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Halloysite nanotubes as polyolefin fillers

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Abstract: Halloysite nanotubes (HNTs) are a promising type of naturally occurring fillers for polymers. We review the recent progress in HNTs characterization, methods of their modification, as well as the morphology and mechanical properties of polyolefin/HNT nanocomposites. Modified HNTs well dispersed in a polyolefin matrix bring an improvement to the mechanical properties of nanocomposites. It seems that the connection of well-known advantages of polyolefins with unique properties of HNTs may result in the large-scale utilization of this type nanocomposite.

Keywords: halloysite nanotubes, aluminosilicate modification, polyolefin nanocomposites.

Nanorurki haloizytowe jako napelniacze poliolefin

Streszczenie: Artykuł stanowi przegląd najnowszej literatury dotyczącej nanokompozytów poliolefinowych napelnianych nanorurkami haloizytowymi (HNT). Omówiono wpływ dodatku HNT na osnowę poliolefinową, ze szczególnym uwzględnieniem morfologii oraz właściwości mechanicznych nanokompozytów poliolefina/HNT. Modyfikowane HNT wykazywały wysoki stopień rozproszenia w osnowie poliolefinowej, dzięki czemu powodowały poprawę właściwości mechanicznych poliolefinowych nanokompozytów napelnianych nanorurkami haloizytowymi. Połączenie korzystnych właściwości poliolefin, ekonomicznych metod ich przetwórstwa oraz unikatowych właściwości HNT pozwoli na szersze rozpowszechnienie nanokompozytów wytworzonych z ich udziałem.

Słowa kluczowe: nanorurki haloizytowe, modyfikacja glinokrzemianów, nanokompozyty poliolefinowe.

In the last two decades, polymer nanocomposites based on unmodified or modified mineral nanofillers (e.g. nanoclays) have attracted a great deal of attention both in science and industry. A large majority of these nanocomposites were prepared on the basis of natural

and synthetic smectites, such as montmorillonite (MMT), halloysite, hectorite or laponite. Importantly, low nanofiller content (1–10 wt %) is usually sufficient to achieve significant enhancement of physical properties or flame retardancy of nanocomposites [1–6].

Up to now, most polymer nanocomposites with mineral fillers have been based on MMT with platelet structure. Recently, naturally occurring halloysites with a unique tubular form, known as halloysite nanotubes (HNTs), have attracted extensive interest. The cylindrical shape of the tubes results from a mismatch in the two-layered alignment of the constituent sheets of silica and alumina. Sometimes, halloysites also form spheroidal

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and plate-like particles due to the variation in crystallization conditions and geological occurrence. The molecular formula of HNTs $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\text{nH}_2\text{O}]$ is similar to kaolinite. Interestingly, HNTs are morphologically similar to multiwalled carbon nanotubes (MWCNTs), which are technologically demanding to produce in bulk and consequently are very expensive. However, in contrast to the inert walls of CNTs, the surfaces and edges of HNTs contain hydroxyl groups, providing an opportunity for further modification with various organic compounds. Therefore, the much cheaper, natural and fully ecological HNTs with unique combination of tubular nanostructure, rich functionality and high aspect ratio may replace the more expensive CNTs in high-performance and multifunctional polymer nanocomposites [7, 8].

HNTs were first described in 1826 by Berthier but extensive research began in the 1940s [9, 10]. Halloysites are extensively used in industry for ceramics, cements and fertilizer products. In the past, they have also been used to produce the highest-quality china [11, 12]. Nowadays, halloysites have regained attention due to their unique structure and new possibilities of applications [13]. A persistent growth of interest in halloysite applications has been observed, especially in the last 6 years, and the tendency is expected to last in the future.

Up to now, most publications on polymer/HNT nanocomposites have focused on polar polymers. However, less studied polyolefin/HNT nanocomposites seem to be also very important. Polyolefins, such as polyethylene (PE) or polypropylene (PP) have been for years the most common group of polymers. Their low price, diversity of physicochemical properties or universal and economical technologies of processing result in applications of polyolefins in packaging, building, electronic and electric engineering or household appliances. These applications require good mechanical and processing properties, which may be improved by nanofillers.

In this article, we review the recent progress in the application of HNTs as polyolefin nanofillers. First, the characteristics of HNTs related with the formation of polyolefin nanocomposites are summarized. Methods of functionalization (modification) of HNTs are presented next and finally, the morphology and chemical structure, as well as the mechanical properties, of polyolefin/HNT nanocomposites are described.

CHARACTERISTICS OF HNTs IN RELATION TO THEIR APPLICATION AS POLYOLEFIN FILLERS

In the last few years, an increasing number of studies have been focused on the preparation of polyolefin/HNT nanocomposites and their properties. In 2008, Natural Nano Inc. announced a pilot – scale production of PP/HNT composites. In turn, in 2010, Applied Minerals Inc. reported that their trials on incorporating a non-toxic, biodegradable halloysite clay as a drop-in additive for the reinforcement of polyolefin composites were com-

plete. In April 2014, Sigma-Aldrich signed an agreement with Applied Minerals to distribute their halloysite (Dragonite™) to researchers worldwide [14].

There are some properties of HNTs that determine their use as a polymer filler [13, 15]:

- Availability in nature and relatively low price.

HNTs were found widely deposited in soils worldwide [16, 17]. Three of the most important deposits are located in the USA, New Zealand and Poland [18]. This material is white in color but sometimes is also slightly red. The stone-like, raw halloysite is easily ground into powder form. From the industrial point of view, the most important point is the relatively low price of HNTs, which is much lower (from 10 to even 500 times) compared with MWCNTs. Therefore, HNTs may be an interesting alternative with significant potential to commercialization, especially in cost sensitive applications.

- Low content of impurities.

Raw HNTs mined directly from nature contain only trace concentrations of impurities such as quartz, kaolinite, alunite, feldspar or metal ions, which may restrict some applications [19]. To obtain the best results in nanocomposite applications, HNTs are usually purified through a water dispersion-centrifugation-drying method [20, 21]. To increase the stability of HNTs in water and to facilitate the separation of individual tubes, hexametaphosphate is added to the halloysite/water suspension [22, 23]. An almost pure HNTs deposit has been found in Utah, USA [24].

- Tubular structure and their reinforcing effect.

HNTs are predominantly tubular (Fig.1a) with an outer diameter of 20–200 nm, inner diameter of 5–70 nm and length of 50–5000 nm [25–27]. In all samples, the tubular particles are cylindrical and open-ended with an electron-transparent central lumen [19]. The crystalline structure of HNTs (Fig. 1b) is of a two-layer type: tetrahedral and octahedral sheets, which constitute the basic structural elements of halloysite. The sheets are connected together through hydrogen bonding and weak Van der Waals interactions [28–31]. The external surfaces of the tubes have a structure of tetrahedral sheet and are mainly composed of siloxane groups (Si-O-Si), whereas the internal surfaces have an octahedral structure with aluminol moieties (Al-OH) [32–37]. HNTs have 11–39 % lumen space with empty structures, 14–47 % pore space and average pore size of 78–100 Å. The aspect ratio of HNTs are rather high, typically *ca.* 10–50. As is known, the higher the aspect ratio, the better the reinforcing effect observed by optimizing the load transfer from the matrix to the nanotubes. The elastic modulus of HNTs is 140 GPa (with theoretical values of 230–340 GPa) [38–40]. BET surface area values of HNTs are in the range of *ca.* 75–82 m²/g. The density of HNTs is relatively low (2.14–2.59 g/cm³) in comparison with other mineral fillers, which is a very important characteristic for light-weight polymer composites applications [13, 19]. As Pasbakhsh described [19] the pore size

