

Halloysite modified by melamine cyanurate and its compositions based on PA6

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Abstract: The results of the investigation on the synthesis and applications of halogen-free hybrid flame retardants (HFR) are presented. HFR were obtained by *in situ* modification of halloysite (HNT) with melamine cyanurate (MC). The reactions were conducted with and without the presence of poly(vinyl alcohol) (PVA) as a protective colloid. The modification of HNT was confirmed by using infrared spectroscopy (IR), scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM/EDS) and transmission electron microscopy (TEM) analyses. The thermal properties of flame retardants were investigated as well. The obtained HFR were introduced into polyamide 6 (PA6). The relationship between a type of HFR and its effectiveness in reducing the flammability as well as in improvement of mechanical properties of polymer composites was investigated. It was found, that depending on the type of applied HFR, the value of the oxygen index (OI) of the obtained composites was within 29–34.5 %. In turn, the use of PVA in the synthesis of HFR increased the flexibility of the compositions containing this type of HFR.

Keywords: melamine cyanurate, halloysite, polyamide 6, flame retardants, flame retardancy, polymer compositions.

Haloizyt modyfikowany cyjanuranem melaminy i jego kompozycje z PA6

Streszczenie: Przedstawiono wyniki prac dotyczących syntezy i zastosowania bezhalogenowych uniepalniaczy (HFR) otrzymywanych w wyniku modyfikacji *in situ* cyjanuranem melaminy (MC) glino-krzemianu warstwowo-rurkowego – haloizytu (HNT). Reakcje prowadzono w obecności poli(alkoholu winylowego) (PVA) lub bez jego udziału. Modyfikację haloizytu potwierdzono metodami spektroskopii w podczerwieni (IR), skaningowej mikroskopii elektronowej ze spektrometrią dyspersji energii promieniowania rentgenowskiego (SEM/EDS) oraz transmisyjnej mikroskopii elektronowej (TEM). Zbadano również właściwości termiczne wytworzonych uniepalniaczy. Uzyskane HFR wprowadzono do poliamidu 6 (PA6), zbadano ich wpływ na palność i właściwości mechaniczne otrzymanych kompozycji. Stwierdzono, że w zależności od rodzaju zastosowanego uniepalniacza wartość indeksu tlenowego (OI) otrzymanych kompozycji mieści się w granicach 29–34,5 %. Stwierdzono też, że zastosowanie PVA w syntezie HFR zwiększa elastyczność kompozycji otrzymanych z udziałem tak modyfikowanego haloizytu.

Słowa kluczowe: cyjanuran melaminy, haloizyt, poliamid 6, uniepalniacze, uniepalnianie, kompozycje polimerowe.

The extensive use of plastics in various fields of everyday life and technology as well as the increasingly rising safety standards for fire hazard result in the need of the modification of plastics with flame-retardant additives. Flame retardants are chemical compounds which inhibit the ignition process and change the course of pyrolysis by reducing the quantity of the flammable and volatile low molecular weight products and promoting the formation of less flammable carbonized layer acting as a bar-

rier between the plastics and the flame. An ideal flame retardant should have the least possible impact on the mechanical properties of plastics and should reduce the negative environmental impact of the gaseous products produced during the combustion of plastics. For many decades, compounds with chlorine or bromine atoms in their structure were used as fire retardants. However, during burning, polymers modified by this type of flame retardants release toxic gases into the atmosphere. These gases are more dangerous to human health than fire. For this reason, there is a continuous search for flame retardants additives that are halogen-free.

Flame retardants based on chlorine or bromine are generally added to the materials in an amount not exceeding 4–5 % by weight. Such quantities have not a significant

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influence on the mechanical properties of plastics modified by this type of flame retardants. However, as previously mentioned, they have a negative impact on the environment. In turn, the halogen-free flame retardants should be added into material in an amount of 15–25 % by weight, and in some cases even 50 % by weight, to achieve a sufficient degree of flame retardancy of the modified plastics. Such amount of the flame retardant has a negative effect on the material performance, *e.g.*, its mechanical properties. One of the halogen-free flame retardants, produced on a large scale, is melamine cyanurate (MC) which is used to reduce the flammability of polyamide 6. The methods of obtaining melamine salts are widely described in the patent literature. This type of compounds can be prepared in the direct reaction of melamine with proper organic or inorganic acid. Melamine is monobasic in its salts, an appropriate salt is obtained with almost 100 percent efficiency, if an equimolecular amount of reagents is used. In the literature, there are many reports on the synthesis of MC. In the Japanese patent [1], the authors propose to carry out the reaction in an aqueous medium at $\text{pH} > 7$, while the authors of the Polish patent [2] propose the range of pH 3–7. In turn, according to the authors of the patent [3], the best results are obtained by carrying out the reaction at pH of not above 1. Because MC makes problems during filtration, due to the extremely fine-grained form, therefore the authors of the patent [4] propose to carry out the synthesis of this compound in the kneader at low water content. According to them this allows to bypass the laborious step of filtering the precipitate.

