

Newly emerging applications of halloysite nanotubes: a review

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Abstract

Halloysite nanotubes (HNTs) are types of naturally occurring 1:1 clays with nanotubular structures and similar chemical composition to kaolin. Due to various characteristics such as nanoscale lumens, high length-to-diameter ratio, relatively low hydroxyl group density on the surface, etc., numerous exciting applications have been discovered for this unique, cheap and abundantly deposited clay. After briefly summarizing applications in controlled release, nanotemplating and sorption, we emphasize the applications of HNTs in the fabrication of polymer nanocomposites. The unique structures and performance of HNT-incorporated polymer nanocomposites processed by various routes are described. The results suggest that these nanocomposites exhibit remarkable performance such as reinforcing effects, enhanced flame retardancy and reduced thermal expansion. Accordingly, HNTs should be of interest in the area of polymer nanocomposites for structural and functional applications.

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Keywords: halloysite nanotubes; nanocomposite; controlled release; reinforcement

GENERAL INTRODUCTION TO HALLOYSITE NANOTUBES

Halloysite nanotubes (HNTs), a type of natural occurring clay minerals with nanotubular structures, are increasing becoming the focus of investigations. As a type of well-crystallized kaolin, HNTs were firstly reported by Berthier as a dioctahedral 1:1 clay mineral of the kaolin group in 1826, and are found widely deposited in soils worldwide.^{1–4} Many countries, such as China,⁵ France,⁶ Belgium⁷ and New Zealand,⁸ have deposits of HNTs.

According to the state of hydration, HNTs are generally classified into two groups: hydrated HNTs with a crystalline structure of 10 Å d_{001} spacing and dehydrated ones with 7 Å d_{001} spacing. The typical crystalline structure of HNTs is shown in Fig. 1. As has been reported,³ the presence, or history, of interlayer water in HNTs is one of the most important features distinguishing HNTs from kaolinite. With the dehydration process, the d_{001} spacing of HNTs changes from 10 to 7 Å and the process is irreversible. HNTs have a similar chemical composition to kaolinite and the ideal chemical formula can be expressed as $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$, where n equals 2 and 0, representing hydrated and dehydrated HNTs, respectively.^{9,10}

Due to the variety of crystallization conditions and geological occurrence, HNTs adopt different morphologies such as tubular, spheroidal and plate-like particles, of which the tubular structure is the most common and valuable.^{3,11} Typically, the inner diameter, outer diameter and length of HNTs are 1–30 nm, 30–50 nm and 100–2000 nm, respectively. The typical morphologies of HNTs are shown in Figs 2 and 3.^{12–14}

As has been reported,¹⁵ HNTs contain two types of hydroxyl groups, inner and outer hydroxyl groups, which are situated between layers and on the surface of the nanotubes, respectively. Due to the multi-layer structure, most of the hydroxyl groups are inner groups and only a few hydroxyl groups are located on

the surface of HNTs. The surface of HNTs is mainly composed of O–Si–O groups, and the siloxane surface can be confirmed from Fourier transform infrared spectra, in which the very strong absorption of O–Si–O (*ca* 1030 cm^{-1}) is observed.¹⁶ Consequently, compared with other silicates such as kaolinite and montmorillonites, the density of surface hydroxyl groups of HNTs is much smaller.

Due to characteristics such as nanoscale lumens, high length-to-diameter (L/D) ratio, low hydroxyl group density on the surface, etc., HNTs have been focused on by researchers recently, as indicated by the rapid growth in related publications. Traditionally, due to the high L/D ratio and superior high-temperature-resistant property, HNTs were exploited to produce high-quality ceramics, such as thin-walled porcelain or crucible products, which has been the main application of HNTs.^{17–20} Recently, scientists and engineers have discovered and developed a large range of exciting new applications for these unique, cheap and abundantly available naturally occurring clays with nanoscale lumens.

After briefly introducing the application of HNTs to controlled release, nanotemplating and sorption, this review then emphasizes their applications in the fabrication of polymer nanocomposites.

