Modification of polyamide 6 fibers with water-glass in the bath method*)

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Abstract: High temperature (HT) bath method was used to produce the flame-retardant polyamide 6 (PA6) fibers, analogous to dyeing using dispersed dyes. The modification process was carried out in a bath containing flame-retardant and a surfactant (dispersant). An ecological commercial product – so-called soda water-glass, *i.e.*, aqueous sodium silicate solution (WG) – was used as flame-retardant. The resulting flame-retardant effect was evaluated on the basis of the limiting oxygen index (*LOI*) method. The thermal properties of the examined fibers were determined using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Basic mechanical testing of fibers was also performed. Fiber burning residues were characterized on the basis of photographs obtained by scanning electron microscopy (SEM). Changes in the supermolecular structure of PA6 fibers after the modification were discussed using wide-angle X-ray scattering (WAXS). As a result of the proposed modification of PA6 fibers a small but sustained increase in the flame-retardant effect was obtained.

Keywords: PA6 fibers, *LOI*, TGA, DSC, WAXS, SEM.

Modyfikacja włókien z poliamidu 6 szkłem wodnym metodą kąpielową

Streszczenie: Włókna z poliamidu 6 (PA6) o zmniejszonej palności wytworzono z zastosowaniem metody kąpielowej HT (*high temperature*), prowadzonej w sposób analogiczny do barwienia włókien barwnikami zawiesinowymi. Kąpiel modyfikująca zawierała uniepalniacz oraz środek powierzchniowo czynny (dyspergator). Środkiem uniepalniającym był ekologiczny produkt handlowy o nazwie szkło wodne sodowe – wodny roztwór krzemianu sodu (WG). Uzyskany efekt trudnozapalności oceniano na podstawie wyznaczonego indeksu tlenowego (*LOI*). Właściwości termiczne badanych włókien określano za pomocą różnicowej kalorymetrii skaningowej (DSC) i analizy termograwimetrycznej (TGA). Wykonano też podstawowe badania wytrzymałości mechanicznej włókien. Pozostałości po spaleniu włókien charakteryzowano na podstawie fotografii uzyskanych techniką elektronowej mikroskopii skaningowej (SEM). Zmiany w strukturze nadcząsteczkowej włókien PA6 poddanych modyfikacji oceniano z wykorzystaniem szerokokątowej dyfraktometrii rentgenowskiej (WAXS). W wyniku zaproponowanej modyfikacji uzyskano niewielkie, ale trwałe zmniejszenie palności włókien PA6.

Słowa kluczowe*:* włókna PA6, *LOI*, TGA, DSC, WAXS, SEM.

Polyamide 6 (PA6) is an excellent engineering material due to its high mechanical strength, low coefficient of friction and chemical resistance [1–6]. Due to the specific technical applications, composites in which PA6 is reinforced by fiberglass are often encountered. This material, in addition to industrial applications, is also used for fiber production. Products made of PA6 fibers (or their significant addition) are often used for the interior design of public utilities buildings and public means of transport. For such types of applications, these must comply with very strict fire safety requirements. Although PA6 does not belong to easily combustible polymers (*LOI* of approx. 24 %), in some cases the level of its flash resistance is insufficient. Consequently, the PA6 fiber material must undergo a flash-resistant modification. Currently, organic and inorganic compounds of phosphorus, silicon, aluminum, and nitrogen are used to modify PA6 [7–11]. Previously used flame-retardants containing halogen atoms (Cl, Br) are withdrawn from use due to their toxicity [12–17]. To obtain flash-resistant PA6 fibers, additive flame-retardants can be admixed to the melt or spinning solution during the spinning process [7, 18–20]. However,

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there are difficulties in selecting a PA6 flame-retardant as it is not easy to match it to the polymer matrix. In addition, to obtain an acceptable technical flame-retardant effect, a very large amount of flame-retardant substance of up to 30 wt % should be added to the polymer. With such high levels of flame-retardant, the strength of the polymer decreases, and obtaining fibers becomes virtually impossible [21, 22]. Obviously, there are exceptions described in the literature, where already at 7 wt % of a flame-retardant, the flash-resistant properties of PA6 fibers have been obtained with good mechanical properties [23]. With few exceptions, including those mentioned above, there are no reports in the literature on flame-retardant modified PA6 fibers. This gap is bridged with the presented work on the application of non-flammable PA6 fibers of aqueous solution of sodium silicate – so-called water-glass. The modification process was carried out in the bath, similarly as for dye method. In this way, PA6 fiber with improved flash resistance was obtained.