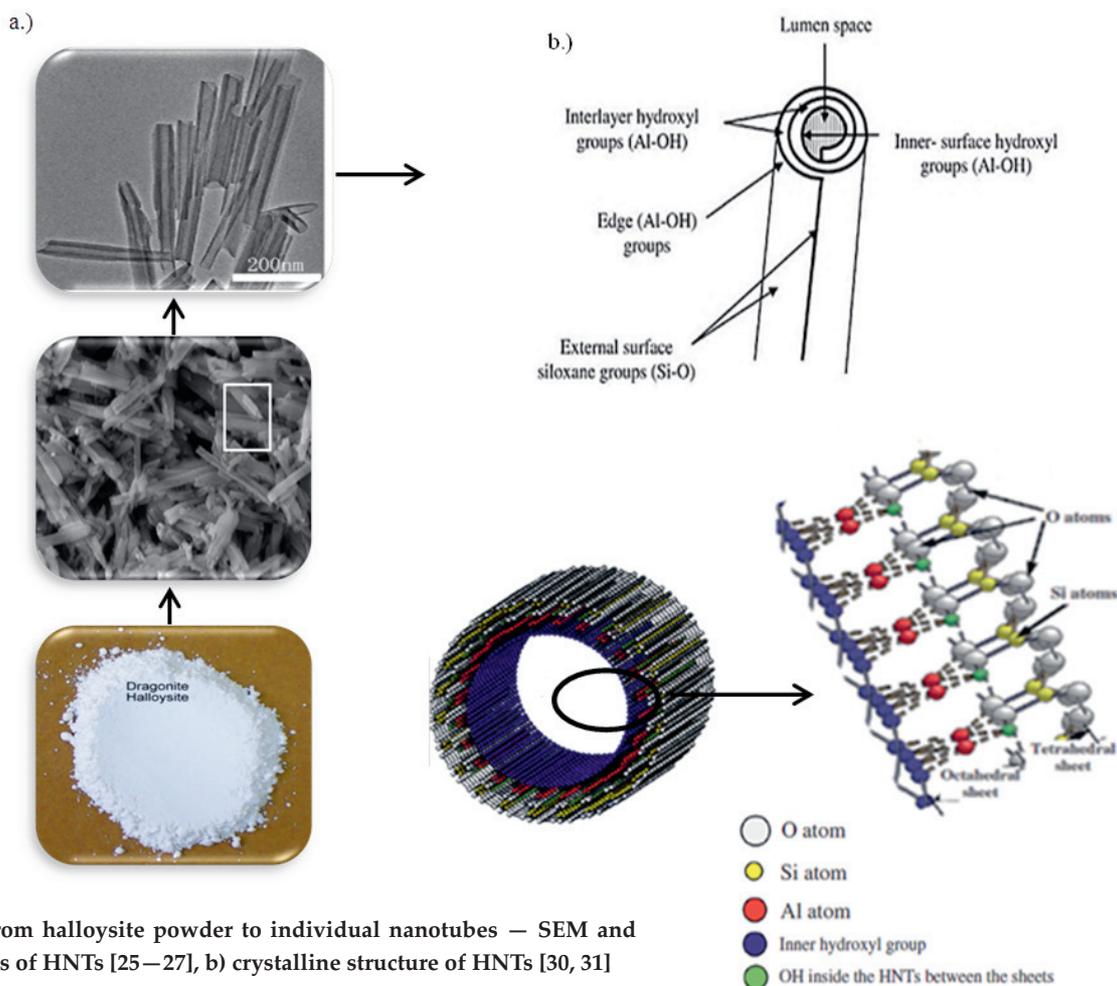


Fig. 1. a) From halloysite powder to individual nanotubes – SEM and TEM images of HNTs [25–27], b) crystalline structure of HNTs [30, 31]

distribution of HNTs is broadly bimodal, corresponding to smaller and larger internal/surface pores, such as spaces between the sheets or central lumen of HNTs. Therefore, the surface of HNTs can be filled or coated

with polymers or many organic substances, enhancing the homogeneity of the nanocomposites [13].

The chemical structures of HNTs were studied by Fourier transform infrared spectroscopy (FT-IR). An example of a FT-IR spectrum of halloysite and a detailed characteristic of particular bands of the spectrum is presented in Fig. 2 and in Table 1.

– Relatively low tube – tube interactions.

HNTs have a limited possibility of creating strong tube – tube interactions and large – area contacts between themselves. This results from geometrical and che-

Table 1. Assignments of FT-IR vibrations of HNTs

Wavenumbers cm^{-1}	Suggested assignments	Reference
3739	Si-OH stretching vibrations	32, 33
3620, 3696, 3661	inner-surface O-H stretching vibrations and in-phase and out-of-phase stretching vibrations	32–37
3566	interlayer water O-H vibration	32
1625	O-H deformation vibrations in physical adsorbed water	32–34
1033	skeleton Si-O stretching vibration (Si-O-Si, O-Si-O)	32, 33, 37
913	inner O-H deformation vibrations	32, 34, 35
794, 754, 689	Si-O symmetric and perpendicular stretching vibrations or O-H (Al-OH) translational vibrations	32, 34, 36
538	Si-O-Al deformation vibrations	31, 33
470, 432	Si-O-Si and Si-O deformation vibrations	31, 33

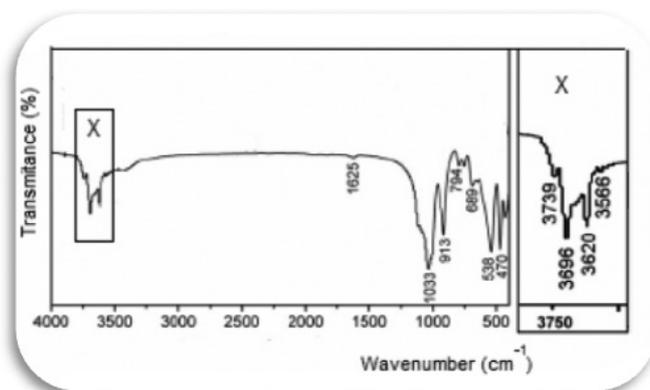


Fig. 2. FT-IR spectrum of HNTs [32]

mical aspects, such as tubular morphologies with relatively high aspect ratio and few hydroxyl groups located on external surfaces of HNTs. Therefore, the interactions caused by secondary bonds like H-bonding or Van der Waals forces between the tubes are relatively weak. Consequently, HNTs can be uniformly dispersed into polymer matrix, which is the crucial factor in obtaining polymer/HNT nanocomposites with better properties compared to unfilled polymers. For comparison, strong intrinsic Van der Waals attractions are observed between CNTs, making their dispersion in polymers a challenging task [41].

– Relatively low hydrophilicity.

In contrast to other nanoclays, the multi-layer, tubular structure of HNTs are connected with their relatively weak hydrophilic character. Most hydroxyl groups (Al-OH) are located inside the tubes, whereas only a few hydroxyl groups (Al-OH and Si-OH) were found on the edges of external surfaces of the tubes (Fig. 1b) [42, 43]. Therefore, HNTs should be readily dispersed into non-polar polyolefin matrices. However, sometimes the weak hydrophilic character of HNTs is insufficient for proper interactions with strong, non-polar polymer chains. In that case, the functionalization processes of HNTs with different organic and inorganic compounds are used.

– Negatively charged surfaces.

Two types of charges exist on the surfaces of HNTs. The first is the permanent negative charge on the silicon tetrahedral sheets, resulting from minor isomorphous substitutions in the tetrahedral sheets. The second is the variable charge caused by protonation or deprotonation of the edge hydroxyl groups. The variable charge is affected by three types of hydroxyl groups: the more reactive silanol (Si-OH) and aluminol (Al-OH) groups on the tube edges and the less reactive Al-OH groups at the interlayer surface. The sign of the charge depends on the pH and charges develop on these hydroxyl groups by direct H^+ or OH^- transfer from aqueous solution, further causing charge heterogeneity. The surface charge has a great significance during modification processes. Long organic chains of modifying compound with positively charged ends, *e.g.* alkylammonium salts with long aliphatic chains can be tethered to the negatively charged surfaces either on interlayer surfaces or more frequently on the edges or external surfaces of HNTs. Consequently, the surface charge facilitates the polymer chains to diffuse between, or into, HNTs [13].

– Electrophilic character.

HNTs are electrophilic. The electron acceptor sites are the aluminum species at the crystal edges and the transition metals of higher valences in the silicate layers. These properties of HNTs can be used to enhance the interfacial interactions in polymer nanocomposites [23].

– Thermal and chemical resistance.

An important advantage of HNTs is their high resistance to heat and chemical substances. The thermal resistance of halloysite reaches 600 °C, which means that

HNTs are suitable for almost all polymers, even with high processing temperatures. Cheng [44] and Frost [45] showed, with TGA and DTA analysis, that the decomposition process of HNTs takes place in three main stages: 1) release of water adsorbed on halloysite particles (50–240 °C), 2) structural decomposition of halloysite (480–640 °C) with dehydroxylation of structural aluminol (Al-OH) groups inside and on the edges of halloysite tubes, 3) formation of amorphous SiO_2 and $\gamma-Al_2O_3$ (around 990 °C) or thermal decomposition of impurities.

– Fire retardant properties.

HNTs are a promising additive for improving the thermal stability and flame retardancy of polyolefins and other polymers. The improvement of thermal stability and flame retardancy resulted from the barrier properties of HNTs combined with an encapsulation process of the polymer's degradation products inside the HNT lumens [46]. Detailed information about the thermal stability and flame retardancy of polyolefin/HNT nanocomposites will be described in our following paper.