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CONTROLLED RELEASE, NANOTEMPLATING AND SORPTION

Controlled or sustained release

As the lumens of HNTs could be loaded with drugs or other chemicals, HNTs are expected to be ideal materials for controlled or sustained release of drugs, other bioactive molecules or other additives, and much related work has been reported. Results show that HNTs are ideal substrates for the controlled or sustained release of drugs or bioactive molecules.^{21–35} Shchukin and co-workers developed a new type of active corrosion protection coatings composed of hybrid sol–gel films doped with HNTs filled with corrosion inhibitors and found that the corrosion inhibitors can be released in a controllable way.^{36,37} HNTs can also be utilized to encapsulate other substances for controlled or sustained release, such as additives for paints and sealants, lubricants, herbicides, pest repellents, household, food and personal products, cosmetics, and other agents that could benefit from controlled release.^{3,38–43}

Nanoreactors or nanotemplates

Filling or loading of nanotubes and using them as nanoreactors have been of interest for decades.^{44–47} However, the relatively high price or the complicated fabrication process confines their application in mass production. Based on their nanotubular structures, recently HNTs have been used as alternative nanoreactors to fabricate nanowires and nanoparticles and for similar purposes. For instance, Luca and Thomson⁴⁸ studied the intercalation and polymerization of aniline within a tubular aluminosilicate, and the results suggest that the polyaniline, which can act as a molecular wire, could be prepared in the lumens of HNTs. According to the studies of Shchukin *et al.*,⁴⁹ HNTs could be used as biomineralization nanoreactors for carrying out enzyme-catalyzed inorganic synthesis. The idea of using HNT lumens as biomimetic nanoreactors offers promising possibilities for studying crystal engineering and fundamental aspects of the biomineralization process. In

addition, many other investigations of HNTs acting as nanoreactors or nanotemplates to prepare nanoparticles, nanowires, nanocoatings, etc., have been reported.^{50–58} Porous carbons rich in mesopores and with large pore volumes have been prepared by polymerization and carbonization of a carbon precursor, sucrose, within HNTs. The process is relatively simple and expected to cost less than the high-temperature carbonization process in the preparation of mesoporous carbons with total pore volume and large specific surface areas.⁵⁹ In addition, as reported by Li *et al.*, polymeric nanotubes and nanowires have been fabricated using HNTs as templates by atom transfer radical polymerization, and, furthermore, a non-woven porous fabric exhibiting interesting wetting characteristics has been prepared by direct casting of a composite dispersion followed by sequent thermal crosslinking.⁶⁰

Recently, HNTs have also been used as catalyst carriers especially in the petroleum refining industry. Rong and Xiao introduced HNTs to the catalytic cracking of heavy oils and studied the catalytic cracking activities.⁶¹ Machado *et al.* encapsulated anionic and cationic metalloporphyrins into the lumens of HNTs and investigated the catalytic activity of these novel materials in the oxidation of organic substrates. The results showed that these novel immobilized catalysts are a promising system for selective oxidation reactions.⁶²

Sorbents for contaminants and pollutants

Due to the nanotubular structures, it is also expected that HNTs will possess the capability of adsorption to specific substances. Recently, applications of HNTs in the adsorption of contaminants and other substances have been reported. Zhao and Liu used HNTs as nano-adsorbents for the removal of the cationic dye methylene blue from aqueous solutions and the experimental results suggested the method worked well.⁶³ Lu *et al.* developed HNTs for environmental treatment on the basis of their nanotubular structure, and the results showed that HNTs are promising for applications in the decomposition and elimination of various pollutants in air and water.⁶⁴ Adsorption onto HNTs of uranium from aqueous solutions was studied by Kilislioglu and Bilgin. The adsorption mechanism and kinetics were studied and the results showed that the adsorption reaction was endothermic and more spontaneous at high temperature.⁶⁵ A novel biofilter containing an organic, bentonite and HNTs was applied for elimination of microbial pollutants from the air of an industrial hatchery. The