EXPERIMENTAL PART

Materials

The materials used in this work were all commercially available technical products. The polyamide (PA6) fibers (multifilament 21 tex f16 t0) supplied by Stilon S.A. (Poland) were used.

The flame-retardant modifier used in this work – water-glass (WG) – CAS 1344-09-8, was supplied by Rudniki S.A. (Poland).

Flame-retardant modification process

The modification consists in inserting flame-retardant compound in dyeing 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: temperatures: 100 °C, 110 °C, 120 °C, 130 °C; treatment time 1 h and heating rate 2.5 deg/min, respectively. The PA6 fibers were treated in the water-glass solution of 1, 3, 5 and 10 %, respectively calculated per fiber weight.

Dispersing agent: dyspergator NNO (a nonionic dispersing agent from Organika-Rokita, Poland) was added into the modification bath in the amount of 1.5 g/dm^3.

After the modification treatment investigated samples were washed in a solution of detergent Pretepon G (Organika-Rokita, Poland) in the amount of 5 g/dm^3. The washing time was 30 minutes and the temperature 60 °C.

Methods of testing

– The obtained flame-retardant effect of PA6 fibers was evaluated using the method of the limiting oxygen index (*LOI*). 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.

– For PA6 multifilament samples tested, the basic strength parameters were determined taking into account the recommendations of EN ISO 2062:2009 standard. Measurements were carried out using Instron 5544 testing machine with a compression-tensile head with a measuring range of 0–2 kN. The tests were carried out with equal break velocity of 200 mm/min for all samples. To determine the strength parameters: average break strength and relative average elongation at break, 50 ruptures were tested for each variant, assuming a random error of 2 % of the average break strength value. The measuring distance between the jaws was 250 mm. The testing was carried out under normal climate conditions (EN ISO 139:2005).

– TGA investigations were performed using Thermogravimetric Analyzer TA Instruments Q500. Measurements were done in a temperature range from 30 to 720 °C with the heating rate of 20 deg/min in air atmosphere (flow 40 cm^3/min).

– Differential scanning calorimetry measurements were performed using a TA Instruments Thermal Analysis System 5100 equipped with TA Instruments 2920 Calorimeter and RCS cooling system. The measurements were registered in the temperature range 0–260 °C, using TA standard aluminum pans, under nitrogen atmosphere (flow 40 cm^3/min) with a heating rate of $\beta_+ = 10$ deg/min. The data were evaluated by means of the Universal V2.6D TA Instruments software.

– Wide-angle X-ray scattering investigations were carried out with a URD-65 Seifert diffractometer. CuK$_\alpha$ radiation was used at 40 kV and 30 mA. Monochromatization of the beam was obtained by means of a nickel filter and a pulse-height analyzer. A scintillation counter was used as a detector. Investigations were performed in the range of angles 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 [24] was used.

– The surface of fibers and remnants after the burning process was examined using a JSM-5500LV scanning electron microscope supplied by JEOL. The samples were mounted on aluminum stubs and coated with gold (JFC 1200, JEOL). Secondary (SE) and back-scattered electron (BSE) observations were conducted with an accelerating voltage of 10 kV. Microphotographs were obtained at magnifications ranging from 50× to 500×.

RESULTS AND DISCUSSION

Research on the effectiveness of flame-retardant modification by *LOI* method

In the course of the research on the possibility of the flame-retardant modification of PA6 fibers in the bath us-

Table 1. Limiting oxygen index (*LOI*) of polyamide 6 fibers modified with water-glass (WG)

Temperature of bath, °C	Content of WG in bath, wt %			
	1	3	5	10
	LOI, %			
100	26.0	26.2	26.2	26.4
110	26.6	26.7	26.7	26.9
120	27.1	27.2	27.5	27.5
130	26.4	26.3	26.5	26.5

ing water-glass, 16 different variants of the modified fibers were obtained (four temperatures and four WG concentrations in the bath). For such a large sample population it was necessary to define a logical path of research in order to identify the most favorable (optimum) variant. Such a procedure allows to avoid the proliferation of costly and time-consuming structural research for modification variants without practical justification, which is often expressed by too low cost-effectiveness of modification and/or significant deterioration in the performance of the modified materials.