It is well-known that introducing some additives to the polymer matrix improves some of its properties but impairs others, especially mechanical properties. On the other hand, the addition of 2–5 % by weight of nanoparticles positively influences the mechanical properties of the polymer. One of nanoadditives, used in the modification of polymers, is halloysite (HNT), a layer-tubular mineral with double layer packages. HNT has excellent mechanical properties and therefore has been used to increase the strength of many polymer nanocomposites [5–7]. Moreover, HNT positively influences their fire retardant properties [6, 8, 9]. It should be noted that about 70 % of HNT is of a layered structure. This mineral can be intercalated using sodium, ammonium, and lead acetate [10].

A lot of information regarding the modification of HNT is available in the literature. Because of tubular structure of HNT both inner lumen and outer wall surface can be modified. HNTs with modified inner lumen can be used as medicine transporters [11].

In turn, a modification of outer wall surface can be carried out using alkali [12], silanes [13–16], compounds of biological origin [17], surfactants [18, 19] and by surface grafting polymerization [20]. From the point of view of improving the thermal and mechanical properties as well as flammability, the most important modification is using silanes and surface grafting polymerization. The use of such modified HNT improves interfacial adhesion

of the HNTs-polymer nanocomposites. As a result, the improvement of the thermal and mechanical properties of thus obtained composites is observed.

In literature, no information on the modification of HNT by MC during its preparation (*in situ*) is available. As well, there are no reports regarding the influence of such modification on the mechanical, thermal and flammability properties of PA6 composites containing this type of filler. There is only one paper reporting the use of the physical mixture of MC and HNT as agents which have a positive impact on the mechanical properties of thermoplastic polymers, *e.g.*, PA6 [21]. Similar information regards physical mixture of melamine and HNT [22]. But in the articles mentioned above, authors do not discuss influence of this type of fillers on the flammability or thermal properties of polymer compositions modified in this way.

A study on the influence of physical mixture of HNT and MC introduced into butadiene-acrylonitrile rubber on the thermal, mechanical and flammability properties of the resulting composites was conducted by Rybiński and Janowska [23]. In turn, L. Li and others [24] investigated the influence of physical mixture of HNT and MC on the thermal stability and flammability of the composites obtained from PA6. An increase in the thermal stability of the composites of PA6 with MC and HNT was observed, moreover, interaction between MC and HNT promotes the formation of more yields of char. The oxygen index of the obtained compositions was in the range of 31.1–31.7 % and depended on the weight ratio and amount of fillers used.

Literature data shows that both HNT as well as melamine salts act as burn inhibitors, and what is more, HNT used as a nanofiller greatly improves the mechanical properties of the modified plastics.

Therefore, it is beneficial to use both of these compounds as flame retardants in thermoplastics. It should be emphasized that HNT occurs in Poland in the form of uniform fields and is much cheaper than foreign HNT.

For this reason the purpose of this research was to investigate the effect of the modification of HNT by MC on the thermal and mechanical properties as well as flammability of compositions obtained from PA6 and such modified HNT. The modification of HNT with MC was carried out during the synthesis of MC with or without the presence of poly(vinyl alcohol) (PVA) as a protective colloid. Its application was aimed at increasing the bulk density of the resulting fillers. The influence of protective colloid on the properties of the filler as well as PA6 compositions obtained with its use were investigated.

EXPERIMENTAL PART

Materials

Melamine (Zakłady Azotowe Puławy, Poland), cyanuric acid (Hebei Haida Chemical Industry CO., LTD, China), halloysite (HNT) (INTERMARK Gliwice, Poland).

As a protective colloid poly(vinyl alcohol) (PVA) fully hydrolyzed was used, M_w app. 200 000 (Merck, Germany), polyamide 6 (PA6) (Tarnamid T-27, Grupa Azoty Tarnów, Poland), commercially flame retarded polyamide 6 (Tarnamid T27MCSV0, Grupa Azoty Tarnów, Poland).

Syntheses

Modification of HNT by melamine salts was carried out according to the method described in the patent applications [25–28]. According to these references, the flame retardants CM10HZ, CM15HZ, CM20HZ and CM25HZ containing, respectively, 10, 15, 20 and 25 parts of HNT per 100 parts of melamine salt, were obtained. The flame retardants were obtained with and without PVA protective colloid.

The modified HNTs were introduced into PA6 using twin screw extruder Berghoff 33 LLD with concurrent screws. The flame retardants were introduced into the polymer matrix in the amounts of 8.5, 10 or 12 % by weight. The filled polyamide 6 was granulated and then injection molded by means of injection molding machine Arburg. In this way, the samples for mechanical and flame retardancy tests were obtained.

Methods of testing

– In order to confirm the modification of HNT by melamine salts, IR spectroscopy (FT IR-Perkin-Elmer 2000 apparatus), scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) (JSM – 6490LV produced by JEOL company) and transmission electron microscopy (TEM) (Zeiss Libra 120Plus apparatus) were used.

– To determine the thermal stability of the obtained additives, thermogravimetric (TG) analysis was done (TGA Q50 V20.8 Bulid 34 apparatus).

