformed (fasciated), which largely prevented their use for textile processing. Explanation to the problem was achieved thanks to the DSC calorimetric studies. Figure 1 summarizes the DSC curves registered in the same range of temperatures (20–290 °C) for conventional polyester fibers – spun at relatively low speeds and PET POY fibers. Thermal analysis clearly shows that the supermolecular structure of POY fibers is almost amorphous immediately after the spinning process. On DSC curve, a very clear cold crystallization peak at the temperature range 120–140 °C is observed. Thus, the use of modification temperature of 130 °C overlapped with the range of temperature of the transition associated with
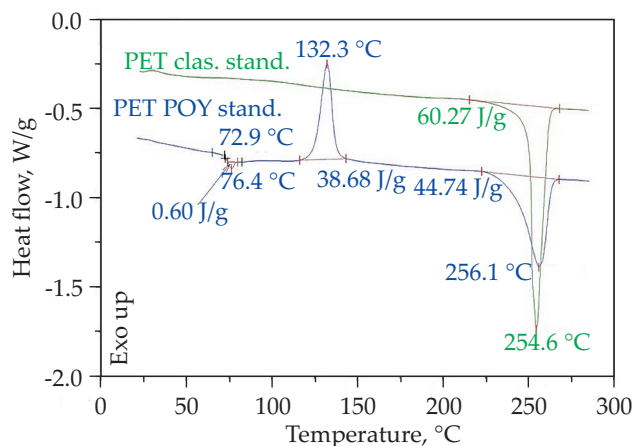
intensive reconstruction of the fiber structure at the supermolecular level. Hence, their consequent macroscopic deformation took place. Lowering the flame retardant modification temperature to 115 °C, which is outside the peak temperature of cold crystallization, unambiguously resolved this problem.

Flammability test

Next to the appropriate application temperature, the second key parameter in determining the efficiency of the flame retardant modification of the fibers is the concentration of the flame retardant particles in the bath. Utilizing the limiting oxygen index method, PET POY fibers modified in a wide range of flame retardant concentrations in the bath were tested for fire resistance (Table 1). For all the variants, a very clear improvement was obtained in flame retardant properties, as compared to the unmodified fibers. The results (which are the mean value of several tests) show, however, that the flame resistance of the tested fibers does not vary in a monotonic manner. The highest value of the *LOI* index – 28.2 % – was recorded for only 0.5 wt % WG content in the bath. Further increase of the modifier concentration did not improve the *LOI* indicator, and several times increasing the concentration of water-glass in the bath, even resulted in a clear deterioration of the resulting flame retardant effect.

T a b l e 1. **Results of limiting oxygen index (*LOI*) measurements of studied PET POY fibers modified with water-glass**

Sample of fibers	*LOI*, %
PET POY stand.	21.7
PET POY+0.3%WG, 115 °C	28.0
PET POY+0.5%WG, 115 °C	28.2
PET POY+1.0%WG, 115 °C	28.0
PET POY+3.0%WG, 115 °C	27.9
PET POY+5.0%WG, 115 °C	25.4
PET POY+10.0%WG, 115 °C	25.0

The results obtained using *LOI* method were confirmed by thermogravimetric analysis. By conducting TGA measurement of the PET fiber samples in air, a complete separation of the process of PET thermal dissociation from the process of ignition, and then combustion, of the carbonization product obtained earlier, was enabled (Fig. 2). The above regularity was already used successfully by the authors in previous works [16, 17] devoted to flame retardant modification of the classic polyester fibers.

As previously mentioned, in the case of PET POY fibers discussed in this paper, the application of TGA technique clearly confirmed the previous results of the *LOI* flammability test (Fig. 3). Analysis of differential weight loss curves (DTG) in terms of combustion of the organic residue of the test samples of fibers in the temperature range from 500 to 630 °C, the most preferred version of the
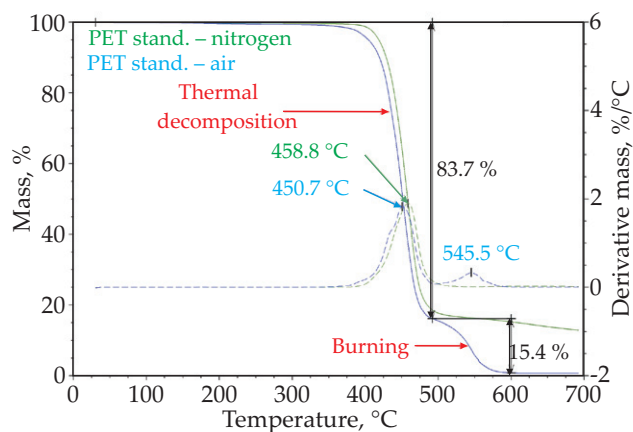