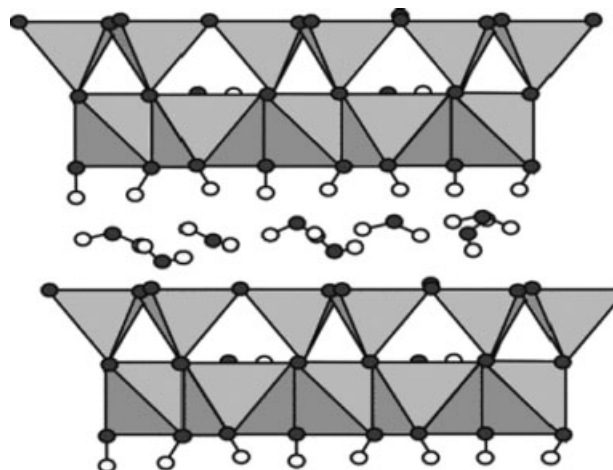


Figure 1. Crystalline structure of HNTs.³

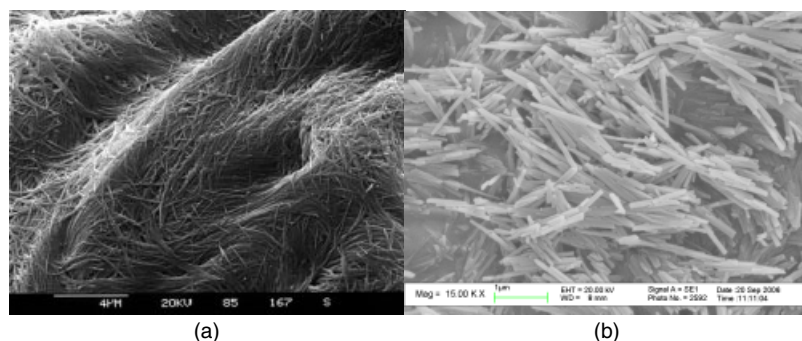


Figure 2. SEM images of HNTs from (a) France and (b) Hubei Province, China.

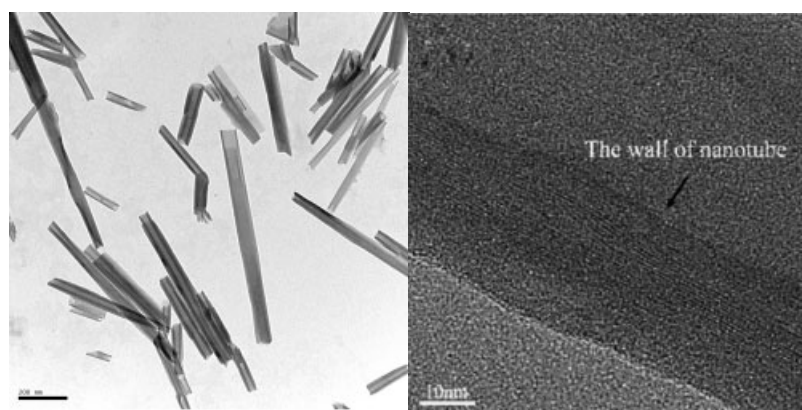


Figure 3. Transmission electron microscopy images of HNTs from (a) Hubei Province, China and (b) New Zealand.

investigation showed the biofilter to be effective in the elimination of potentially pathogenic bacteria, dust and endotoxins from the air of the hatchery.^{66,67}

FABRICATION OF POLYMER/HNT NANOCOMPOSITES AND THEIR PROPERTIES

As described above, HNTs are nanotubes with high L/D ratio and possess a low density of surface hydroxyl groups compared with other silicates. Consequently it is expected that HNTs will be promising as reinforcing fillers for polymer materials. Recently, an increasing number of studies have focused on the fabrication of polymer/HNT nanocomposites and their properties. In 2008 NaturalNano Inc. announced a pilot-scale production of polypropylene (PP) with 5–13% of functionalized HNTs. Recently, researchers introduced HNTs to various polymeric matrices such as PP, polyamide, epoxy resin and rubbers to form nanocomposites. Many approaches and techniques have been utilized to realize nanocomposites with unique structures and desired performance. The fabrication of polymer/HNT nanocomposites and their properties are reviewed in the following.

Fabrication of HNT-incorporated polymer nanocomposites

For thermoplastics such as polyolefins and polyamides, melt blending is an industrially favored method to fabricate their composites with inorganics. Due to the easy dispersibility of HNTs, it is expected that HNTs could be dispersed relatively uniformly in thermoplastics by direct melt blending, especially for polymers with high polarity such as polyamides. As has been reported, some HNT-incorporated polymer nanocomposites such as those

of polyamide 6 (PA6), PP and poly(butylene terephthalate) have been prepared successfully via a melt-blending process without any surface modification of HNTs.^{13,68,69}

Compatibilization between polyolefins and inorganics is challenging due to the great polarity discrepancy and the chemical inertness of the polyolefins. To increase the compatibility between PP and HNTs, Du *et al.*⁷⁰ proposed a two-step method of grafting PP chains onto the surface of HNTs, which is shown in Fig. 4. The investigation suggests that the approach works well and can effectively increase the mechanical performance of nanocomposites.