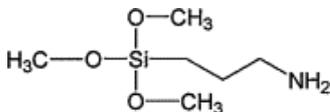
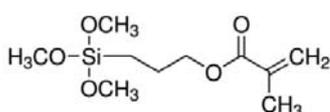
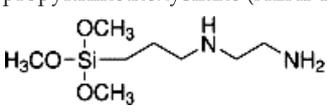
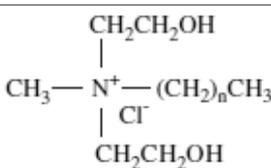
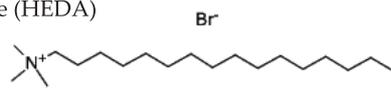
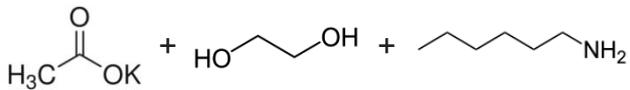
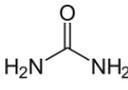
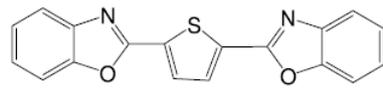
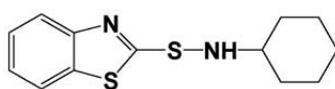
The advantages of HNTs presented above make them promising reinforcing fillers for polyolefins. What is important, due to their structure and chemical character, HNTs can be more easily dispersed into polyolefin matrices in comparison with other nanofillers, such as MMT. This is a crucial factor for obtaining nanocomposites with better mechanical properties, higher thermal stability and reduced flammability. However, due to the great polarity discrepancy between HNTs and non-polar polyolefins and thus a low compatibilization degree due to a weak, but still existing, tendency of HNTs to agglomerate, the synthesis of homogeneous nanocomposites is still a challenging task. Therefore, below we discuss different solutions of the optimization of the homogeneity by strengthening interfacial interactions and dispersion of nanotubes in polyolefin/HNT nanocomposites.

METHODS OF HOMOGENEITY IMPROVEMENT IN POLYOLEFIN/HNT NANOCOMPOSITES

Functionalization of HNTs

One of the most commonly used ways to obtain the proper dispersion of HNTs in a polyolefin matrix is the functionalization (modification) of HNTs by different organic compounds. The chemical formulas of the main compounds used for covalent and non-covalent functionalization of HNTs are compiled in Table 2. Due to enhanced homogeneity, the polyolefin nanocomposites based on modified HNTs usually exhibit improved mechanical and thermal properties compared to the same composites with unmodified HNTs [13]. Changes in the degree of HNT dispersion and their interfacial interactions with polyolefin chains caused by HNT modification were usually determined with scanning and transmission electron microscopy (SEM, TEM), X-ray diffraction (XRD) or FT-IR methods.

Table 2. Main directions of HNTs functionalization for polyolefin/HNT composites

Substance	Functionalization process	Ref.
Covalent functionalization		
Aminopropyltrimethoxysilane (APTMS)		47, 54, 55
γ -Methacryloxypropyl trimethoxysilane (MPS)		Silane coupling solvent: toluene or ethanol conditions: 100 °C, 24 h
(2-Aminoethyl)-3-aminopropyltrimethoxysilane (AEAPTMS)		
Non-covalent functionalization		
Methyl, tallow, bis 2-hydroxyethyl, quaternary ammonium salt (n = 14–18)		Electrostatic attraction interactions solvent: 5 % K ₂ CO ₃ conditions: 80 °C, 24 h
Hexadecyl-trimethyl-ammonium bromide (HEDA)		Electrostatic attraction interactions conditions: 80 °C, 24 h without solvent
K-acetate + ethylene glycol + n-hexylamine		Intercalation conditions: 20–150 °C, 4–48 h
Urea		Intercalation mixing in laboratory planetary mill
2,5 bis(2-benzoxazolyl) thiophene (BBT)		23
N-cyclohexyl-2-benzothiazole sulfonamide (CBS)		Electron transfer intercalation vigorous blending
2,2'-(1,2-ethenediyl)di-4,1-phenylene bisbenzoxazole (EFB)		59
Melamine (MEL), Melamine cyanuric acid (MCA) Diphenyl guanine (DPG) 2,4,6-Trimercapto-s-triazine (TCY) Tri-(2-hydroxyethyl) isocyanurate (THEIC) Beta-cyclodextrin (beta-CD)	Hydrogen bonding added with HNTs during the polyolefin/HNTs processing	21

Covalent functionalization

The hydroxyl groups located on the inner surfaces and on the edges of HNTs provide reactive sites for the covalent attaching of chemical species. The siloxane groups (Si-O-Si) of HNTs are regarded as nonreactive. Usually, modification of internal surfaces of HNTs is rele-

vant for immobilization and controlled release applications, while modification of the external surfaces and edges is beneficial for nanocomposite formation.

The main advantage of covalent functionalization is the reduction of hydrophilicity of HNT surfaces by shielding their hydroxyl groups through the incorporation of new functional groups (usually hydrocarbons)

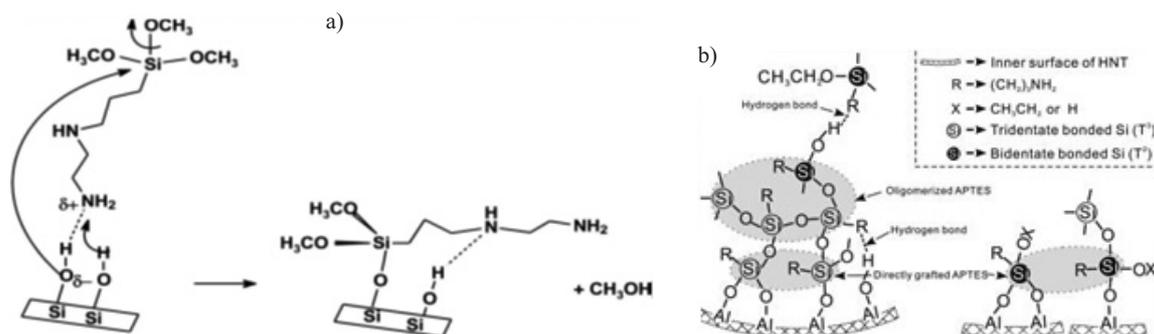


Fig. 3. Grafting reaction scheme between HNTs and organosilane proposed by: a) Barrientos-Ramirez [49], b) Yuan [34]

[13]. The most common method is silane grafting via the condensation of hydrolyzed silanes and external hydroxyl groups of HNTs. The process of modifying HNTs is usually carried out in toluene or ethanol at 100 °C for 24 h. Before grafting, halloysite is often thermally treated at 400 °C for 2 h [47, 48]. The mechanism of silane (AEAPTMS and APTMS) grafting on the HNTs surfaces proposed by Barrientos-Ramirez [49] and Yuan [34] is presented in Fig. 3. The authors stated that the amino groups may catalyze the reaction between methoxy groups of silane and OH groups (Si-OH or Al-OH) of HNTs [50]. Besides, hydrogen bonding between amino groups of the aminosilane and the Si-OH groups of HNTs might occur. In the FT-IR spectrum of functionalized HNTs, beside the absorption bands of raw HNTs, absorption of functional groups of aminosilane at 3485 and 3350 cm^{-1} (N-H₂ stretching), 2938 and 2842 cm^{-1} (N-H stretching and symmetric C-H₂ stretching), 1654 cm^{-1} (N-H bending), 1556 cm^{-1} (N-H₂ scissoring), as well as 1466 cm^{-1} (C-H₂ scissoring), 1385 cm^{-1} (C-H₂ wagging) and 1329 cm^{-1} (Si-CH scissoring) and 1195 cm^{-1} (C-N stretching) were observed. On the basis of XRD analysis the authors proved no modification of basal spacing of HNTs. Thus the aminosilanes did not intercalate between HNT layers and remained on the surfaces. The authors believed that most interlayer located Al-OH groups of HNTs are unavailable for grafting because they are blocked by the strong hydrogen bonds between layers. As a consequence, grafting took place just on the outer Si-OH groups. Yuan [34] founded that modification of HNTs by APTMS included not only the direct grafting of APTMS onto the OH groups of HNTs, but also oligomerization of APTMS. In this process, the hydrolyzed APTMS molecules condensed among themselves and with already grafted APTMS to form a cross-linked structure (Fig. 3b). The authors believed that thermal pretreatment of HNTs plays an important role in the mechanism of grafting. Direct grafting occurs for HNTs thermally treated at 400 °C, whereas both direct grafting and cross-linked structure formation occur without the pretreatment of HNTs. Moreover, a devolatilization can dramatically enhance the loading of hydrolyzed APTMS into the lumens of HNTs and increase the grafting yield. Silane grafting can also be used as an additional pretreatment

before further modifications of HNTs. For example, Joo [51] prepared HNTs-COOH by mixing the aminosilane grafted HNTs with succinic acid anhydride in dimethyl formamide.

Du [52] showed that after functionalization with organosilane (MPS), HNTs were dispersed more uniformly in the PP matrix. Without modification, HNTs formed some aggregates in the PP matrix. Furthermore, many cavities and sharp interfaces, which were found on the fracture surfaces of PP/unmodified HNTs composites, are reduced in composites with modified HNTs. It is clearly proved that surface modification of HNTs with organosilane significantly improves the interfacial interaction of HNTs with PP chains. In the next paper, Du [53] described that, after functionalization by APTMS, an even higher content (30 wt %) of HNTs can be well dispersed in PP matrix. In turn, Pal [54] observed individually dispersed HNTs in COC (cycloolefin copolymer) matrix after two-step functionalization of HNTs with APTMS and then PE-g-MA (polyethylene grafted with maleic anhydride), whereas raw HNTs formed agglomerates in the matrix. The probable mechanism of HNT – APTMS interactions with PE-g-MA and COC are presented in Fig. 4. After the modifications, HNTs adopt a chain containing an ethylene moiety that can physically interact by chain entanglement at the interface with the ethylene part of the COC.