Fig. 1. DSC curves for standard PET fibers and PET POY, analysis of: glass transition, cold crystallization, melting and non-isothermal crystallization

Fig. 2. TG and DTG curves for PET standard fibers, respectively: measurement performed in nitrogen atmosphere (green), in air atmosphere (blue)
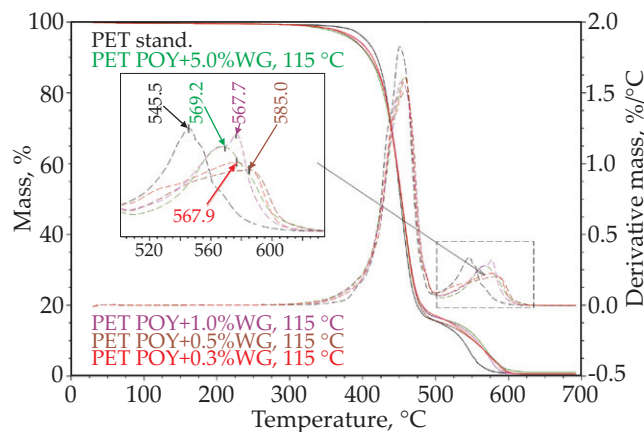

Fig. 3. TG and DTG curves for PET standard and PET POY fibers (measurements performed in air atmosphere), respectively: unmodified standard (black), modified in the bath (WG 5.0 wt %) at 115 °C (green), modified in the bath (WG 1.0 wt %) at 115 °C (pink), modified in the bath (WG 0.5 wt %) at 115 °C (brown), modified in the bath (WG 0.3 wt %) at 115 °C (red)

modification (0.5 wt % of WG in the bath) shows a shift of the maximum temperature by nearly 40 °C towards higher temperatures, as compared to the untreated fibers.

Structural studies

The structural implications of the applied method were searched on the basis of DSC calorimetry and X-ray studies within the wide (WAXS) and the small (SAXS) scattering angles. The analysis of recorded DSC curves indicates that, except for unmodified PET POY fibers (already discussed blue curve in Fig. 1), the nature of curves registered for all variants of the bath modification at 115 °C, is the same. It is characterized by the complete absence of the cold crystallization peak, and the established values of the temperature and enthalpy of melting differ very slightly (Table 2). The following table shows the temperature and enthalpy for the characteristic variants selected from the population of all kinds of studied PET POY fibers: the so-called green fibers, fibers processed only in a blank bath only, and fibers modified with a minimum (0.3 %), the best (0.5 %) and the highest (10.0 %) content of flame retardant in the bath. The degree of crystallinity determined on the basis of DSC method for the fibers treated in a blank bath (pure water at a temperature of 115 °C) is only slightly more than 1 % higher compared with PET POY fibers modified using water-glass at a concentration of as much as 10 % in the bath. Minimum melting peak temperature, correlated with the average size

of the crystallites, does not change significantly with an increase in the concentration of the modifier.

In conclusion of the foregoing discussion, it should, therefore, be noted that in the light of DSC calorimetric studies, the modification of the crystalline structure of PET POY fibers is almost exclusively based on the heat treatment of fibers (comparison of the results for the raw fibers and the fibers treated in the blank bath). The fact is manifested by increased content of the crystalline fraction in the fiber structure by approx. 30 % independently on the concentration of the flame retardant in the bath.

Deeper structural conditions of the applied flame retardant modification were investigated on the basis of X-ray diffraction studies.

The wide-angle PET POY fibers tests revealed only a diffusive nature of the scattering in the case of unmodified fibers, reflecting the lack of the crystalline fraction in their structure (Fig. 4). The nature of WAXS diffraction patterns for all the other variants of tested fibers (treated at 115 °C) is different and typical of PET fibers conventionally formed from the melt at relatively low speeds.