Taking into account the above considerations, in our case the study started with the determination of the *LOI* – the basic indicator defining the effectiveness of the proposed flame-retardant modification for all variants of modified PA6 fibers (Table 1).

The unmodified PA6 fibers show a limiting oxygen index value of 24.2 %. Treating these fibers in a blank bath (water at 120 °C) did not change the value.

By analyzing the data in the Table 1 it should be noted that the *LOI* index improvement (increase) was obtained for all modified fibers, with *LOI* values not changing strictly monotonically, both with the increase of temperature and WG concentration in the bath. Definitely the most advantageous was the modification at 120 °C, which is a certain analogy to the dyeing efficiency of PA6 with dispersed dyes [25]. The temperature dependence of the *LOI* index is more pronounced than its changes due to the increase in WG concentration in the bath within the analyzed range (0 to 10 %).

Study of mechanical properties

Tensile strength of the initial PA6 multifilament is higher by approx. 2–5 % than that of the PA6 multifilament processed at 120 °C, and the elongation at break is approx. 100 % lower. The breaking forces and elongation at break for water-glass modified fibers are similar within the limits of statistical error, regardless of the amount of WG used, and exhibit values similar to those for the blank bath (Table 2).

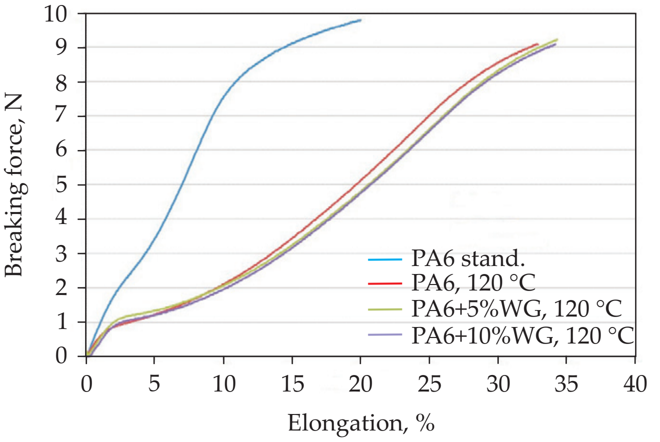

Fig. 1. Characteristic stress-strain curves for tested PA6 filaments: unmodified standard (blue), treated in water at 120 °C (red), modified in the bath with water-glass (WG 5 wt %) at 120 °C (green), modified in the bath with water-glass (WG 10 wt %) at 120 °C (purple), respectively

Also the profile of the stretching curves is similar. Compared to the reference sample stretching (unmodified PA6 multifilament), the stretching curves for heat-treated fiber samples differ substantially (Fig. 1), as evidenced by literature [26]. These fibers show lower values of elastic limit and yield point, and corresponding areas of elastic, plastic and permanent set deformations.

Summarizing the results of conducted mechanical tests it should be stated that the applied flame-retardant modification resulted in only a slight reduction in the mechanical parameters of the fibers to a level that is fully acceptable in their potential uses. Although WG does not significantly affect the strength, but the processing temperature has an effect on the stretching curve and a significant increase in the elongation at break.

TGA measurements

The results of flame-retardant properties improvement of the discussed PA6 fibers obtained in *LOI* tests were

Table 2. Mechanical parameters of PA6 fibers modified with water-glass

Sample	Breaking force N	Coefficient of variation of breaking force %	Elongation at break %	Coefficient of variation of elongation at break %
PA6 stand.	9.79	2.28	19.98	6.15
PA6, 120 °C	9.38	3.30	35.23	6.78
PA6+1%WG, 120 °C	9.29	4.07	35.09	4.16
PA6+3%WG, 120 °C	9.25	3.74	34.87	5.37
PA6+5%WG, 120 °C	9.23	3.76	34.28	5.98
PA6+10%WG, 120 °C	9.19	4.65	34.16	8.69

