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Thermal stability and flammability of polyolefin/halloysite nanotubes composites

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Abstract: Halloysite nanotubes (HNTs) have become promising halogen-free flame retardants of polyolefin's. Due to their tubular structure, HNTs can create stable barrier against heat and mass transport processes. Encapsulation of polymer's degradation products inside HNTs lumens seems to be important factor, too. Different aspects of HNTs dispersion in polyolefin's matrices such as modification of HNTs and/or presence of coupling agents or special processing techniques were presented. HNTs can act as flame retardants without sacrificing mechanical properties only after homogeneous dispersion in polymer matrix.

Keywords: polyolefin nanocomposites, halloysite nanotubes, thermal stability and flame retardancy.

Stabilność termiczna i palność kompozytów poliolefiny/nanorurki haloizytowe

Streszczenie: Najnowsze badania w zakresie uniepalniania poliolefin są ukierunkowane na zastosowanie dodatku nanorurek haloizytowych (HNT) jako bezhalogenowego środka zmniejszającego palność, a jednocześnie zachowującego właściwości mechaniczne osnowy. Powstająca na powierzchni płonącego nanokompozytu, zawierającego HNT, warstwa tzw. zgorzeliny ogranicza przenikanie gazów oraz ciepła i zabezpiecza materiał przed dalszym paleniem. Unikatowa struktura HNT umożliwia dodatkowo pochłanianie produktów termicznego rozkładu poliolefinowej osnowy. Na podstawie dostępnej literatury dokonano oceny wpływu różnych czynników, m.in. modyfikacji nanorurek haloizytowych i/lub dodatku kompatybilizatora i/lub doboru odpowiedniej metody przetwórstwa, na zwiększenie stabilności termicznej oraz odporności ogniowej nanokompozytów poliolefinowych z udziałem nanorurek haloizytowych.

Słowa kluczowe: nanokompozyty poliolefinowe, nanorurki haloizytowe, stabilność termiczna, odporność ogniowa.

Plastic materials, especially the ones based on polyolefin's, are used nowadays in almost every field of our lives. Because of their very competitive price/performance ratio, polyolefin's materials are used *e.g.*, in packaging, building and electrical industries. However high flammability and melt dripping are topics limiting their

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applications in some cases [1, 2]. Therefore methods of reducing the flammability of polyolefin's attracted great deal of attention for many years. Generally it has been proved that incorporation of flame retardant additives is the most effective method of enhancing flame retardancy of polymer materials [3]. Until 90's, halogenated flame retardants had the largest share in the market. However, their use has been increasingly contested due to potential toxicity of their decomposition products, as well as their persistency in the environment and bioaccumulation [4]. Therefore general trend is to substitute these flame retardants by non-halogenated alternatives, such as the most popular metal hydroxides [5]. Their environment friendly character *i.e.*, nontoxicity and low corrosivity, as well as low cost are main advantages of these flame retardants. However metal hydroxides act effective only above the concentration of 50 wt % in polymer matrix, what causes a dramatic deterioration of their mechanical properties and limits a certain applications of the plastics [6—9].

For several years much attention has been devoted to the use of mineral nanoparticles, mainly montmorillonite (MMT), as flame retardant systems auxiliary additives [10, 11]. As was shown by Gilman [12] aluminosilicate particles have to be nanodispersed for improving fire-resistance properties. It is commonly known that for enhancement of nanocomposites thermal stability the barrier properties of aluminosilicates are responsible [13, 14]. Gilman [12, 14] explained action of aluminosilicates through the thermal barrier effects, protecting the burning surface against the contact with fire and limiting mass transport processes, which slows down the outflow of thermal degradation volatile products. High thermal stability of the aluminosilicates has direct implications for flame retardancy improvement.

Recently it has been reported that halloysite with a tube-like structure can more effective support flame retardant systems than layered MMT [15, 16]. The effect results from the unique crystal structure and few hydroxyl groups existing on the halloysite nanotubes (HNTs) surfaces, what leads to relatively easy dispersion of HNTs in polymeric matrix. Usually 2—10 wt % content of HNTs in nanocomposite is sufficient enough to enhance thermal stability and flame retardancy of the materials [17]. Detailed descriptions of the structure and properties of HNTs were presented in our previous paper [18]. It is known that homogeneous dispersion of filler, in this case of HNTs, in polymer matrix is the key factor for improvement of thermal stability and flammability reduction of composites. On the other hand interactions between polymer matrix and the fillers surface are the driving force for homogeneous dispersion of the latter [19—22].