– The grain size (Mastersizer apparatus with Scirocco 2000 adapter) and the bulk density of the obtained additives were determined as well. Bulk density was determined according to the method described in the literature [29].

– Oxygen index (OI) was measured by means of FTT (England) apparatus according to the standard ASTM D 2863-97. Horizontal and vertical flammabilities were determined using UL-94 chamber (FTT England apparatus) according to the standard PN-EN 60695-11-10.

– Mechanical properties were determined according to the standards PN-EN ISO 527, PN-EN ISO 178 using single-column testing machine Instron 3345. Charpy impact strength was determined according to the standard PN-EN ISO 179/180 using impact strength hammer Roell Zwick 4J.

RESULTS AND DISCUSSION

In last decades, melamine and its derivatives, especially salts, have drawn attention as flame retardants.

Melamine salts are obtained in a direct reaction of melamine with an appropriate organic or inorganic acid.

This paper describes the results of the studies concerning the modification of HNT using MC. MC is the most popular halogen-free flame retardant, which is used to decrease flammability of PA6. The modification of HNT was carried out with or without the use of PVA as a protective colloid in order to increase the bulk density of the final product. The higher value of bulk density facilitates the dosing of the flame retardant into plastics. Moreover the presence of the protective colloid decreases the viscosity of the reaction mixture. Conducting the reactions without a protective colloid results in an increase in the viscosity of the reaction mixture. This causes an increasing of a local temperature and in the industrial applications significantly impedes the feeding into the drying zone.

The analysis of the obtained products has shown that an application of PVA during the synthesis of hybrid flame retardants (HFR) causes an increase in their bulk density (Table 1). It is very useful from the user's point of view.

In order to confirm the modification of HNT by MC, IR analysis of the obtained products was made, showing the presence of both HNT and melamine salt (Table 2).

Table 1. Analysis of bulk density of synthesized HFRs

Type of HFR	Bulk density of HFR synthesized without PVA kg/m ³	Bulk density of HFR synthesized in the presence of PVA kg/m ³
CM10HZ	300	406
CM15HZ	352	476
CM20HZ	328	486
CM25HZ	432	492

Table 2. IR analysis of synthesized HFRs

Frequency	Source	Type of band
3697–3620	Al-OH in halloysite	Valence
3390	-NH ₂ participating in the hydrogen bonds	As above
3231	-N-H in -NH ₃ ⁺ group	As above
2820–2694	-N-H in cyanuric acid	As above
2560	-NH ₃ ⁺ group	As above
1781–1740	C=O group in cyanuric acid	As above
1663–1536	-N=C< in heteroaromatic system	As above
1448	=N-C<< bond joining a substituent to the aromatic ring	As above
1033	=C-N= in heteroaromatic ring	As above
920	S-triazine ring	As above
567	Al-O group in halloysite	As above

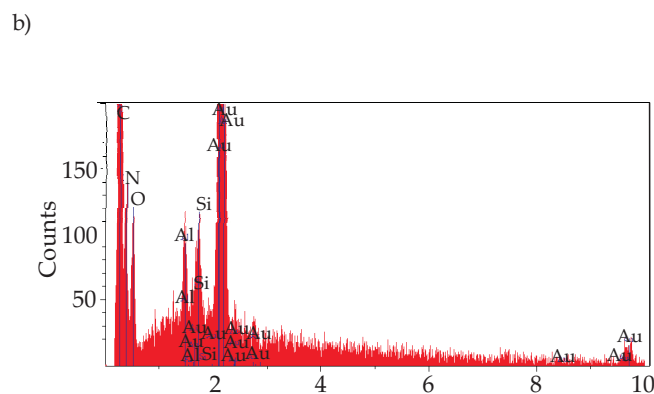
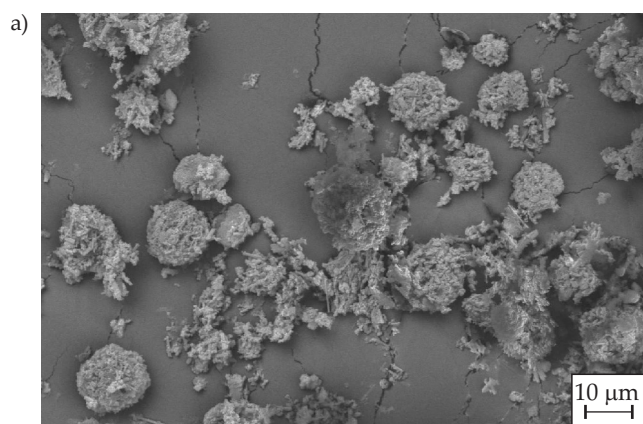


Fig. 1. a) SEM, b) EDS analysis of halloysite modified by melamine cyanurate in the presence of PVA