According to Daubeney, Bunn and Brown [34], PET crystallizes in a triclinic system and the edges of the unit cell are single monomeric unit of PET homopolymer. PET chains assume an approximately planar configuration. The chain plane is almost parallel to the (100) lattice plane.

T a b l e 2. **Values of: melting temperature (T_m), melting enthalpy (ΔH_m), cold crystallization temperature (T_r), cold crystallization enthalpy (ΔH_r) and degree of crystallinity (κ) calculated on the basis of a DSC curve**

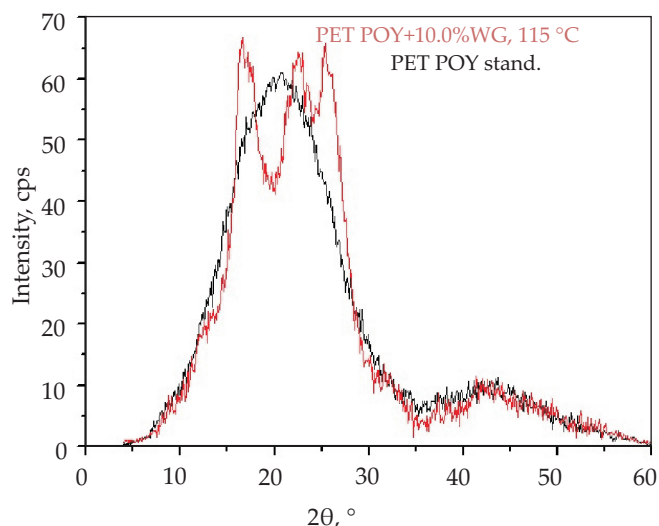| Sample of fibers	T_r, °C	ΔH_r, J/g	T_m, °C	ΔH_m, J/g	κ_{DSC}, %
PET POY stand.	132.3	38.7	256.1	44.7	4.3
PET POY, 115 °C	–	–	257.2	46.8	33.4
PET POY+0.3%WG, 115 °C	–	–	257.4	46.8	33.3
PET POY+0.5%WG, 115 °C	–	–	257.4	46.7	33.3
PET POY+10.0%WG, 115 °C	–	–	257.1	45.0	32.1

Fig. 4. Comparison of WAXS patterns of standard (unmodified) PET POY fibers (black) and PET POY fibers modified with WG (10.0 wt %) in 115 °C (red)
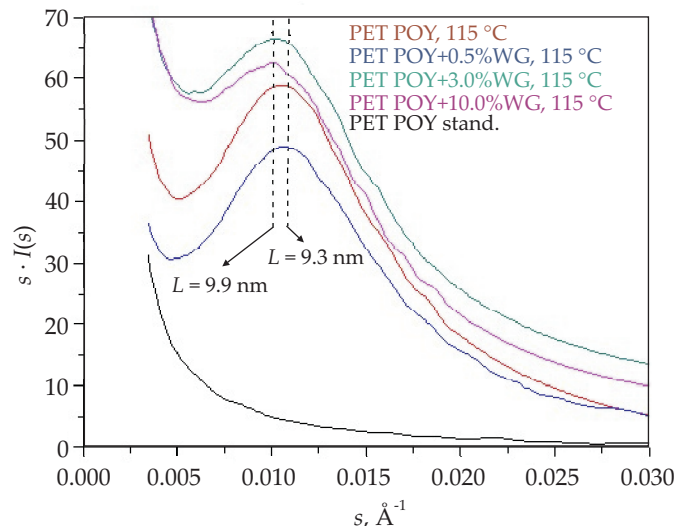

Fig. 5. Normalized SAXS curves (where s is the scattering vector; $s = 2\sin\theta/\lambda$) for unmodified PET POY fibers (black) and fibers modified in the bath of temperature 115 °C (other colors, respectively)

The crystalline structure of PET POY fibers is developed in the process of their heat treatment accompanying the flame retardant modification. The determined value of mass degree of crystallinity (Table 3) is at a level of approx. 32 % irrespective of the water-glass content in the bath. This confirms the conclusion drawn from the results of the DSC studies that the impact of modifier on the formation of the crystalline phase of PET POY fibers is substantially negligible, with a minor exception of the fibers modified with a content of WG in the bath that is 20 times higher than the optimal variant, where a slight reduction in the degree of crystallinity can be noticed. Average crystallite size values, determined from WAXS measurements, using the Scherrer equation, in a direction perpendicular to a family of lattice planes (101) and (100), also show no specific tendencies.