Modifications of HNTs rely on intercalation or grafting of organic compounds, usually with long aliphatic carbon chains, on the surface or rarely in the interlayer space of the halloysite. A polar group of the modifier can interact with -OH group of HNTs, whereas the aliphatic chains enhance the hydrophobic character of HNTs and in consequence the adhesion to polyolefin matrix [16, 23]. The processes may improve thermal stability and fire properties of polyolefin/HNTs nanocomposites. The methods of HNTs modification were presented in our previous paper [18]. The second approach to nanocomposite synthesis is to use agent known as compatibilizer. Usually compatibilizer is functionalized (co)polymer or other compound containing polar functionalities, such as maleic anhydride (MA), hydroxyl or amino groups. Polar groups of the compatibilizer can interact with HNTs, whereas the non-polar chains remain miscible with polymer matrix [24—26].

In this paper the review of several strategies for improvement of compatibility between non-polar polyolefin's and HNTs, and in consequence a betterment of thermal stability and flame retardancy of their composites, are presented. HNTs can be dispersed relatively uniformly in thermoplastics via melt blending, especially in polymers with medium and high polarity, such as polyamides [27—30]. However compatibilization of HNTs with polyolefin's, such as polypropylene (PP) or polyethylene (PE) is challenging due to great polarity discrepancy and the chemical inertness of the polyolefin's. Different factors influencing the degree of HNTs dispersion in polyolefin matrix and thus thermal stability and flammability, including prior modifications of nanotubes with organic compounds and/or usage of coupling agents during composites preparation or special processing techniques applied, are the subjects of the paper. Synergistic action of HNTs with non-halogenated flame retardants is considered, too.

THERMAL STABILITY OF POLYOLEFIN/HNTs COMPOSITES

Mechanism of polyolefin/HNTs composites degradation during thermogravimetric analysis (TGA) depends greatly on the atmosphere used. The analysis performed under oxygen can provide more realistic information about the thermal behavior on the material in real life than experiments conducted under inert atmosphere. In both cases volatile products of polyolefin degradation may be entrapped into the hollow interiors (lumens) of HNTs, what increases thermal stability of polyolefin. However a difference can be observed in the main step of mass loss. Under oxidative condition, mass loss for PP and PP/HNTs starts at the temperature *ca.* 100 °C lower than was observed in the case of N_2 atmosphere. It has been reported [31] that the presence of oxygen initiates at temperature of *ca.* 200 °C radical depolymerization of PP going through hydroperoxidation of C-H bonds. In this case HNTs showed a barrier effect against oxygen diffusion in both initial and main step of polyolefin degradation, however without promoting the char formation. Under N_2 atmosphere the step of depolymerization usually occurs above 450 °C; in the same temperature the decomposition of hydroxyl groups (Al-OH) of HNTs also occurs, which can have catalytic effect on the polyolefin degradation as a Brönsted active sites. In consequence, a decrease of thermal stability of the polyolefin was observed. The catalytic effect of nanoclays on thermal degradation of PP has already been reported by Marcilla [32]. Nevertheless some authors proved that good dispersion of HNTs obtained by combined effect of a compatibilizer presence and water-assisted extrusion process can dominate over the unfavourable catalytic effect of HNTs. Thermal stability under both air and nitrogen atmospheres and the kinetics of thermo-oxidative degradation of PP nanocomposites with 8 wt % of unmodified HNTs were analysed by Lecouvet [33]. Du [17] first described PP/HNTs nanocomposites modified with organosilane, namely methacryloxypropyl trimethoxysilane (MPS). TGA (N_2) showed that the temperatures of 5 and 10 % of mass loss ($T_{5\,\%}$ and $T_{10\,\%}$, respectively) were *ca.* 70 °C higher for nanocomposite containing 10 wt % of modified HNTs than for unfilled PP. The improvement of thermal stability was described as a combination of barrier properties and entrapment mechanism of HNTs. The more uniform dispersion of modified HNTs in PP matrix causes higher randomness of lumens′ ends and in consequence the entrapping of degradation products could be more effective. This mechanism is presented in Fig. 1. It was also suggested that the presence of iron in HNTs may play important role by acting as a scavenger of free radicals during the process of composite degradation. Similar results were described by Pedrazzoli [34], who examined the influence of unmodified and modified HNTs on thermal stability of linear low-density polyethylene (PE-LLD). HNTs were modified with K-acetate, ethylene glycol and *N*-hexylamine mixture. In that case $T_{10\,\%}$ values of PE-LLD/modified HNTs nanocomposites were only 10 °C higher than for neat PE-LLD. In U.S. patent [35] the PP nanocomposites with 5 wt % of HNTs modified by benzalconium chloride exhibited increase of $T_{5\,\%}$ from 390 °C to 412 °C.

