Halloysite nanotubes: prospects and challenges of their use as additives and carriers – A focused review

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ABSTRACT: There is increasing research interest in potential applications of halloysite as fillers for polymer composites, controlled drug delivery, carriers for the supply and sustained release of active agents for anticorrosion coatings, in nanoreactors or nanotemplates, and for the uptake of contaminants or pollutants and support for catalysts. In this review, recent findings in terms of the prospects and challenges of using halloysite nanotubes (HNTs) in different polymeric matrices targeting a range of old and new applications are discussed and evaluated. The compositions include chitosan/halloysite membranes as bone-tissue scaffolds, polylactic acid (PLA)/halloysite membranes for food-packaging applications and their antimicrobial activities, instrumented impact properties of epoxy/halloysite nanocomposites and the role of halloysite in the self-healing of epoxy composites, polyacryronitrile (PAN)/halloysite membranes for use in water filtration as well as a review of some recent applications of halloysite/alginate beads in the adsorption of contaminants such as lead.

Halloysite nanotubes (HNTs) are promising nanofillers because of their hollow lumen space ranging from 5 to 70 nm in width (depending on its origin), distribution of hydroxyl groups on their edges and inner surfaces as well as large aspect ratios and surface areas (Pasbakhsh *et al.*, 2013). The lumen in HNTs makes them capable of carrying drugs and agents to be used as nanocontainers/nanofillers for various applications such as sustained-release drug delivery.

Using HNTs as fillers in polymer composites has brought new insights to this research area due to the good dispersibility of HNTs within many types of non-polar polymers. This good dispersibility mainly derives from positioning of SiO_2 tetrahedra on the outer surfaces of HNTs, whereas the Al octahedra locate on the inner walls and edges of the tubules, from their relative inflexibility and tubular morphology, unusual charge distribution and unique crystal structure (Ismail *et al.*, 2008). However, when HNTs are used simultaneously as carriers and reinforcement, or when they are used at concentrations of >5–10 wt.% the structure–property relationship (here dispersion–reinforcement) has remained a challenge which has rarely been studied satisfactorily in the literature so far. Abdullayev *et al.* (2011) loaded the lumen space of HNTs with silver as an antimicrobial agent incorporated into a paint coating, where the silver-loaded HNTs acted against bacterial growth as well as stress-induced crack formation at the same time. In another study, corrosion inhibitors were loaded into the lumen of HNTs and

10 wt.% of the product was incorporated in a latex paint-based material to obtain successful anticorrosive performance (Abdullayev et al., 2009, 2013).

When it comes to the use of HNTs for self-healing applications, they have mainly been used in anti-corrosion coatings principally as carriers of anti-corrosion agents (Shchukin et al., 2008; Abdullayev et al., 2009, 2013) as well as in reinforcement of microvascular containers (Olugebefola et al., 2014) but, to date, not as carriers in a bulk composite structure (Vahedi et al., 2015). However there have been very few studies on the use of HNTs as nanocarriers for sustained release of drugs or agents that involve the reinforcement and controlled release characteristics at the same time (e.g. Wei et al., 2012).

This focused review aims to provide insight and information on the utilization of HNTs as multifunctional fillers in potential applications such as packaging, tissue scaffolds, self-healing materials, filtration membranes and heavy-metal absorbents, mainly arising from our group's recent studies as well as some related studies in the literature.

DISCUSSION

Modification of halloysite: new insights and challenges

Surface modification of HNTs has been employed as an effective method to enhance their performance in various applications such as polymer reinforcement (Deng et al., 2009; Pasbakhsh et al., 2010) and as nanocontainers (Yah et al., 2012; Yuan et al., 2012). Silane modifiers are widely reported modifiers which have been used for surface treatment of HNTs (Liu et al., 2007; Yuan et al., 2008; Deng et al., 2009; Pasbakhsh et al., 2010). Depending on requirements, various chemical groups such as amine, methacrylate and epoxy can be grafted on the surface of HNTs using different types of silane coupling agents (amino silanes, 3-(methacryloxypropyl) trimethoxysilane (γ–MPS) (Du et al., 2007; Liu et al., 2011) and γ-glycidoxypropyltrimethoxy silane (GMS) (Liu et al., 2007). The grafting reaction takes place through hydroxyl groups on the HNTs' surfaces and edges while silane coupling agent molecules can also react with each other and form undesirable oligomerized or polymerized silane networks on the HNTs' surfaces (Yuan et al., 2008; Vahedi & Pasbakhsh, 2014a). The efficiency of grafting and properties of the grafted (3-Aminopropyl)triethoxysilane (APTES) network was affected heavily by pretreatments (both

thermal treatments (Yuan et al., 2008; Vahedi & Pasbakhsh, 2014a) and with NaOH (Vahedi & Pasbakhsh, 2014a)) as well as the post-cure condition of the HNTs which improved significantly their performance as nanofillers (Vahedi & Pasbakhsh, 2014b). NaOH pretreatment could activate the HNTs by increasing the amount of OH groups on their external surfaces while thermal treatment could result in removal of the interlayer water of HNTs and also dehydroxylation of surfaces. Having OH groups readily available at the edge of HNTs makes their modification much easier compared to other types of nanofillers such as layered silicates which need an intercalation between layers beforehand. Their parallel-sided shapes make sure HNTs are less agglomerated during the modification process compared with carbon nanotubes or silicate layered nanoclays. The HNTs do not need to be separated or exfoliated from each other using complex treatment processes as for nanoclays such as montmorillonite. On the other hand, modification of HNTs needs more careful and complex procedures including encapsulation of different molecules into the negatively charged lumen space of HNTs.