XRD results (Fig. 5) confirmed a good dispersion of HNTs, as well as interfacial interactions, in COC/modi-

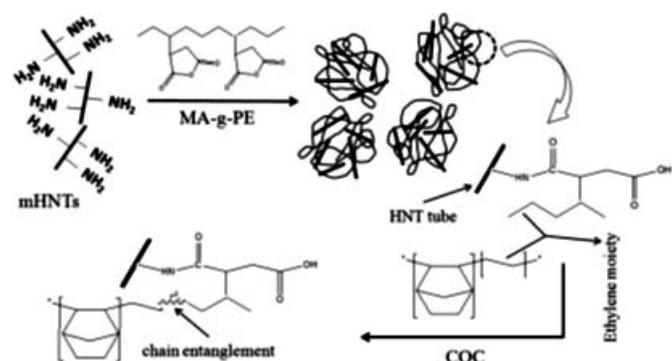


Fig. 4. Mechanism of interactions between two-step modified HNTs and COC matrix [54]

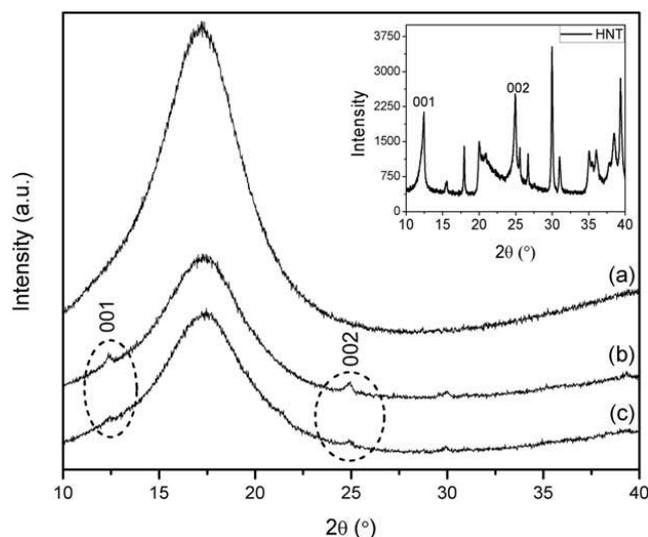


Fig. 5. XRD patterns of: a) pure COC, b) COC/unmodified HNTs, c) COC/modified HNTs [54]

fied HNTs nanocomposite. Partial intercalation of modified HNTs by COC chains, leading to the dispersion of modified HNTs all over the COC matrix, was clearly seen.

Non-covalent functionalization

The relatively low content of hydroxyl groups on HNT surfaces limits the number of reactive sites for covalent bonding and hence covalent functionalization may be unsatisfactory in some cases and then non-covalent functionalization might be a better modification strategy.

Du [21], for the case of PP/HNTs and PE-HD/HNT nanocomposites, believed that a proton donor or acceptor (Table 2), including MEL, MCA, DPG, TCY, THEIC, beta-CD, added simultaneously with HNTs to the polyolefin matrix during processing can interact with HNTs via hydrogen bonding (HB) and then bridging HNTs with the polymer matrix [21]. HB formation was studied with FT-IR analysis. Si-O and N-H (1030 , 1007 cm^{-1} and

1653 , 1553 cm^{-1} , respectively) absorptions on HNT/MEL spectrum proved the formation of HB between Si-OH groups of HNTs and NH_2 groups of MEL.

HNTs can also intercalate with organic compounds through an ion exchange reaction, which was described by Joussein [16]. However, as Pasbakhsh showed [19], the parameter determining the ionic exchange capability — cation exchange capacity (CEC) value — is very low for HNTs (around 2 meq/100 g); for comparison, the CEC of montmorillonite usually averages around 150 meq/100 g. Generally, HNTs did not need to be intercalated because of their tubular microstructure and relatively good dispersion in polar polymers. However, there are a few works [55–58] focused on the intercalation of HNTs in order to obtain better dispersion into polyolefin matrix (table 2). Pedrazzoli [57] proved that HNTs can be finely dispersed within a PE-LLD matrix after HNTs intercalation with K-acetate, ethylene glycol and *N*-hexylamine mixture. In XRD patterns of PE-LLD nanocomposites (Fig. 6a), they observed the characteristic peaks of HNTs ($2\theta = 20.4^\circ$ and 24.7°), whose intensity slightly increases with increasing HNTs content (1–8 wt %). These peaks may confirm the presence of structures with limited intercalation and can be attributed to the formation of nanocomposites. In FT-IR spectra (Fig. 6b), the characteristic peaks of HNTs, as well as modifying compounds (*ca.* 1500 and 1300 cm^{-1} , attributed to the C=O and CH_3 vibrations, respectively), were observed. In turn, in spectra of PE-LLD/unmodified HNTs, the HNT characteristic peaks are almost invisible, indicating a low degree of chemical interaction in this composite. Similar results were also obtained for urea-intercalated PP/HNTs nanocomposites by Khunova [55]. Moreover, Ning [56] obtained a good dispersion of HNTs (1–10 wt %) in a PP matrix after intercalation of HNTs with a quaternary ammonium salt. SEM images showed that the interface of PP/modified HNTs was smoother and no obvious cavities were seen, suggesting a good interfacial interaction.

The occurrence of several metal atoms (aluminum, iron, transition metals with unoccupied orbitals) on HNT

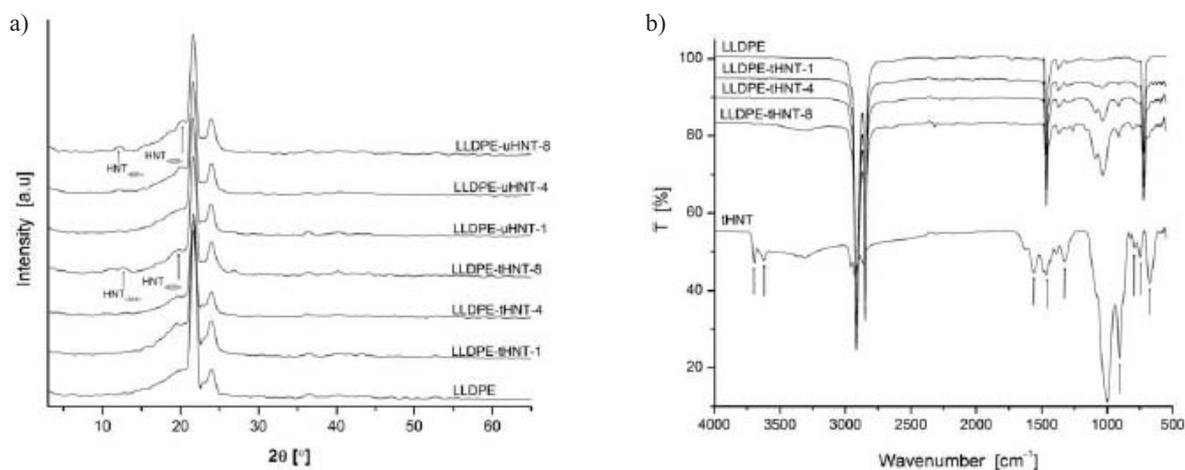


Fig. 6. a) XRD patterns, b) FT-IR spectra of PE-LLD and its nanocomposites with modified (tHNT) and unmodified HNT (uHNT) [57]

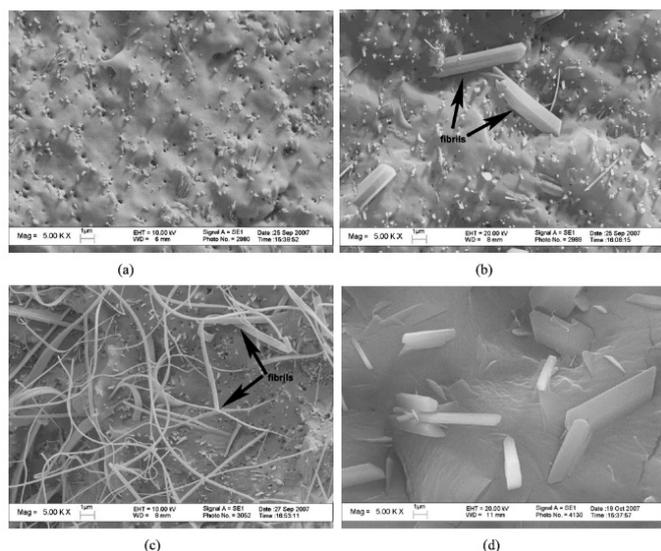


Fig. 7. SEM of the fractured surface of PP/HNTs (30 wt %)/BBT nanocomposites: a) PP/HNTs, b) PP/HNTs/BBT (3 wt %), c) PP/HNTs/BBT (10 wt %), d) PP/BBT (10 wt %) [23]

surfaces offers numerous opportunities for improving the interfacial adhesion between HNTs and polyolefin chains via electron transfer interactions [13]. Liu proved that electron-transferring modifiers, such as BBT [23], EFB [59] or CBS [60] also contributed to the uniform dispersion of HNTs in PP matrices through interactions with HNTs. Interestingly, apart from the nanotubes, some fibrils were also observed in PP/HNT/BBT or PP/HNT/CBS nanocomposites. As HNTs could not be aligned into such continuous fibrils, the authors attributed their formation to the organization of BBT molecules. SEM images indicated (Fig. 7) that in the absence of HNTs, BBT itself could not be organized into fibrils. Moreover, DSC results showed a significant increase of PP/HNTs nanocomposites crystallinity after incorporating BBT, which was connected with the growth of PP crystals along the fibrils.