Some other methods, such as fabricating composites by hydrogen bonding and charge transfer mechanisms, have also been proposed for the fabrication of PP/HNT nanocomposites. Du *et al.* demonstrated a facile method to fabricate PP/HNT nanocomposites by the formation of a reinforcing inorganic network in a polymer matrix via a hydrogen-bonding self-assembly process.^{71,73} The authors believe that, with the incorporation of certain organics with hydrogen-bonding functionalities, HNTs could form a network structure via the hydrogen bonding between the hydroxyls and oxygen atoms from Si–O–Si on the HNT surfaces and the functionalities of the organics. It is expected that the process could facilitate the dispersion of HNTs in the matrix and, more importantly, the assembled inorganic network partially transfers the stress, resulting in a significantly improved mechanical performance of the composites. Another approach to fabricating PP/HNT nanocomposites was proposed by Liu *et al.* via an electron charge-transfer mechanism.^{72–75} Two types of nanocomposite, a 2,5-bis(2-benzoxazolyl)thiophene (BBO)/HNT nanocomposite and a 2,2'-(1,2-ethenediyl)di-4,1-

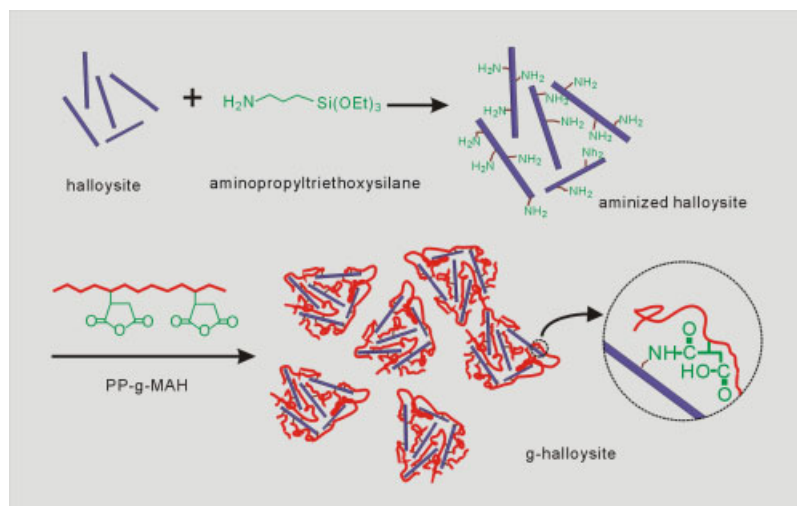


Figure 4. Surface grafting of HNTs.

phenylene)bisbenzoxazole/HNT nanocomposite, were fabricated by Liu *et al.* via this charge-transfer mechanism.

For rubber/clay nanocomposites, it is well known that a good dispersion of the clay and strong interfacial interactions are two crucial factors in determining the performance of the nanocomposites.⁷⁶ As described previously, due to fewer hydroxyl groups on their surfaces, HNTs can only with difficulty be effective fillers for rubber due to the unsatisfactory interfacial bonding. Different ways have been attempted for better interfacial bonding. Recently, Guo *et al.* utilized methacrylic acid (MAA) to improve the performance of styrene–butadiene rubber (SBR)/HNT nanocomposites by direct blending.⁷⁷ Carboxylated butadiene–styrene rubber (xSBR) is a copolymer of styrene, butadiene and a small amount of acrylic acid. Due to the presence of carboxyl groups, it is expected that HNTs will have good compatibility with xSBR. HNTs and xSBR have been utilized to prepare nanocomposites with strong interfacial interactions via hydrogen bonding.⁷⁸ In order to obtain a good dispersion of HNTs in xSBR, a co-coagulation process of xSBR latex and HNTs aqueous solution was utilized. The process is shown in Fig. 5.

Dispersion of HNTs and morphologies of nanocomposites

Due to their fewer surface hydroxyl groups, it is expected that HNTs will disperse better than other silicates such as montmorillonite and kaolinite. It is reported that HNTs can be dispersed relatively uniformly by a direct melt-blending method, especially in polyamides with high polarity (Fig. 6).^{13,68} Du *et al.* found that the approaches to fabricating nanocomposites via hydrogen bonding also facilitate the dispersion of HNTs in PP matrices. Morphological investigation suggests that with the introduction of hydrogen bonding, the dispersion of HNTs is obviously improved. In another approach to fabricating PP/HNT nanocomposites via an electron charge-transfer mechanism,⁷² it is concluded that the electron transfer between HNTs and BBOT induces the formation of BBOT microfibers and the hybrid fibrils formed induce the transcrystallization of PP on the fibrils. The morphology of the nanocomposites is shown in Fig. 7.