Liu [26] studied the influence of *N*-cyclohexyl-2-benzothiazole sulphonamide (CBS) as a compatibilizer in PP/HNTs nanocomposites. In composites with CBS better dispersion of nanotubes in PP matrix, as well as better interfacial adhesion were observed in SEM and TEM images. In consequence, with the increase of CBS content (1—10 wt %) nanocomposites showed considerably higher degradation temperatures in relation to uncompatibilized PP/HNTs and neat PP. Authors concluded, that the benzothiazole groups of CBS show the shielding effect for the acidic sites on HNTs surfaces and prevent the catalytic effect of HNTs during PP degradation. Lecouvet [24] studied the role of maleic anhydride grafted polypropylene (PP-*g*-MA) on thermal stability of PP/HNTs nanocomposites. In this case, the uncompatibilized composites with 8 wt % of HNTs showed *ca.* 40 °C reduction of the $T_{5\,\%}$ value compared to the neat PP. The authors suspected that it resulted from catalytic action of HNTs on PP thermal degradation. In the presence of compatibilizer predominantly heterogeneous morphology of the composite was still observed, causing only slightly higher value of the $T_{5\,\%}$ in comparison with neat PP.

As it was clearly shown in some papers neither modification of HNTs nor compatibilizer addition alone was sufficient to improve thermal stability of polyolefin/HNTs nanocomposites. It was the reason to try both of the methods at once. Such strategy was described by Pal [36], who focused on specific group of polyolefin's, namely cycloolefin's copolymers (COC). The enhancement of thermal properties of COC was achieved by the modification of HNTs with organosilane [*N*-(β-aminoethyl)-γ-aminopropyltrimetoxysilane] and addition of a compatibilizer (PE-*g*-MA). Intriguingly, to achieve a better results the PE-*g*-MA and modified HNTs mixture was firstly reacted at 100 °C for 2 h. Only 1 wt % of such prepared HNTs was effective — an increase of the $T_{10\,\%}$ value from 439 to 461 °C was observed. Authors stated that PE-*g*-MA acts as a bridge between the modified HNTs and COC, what enhances interfacial interactions, dispersion and finally thermal stability. They also believed that both barrier property and the entrapment of volatile products by HNTs during COC degradation are important factors.

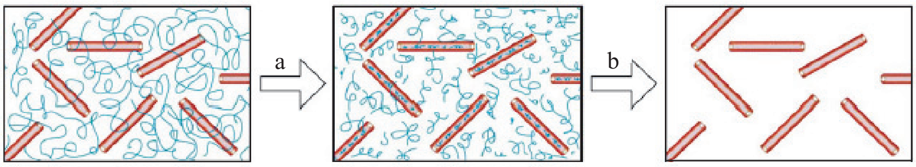

Fig. 1. Scheme of entrapment mechanism of thermal decomposition of PP/HNTs nanocomposites: a) entrapping of decomposition products by HNTs lumens; b) escaping of decomposition products from HNTs lumens (according to [17])

However in some cases combination of compatibilizer addition and modification of HNTs may not be the best solution, because of environmental issues of some modifiers and practical limitations, such as cost or difficulty in achievement of controllable and repeatable results. Therefore water-assisted extrusion process was applied recently by Lecouvet [24] to prepare PP/unmodified HNTs nanocomposites with improved thermal stability.

The authors suggest that water plays a dual role during the melt blending: promotes the clay dispersion and enables the formation of bonds between compatibilizer used (PP-*g*-MA) and the HNTs. The $T_{5\,\%}$ value increased by *ca*. 10 °C for PP/HNTs/compatibilizer composite prepared during water-assisted extrusion process, compared to the neat PP. Only for these nanocomposites individually dispersed nanotubes in SEM and TEM images were observed. It was stated that good dispersion of HNTs in the matrix could dominate the unfavourable catalytic effect of HNTs via the formation of a tortuous diffusion path and encapsulation of the products of initial degradation of PP.