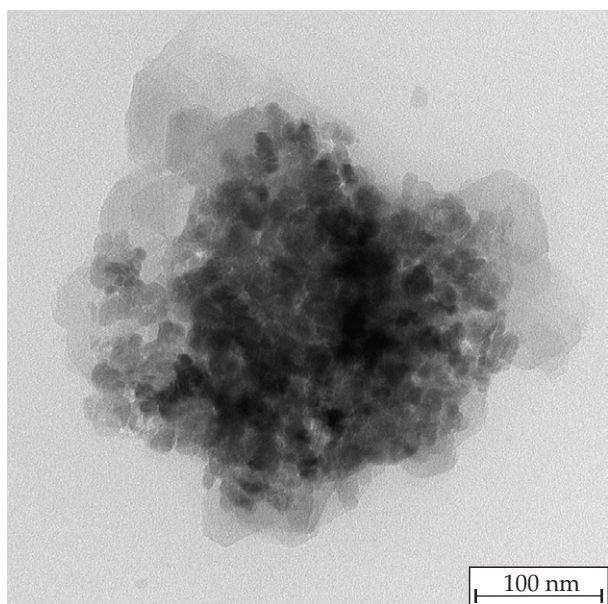


Fig. 2. TEM analysis of halloysite modified by melamine cyanurate in the presence of PVA

The HNT modification by MC was confirmed by scanning electron microscopy coupled with EDS analysis (Fig. 1). SEM micrographs showed that MC covered the surface of the HNT plates. EDS analysis indicated the presence of nitrogen and carbon on the HNT surface.

Transmission electron microscopy (TEM) also confirmed that MC is deposited on the HNT surface. In Figure 2 crystals of MC which cover the HNT plates are visible. Thus, it is the evidence that modification was carried out successfully. In Figure 2 we can also see a tubular structure of the aluminosilicate.

The above analyses (SEM and TEM) confirmed that the obtained hybrid flame retardant is not only a physical mixture but a physically modified aluminosilicate.

TG analysis was made in order to determine the thermostability of the obtained FR additives.

On the TG curve of the raw HNT (Fig. 3), we can see two endothermic peaks. The first one occurs at a temperature of 42.2 °C (mass loss 1.3 %) and comes from the elimination of water from the external surface of HNT.

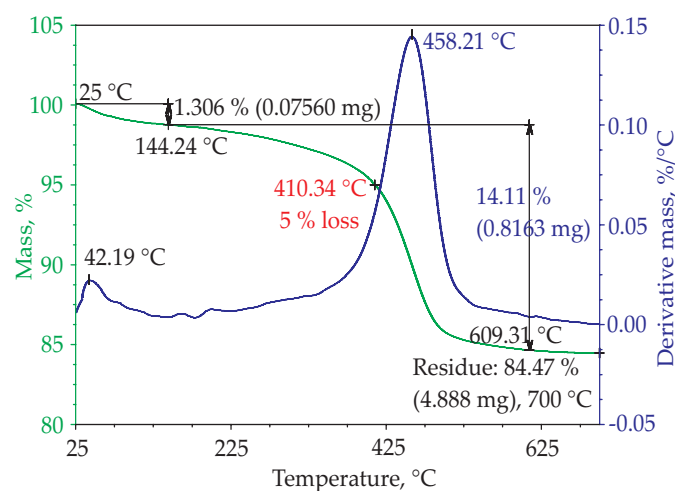


Fig. 3. TGA curve of raw halloysite

The second peak occurs at 458.2 °C and it is connected with the elimination of hydroxyl groups which are permanently bonded to the crystallographic network of the aluminosilicate. Their mass loss is 14.1 % and is very close to the theoretically calculated – 13.95 %.

In turn, on the TG curve of the commercial MC (Fig. 4), one can observe only one endothermic peak at 404.5 °C. It comes from a decomposition of melamine salt. In the case of HNT modified by melamine salts, one can observe one endothermic peak which is shifted toward lower temperature (382/388 °C), in comparison to the peak which occurs on the TG curve of commercial MC (Fig. 5).

The modification of the HNT using salts of melamine in the presence of protective colloid PVA does not change the thermal stability of the final product. The high thermal stability of the modified HNT indicates that it can be used as an agent increasing the thermal stability and reducing the flammability of plastics filled by this type of additive.

The obtained hybrid halogen-free flame retardants, synthesized with and without the presence of the protective colloid, were introduced into PA6 in amount of 8.5, 10 and 12.5 % by weight using a twin-screw extruder. Then the modified plastics were granulated and injection molded. The resulting samples were used for the determination of oxygen index (OI), the vertical and horizontal flammability and mechanical properties as well.