Incorporation of MAA would facilitate significantly the dispersion of HNTs in SBR matrix.⁷⁷ The excellent dispersion of HNTs in the vulcanizates is evidenced by the good transparency. Using the co-coagulation process of xSBR latex and HNTs, xSBR/HNT

nanocomposites with good interfacial bonding and uniform dispersion of HNTs were achieved.⁷⁸ Hybrids containing up to 65 wt% HNTs were fabricated in an SBR matrix with the *in situ* formation of zinc disorbate by Guo *et al.* Apart from the mechanical strength and heat resistance comparable to general engineering plastics, the hybrids exhibit very good transparency, which is attributed to the excellent dispersion of the nanotubular clay.⁷⁹

For thermosetting resins, which are traditionally processed by casting or potting, it is rather difficult to achieve a uniform dispersion of HNTs. For a satisfactory state of dispersion, Liu *et al.* fabricated epoxy/HNT nanocomposites with good dispersion of HNTs via co-curing with cyanate ester resin and surface modification of HNTs.^{80,81}

Properties of HNT-incorporated nanocomposites

Mechanical performance

Mechanical properties, especially the modulus of PP, can be effectively improved using HNTs. As indicated in Tables 1 and 2, the flexural properties, tensile strength and impact strength all are noticeably improved with the incorporation of HNTs.^{13,68,69} It is expected that the reinforcing effects of HNTs on PP and PA6 be correlated to the rod-like and high aspect ratio structures of HNTs and the unique surface chemical properties. In addition, investigation shows that only traces of heavy metals were detected, much lower than standards of the restriction of harmful substances of the European Union. Consequently it can be concluded that HNTs are a type of ‘green’, unique and promising reinforcing material for thermoplastics.

The mechanical properties of PP/HNT nanocomposites can be further improved by introducing organics bearing functionalities via hydrogen bonding or charge transfer (Tables 1 and 2)⁷¹ (Du ML, Guo BC, Liu MX, Cai XJ and Jia DM, unpublished). The assembled inorganic network or aggregates, which can partially transfer the stress, and the unique transcrystallization behavior are responsible for the improved mechanical properties^{71–73} (Du ML, Guo BC, Liu MX, Cai XJ and Jia DM, unpublished). These methods provide novel reinforcing routes to polymer nanocomposites with improved mechanical properties.

Epoxy/HNT nanocomposites also exhibit markedly increased storage moduli and flexural strength. The markedly positive effects of the HNTs on the performance of epoxy resins are correlated

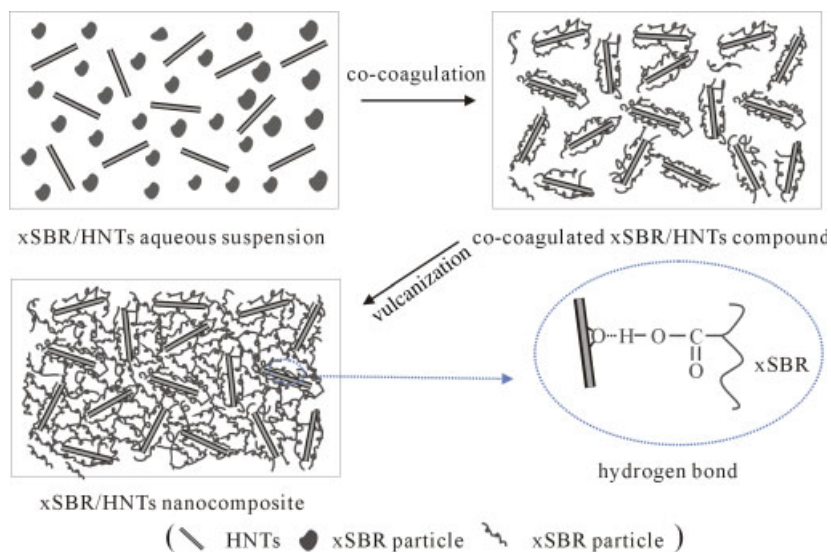


Figure 5. Preparation process of xSBR/HNT nanocomposites.