It is worth noting here that the degree of crystallinity values obtained using DSC and WAXS methods are largely compatible, differing only by approx. 1 % (*i.e.*, within the error limits of both methods). The only exception to this are "green" PET POY fibers, for which DSC method indicated low crystallinity of just above 4 %, as opposed to the WAXS method according to which it was conside-

T a b l e 3. Parameters of structure of PET POY fibers obtained from WAXS measurements

Sample of fibers	Degree of crystallinity κ_{WAXS}, %	Dimensions of crystallites $D_{(hkl)}$, nm	
		$D_{(101)}$	$D_{(100)}$
PET POY stand.	Almost amorphous		
PET POY, 115 °C	32.1	4.3	2.9
PET POY+0.5%WG, 115 °C	32.2	4.1	3.0
PET POY+3.0%WG, 115 °C	32.2	4.4	2.9
PET POY+10.0%WG, 115 °C	31.7	4.3	3.0

red nearly amorphous. This situation is entirely justified since in the case of transformation of thermally metastable POY fiber structure during the DSC measurement, the precise evaluation of the fuzzy temperatures of cold crystallization effect becomes practically impossible.

Analysis of the small-angle X-ray scattering curves provided an opportunity for a deeper look at the nanostructure of PET POY fibers (Fig. 5). The comparison of one-dimensional SAXS diffraction patterns reveals the lack of any electron density fluctuations, expressing the existence of a lamellar arrangement in the direction parallel to the axis of the fibers for unmodified POY fibers. In the process of heat treatment of these fibers a lamellar system develops, the presence of which is confirmed by the clear diffraction peak occurring in the small-angle patterns. The position of the discussed peak determines the value of the so-called long period of the structure, whose size was determined at 9.3 nm based on the Bragg equation for fibers treated only in a blank bath and at low flame retardant contents. At very high WG concentrations in the bath (more than 3 wt %) this value increases to 9.9 nm. At the same time, the crystalline lamella thickness l_c determined on the basis of a correlation function, does not change, regardless of the modifier concentration in the bath. This leads to the conclusion that, at relatively low concentrations, water-glass is located only in the interfibrillar areas of PET POY fibers material, while at relatively high concentrations of flame retardant, exceeding the optimum concentration by several times, it begins to penetrate intrafibrillar amorphous regions, which, however, does not increase its efficiency in the process of fiber burning.

CONCLUSIONS

Based on the studies, conclusions were developed both for the technological parameters of the proposed flame

retardant modifications, as well as for its structural implications.

– Based on DSC results the maximum temperature (115 °C) of flame retardant modification of PET POY fibers, using bath method, was established.

– Application of bath method and water-glass (as the flame retardant), significantly reduces the flammability of the examined fibers (Table 1). The obtained flame retardant effect is permanent. Flammability reduction reached by surface modification is slightly lower than for chemical modification (during the polycondensation process) or physical modification (mix of flame retardant and the polymer in the melt) [18]. However, both chemical and physical methods make technological difficulties and are much more expensive that the surface modification method presented in our work.

– Using the limiting oxygen index method, the flame retardant concentration in the bath (0.5 wt %) was determined on a level assuring the maximum flame resistant effect (*LOI* = 28.2 %).

– Thermogravimetric studies performed in air atmosphere enabled precise monitoring of flame retardant effect. Thermogravimetric studies clearly confirmed *LOI* results.

– The applied surface flame retardant modification does not affect quality of the crystalline fraction of PET POY fibers (Tables 2 and 3), compared to the alternative chemical and physical methods which significantly change the degree of crystallinity.

– At relatively low concentrations, water-glass is located only in the interfibrillar areas of PET POY fiber material, while at relatively high concentrations of flame retardant; exceeding the optimum concentration by several times, it begins to penetrate intrafibrillar amorphous regions.