The number of patents or patent applications focusing on modification methods of HNTs is relatively low. In one patent [61], the authors claimed the method of HNT modifications with balmy rosin and balmy rosin esters or glycidol methacrylate. HNTs were mixed with modifying agent in acetone, in the presence of benzoyl peroxide, at the temp. of 70 °C under reflux, and then used as a reinforcing agent for PP. In another patent application [62], the method of thermal or ultrasound modifications of HNTs were described as a sufficient method of improving thermal stability and mechanical properties of PP/HNTs composites. A U.S. patent [63] described a method of modifying HNTs with functionalized block copolymer for improving compatibility with thermoplastic or thermoset polymers. In another U.S. patent [64], it was demonstrated that HNTs modified with benzalconium chloride contribute to the improvement of the mechanical properties of PA 6 and thermal stability of PP.

Other methods of homogeneity improvement in polyolefin/HNT nanocomposites

In some cases, functionalization of HNTs can be insufficient to obtain a high degree of HNT dispersion in polyolefin matrix. Therefore, considerable attention has been focused on the improvement of HNT dispersion by connection of HNT functionalization with a compatibilizer addition and/or specific processing methods. Lecouvet [65] obtained nanocomposites of PP/unmodified HNTs (8–16 wt %) with well-dispersed nanotubes by the addition of compatibilizer (PP-g-MA) with water-assisted extrusion (Fig. 8). In PP/HNT composites prepared with the use of compatibilizer but by simple extrusion, huge

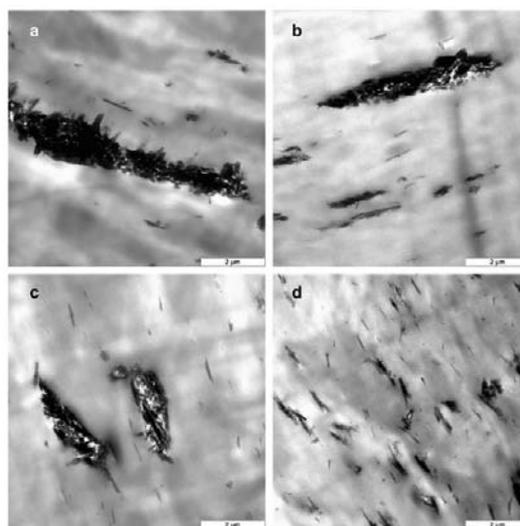


Fig. 8. TEM images of single extruded: a) PP/HNTs (8 wt %), b) PP/PP-g-MA/HNTs and water-assisted extruded composites, c) PP/HNTs, d) PP/PP-g-MA/HNTs [65]

aggregates of HNTs, with only a few individual nanotubes in SEM and TEM images, were observed. Also, separate use of a compatibilizer or water-assisted extrusion process was insufficient. It was concluded that water injected into the extruder high compression zone remains liquid and promotes an even HNT distribution. Besides, the anhydride groups in PP-g-MA are hydrolyzed to carboxylic diacid by water and may form interfacial hydrogen bonding with siloxane (Si-O) and aluminol (Al-O) groups of HNTs. In one paper [66], Lecouvet observed individually dispersed HNTs (0.5–3 wt %) in a PP/IFR (intumescent flame retardant) system obtained through dilution of masterbatch of PP/HNTs (8 wt %) extruded in the presence of water with neat PP and IFR. Moreover, Zhao [67] observed that HNTs (0.5–3.0 wt %) were also well dispersed in a PE-LD/IFR system after processing all compounds together in a two-step process first with high-speed mixer and then with twin-screw extruder.

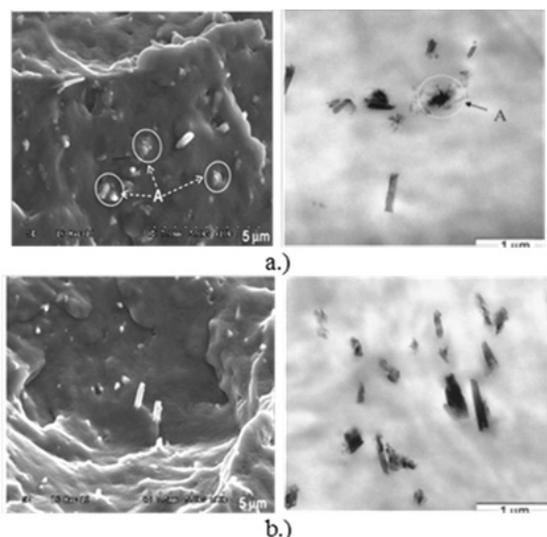


Fig. 9. SEM and TEM images of: a) PP/6 wt % unmodified HNTs, b) PP/6 wt % modified HNTs nanocomposites; A — aggregates of nanotubes [68]

Wang [22] studied the effects of water-assisted injection molding (WAIM) or compression molding (CM) on the orientation of HNTs in PP/unmodified HNT (2–8 wt %) nanocomposites. As the authors expected, samples prepared by the WAIM method showed a high orientation of HNTs in the flow direction due to shear flow across the mold cavity during the high-pressure water penetration. In turn, in the case of CM nanocomposites, randomly orientated, well dispersed nanotubes were observed as a result of the very low shear rate in the process.

A homogeneous dispersion of HNTs in PP matrices was also obtained by the masterbatch dilution method. Prashantha [68] diluted PP masterbatches containing unmodified and quaternary ammonium salt modified HNTs. In opposition to nanocomposites with unmodified HNTs (Fig. 9a), well-dispersed HNTs were observed in PP/modified HNT nanocomposites (Fig. 9b). The authors explained that quaternary ammonium salt functional groups present on the HNTs surfaces decreased their surface free energy and hindered nanotube/nanotube interactions. The effects finally facilitate the breakup of aggregates during the extrusion process and improve the interfacial interactions between HNTs and the PP matrix.

Recently, Lin [69] confirmed that the addition of unmodified HNTs and compatibilizer (SEBS-*g*-MA — maleic anhydride grafted styrene — ethylene — butylene — styrene block copolymer) is an effective way to improve interfacial adhesion in PP/PET blends. However, HNTs were well dispersed only in the blend prepared as a two-step process, *i.e.* first mixing HNTs with SEBS-*g*-MA and then extruding with PP/PET blend. Moreover, HNTs were selectively dispersed in PP/PET/SEBS-*g*-MA/HNT blends and part of the HNT, together with SEBS-*g*-MA, form a “coat” on the PET phase, resembling an encapsulation structure (Fig. 10).

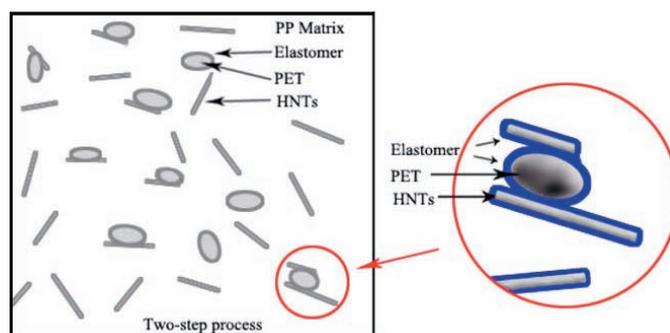


Fig. 10. Schematic representation of encapsulation model in PP/POM/SEBS-*g*-MAH/HNTs blend (blue layer is SEBS-*g*-MA) [69]

It can be concluded that the driving forces for the homogeneous dispersion of HNTs in polyolefin matrices are interfacial interactions and high shear forces during melt mixing. Use of a twin-screw extruder (rarely internal mixer) is the most common and industrially favored method of polyolefin/HNT nanocomposite preparation. Several strategies for the improvement of HNT dispersion in polyolefin matrix, including functionalization of HNTs with different organic compounds and/or compatibilizer addition, or masterbatch dilution, as well as water-assisted extrusion techniques have been proposed.