It was found that orientation of nanoclays particles also influenced thermal stability of nanocomposites. In order to study the effect of HNTs orientation Wang [37] prepared PP/HNTs nanocomposites with highly oriented (water-assisted injection moulding — WAIM) and randomly distributed (compression moulding — CM) nanotubes. TGA (N_2 atmosphere) showed that $T_{5\,\%}$ and $T_{10\,\%}$ values for PP increased in the presence of both highly and randomly oriented HNTs. However the best results were obtained for nanocomposites with 2 wt % of highly oriented HNTs, whereas for nanocomposites with 5 and 8 wt % of highly oriented HNTs decrease of temperature at maximum mass loss (T_{max}) was visible. The authors suggested that HNTs may have two opposite effects on thermal degradation of PP under N_2 atmosphere. Namely, thermal stability increases as a result of entrapment of volatile products in initial stage of PP degradation ($T_{5\,\%}$ and $T_{10\,\%}$) [17, 24, 38], but on the other hand, decrease of the T_{max} for nanocomposites with 5 and 8 wt % of HNTs can result from the unfavourable presence of HNTs aggregates [17, 24] and from the catalytic effect of HNTs on PP degradation [32]. Moreover, on the differential scanning calorimetry (DSC) curves of nanocomposites only one endothermic peak in the temperature range 300—500 °C was observed. It may results not from the barrier effect but from the stabilizing effect of HNTs on PP macromolecules as a result of interactions between macromolecules and HNTs surface cause by shear-induced interfacial crystallization. Similar mechanism was also suggested in the case of PP/MMT nanocomposites by Galeski and Golebiewski [39].

Recently modified HNTs were used not only as fillers but also as compatibilizers for blends of non-polar polyolefin's with polar polymers. Such systems may combine advantages of different polymers and polymer/HNTs nanocomposites [40—42]. Pal [36] studied effect of both unmodified and modified HNTs on thermal stability of 1:1 PP/POM (polyoxymethylene) immiscible blend. HNTs have been modified with *N*-(β-aminoethyl)-γ-aminopropyltrimetoxysilane (APTMS). TGA (N_2) results showed that after addition of 1 wt % of unmodified HNTs the $T_{5\,\%}$ value increased from 259 °C to 263 °C. Moreover POM/PP blend with 1 wt % of modified HNTs showed a further increase up to 270 °C. The authors concluded that thermal degradation has diminished because of both good interactions between the blend and the modified HNTs as well as barrier properties of HNTs.

FLAME RETARDANCY OF POLYOLEFINE/HNTs COMPOSITES

The enhancement of flame retardancy in the case of composites under consideration results from the migration of HNTs to the surface of the composite during combustion process and formation of an inorganic residue. This residue *i.e.*, char, acts as a protection against both external flame ingress and mass transport and reduces the amount of volatile degradation products available for the flame. It seems that the mechanism of combustion is similar to that of TGA experiment in air atmosphere. However, some researches stated that the entrapment mechanism important for the improvement of thermal stability does not play any role in the combustion process and barrier effect of HNTs determines flammability of the nanocomposites. They explained this fact that the volatilization products are produced in a short time in the cone calorimeter and are preferentially transferred to the surface of combustion polymer.

In order to determine the fire behavior of nanocomposites several test methods may be used but the cone calorimeter experiment seems to give the most valuable information [43]. During cone calorimetry tests one can analyse the behavior of materials when exposed to heat and a source of ignition. Due to relatively small sample size used for testing, cone calorimetry is a quick, low cost way to conduct research on fire performance of materials. The main result of the measurement is heat release rate (*HRR*) *i.e.*, the amount of energy given off by the specimen versus time, but other important parameters can be calculated, such as: peak rate and average rate of heat release, total heat released (*THR*), effective heat of combustion, specific extinction area (*SEA*), exhaust flow rate (*EFR*), mass loss rate (*MLR*) and final sample mass, time to ignition (*TTI*), CO, CO_2, and other gases concentrations or smoke density [11].