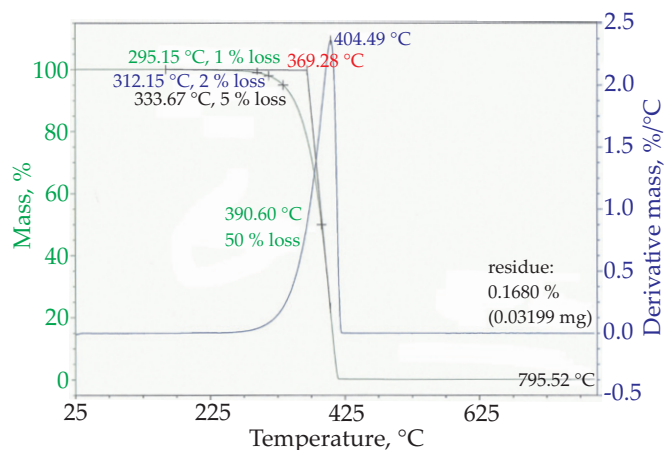


Fig. 4. TGA curve of melamine cyanurate obtained in the presence of PVA

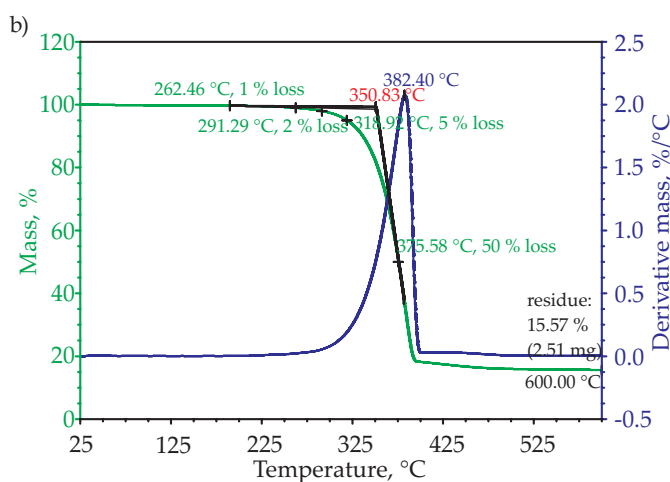
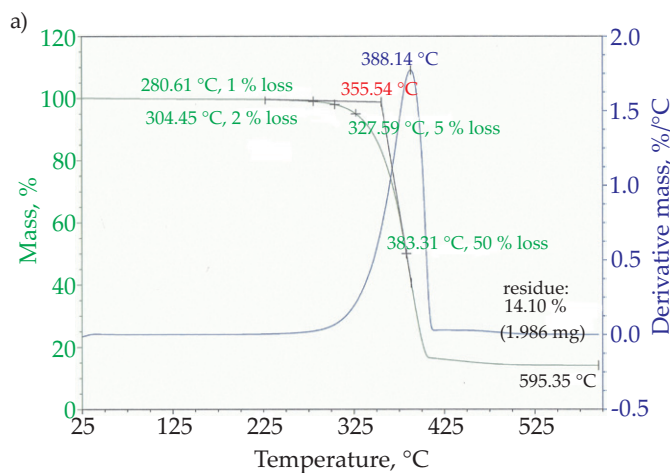


Fig. 5. TGA curve of halloysite modified by melamine cyanurate; synthesis carried out: a) in the presence of PVA, b) in the absence of PVA

At the beginning, the morphology of the obtained compositions was examined. SEM analysis showed that additives based on HNT were well dispersed in PA6 matrix (Fig. 6). Using PVA during the synthesis of the additive did not cause the agglomeration of the additive in the polymer matrix.

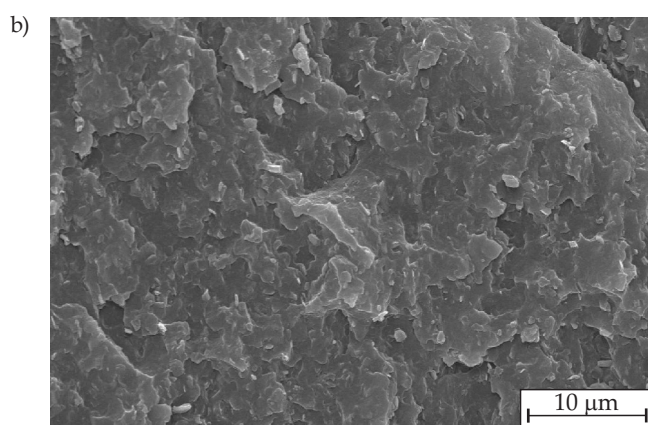
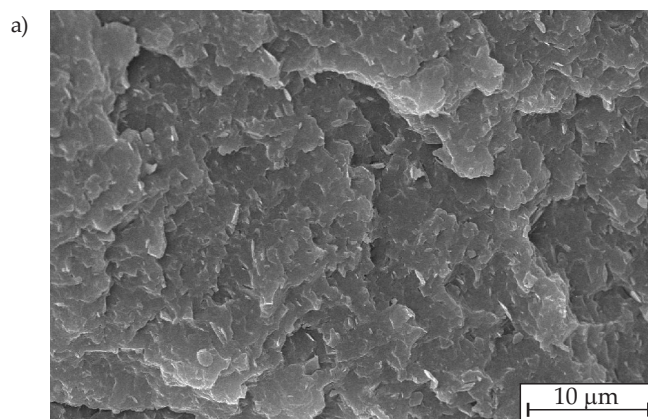


Fig. 6. SEM analysis of PA6 filled with hybrid flame retardant synthesized: a) in the presence of PVA, b) in the absence of PVA

Such good distribution has a significant influence on the mechanical and flame retardant properties of the filled polymer.

In order to verify the degree of the reduced flammability of the obtained compositions *OI* was determined. The results are shown in Table 3.