MECHANICAL PROPERTIES OF POLYOLEFIN/HNT NANOCOMPOSITES

Jia [70] observed a significant improvement of tensile strength, flexural strength and flexural modulus of PE-LLD (LLD-PE) even after the addition *ca.* 40 wt % of HNTs. Further improvement of the mechanical properties was obtained by the addition of 5 wt % of a compatibilizer, in this case PE-LLD grafted with maleic anhydride, methyl methacrylate and butyl acrylate. The authors explained that anhydride and ester groups present in the compatibilizer can form both intermolecular hydrogen bonds with OH groups and dipole-dipole interactions with Si-O groups of HNTs. Simultaneously, the compatibilizer can strengthen the interfacial bonding between PE-LLD and HNTs and facilitate the dispersion of HNTs in PE-LLD matrix. Moreover, poly(butyl acrylate) segments of the compatibilizer can also improve the toughness of the nanocomposites. Du [52, 53] obtained remarkable mechanical properties of PP/HNTs nanocomposites containing 30 wt % of HNTs. The tensile strength, Young modulus, flexural modulus and flexural strength increased gradually with higher HNT contents. The best properties were observed for nanocomposites with organosilane modified HNTs. In turn, elongation at break of the nanocomposites, especially with 15 and 30 wt % of HNT load, significantly decreased compared to neat PP (from about 350 % to 100 % of elongation value). However, comparatively, elongation at break of PP/MMT (15 wt %) nanocomposites is not higher than 50 % [71, 72].

Prashantha also proved the best reinforcement potential of HNTs as compared to MMT and CNTs. The authors explained that CNTs and MMT have a stronger tendency to form agglomerates, which act as crack initiation sites and lead to sudden failure of the material. Therefore, HNTs seem to be a more favorable filler of polyolefin matrices than MMT and CNTs.

Pedrazzoli [57] observed that HNTs modified by a mixture of K-acetate, ethylene glycol and *N*-hexylamine are responsible for a significant increase (about 94 %) of the elastic modulus in comparison with PE-LLD matrix. Moreover, in PE-LLD/modified HNT nanocomposites, the stiffening effect of HNTs up to 8 wt % of HNT content only slightly reduces PE-LLD ductility. In that case, the yield stress of the composite was slightly higher compared with neat PE-LLD, whereas the stress and elongation at break moderately decrease with increasing the HNT content.

The toughening mechanism of HNTs during fracture of nanocomposites was assessed through the essential work of fracture (EWF) method under specific tensile conditions [57]. The total fracture energy can be portioned into an essential work required to create new fracture surfaces and nonessential work dissipated by the plastic deformation of the outer plastic zone. The force-displacement curves and SEM images (Fig. 11a) obtained during EWF testing showed that, after yielding, the specimens of PE-LLD/unmodified HNTs cracked abruptly without a stable propagation phase, whereas PE-LLD/modified HNTs specimens exhibited ductile fracture. The two-fold increase of fracture toughness (expressed as EWF value) in PE-LLD/8 wt % modified HNTs nanocomposite the authors assigned to the reinforcing effect of modified HNTs. Conversely, the reinforcing effect of unmodified HNTs is predominated by loss in ductility, which is in accordance with the results of quasi-static tensile tests (Fig. 11b).

On the other hand, Knuhova [55] did not observe any improvement in tensile strength and tensile modulus of PP/5 wt % HNT nanocomposites, even after intercalation of HNTs by urea. One reason of this might be identical *d*-spacings of urea-intercalated HNTs and PP/urea-intercalated HNT nanocomposites, leading to restricted intercalation of PP chains in the HNTs structure. The authors believed that urea modification of HNTs led to an increase in HNT hydrophilicity and caused a low affinity to the hydrophobic PP matrix. After modification of HNTs by quaternary ammonium salt or organosilane, the authors obtained similar results. Moreover, in a U.S. patent [64], it was demonstrated that HNTs modified by quaternary ammonium salt did not improve the mechanical properties of PP and thus the mechanical properties of composites were similar to the neat PP, even after using PP-*g*-MA as a compatibilizer. As Ning [56] stated, this can result from decreased or unchanged crystallinity of PP in PP/HNT nanocomposites in comparison to neat PP. It is well known that only an increased crystallinity of poly-

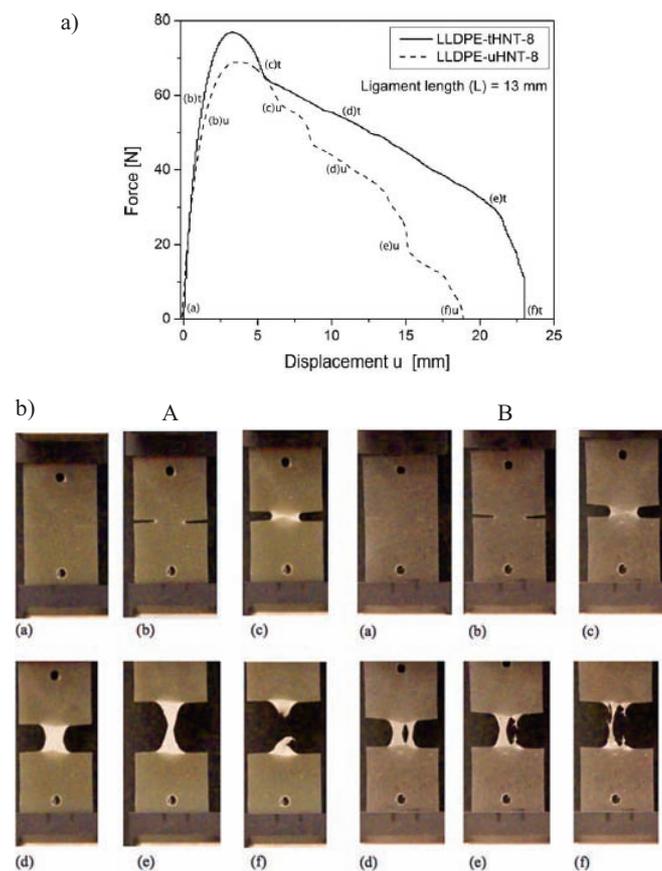


Fig. 11. a) The force-displacement curves, b) serial photographs of: A) PE-LLD-tHNT-8, B) PE-LLD-uHNT-8 specimens during the EWF tests at different times (tHNTs – modified HNTs, uHNTs – unmodified HNTs) [57]

mer can contribute to the improvement of mechanical properties of polymer composites.

Therefore, to obtain more favorable mechanical properties, modification of both HNTs and PP matrix was applied. Knuhova [55], beside modifications of HNTs, also simultaneously modified the PP matrix with DBMI (4,4'-diphenylmethylenedimaleinimide). As a result, significant increases in tensile strength and tensile modulus of PP/DBMI/HNT nanocomposites were observed. The best results were for PP/DBMI/urea-intercalated HNT nanocomposites probably due to the coupling effect of urea between the HNTs and PP via reaction between the OH groups of HNTs and imide ring of DBMI.

The enhanced mechanical properties of polyolefin/HNT nanocomposites were also achieved by using different proton donors as special modifiers of HNTs and/or polyolefin matrix, which can interact either with HNTs or both HNTs and polyolefin matrix. Du [21] stated that proton donors, such as MEL or MCA (Table 2) improve the tensile strength and flexural properties of PP/HNTs and PE-HD/HNT nanocomposites via hydrogen bonding bridging of HNTs in the polyolefin matrix. This effect was observed even at 1 wt % addition of proton donor and with high loading of HNTs, *ca.* 30 wt %. This probably results from transferring of loaded stress

by bridged HNT structures. However, these structures can restrict the mobility of polyolefin chains, leading a higher rigidity and reduced impact strength to the nanocomposites. On the other hand, Liu [23] obtained similar results after using BBT as a transfer electron modifier. Interestingly, the positive reinforcing effect of BBT was attributed to the formation of BBT fibrils in the PP/HNT nanocomposites (Fig. 8). Authors explained that the presence of the fibrils leads to significant improvement of PP crystallinity and consequently the tensile and flexural properties of the nanocomposites increased. In that case, the decrease of impact strength was assigned to the presence of a PP transcrystalline layer on the BBT fibril surface with high rigidity and lower deformability. Slightly better results were obtained by Liu [59] in the way of modification of both HNTs and PP matrix with CBS (see Table 2) – an accelerator popular in the rubber industry. In this case, CBS reacted both with the PP matrix through a grafting reaction and with HNTs via an electron transferring mechanism, leading to the intensification of interfacial bonding in PP/HNT systems. A slight decrease of tensile strength and flexural modulus above 7 wt % content of CBS in nanocomposites correlated with the presence of stress concentration points, *i.e.* HNT aggregates and CBS fibrils.

In a Polish Patent Application [62], thermally treated HNT (1–10 wt %)/PP nanocomposites with an elastic modulus *ca.* 80 % higher in comparison to unfilled PP and PP/unmodified HNT composites were presented. In another application [61], the authors noted that composites with 3 wt % HNTs modified by balmy rosin and balmy rosin esters or glycidol methacrylate showed nearly a 400 % increase in Charpy impact strength value, 2-fold increase in tensile strength and 15–30 % increase in flexural elasticity modulus in relation to unfilled PP.