REFERENCES

[1] Zhang J., Ji Q., Zhang P. *et al.*: *Polymer Degradation and Stability* **2010**, *95*, 1211.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2010.04.001

[2] Didane N., Giraud S., Devaux E. *et al.*: *Polymer Degradation and Stability* **2012**, *97*, 879.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2012.03.038

[3] Didane N., Giraud S., Devaux E. *et al.*: *Polymer Degradation and Stability* **2012**, *97*, 2545.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2012.07.006

[4] Didane N., Giraud S., Devaux E.: *Polymer Degradation and Stability* **2012**, *97*, 1083.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2012.04.010

[5] Zhang X., Zhong Y., Mao Z.P.: *Polymer Degradation and Stability* **2012**, *97*, 1504.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2012.05.006

[6] Alongi J.: *Fibers and Polymers* **2011**, *12*, 166.

[7] Borysiak S.: *Journal of Thermal Analysis and Calorimetry* **2015**, *119*, 1955.
http://dx.doi.org/10.1007/s10973-014-4341-y

[8] Doğan M., Erdoğan S., Bayramlı E.: *Journal of Thermal Analysis and Calorimetry* **2013**, *112*, 871.
http://dx.doi.org/10.1007/s10973-012-2682-y

[9] Jitjaicham M., Kusuktham B.: *Silicon*, Published online: 03 March 2017.
http://dx.doi.org/10.1007/s12633-016-9494-9

[10] Chen D.Q., Wang Y.Z., Hu X.P. *et al.*: *Polymer Degradation and Stability* **2005**, *88*, 349.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2004.11.010

[11] Liang S., Neisius N.M., Gaan S.: *Progress in Organic Coatings* **2013**, *76*, 1642.
http://dx.doi.org/10.1016/j.porgcoat.2013.07.014

[12] Carosio F., Laufer G., Alongi J. *et al.*: *Polymer Degradation and Stability* **2011**, *96*, 745.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2011.02.019

[13] Varesano A., Tonin C., Ferrero F. *et al.*: *Journal of Thermal Analysis and Calorimetry* **2008**, *94*, 559.
http://dx.doi.org/10.1007/s10973-007-8639-x

[14] Fakin D., Kleinschek K.S., Kurecic M. *et al.*: *Surface and Coatings Technology* **2014**, *253*, 185.
http://dx.doi.org/10.1016/j.surfcoat.2014.05.035

[15] Toda T., Yoshida H., Fukunishi K.: *Polymer* **1997**, *38*, 5463. http://dx.doi.org/10.1016/S0032-3861(97)00093-1

[16] Gawłowski A., Fabia J., Graczyk T. *et al.*: *Journal of Thermal Analysis and Calorimetry* **2016**, *125*, 1327.
http://dx.doi.org/10.1007/s10973-016-5498-3

[17] Fabia J., Gawłowski A., Graczyk T. *et al.*: *Polimery* **2014**, *59*, 557.
http://dx.doi.org/10.14314/polimery.2014.557

[18] Baseri S., Karimi M., Morshed M.: *European Polymer Journal* **2012**, *48*, 811.
http://dx.doi.org/10.1016/j.eurpolymj.2012.01.017

[19] Liu L.B., Sumita M., Asaka K.M.: *Journal of Materials Science* **1988**, *23*, 2683.
http://dx.doi.org/10.1007/BF00547437

[20] Warner S.B.: *Journal of Thermal Analysis* **1983**, *28*, 17.
http://dx.doi.org/10.1007/BF02105275

[21] Geller V.E.: *Fibre Chemistry* **2006**, *38*, 298.
http://dx.doi.org/10.1007/s10692-006-0084-2

[22] Bhat N.V., Kale M.J.: *Fibers and Polymers* **2012**, *13*, 936.
http://dx.doi.org/10.1007/s12221-012-0936-8

[23] Kim H.A., Kim S.J.: *Fibers and Polymers* **2016**, *17*, 427.
http://dx.doi.org/10.1007/s12221-016-5942-9

[24] Chen Y., Peng H., Li J. *et al.*: *Journal of Thermal Analysis and Calorimetry* **2014**, *115*, 1639.
http://dx.doi.org/10.1007/s10973-013-3461-0