Lecouvet [24] proved that the fire properties, such as p*HRR* (peak of heat release rate) and *THR* for PP/PP-*g*-MA/HNTs composites were improved compared to the neat PP, but were similar as for uncompatibilized composite. Most probably it was due to obtaining heterogeneous morphology of compatibilized composites. Moreover, in the case of composites with predominant aggregation of HNTs, prepared without a compatibilizer, HNTs residue was more fragile and cracked. As it was reported by many authors [16, 17, 37] only homogeneous dispersion of HNTs can lead to formation an effective physical barrier for mass and energy transport and enhancement fire retardancy of polymer. Better dispersion of HNTs and in consequence improved fire properties of PP/HNTs composites the authors obtained using a synergetic combination of compatibilizer addition and water-assisted extrusion process. The improvement of fire properties was observed with the increasing of HNTs content. The crucial role in enhancement of fire retardancy of these nanocomposites was assigned to the rigid and stable HNTs residue observed after combustion. This effective physical barrier reduced the p*HRR* value from 622 to 219 kW/m^2 and *THR* from 75 to 55 MJ/m^2, in comparison with neat PP. It is worth noting that HNTs barrier can only delay the volatilization of PP degradation products but not prevent it. Unfavourable reduction of *TTI* values for all nanocomposites was observed and explained by authors in three possible ways: i) higher viscosity of the nanocomposites at the initial step of burning decreases the apparent heat conductivity, ii) higher heat accumulation at the nanocomposites surface speeds up the ignition temperature of material, iii) nanocomposites with HNTs may tend to absorb and/or scatter incident radiation mainly near the surface, reducing the time required to reach the ignition temperature.

Du [17] achieved even better fire properties of PP/HNTs nanocomposites, but in this case proper dispersion of HNTs in PP matrix was achieved by surface modification of HNTs with organosilane compounds. The best results were obtained at high content of uniformly dispersed, modified HNTs (30 wt %) in the matrix. The *HRR*, *SEA* and *MLR* values for this nanocomposite were reduced, whereas the *TTI* was increased by almost half, compared to neat PP. The curve of *HRR* for neat PP also was changed from sharp to flat after incorporation of modified HNTs (Fig. 2). In result the time to burn out was much longer than in case of neat PP. Authors suspected that the presence of iron dioxide(II) (0.3 wt % in HNTs) may also play role in reduction of flammability of the nanocomposites.

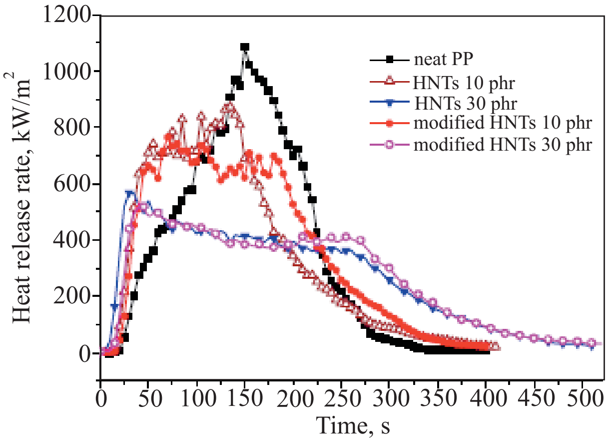

Fig. 2. ***HRR*** **of neat PP and PP/unmodified HNT and PP/modified HNTs nanocomosites (according to [17])**

As it was presented above, HNTs can improve thermal stability and reduce flame intensity (*i.e. HRR*) during cone calorimeter test. However, usually other parameters such as time to ignition (TTI) and other fire testing methods *e.g.*, UL-94 standard or limiting oxygen index (*LOI*) method are of great importance for assessing fire safety of polymer materials [45]. Addition of HNTs alone to polymer matrix do not guarantee meeting of the requirements, therefore HNTs should be seen as a part of flame retardant systems rather than a flame retardant on its own. His role should be to enhance the effectiveness of typical flame retardants, such as metal hydroxides.

In the case of polyolefines, synergistic flame retardant action of HNTs with intumescent flame retardant (IFR) has been studied recently. It was stated that during the combustion process, IFR forms an expanded charring layer at the burning surface, which can protect the matrix beneath from the heat flux and fire [44]. However the insulating properties of the intumescent coatings depend on their mechanical and thermal stability. Due to required loading level of IFR in polyolefine matrix (25—30 wt %), reduced flammability can sometimes be achieved at the expense of mechanical properties. So, it is expected that the reduction of IFR content in polyolefines matrices and introduction of smaller amount of HNTs (0.5—5 wt %) may improve mechanical and thermal properties of the IFR protective layer, either by physical and/or chemical synergistic effect. Lecouvet [45] studied effect of unmodified HNTs with IFR agent, based on a coated ammonium polyphosphate (APP) on thermal stability and fire properties of PP/APP/HNTs system. The results suggest that synergistic mechanism exists between APP and HNTs only for certain ratio of the components (1.5—3 wt % HNTs and 17—18.5 wt % APP). Cone calorimetry showed that the substitution of IFR by 3 wt % of HNTs resulted in improved flame retardancy (30 and 40 % reduction of two *HRR* peaks, assigned to build-up of an intumescent char and to char degradation through crack formation, respectively) and in prolonged time to reach the second *HRR* peak, from 530 to 740 s. At the same time a shift from V-1 to V-0 classification of UL-94 test was achieved for 1.5 wt % HNTs. On the basis of SEM, TEM, TGA and NMR results it was concluded that HNTs contribute to mechanical and thermal stabilization of intumescent char on the burning polymer surface. HNTs act as aluminosilicate „skeleton-frame" and react with APP and/or its degradation products via Al-O-P bonds. As a consequence, thermally stable at temperature above 500 °C, denser and tougher intumescent char, inhibiting heat and mass transfers between the flame zone and the condensed phase was obtained (Fig. 3). Furthermore, by analysis of the storage modulus (*E'*) as a function of temperature, the influence of HNTs on the thermo-mechanical behavior of IFR/PP was examined. As it was reported in [46], reinforcing effect of HNTs in polymer matrix results from high intrinsic stiffness and nanoscale dispersion in polymer matrix. However, contrary to expectations, PP/IFR/HNTs nanocomposites showed limited enhancement of *E'* value. Authors explained it by relatively low HNTs content (3 wt %) in relation to IFR, which