One can see that the method used for the synthesis of hybrid flame retardant has a negligible impact on the value of the oxygen index of final compositions. As can be seen, all of the samples obtained from PA6 filled with HNT modified by MC have an oxygen index higher than 29 vol %. It is not important whether the flame retardant was obtained in the presence of PVA or without it. Small differences in the values of the *OI* have no impact on reaching the highest class of vertical (V0) and horizontal (FH1) flammability according to the UL94 test.

In the case of mechanical properties, it was stated that carrying out the syntheses of hybrid flame retardants in the presence of the protective colloid did not negatively affect the mechanical properties of the filled plastic. One can see that if the flame retardant was synthesized in the presence of PVA, modulus of elasticity (Fig. 7) has higher value than in the case when the polymer was filled with the flame retardant synthesized without PVA. But in both cases, the Young modulus (Fig. 8) and the modulus of elasticity (Fig. 7) have higher values than commercial flame retarded PA6 (T27MCSV0). So it is the evidence that HNT improves

Table 3. Oxygen index and vertical flammability of compositions obtained from PA6 and halloysite modified by melamine cyanurate

Sample	Amount of filler (parts per 100 parts of polymer composition by weight)	Amount of halloysite (parts per 100 parts of polymer composition by weight)	Oxygen index vol %	Vertical flammability
PA6	–	–	24.0	–
Filler: halloysite modified by melamine cyanurate without PVA				
PA6CM10HZ	8.5	0.8	29.7	V0
	10.0	1.0	31.5	V0
	12.5	1.2	33.0	V0
PA6CM15HZ	8.5	1.3	30.4	V0
	10.0	1.5	31.2	V0
	12.5	1.9	32.0	V0
PA6CM20HZ	8.5	1.7	30.0	V0
	10.0	2.0	30.3	V0
	12.5	2.5	31.0	V0
PA6CM25HZ	8.5	2.1	30.8	V0
	10.0	2.5	32.5	V0
	12.5	3.1	34.6	V0
Filler: halloysite modified by melamine cyanurate in the presence of PVA				
PA6CM10HZ_0.5PVA	8.5	0.8	29.0	V0
	10.0	1.0	30.0	V0
	12.5	1.2	30.5	V0
PA6CM15HZ_0.5PVA	8.5	1.3	30.1	V0
	10.0	1.5	30.5	V0
	12.5	1.9	30.3	V0
PA6CM20HZ_0.5PVA	8.5	1.7	30.0	V0
	10.0	2.0	29.8	V0
	12.5	2.5	29.9	V0
PA6CM25HZ_0.5PVA	8.5	2.1	29.3	V0
	10.0	2.5	29.6	V0
	12.5	3.1	29.6	V0

PA6CM10HZ, PA6CM15HZ, PA6CM20HZ, PA6CM25HZ: mean composition of PA6 with additive containing 10, 15, 20 and 25 parts of halloysite per 100 parts of flame retardant, respectively.

PA6CM10HZ_0.5PVA, PA6CM15HZ_0.5PVA, PA6CM20HZ_0.5PVA, PA6CM25HZ_0.5PVA: mean composition of PA6 with additive synthesized in the presence of PVA, containing 10, 15, 20 and 25 parts of halloysite per 100 parts of flame retardant, respectively.

the mechanical properties of the polymer filled with the hybrid flame retardant. The significant influence of HNT and PVA, which were used during the synthesis of the hybrid flame retardant, is visible when the Charpy impact strength is analyzed (Fig. 9). This parameter reaches values of about 50–80 % higher for PA6 filled with the hybrid flame retardant synthesized with PVA than for commercial flame retarded PA6. It depends on the quantity of HNT and PVA used during the synthesis of the additive. The flexural strength (Fig. 10) exhibits the same relationship. The most visible influence of PVA which was used

during the synthesis of hybrid flame retardant occurs when we analyze the tensile strength at yield (Fig. 11). It can be seen that the use of PVA during the synthesis of the hybrid flame retardant causes that the values of tensile strength at yield are higher than those of the polyamide filled with the hybrid flame retardant synthesized without PVA. So, if we want to obtain a composite material with enhanced stiffness, we can introduce a filler synthesized without using PVA. But if we want to obtain a composite with increased elasticity we may use a flame retardant synthesized in the presence of PVA.

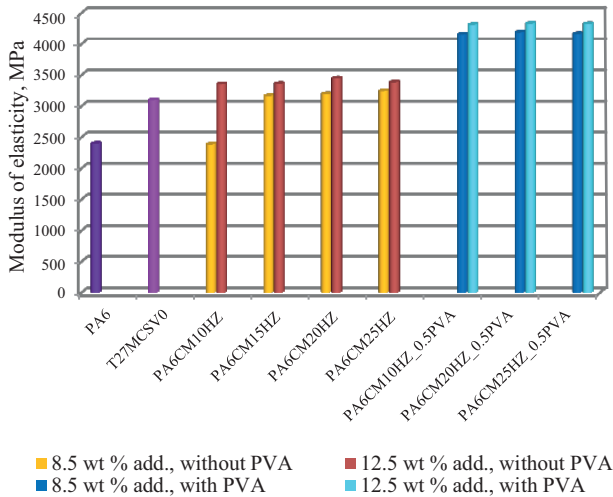


Fig. 7. Dependence of modulus of elasticity of composites on amount and kind of filler