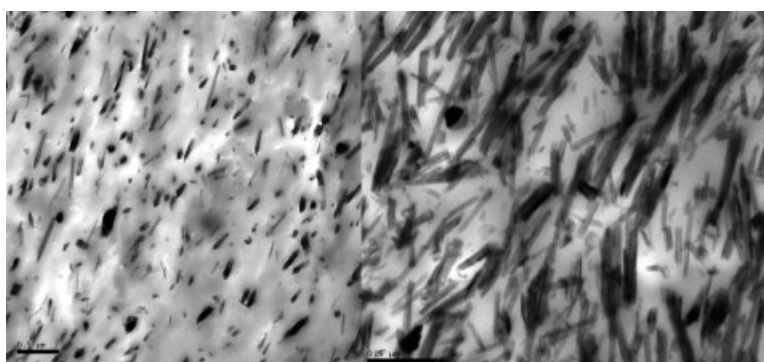


Figure 6. Transmission electron microscopy images of PA6/HNT (100/10) nanocomposite (left) and SBR/HNT/MAA (100/40/2) nanocomposite (right).

with the unique characteristics of the HNTs, the uniform dispersion and the possible interfacial reactions between the modified HNTs and the matrix. Epoxy/HNT nanocomposites with high impact strength were successfully prepared by Ye *et al.* without sacrificing flexural modulus, strength and thermal stability.¹⁴ The toughening mechanisms were investigated and it was believed that the large

amount of micro-cracking, nanotube bridging/pull-out/breaking and crack deflection were responsible for the unusual 400% increase in impact strength.

Carbon black has been used as a reinforcing filler for rubbers for a long time, and recently silica, especially fumed silica, has also been utilized as an alternative to carbon black due to the

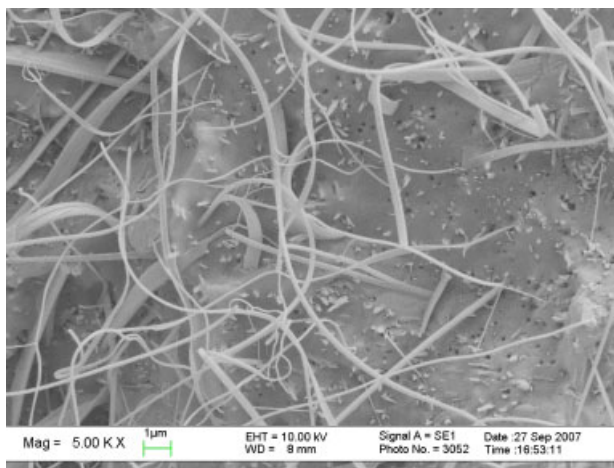


Figure 7. SEM image of impact-fractured surface of PP/HNT/BBOT nanocomposite.

Table 1. Mechanical properties and crystallinity of PP and PP nanocomposites

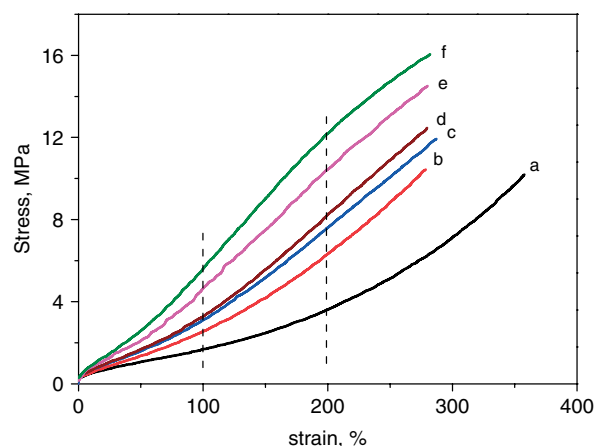
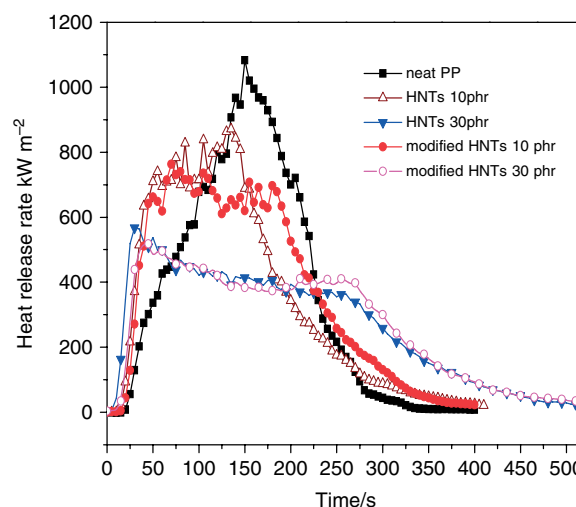
Material ^a	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (kJ m ⁻²)	Crystallinity (%)
Neat PP	1.37	44.5	33.5	4.05	45.7
PP/HNT (100/5)	1.75	51.5	35.2	5.51	–
PP/HNT (100/30)	2.06	52.8	33.2	4.22	–
PP/HNT/MEL (100/30/3.75)	2.65	58.5	35.5	3.55	–
PP/HNT/MEL (100/30/10)	2.70	57.3	34.4	3.39	–
PP/HNT/BBOT (100/30/1)	2.42	56.6	36.5	3.91	60.4
PP/HNT/BBOT (100/30/10)	2.83	61.4	38.8	3.13	62.7