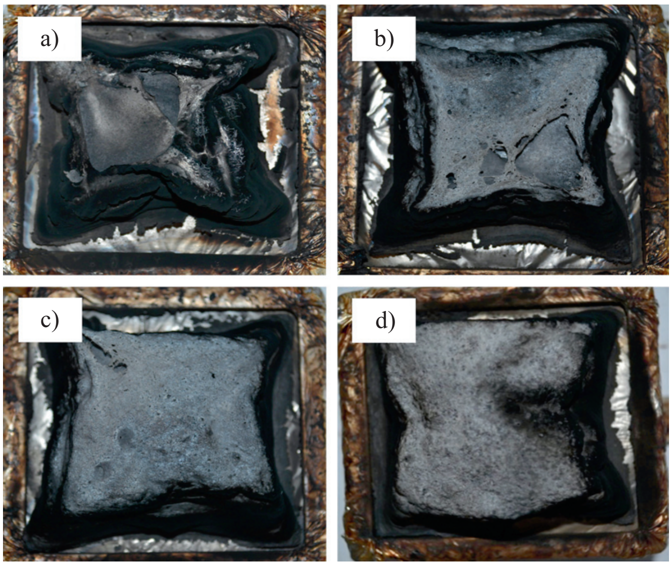

Fig. 3. Top view of cone calorimeter residues of: a) PP/IFR (20 wt %), b) PP/IFR/HNTs (0.5 wt %), c) PP/IFR/HNTs (1.5 wt %), d) PP/IFR/HNTs (3 wt %) intumescent nanocomposites (according to [44])

controls the final mechanical properties of HNTs/IFR/PP nanocomposites.

Zhao and co-workers [47] described a similar synergistic flame-retardant mechanism of HNTs with IFR for low density polyethylene (PE-LD). The best results for *LOI*, UL-94 and cone calorimetry parameters were obtained for 2 wt % addition of HNTs in PE-LD/IFR system. Authors suggested that the synergistic effect of HNTs used with IFR was based only on physical reinforcement by HNTs *i.e.*, migration of HNTs to the surface during the combustion process and formation of a more compact barrier. It is also worth mentioning that mechanical properties, such as tensile strength and elongation at break of PE-LD/IFR/HNTs nanocomposites were slightly improved compared to PE-LD/IFR.

CONCLUSIONS

Based on this review it can be concluded that HNTs are promising additive able to improving thermal stability and flame retardancy of polyolefin's and their blends with some polar polymers as well. What is important, HNTs can be considered as „green", inexpensive and easily obtainable functional filler. It was shown that thermal stability and flame retardancy of HNTs/polyolefin nanocomposites were influenced by many factors: modification of HNTs, compatibilizer addition and method of nanocomposite production. The most critical parameter was homogeneous dispersion of HNTs in polyolefin's matrices. Usually 2—20 wt % content of HNTs in nanocomposite was sufficient to enhance thermal stability or reduce flammability of polyolefin's. Improvement of thermal stability and flame retardancy resulted from the barrier properties of HNTs combined with an encapsulation process of polymer degradation products inside the halloysite tubes. During combustion of nanocomposites a rigid and stable inorganic residue was formed, acting as a barrier to heat and mass transport processes. The best results gave combined usage of HNTs with conventional non-halogenated flame retardants.

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