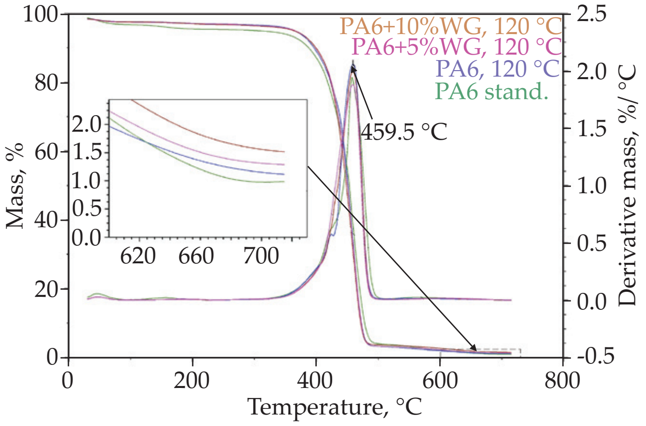

Fig. 2. TG and DTG curves registered during measurements provided in nitrogen atmosphere, for PA6 fibers: unmodified standard (green), treated in water at 120 °C (blue), modified in the bath with water-glass (WG 5 wt %) at 120 °C (pink), modified in the bath with water-glass (WG 10 wt %) at 120 °C (maroon), respectively

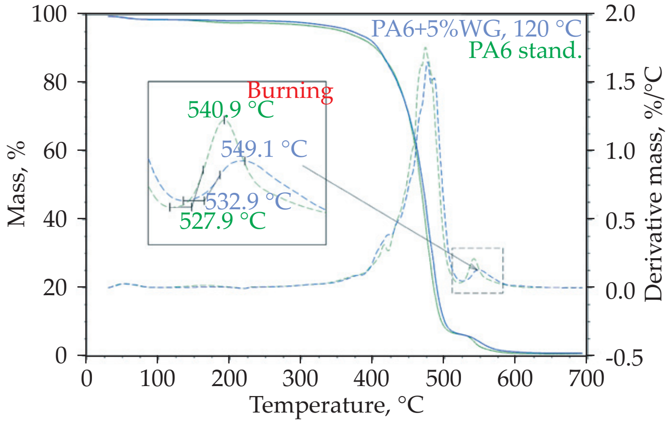

Fig. 3. TG and DTG curves registered during measurements provided in air atmosphere, for PA6 fibers: unmodified standard (green), modified in the bath with water-glass (WG 5 wt %) at 120 °C (blue), respectively

verified using the thermogravimetric analysis method. In addition to the fundamental process reflecting the 1-stage thermal dissociation of PA6, with the highest mass loss rate expressed by the maximum of DTG curves at approx. 460 °C, the TGA measurements of the tested fibers, carried in standard inert atmosphere, in the range of 30–720 °C (Fig. 2), show loss of sample weight associated with dehydration.

This effect is very pronounced for unmodified PA6 fibers (which due to the relatively high moisture sorption of these fibers is obvious) and is significantly reduced for water-glass modified fibers, with the solution penetrating the fibers instead of water. Confirmation of this observation is a comparison of the amount of residues (carbonization products) after the process of thermal decomposition of fibers up to 720 °C (magnified in Fig. 2). The residue for 10 % water-glass modified fiber is 0.5 % greater than that of the unmodified fiber sample.

As mentioned above, proper confirmation of the results of the *LOI* tests was obtained by TGA analysis of fibers heated in air. As in earlier works on PET fiber modification [27] we used the fact that the decomposition of PA6 in the air and the combustion process of the resulting carbonization product are clearly separated in temperatures (Fig. 3).

Based on the analysis of the DTG differential curves at the ignition and burning of carbonization products, the maximum corresponding to the highest burning rate was found to be shifted towards higher temperatures. In case of the most advantageous variant of the modification (5 % WG, 120 °C) this shift was just over 8 °C (magnification, Fig. 3). It should also be noted that the fibers modified in this way ignite at the temperature 5 °C higher than unmodified ones. This additionally confirms the improvement of the flame-retardant properties of the fibers as a result of the proposed modification.

DSC studies

Explanations of the impact of the used flame-retardant on the fiber structure were sought based on calorimetric studies applied to a series of fibers modified according to the most preferred temperature variant (120 °C).

The nature of the DSC curves registered for all variants of WG concentration in the bath as well as for the unmodified fibers is exactly the same. The curves show two endothermic effects. The first one, of relatively light intensity, corresponds to the moisture evaporation, while the second one, important for structural reasons, shows the melting of the crystalline fraction of the fibers. The values of temperature and melting enthalpy determined from the DSC curves differ only slightly (Table 3).