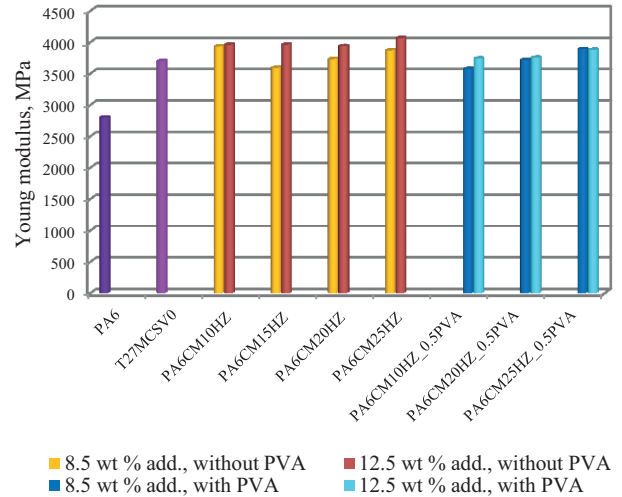


Fig. 8. Dependence of Young modulus of composites on amount and kind of filler

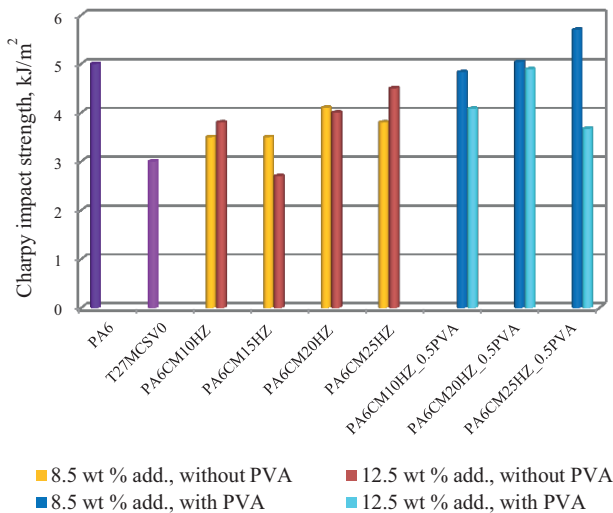


Fig. 9. Dependence of Charpy impact strength of composites on amount and kind of filler

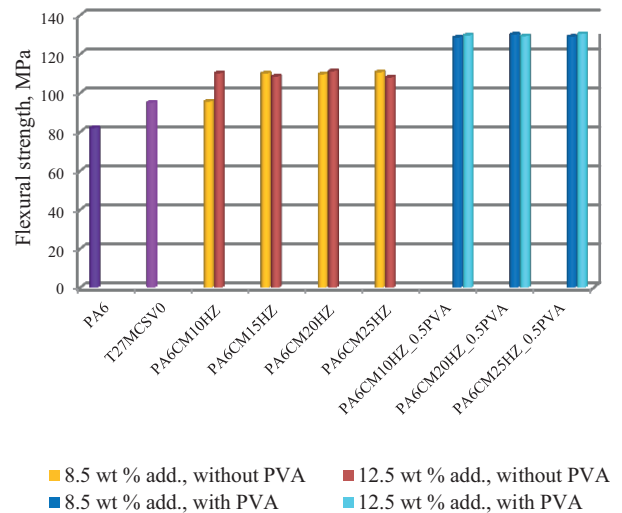


Fig. 10. Dependence of flexural strength of composites on amount and kind of filler

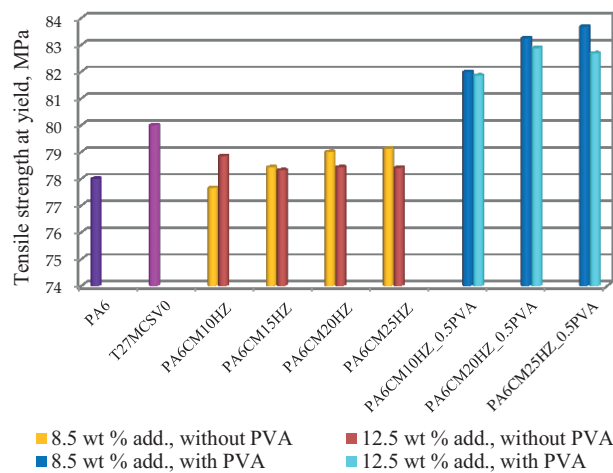


Fig. 11. Dependence of tensile strength at yield of composites on amount and kind of filler

Summarizing, HNT fulfilled its role, *i.e.*, the mechanical properties of the polymer filled with this type of flame retardant have been improved.