Moreover, beside single polyolefin systems, HNTs are also used in blends of polyolefins with other polymers. Lin [69] stated that the formation of an unique morphology with encapsulation structure (Fig. 10) during two-step processing of PP/PET/SEBS-*g*-MAH/HNTs blend was crucial for substantial improvement of the mechanical performance of PP/PET blends. HNTs selectively dispersed at the interphase improve the capability of stress transfer from the PP to PET phase thus reinforcing the PP/PET interphase. As a consequence, remarkably higher flexural and tensile properties of the blends were observed. Moreover, introduction of higher amounts of HNTs (from 0.5 to 10.0 wt %) led to better properties. Pal [47] suggested that HNTs modified with organosilane play a double role in polar-nonpolar PP/POM blend: as a reinforcing (filler) and bridging agent (compatibilizer). Therefore, the tensile properties of the PP/POM/modified HNTs were higher than the PP/POM and PP/POM/unmodified HNTs.

HNTs were also used as reinforcing agent of intumescent flame retardant (IFR) systems for polyolefins. Zhao [73] found that not only flame retardancy, but also the

tensile properties of PE-LD/IFR composites can be promoted by the addition of a small amount of HNTs. The authors observed that both tensile strength and elongation at break of PE-LD/IFR systems were increased compared with neat PE-LD with the presence of 0.5–2.0 wt % of HNTs. They believed that it mainly resulted from a good dispersion of HNTs in the PE-LD/IFR composite.

The results of tensile properties are usually confirmed by dynamic mechanical properties. It is generally believed that well-dispersed HNTs can effectively restrict the motion and relaxation of polymer chains thus remarkably enhancing stiffness and load bearing capability, as well as the glass transition temperature of the material. Many authors proved the improvement of dynamic mechanical properties of polyolefin/HNT nanocomposites in comparison with neat polyolefin. Pedrazzoli [57] described a significant improvement of creep stability and storage modulus, as well as glass transition temperature (T_g), of PE-LLD after the introduction of HNTs (1–8 wt %), especially modified HNTs. Similar results for storage modulus (E') were also obtained by Pal [54] in the case of COC/1 wt % HNT nanocomposites, where HNTs were modified with APTMS. In turn, Prashantha [68] obtained an increase of E' and T_g values for PP/HNT nanocomposites prepared by the masterbatch dilution method. As in previous examples, the best results exhibited nanocomposites with modified HNT.

It was demonstrated that incorporation of HNTs into polyolefin matrix usually leads to a significant improvement of the mechanical properties of polyolefin/HNT nanocomposites compared with neat polyolefin. The reinforcing effect of HNTs in polyolefin matrix was attributed to such main factors, as: 1) high intrinsic stiffness of nanotubular structure, as well as high aspect ratio, of HNTs, 2) strong interfacial interactions between HNTs and polyolefin matrix, 3) good dispersion of uniformly orientated HNTs along the stretching direction, acting as a “skeleton” bearing stress and fracture energy, 4) nucleating effect of HNTs leading to improved mechanical properties of the polyolefin matrix, such as PP by higher crystallinity and lower spherulite size.

These factors are mainly assigned to the nanocomposites with functionalized HNTs or containing a compatibilizer. It was also suggested that functionalized HNTs can play a double role in polyolefin blends with polar polymers, either as a reinforcing or compatibilizing agent. The increase of strength and modulus during tensile and flexural, as well as bending tests, were mainly observed. Moreover, the higher crystallinity of polyolefins after HNT incorporation resulted in higher modulus and strength of polyolefin/HNT nanocomposites. However, a higher rigidity often led to lower deformability, thus elongation at break and impact strength were slightly decreased. In nanocomposites without any functionalization, insufficient interfacial interactions and worse dispersion of HNTs were observed, leading to unchanging or even decreasing mechanical properties in comparison with neat polymer.

CONCLUSIONS

It can be concluded that HNTs are promising reinforcing fillers of polyolefins and their blends with other polymers. The number of publications concerning the functional properties of polyolefin/HNT nanocomposites is still growing. The properties result from a unique combination of tubular structure, large aspect ratio, high mechanical strength and rich functionality of HNTs. It is important that naturally occurring HNTs are of a "green" type of material, free from harmful substances. Natural HNTs can be a much cheaper substitute for synthetic CNTs in high-performance and multifunctional polymer nanocomposite applications. HNTs exhibit a low tendency to agglomeration and weak hydrophilic character, which leads to good dispersion in the polyolefin matrix. Incorporation of HNTs into the polyolefin matrix provided a better reinforcement effect than it was observed in the case of MMT or even CNTs.

Critical factors determining the mechanical properties of polyolefin/HNT nanocomposites are a high dispersion of nanotubes and strong interfacial interaction between HNT surface and polyolefin chains. The concentration of HNTs is also an important factor, although in some cases both low and high content of HNTs led to satisfactory results. Nevertheless, only functionalization of HNTs and/or a compatibilizer addition gave the opportunity to perform these requirements. Therefore, a great potential lies in the functionalization of HNTs, as it may provide an enhancement of the functional properties of polyolefin/HNT nanocomposites.

Reinforced polyolefin nanocomposites with HNTs have many potential applications, including packaging, building materials, as well as insulating enclosures or household equipment. Therefore, it seems that the connection of polyolefins' diversified physicochemical properties, economic processing, as well as low price with unique properties of HNTs, may result in large-scale utilization of polyolefin/HNT nanocomposites. The most important limitation is still the insufficient adhesion between HNTs and non-polar polyolefins, demanding expensive modification processes.

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REFERENCES

- [1] Legaly G.: *Applied Clay Science* **1999**, 15, 1. [http://dx.doi.org/10.1016/S0169-1317\(99\)00009-5](http://dx.doi.org/10.1016/S0169-1317(99)00009-5)
- [2] Alexandre M., Dubois P.: *Materials Science and Engineering: R: Reports* **2000**, 28, 1. [http://doi.org/10.1016/S0927-796X\(00\)00012-7](http://doi.org/10.1016/S0927-796X(00)00012-7)
- [3] Pavlidou S., Papaspyrides C.D.: *Progress in Polymer Science* **2008**, 33, 1119. <http://dx.doi.org/10.1016/j.progpolymsci.2008.07.008>
- [4] Kurt E., Geckeler H.Nishide: „Advanced Nanomaterials”, Wiley-VCH GmbH & Co. KGaA, Weinheim 2010, Vol. 1, pp. 195–247.
- [5] Moroń L., Kudła S.: *Przemysł Chemiczny* **2012**, 91, 1889.
- [6] Kudła S., Szpilka K., Bujnowicz K.: *Przemysł Chemiczny* **2013**, 92, 1792.
- [7] Rooj S., Das A., Heinrich G.: *European Polymer Journal* **2011**, 47, 1745. <http://dx.doi.org/10.1016/j.eurpolymj.2011.06.007>
- [8] Ng K.M., Lau Y.T.R., Chan Ch.M., Weng L.T., Wu J.: *Surface and Interface Analysis* **2011**, 43, 795. <http://dx.doi.org/10.1002/sia.3627>
- [9] Macewan D.M.C.: *Nature* **1946**, 159. <http://dx.doi.org/10.1038/157159b0>
- [10] Constanzo P.M., Giese R.F.: *Clays and Clay Minerals* **1986**, 34, 105. <http://dx.doi.org/10.1346/CCMN.1986.0340115>
- [11] Deepak R., Agrawal Y.K.: *Reviews on Advanced Materials Science* **2012**, 30, 282.
- [12] Zhi M., Wang J., Xiang G. et al.: *Progress in Chemistry* **2012**, 24, 275.
- [13] Liu M., Jia Z., Jia D. et al.: *Progress in Polymer Science* **2014**, 39, 1498. <http://dx.doi.org/10.1016/j.progpolymsci.2014.04.004>
- [14] http://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/Sigma-Aldrich/General_Information/1/applied-minerals-press-release.pdf (access date: 19.09.2014).
- [15] Deepak R., Agrawal Y.K.: *Reviews on Advanced Materials Science* **2012**, 32, 149.
- [16] Joussien E., Petit S., Churchman J. et al.: *Clay Minerals* **2005**, 40 (4), 383. <http://dx.doi.org/10.1180/0009855054040180>
- [17] Nakagaki S., Wypych F.: *Journal of Colloid and Interface Science* **2007**, 315, 142. <http://dx.doi.org/10.1016/j.jcis.2007.06.032>
- [18] Churchman G.J., Theng B.K.G.: *Applied Clay Science* **2002**, 20, 153. [http://dx.doi.org/10.1016/S0169-1317\(01\)00098-9](http://dx.doi.org/10.1016/S0169-1317(01)00098-9)
- [19] Pasbakhsh P., Churchman G.J., Keeling J.L.: *Applied Clay Science* **2013**, 74, 47. <http://dx.doi.org/10.1016/j.clay.2012.06.014>
- [20] Du M., Guo B., Wan J. et al.: *Journal of Polymer Research* **2010**, 17, 109. <http://dx.doi.org/10.1007/s10965-009-9296-5>
- [21] Du M., Guo B., Liu M. et al.: *Physica B: Condensed Matter* **2010**, 405, 655. <http://dx.doi.org/10.1016/j.physb.2009.09.082>
- [22] Wang B., Huang H.X.: *Polymer Degradation and Stability* **2013**, 98, 1601. <http://dx.doi.org/10.1016/j.polymdegradstab.2013.06.022>
- [23] Liu M., Guo B., Zou Q. et al.: *Nanotechnology* **2008**, 19, 205709. <http://dx.doi.org/10.1088/0957-4484/19/20/205709>
- [24] Garcia Garcia F., Rodriguez S.G., Kalytta A. et al.: *Zeitschrift für anorganische und allgemeine Chemie* **2009**, 635, 790. <http://dx.doi.org/10.1002/zaac.200900076>
- [25] http://digitalfire.com/4sight/material/dragonite_halloy-site_3179.html?logout=yes (access date: 19.09.2014)
- [26] <http://www.azonano.com/news.aspx?NewsID=25106> (access date: 19.09.2014)
- [27] Jinhua W., Xiang Z., Bing Z.: *Desalination* **2010**, 259, 22. <http://dx.doi.org/10.1016/j.desal.2010.04.046>