Table 3. Values of: melting temperature (T_m), melting enthalpy (ΔH_m) and crystallinity (κ) calculated on the basis of a DSC curves

Sample	Melting temperature T_m, °C	Melting enthalpy ΔH_m, J/g	Crystallinity κ_{DSC}, %
PA6 stand.	219.4	89.5	38.9
PA6, 120 °C	218.8	99.6	43.3
PA6+5%WG, 120 °C	219.3	100.3	43.6
PA6+10%WG, 120 °C	219.0	100.1	43.5

The most important change in crystallinity (less than 3 %) is for fibers that are unmodified and treated in a blank bath. Further increasing (even 10 times) of WG concentration in the bath results in only slight changes in the degree of crystallinity, falling within the error range of the method. Similarly, the minimum melting peak temperature, correlated with the average size of the crystallites, does not change significantly either as the concentration of the modifier is increased.

T a b l e 4. Parameters of structure of PA6 fibers obtained from WAXS measurements

Sample	Content of crystalline phase κ, %			Dimensions of crystallites $D_{(hkl)}$, nm	
	κ_c	κ_α	κ_β	$D_{(101)}$	$D_{(002)/(202)}$
PA6 stand.	45.3	38.1	7.2	5.4	3.7
PA6, 120 °C	48.1	42.5	5.6	8.6	5.5
PA6+5%WG, 120 °C	48.4	43.0	5.4	9.2	5.6
PA6+10%WG, 120 °C	47.9	42.3	5.6	9.1	5.3

κ_c – degree of crystallinity, κ_α – crystalline phase α, κ_β – crystalline phase β.

Structural investigations WAXS and SEM

PA6 exhibits a varied crystallographic polymorphism. In general, two most important forms of crystallites, α and γ, are distinguished, and the remaining fractions are treated as variants of major forms occurring in specific cases. The most thermodynamically stable form α and metastable form β are predominant in the fibers. The monoclinic α form is a thermodynamically stable fraction, obtained mainly by non-isothermal crystallization during the relatively slow cooling of the molten polymer, isothermal crystallization at higher temperatures and by reheating previously cooled down melt PA6 [28]. The pseudo hexagonal β form is less stable and has a lower density. It is formed mainly as a result of the rapid cooling (quenching) of PA6 melt [29].

The crystalline structure of the classical PA6 fibers is formed during the forming process and, as noted above, is dominated by the most thermodynamically stable crystalline form α [30]. This structure is additionally rebuilt during the process of fiber stretching and their thermal stabilization [31]. The rebuilding indicated above is primarily manifested by the increase in the content of the crystalline form α-PA6.

In this work, such PA6 fibers – classically formed from the melt and then stretched and thermally stabilized – were subjected to a flame-retardant modification in the bath. Therefore, despite the high-temperature processing of the fibers during the modification, as expected, no dramatic reconstruction of their crystalline structure was observed (Fig. 4, Table 4).

A change in the fiber crystallinity (2.8 % *vs.* unmodified fibers) was obtained only for the blank bath treatment variant (120 °C for 1 h). The total demonstrated crystallinity increase was contributed by the increase in the content of the α phase (by 4.4 %), while reducing (by 1.6 %) the amount of the unstable β variant in the fiber structure. This was accompanied by an increase in the mean size of crystallites calculated in the direction perpendicular to the families of network planes (101) and (002)/(202) based on the Scherrer equation. The addition of WG as flame-retardant to the water bath, regardless of its concentration, did not cause significant quantitative changes within the crystalline phase (Table 4). Thus,

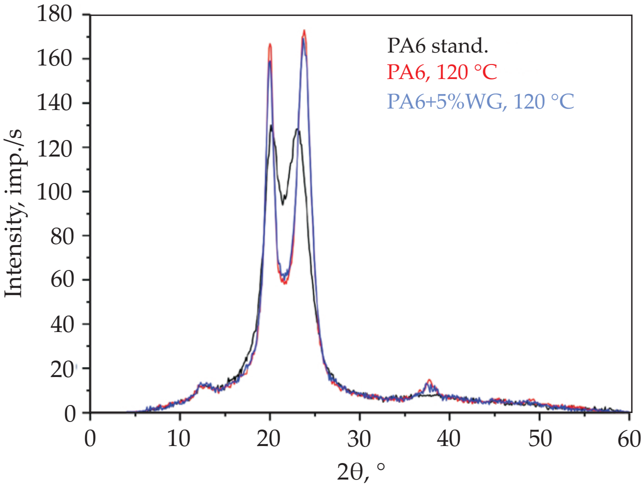

Fig. 4. Comparison of WAXS patterns of: standard PA6 fibers (black curve), PA6 fibers treated at 120 °C (red curve) and modified in the bath (WG 5 wt %) at 120 °C (blue curve), respectively