CONCLUSIONS

As a result of the modification of HNT by MC, new hybrid halogen-free flame retardants with good thermal properties were obtained. The application of a protective colloid led to an increase in bulk density of the flame retardant. The resulting polymer compositions of polyamide 6 and hybrid flame retardants are characterized by a high value of oxygen index. The highest class of vertical (V0) and horizontal (FH1) flammability in the flammability test – UL94 were also achieved by the obtained compositions. The mechanical properties of PA6 filled with hybrid flame retardants have been improved in comparison with commercial flame retarded PA6 – T27MCSV0.

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REFERENCES

- [1] JP Pat. 5 632 470 (1981).
- [2] PL Pat. 100 877 (1978).
- [3] US Pat. 5 202 438 (1993).
- [4] JP Pat. 5 455 587 (1979).
- [5] Ning N., Yin Q., Luo F. *et al.*: *Polymer* **2007**, 48, 7374. <http://dx.doi.org/10.1016/j.polymer.2007.10.005>
- [6] Nakamura R., Netravali A.N., Morgan A.B. *et al.*: *Fire and Materials* **2013**, 37, 75. <http://dx.doi.org/10.1002/fam.2113>
- [7] Ismail H., Pasbakhsh P., Fauzi M.A., Bakar A.A.: *Polymer Testing* **2008**, 27, 841. <http://dx.doi.org/10.1016/j.polymertesting.2008.06.007>
- [8] Du M., Guo B., Jia D.: *European Polymer Journal* **2006**, 42, 1362. <http://dx.doi.org/10.1016/j.eurpolymj.2005.12.006>
- [9] Marney D.C.O., Russell L.J., Wu D.Y. *et al.*: *Polymer Degradation and Stability* **2008**, 93, 1971. <http://dx.doi.org/10.1016/j.polymdegradstab.2008.06.018>
- [10] Mellouk S., Cherifi S., Sassi M. *et al.*: *Applied Clay Science* **2009**, 44, 230. <http://dx.doi.org/10.1016/j.clay.2009.02.008>
- [11] Tan D., Annabi-Bergaya F., Yu H. *et al.*: *Microporous and Mesoporous Materials* **2013**, 179, 89. <http://dx.doi.org/10.1016/j.micromeso.2013.05.007>
- [12] Zeng S., Reyes C., Liu J. *et al.*: *Polymer* **2014**, 55, 6519. <https://doi.org/10.1016/j.polymer.2014.10.044>
- [13] Raji M., El Mehdi Mekhzoum M., Rodrigue D. *et al.*: *Composites Part B* **2018**, 146, 106. <https://doi.org/10.1016/j.compositesb.2018.04.013>
- [14] Krishnaiah P., Ratnam Ch.T., Manickama S.: *Applied Clay Science* **2017**, 135, 583. <https://dx.doi.org/10.1016/j.clay.2016.10.046>
- [15] Albdiry M.T., Ku H., Yousif B.F.: *Engineering Failure Analysis* **2013**, 35, 718. <https://dx.doi.org/10.1016/j.engfailanal.2013.06.027>
- [16] Carli L.N., Daitx T.S., Soares G.V. *et al.*: *Applied Clay Science* **2014**, 87, 311. <https://dx.doi.org/10.1016/j.clay.2013.11.032>
- [17] Ibrahim G.P.S., Isloor A.M., Moslehyani A., Ismail A.F.: *Journal of Water Process Engineering* **2017**, 20, 138. <http://dx.doi.org/10.1016/j.jwpe.2017.09.015>
- [18] Cavallaro G., Lazzara G., Milioto S., Parisi F.: *Langmuir* **2015**, 31, 7472. <http://dx.doi.org/10.1021/acs.langmuir.5b01181>
- [19] Feng K., Hong G.-Y., Liu J. *et al.*: *The Chemical Engineering Journal* **2018**, 331, 744. <http://dx.doi.org/10.1016/j.cej.2017.09.023>
- [20] Paran S.M.R., Naderi G., Ghoreishy M.H.R.: *Applied Surface Science* **2016**, 382, 63. <https://dx.doi.org/10.1016/j.apsusc.2016.04.087>
- [21] Du M., Guo B., Liu M., Jia D.: *Polymer Journal* **2007**, 39, 208. <http://dx.doi.org/10.1295/polymj.PJ2006104>
- [22] Du M., Guo B., Liu M. *et al.*: *Physica B* **2010**, 405, 655. <http://dx.doi.org/10.1016/j.physb.2009.09.082>
- [23] Rybinski P., Janowska G.: *Thermochimica Acta* **2013**, 557, 24. <https://dx.doi.org/10.1016/j.tca.2013.01.030>
- [24] Li L., Wu Z., Jiang S. *et al.*: *Polymer Composites* **2015**, 36 (5), 892. <http://dx.doi.org/10.1002/pc.23008>
- [25] PL Pat. 219 038 (2014).
- [26] PL Pat. 219 039 (2014).
- [27] PL Pat. 223 177 (2015).
- [28] PL Pat. 225 006 (2016).
- [29] Szulc K., Lenart A.: *Journal of Food Science* **2010**, 75, 276. <http://dx.doi.org/10.1111/j.1750-3841.2010.01634.x>

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