^a MEL, melamine.**Table 2.** Mechanical properties of engineering plastics and their nanocomposites

Material ^a	Flexural modulus (GPa)	Flexural strength (MPa)	Tensile strength (MPa)	Impact strength (kJ m ⁻²)
Neat PA	2.71	110.0	77.0	5.25
PA/HNT (100/5)	3.23	118.5	82.1	5.75
PA/HNT (100/8)	3.85	127.4	77.5	5.25
PA/HNT (100/10)	4.13	130.9	84.4	5.75
PA/HNT (100/13)	4.56	135.5	84.1	6.50
Neat PBT	2.3	79.7	52.3	5.65
PBT/HNT (100/5)	2.6	82.7	54.9	4.65
PBT/HNT (100/10)	3.0	90.1	58.0	3.78
PBT/HNT (100/20)	3.9	92.9	56.0	3.46
PBT/HNT (100/30)	4.7	82.7	45.2	3.20

^a PA, polyamide; PBT, poly(butylene terephthalate).

future petroleum crisis. However, most other inorganic fillers such as montmorillonite, kaolinite and calcium carbonate still lack alternatives. Preliminary results show that HNTs have promising prospects in the rubber industry. With the incorporation of MAA, both the stress and strain of SBR/HNT vulcanizates increased significantly. Using the co-coagulation process, Du *et al.*⁷⁸ obtained HNT/sXBR nanocomposites with strong interfacial bonding; the mechanical properties, especially the modulus and hardness, are significantly increased on inclusion of HNTs (Fig. 8). Surprisingly, incorporations of 2 and 5 phr HNTs lead to increases of 7 and 15 degrees in hardness, respectively. Traditionally, about 3–4 phr silicate or carbon black is needed to achieve a 1 degree increase in hardness.^{82–85} It is believed that the significant reinforcing effects of HNTs on xSBR are because of the uniform dispersion of HNTs as a result of the co-coagulation process and strong interfacial interaction due to the hydrogen bonding between the nanotubes and the matrix. In addition, Liu and co-workers^{86,87} studied the structure and properties of natural rubber/HNT nanocomposites. The results indicated that HNTs show good dispersion in the

**Figure 8.** Stress–strain curves of xSBR and xSBR/HNT nanocomposites: (a) xSBR; (b) xSBR/HNT (100/2); (c) xSBR/HNT (100/5); (d) xSBR/HNT (100/10); (e) xSBR/HNT (100/20); (f) xSBR/HNT (100/30).**Figure 9.** Effects of HNTs on the flame-retardant property of PP.

natural rubber matrix and the mechanical performance of the nanocomposites is improved to some extent with HNT loading.

Thermal stability and flame retardancy

Apart from acting as reinforcing agents, HNTs have also been demonstrated as effective flame-retardant agents for PP. As reported by Du *et al.*,⁸⁸ HNTs show outstanding properties for improving the thermal stability and flammability of PP, as shown in Fig. 9. The thermal stability and flame-retardant effects of HNTs on PP are believed to result from the hollow tubular structures of HNTs, the barriers for heat and mass transport and the presence of iron in the HNTs. The results suggest that HNTs are promising as non-halogen flame-retardant fillers. Although HNTs can improve the thermal stability of PP substantially, incorporation of HNTs into PP leads to inferior resistance to thermal oxidation aging, however, which is correlated with the number of acidic sites and volume of entrapped oxygen in the lumen of HNTs and cavities in the PP nanocomposites.^{89,90}

Similarly, HNTs also show high flame-retardant efficiency when combined with other polymers such as PA6 and linear low-density polyethylene (LLDPE). Luo⁹¹ studied the flame-retardant

behavior of PA6/HNT nanocomposites and found that the HNTs exhibited a unique flame-retardant effect on PA6. Marney *et al.* also investigated the flame-retardant effect of HNTs on PA6 and found that the HNTs influence the fire performance of the composites and that HNTs serve as a thermal insulation barrier at the surface of the composites during burning.⁹² The effects of HNTs on the flame retardancy of LLDPE were studied by Jia *et al.*, with the results suggesting that HNTs are expected to be promising flame-retardant nanofillers for LLDPE.⁹³