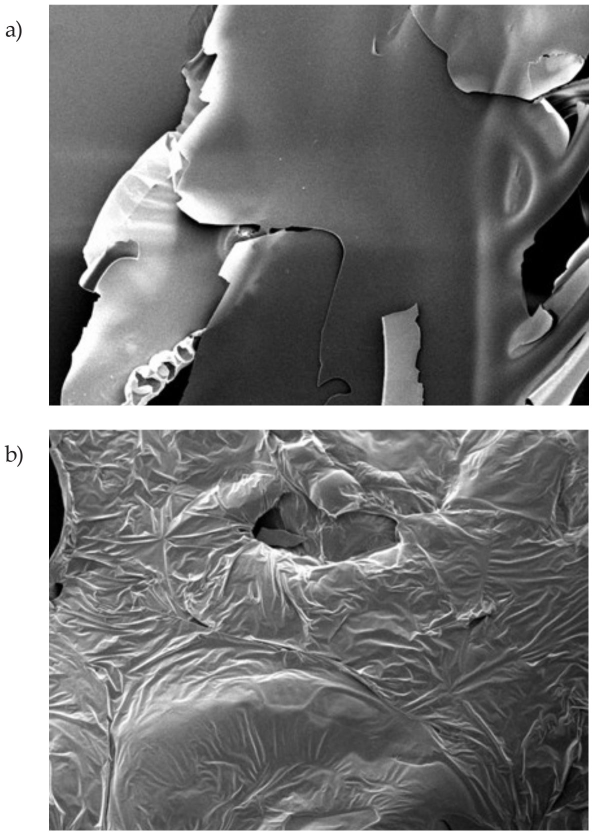

Fig. 5. SEM microphotographs of scorching after the process of burning of PA6 fibers: a) unmodified, b) modified with water-glass in the bath (applied magnification 500×)

summarizing the above considerations, it should be stated that the structural conditions at the supermolecular level, in the case of the proposed flame-retardant modification of PA6 fibers are practically negligible.

In view of the above, the explanation of the reason for the noticeable improvement of the flame-retardant properties of the tested fibers was sought based on the analysis of SEM microscopic images for scorching resulting from the burning of fibers in the air atmosphere.

The microphotograph of the fragment of the scorch formed in the immediate vicinity of the flame, in the case of unmodified fibers (Fig. 5a), illustrates a completely smooth, homogeneous scorch surface, showing very low viscosity of the burning PA6 material formed after melting of the fibers.

The surface of a fragment of scorch formed during the attempt to burn water-glass modified fibers (Fig. 5b) is quite different. In this case, the entire surface of the scorch is covered with a flexible coating, which probably impedes the release of PA6 gaseous decomposition products into the flame zone. In this way, an effective delay is achieved both in terms of the ignition of the sample (as evidenced by the *LOI* and TGA results) as well as the dynamics of the flame propagation.

CONCLUSIONS

Summarizing, it should be noted that the use of water-glass, as an environmentally friendly flame-retardant, for the modification of bath for classic PA6 filament fibers resulted in the intended and lasting improvement in the flame-retardancy. However, the efficiency of the proposed technology is not too high. Compared to previous authors work on analogous modification of PET fibers [27] the result obtained for PA6 fibers is significantly worse. For PET fibers, a relative increase in the *LOI* index by almost 30 % was achieved, compared to just over 16 % for PA6 fibers discussed in this paper. The increase in the *LOI* value was reflected in the shift of the maximum on the DTG curves showing the greatest dynamics of burnt fiber weight loss. For PET fibers, in the most favorable modification variant, the shift was about 40 °C while for PA6 fibers – just over 8 °C, which clearly confirms the results of the *LOI* tests.

It is also worth noting that the largest relative increase in the *LOI* index of approximately 12 % is observed at the transition from unmodified PA6 fibers to those modified with the WG concentration in the bath that is the lowest of all tested variants (1 %). Further increasing of WG concentrations in the bath, even several times, brings only a slight increase in the index, and in the light of the above is practically unreasonable. The same situation is for increasing the application temperature to over 120 °C.

Thus, given the relative lack of complexity of the proposed modification, low application costs, and durability of the improved PA6 fiber flame-retardant effect, it is certainly worth to develop the bath method to improve its efficiency. In this respect, further studies with other flame-retardants should be considered, especially in synergistic system compositions.

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