[25] Wang Y., Zhang L., Yang Y. *et al.*: *Journal of Thermal Analysis and Calorimetry* **2015**, *122*, 1331.
http://dx.doi.org/10.1007/s10973-015-4875-7

[26] Khandual A.: "Environmental Footprints and Eco-design of Products and Processes", Chapter "Green

Fashion Vol. 2", (Eds. Muthu S.S., Gardetti M.A.), Singapore 2016, pp. 171–227.
http://dx.doi.org/10.1007/978-981-10-0245-8_6

[27] Horrocks A.R.: *Polymer Degradation and Stability* **2011**, *96*, 377.
http://dx.doi.org/10.1016/j.polymdegrad-stab.2010.03.036

[28] Lu S.Y., Hamerton I.: *Progress in Polymer Science* **2002**, *27*, 1661.
http://dx.doi.org/10.1016/S0079-6700(02)00018-7

[29] Dasaria A., Yub Z.Z., Caic G.P. *et al.*: *Progress in Polymer Science* **2013**, *38*, 1357.
http://dx.doi.org/10.1016/j.progpolymsci.2013.06.006

[30] Malucelli G., Carosio F., Alongi J. *et al.*: *Materials Science and Engineering: R: Reports* **2014**, *84*, 1.

http://dx.doi.org/10.1016/j.mser.2014.08.001

[31] Chen X., Song W., Liu J. *et al.*: *Journal of Thermal Analysis and Calorimetry* **2015**, *120*, 1819.
http://dx.doi.org/10.1007/s10973-015-4428-0

[32] Ji Q., Wang X., Zhang Y. *et al.*: *Composite Part A: Applied Science and Manufacturing* **2009**, *40*, 878.
http://dx.doi.org/10.1016/j.compositesa.2009.04.010

[33] Rabiej M.: *Journal of Applied Crystallography* **2017**, *50*, 221.
https://doi.org/10.1107/S160057671601983X

[34] Daubeney R. de P., Bunn C.W., Brown C.J.: *Proceedings of the Royal Society A: Mathematical, Physical and Engineering Sciences* **1954**, *226A*, 531.
http://dx.doi.org/10.1098/rspa.1954.0273

Received 3 IV 2017.

W kolejnym zeszycie ukażą się m.in. następujące artykuły:

M. Budnicka, A. Gadomska-Gajadhur, P. Ruśkowski, L. Synoradzki – Polimery biodegradowalne w leczeniu gruźlicy. Cz. II. Wymagania i charakterystyka materiałów

J. Ryszkowska, M. Auguścik, M. Zieleniewska, L. Szczepkowski, M. Kurańska, S. Bąk, M. Antos-Bielska, A. Prociak – Półsztywne pianki poliuretanowe z poliolem rzepakowym o różnej lepkości (*j.ang.*)

M. Urbaniak – Diagram temperatura zeszklenia-temperatura sieciowania-przemiana (T_gTT) dla układu epoksydowego EPY® (*j.ang.*)

R. Malinowski, K. Janczak, K. Moraczewski, A. Raszkowska-Kaczor – Analiza stopnia spęcznienia i frakcji żelowej usieciowanych radiacyjnie mieszanin polilaktyd/poli(adypinian-*co*-tereftalan butylenu)

S. Kuciel, P. Kuźniar, M. Nykiel – Polimery biodegradowalne w strumieniu odpadów zmieszanych – problemy recyklingu polietylenowych materiałów opakowaniowych (*j.ang.*)

A. Nastaj, K. Wilczyński – Optymalizacja procesu wytłaczania jednoślimakowego tworzyw polimerowych – badania doświadczalne

S. Paszkiewicz, A. Szymczyk, I. Irska, D. Pawlikowska, E. Piesowicz – Synteza i charakterystyka nowych reaktywnych mieszanin polimerowych opartych na poużytkowych foliach z poli(tereftalanu etylenu) oraz poli(tlenku tetrametylenu) (*j.ang.*)

T. Dziubek – Zastosowanie współrzędnościowych metod pomiarowych do oceny właściwości użytkowych polimerowych kół zębatych (*j.ang.*)