- [28] Du M., Gou B., Jia D.: *Polymer International* **2010**, 59, 574. <http://dx.doi.org/10.1002/pi.2754>
- [29] Yah W.O., Takahara A., Lvov Y.M.: *Journal of the American Chemical Society* **2012**, 134, 1853. <http://dx.doi.org/10.1021/ja210258y>
- [30] Albdiry M.T., Yousif B.F.: *Materials and Design* **2014**, 57, 279. <http://dx.doi.org/10.1016/j.matdes.2013.12.017>
- [31] Pasbakhsh P., Ismail H., Fauzi M.N.A., Bakar A.A.: *Applied Clay Science* **2010**, 48, 405. <http://dx.doi.org/10.1016/j.clay.2010.01.015>
- [32] Hu P., Yang H.: *Applied Clay Science* **2013**, 74, 58. <http://dx.doi.org/10.1016/j.clay.2012.10.003>
- [33] Zhang Y., Fu L., Yang H.: *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2012**, 414, 115. <http://dx.doi.org/10.1016/j.colsurfa.2012.08.003>
- [34] Yuan J., Southon P.D., Liu Z. et al.: *The Journal of Physical Chemistry C* **2008**, 112, 15742. <http://dx.doi.org/10.1021/jp805657t>
- [35] Horwath E., Kristof J., Mako E. et al.: *Journal of Thermal Analysis and Calorimetry* **2011**, 105, 53. <http://dx.doi.org/10.1007/s10973-011-1522-9>
- [36] Frost R.L., Locos O.B., Kristof J. et al.: *Vibrational Spectroscopy* **2001**, 26, 33. [http://dx.doi.org/10.1016/S0924-2031\(01\)00108-4](http://dx.doi.org/10.1016/S0924-2031(01)00108-4)
- [37] Cheng H., Yang J., Liu Q. et al.: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2010**, 77, 856. <http://dx.doi.org/10.1016/j.saa.2010.08.018>
- [38] Lecouvet B., Horion J., Haese C.D. et al.: *Nanotechnology* **2013**, 24, 105704. <http://dx.doi.org/10.1088/0957-4484/24/10/105704>
- [39] Lu D., Chen H., Wu J. et al.: *Journal of Nanoscience and Nanotechnology* **2011**, 11, 7789. <http://dx.doi.org/10.1166/jnn.2011.4720>
- [40] Guimares L., Enyashin A.N., Seifert G. et al.: *The Journal of Physical Chemistry C* **2010**, 114, 11358. <http://dx.doi.org/10.1021/jp100902e>
- [41] Xie X.L., Mai Y.W., Zhou X.P.: *Materials Science and Engineering: R: Reports* **2005**, 49, 89. <http://dx.doi.org/10.1016/j.mser.2005.04.002>
- [42] Farmer V.C.: *Science* **1964**, 145, 1189.
- [43] Frost R.L., Tran T.H., Kristof J.: *Clays and Clay Minerals* **1998**, 46, 280. <http://dx.doi.org/10.1346/CCMN.1998.0460307>
- [44] Cheng H., Yang J., Liu Q. et al.: *Thermochimica Acta* **2010**, 507–508, 106. <http://dx.doi.org/10.1016/j.tca.2010.05.007>
- [45] Cheng H., Liu Q., Yang J. et al.: *Thermochimica Acta* **2010**, 511, 124. <http://dx.doi.org/10.1016/j.tca.2010.08.003>
- [46] Rybiński P., Janowska G.: *Polimery* **2013**, 58, 327. <http://dx.doi.org/10.14314/polimery.2013.327>
- [47] Pal P., Kundu M.K., Malas A. et al.: *Journal of Applied Polymer Science* **2014**, 131, 39587. <http://dx.doi.org/10.1002/APP.39587>
- [48] Zhang J.J., Liang Q. et al.: *Journal of Applied Polymer Science* **2010**, 117, 3054. <http://dx.doi.org/10.1002/app.32087>
- [49] Barrientos-Ramírez S., Ramirez G.M., Ramoz-Fernandez E.V. et al.: *Applied Catalysis A: General* **2011**, 406, 22. <http://dx.doi.org/10.1016/j.apcata.2011.08.003>
- [50] White L.D., Tripp C.P.: *Journal of Colloid Interface Science* **2000**, 232, 400. <http://dx.doi.org/10.1006/jcis.2000.7224>
- [51] Joo Y., Jeon Y., Lee S.U. et al.: *The Journal of Physical Chemistry C* **2012**, 116, 18230. <http://dx.doi.org/10.1021/jp3038945>
- [52] Du M., Guo B., Jia D.: *European Polymer Journal* **2006**, 42, 1362. <http://dx.doi.org/10.1016/j.eurpolymj.2005.12.006>
- [53] Du M., Guo B., Cai X.: *e-Polymers* **2008**, 8, 1490. <http://dx.doi.org/10.1515/epoly.2008.8.1.1490>
- [54] Pal P., Kundu M.K., Malas A. et al.: *Polymer Composites* **2014**, online version of record published before inclusion in an issue. <http://dx.doi.org/10.1002/pc.23016>
- [55] Khunova V., Kristof J., Kelnar I. et al.: *eXPRESS Polymer Letters* **2013**, 7, 471. <http://dx.doi.org/10.3144/expresspolymlett.2013.43>
- [56] Ning N., Yin Q., Luo F. et al.: *Polymer* **2007**, 48, 7374. <http://dx.doi.org/10.1016/j.polymer.2007.10.005>
- [57] Pedrazzoli D., Pegoretti A., Thomann R. et al.: *Polymer Composites* **2014**, online version of record published before inclusion in an issue. <http://dx.doi.org/10.1002/pc.23006>
- [58] Cheng H., Liu Q., Yang J. et al.: *Journal of Molecular Structure* **2011**, 990, 21. <http://dx.doi.org/10.1016/j.molstruc.2011.01.008>
- [59] Liu M., Guo B., Du M. et al.: *Polymer Journal* **2008**, 40, 1087. <http://dx.doi.org/10.1295/polymj.PJ2008133>
- [60] Liu M., Guo B., Lei Y. et al.: *Applied Surface Science* **2009**, 255, 4961. <http://dx.doi.org/10.1016/j.apsusc.2008.12.044>
- [61] *Pol. Pat.* 213 655 (2013).
- [62] *Pol. Pat.* 211 051 (2012).
- [63] *USA Pat.* 8 557 907 (2013).
- [64] *USA Pat.* 8 217 108 (2012).
- [65] Lecouvet B., Sclavons M., Bourbigot S. et al.: *Polymer* **2011**, 52, 4284. <http://dx.doi.org/10.1016/j.polymer.2011.07.021>
- [66] Lecouvet B., Sclavons M., Bailly C. et al.: *Polymer Degradation and Stability* **2013**, 98, 2268. <http://dx.doi.org/10.1016/j.polymdegradstab.2013.08.024>
- [67] Zhao J., Deng Ch.L., Du S.L. et al.: *Journal of Applied Polymer Science* **2014**, 40065, 1. <http://dx.doi.org/10.1002/app.40065>
- [68] Prashantha K., Lacrampe M.F., Krawczak P.: *eXPRESS Polymer Letters* **2011**, 4, 295. <http://dx.doi.org/10.3144/expresspolymlett.2011.30>
- [69] Lin T., Zhu L., Chen T. et al.: *Journal of Applied Polymer Science* **2013**, 129, 47. <http://dx.doi.org/10.1002/APP.38700>
- [70] Jia Z., Luo Y., Guo B. et al.: *Polymer-Plastics Technology and Engineering* **2009**, 48, 607. <http://dx.doi.org/10.1080/03602550902824440>
- [71] Jang L.W., Kim E.S., Kim H.S. et al.: *Journal of Applied Polymer Science* **2005**, 98 (3), 1229. <http://dx.doi.org/10.1002/app.22246>
- [72] Svoboda P., Zheng C.C., Wang H. et al.: *Journal of Applied Polymer Science* **2002**, 87 (7), 1562. <http://dx.doi.org/10.1002/app.10789>
- [73] Zhao J., Deng Ch.L., Du S.L. et al.: *Journal of Applied Polymer Science* **2014**, 40065, 1. <http://dx.doi.org/10.1002/app.40065>