Crystallization behavior

Nanosized inorganic inclusions generally influence the crystallization process of semi-polymer nanocomposites such as PP nanocomposites.^{94,95} The crystallization behaviors of HNT-incorporated PP nanocomposites have been investigated. Ning *et al.*⁹⁶ found that well-dispersed HNTs in a PP matrix can serve as nucleation agents, resulting in an enhancement of the overall crystallization rate. In addition, the results suggested that nucleation and growth of spherulites are two independent processes in the composites studied. Du *et al.*⁹⁷ also investigated crystallization behaviors of PP/HNT nanocomposites and, similarly, the results suggested that HNTs act as nucleating agents during the crystallization process of PP. These investigations suggest that, similar to other nanosized inorganics such as silica and montmorillonite, HNTs serves as nucleation agents and facilitate the crystallization of the nanocomposites. The microfibrils composing HNTs and BBOT show an ability to induce transcrystallization of PP on the fibrils.^{72,98} Consequently, the crystallinity of the nanocomposites is obviously improved, as shown in Table 1. Liu *et al.* also found that HNTs possess a dual nucleating ability for α -PP and β -PP under appropriate kinetic conditions, and the formation of β -PP in the composites is correlated with the unique surface characteristics of the HNTs.⁹⁹

It is well known that PA6 has an interesting polymorphism behavior, as reported as early as 1947.¹⁰⁰ Nanosized fillers such as carbon nanotubes and organic montmorillonite show marked effects on the crystallization behavior of PA6, and numerous studies on the crystallization kinetics of PA6 with nanosized inclusions have been performed.^{101–107} Recently, Guo *et al.*¹⁰⁸ studied the non-isothermal crystallization behavior and the polymorphism of PA6 and PA6/HNT nanocomposites. The results showed that HNTs act as nucleating agents and accelerate the crystallization and induce the formation of γ -phase crystals. The crystallization behavior of the PA6/HNT nanocomposites is correlated with the multiple roles of HNTs in the crystallization.

Reduced coefficient of thermal expansion

Introduction of interfacial reactions in thermosetting systems may effectively reduce the thermal expansion of the cured resin. Investigations have shown that the coefficient of thermal expansion (CTE) of epoxy/HNT hybrids with low HNT concentration is substantially lower than that of the plain cured resin.⁸⁰ As summarized in Table 3, the CTEs of hybrids with a HNT concentration of 12 wt% are 19.6 and 21.8% lower than those for the neat epoxy resin for the temperature ranges 25–100 and 100–160 °C, respectively. It is believed that interfacial reactions take place during the curing of the hybrids between the aluminols and silanols and the cyanate ester and consequently the covalently linked interface formed is responsible for the improved performance and morphological characteristics of the hybrids.

Table 3. CTE of hybrids for two temperature ranges

Sample ^a	wt% (vol%)	25–100 °C		100–160 °C	
		CTE (ppm °C ⁻¹)	Decrease (%)	CTE (ppm °C ⁻¹)	Decrease (%)
Neat resin		51.26	–	77.26	–
HNTs	4.0 (1.97)	48.68	5.0	70.06	9.3
	8.0 (4.03)	46.35	9.6	68.59	11.2
	12.0 (6.17)	41.19	19.6	60.40	21.8
Silica	20.0 (10.55)	Decrease	19.4% (below T_g)		
Modified ATT	13.7 (7.47)	Decrease	25.0% (below T_g)		
MMT	15.0 (8.58)	Decrease	27.0% (below T_g)		

^a ATT, attapulgite, MMT, montmorillonite.

CONCLUSIONS

Due to characteristics such as nanosized lumens, high L/D ratio, low hydroxyl group density on the surface, etc., more and more exciting applications have been discovered for these unique, cheap and abundantly deposited clays. So far, HNTs have been widely used in controlled or sustained release, in nanoreactors or nanotemplates and for the elimination of contaminants or pollutants. Recently, research has focused on HNT-incorporated polymer nanocomposites. The investigations suggest that the nanocomposites exhibit markedly improved properties, such as superior mechanical performance, much higher flame retardancy and thermal stability, reduced CTE, etc. Based on this review, it can be concluded that HNTs possess promising prospects in the preparation of new structural and functional materials.

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