ZnO deposition on the inner and outer walls of HNTs

In order to give antimicrobial properties to HNTs, deposition of ZnO on their surfaces has been carried out with a two-step solvothermal method using zinc nitrate followed by a calcination process (De Silva et al., 2015). Encapsulation of ZnO within the lumen space was accomplished using an evacuation process. Transmission electron microscopy (TEM) images confirmed the encapsulation of ZnO (Fig. 1a). The size of the deposited ZnO nanoparticles ranged from 2 to 20 nm. The solvothermal method used did not exert any control over the particle size and the deposition was inhomogeneous. Although the majority of ZnO was deposited on the surfaces of HNTs, traces of undeposited ZnO (excess ZnO) could be found in the samples as detected by XRD and micrographs. This aspect would benefit from further investigation (removing undeposited ZnO after the solvothermal process). The advantage of this type of deposition is that different metal oxides (Zn, Fe, Mg, etc.) with positive charges can be deposited on the negatively charged outer surface of HNTs to give multifunctional ability to the HNTs which are incorporated in a polymer or ceramic matrix. Because HNTs are acting as nano-carriers, the synergistic effect of both the reinforcing ability of the HNTs and the properties of
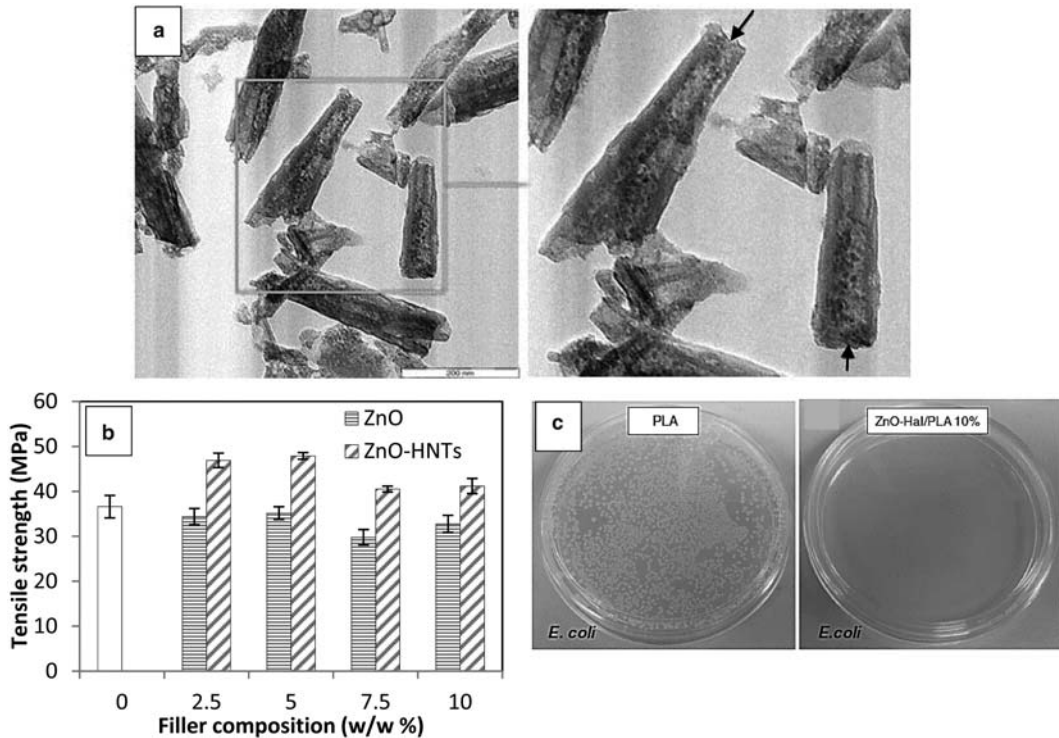
FIG. 1. (a) ZnO deposited on the surface and in the lumen of HNTs. (b) Tensile strength and (c) antimicrobial properties of PLA nanocomposites (part c reproduced from De Silva *et al.*, 2015 with the permission of Elsevier).

the metal oxides (antimicrobial, UV-shielding, *etc.*) can be achieved. However, it is very difficult to have precise control on the distribution, concentration and sometimes also the size (especially at lower loading % ages) of the metallic oxides on HNTs.

Chitosan/HNT membranes as bone-tissue scaffolds

In a recent study by Govindasamy *et al.* (2014), HNTs were incorporated into the chitosan biopolymer for possible use in bone-tissue engineering. According to Lvov *et al.* (2015), one challenge is that HNTs are not biodegradable and therefore they cannot be used for intravenous injection. Nonetheless, future studies could focus on the feasible and safe amount of HNTs which can be used, sustained and/or degraded in the body. Even so, HNTs can be used for drug-delivery systems, oral drug formulations, skin care, medical implants, and dentistry as they have no *in vitro* or *in vivo* toxicity (Lvov *et al.,* 2015). In an earlier study by these authors (Govindasamy *et al.*, 2014), the

feasibility of using these chitosan/HNT bionanocomposites fabricated by an electrospinning method has been proven by observing the formation of an apatite layer in the membranes. Electrospun chitosan/polyethylene oxide (PEO)/HNTs membranes with different HNT concentrations (0, 1, 3, 5, 7 and 10 wt.%) were fabricated and characterized in their study (Fig. 2a,b). Chitosan/PEO membranes show the formation of uniform fibres in random orientations. In chitosan/PEO/HNTs, some HNTs are attached to the fibres while at higher concentrations of HNTs they are agglomerated in clumps (Fig. 2c). In addition, some of the fibres show breakages in the membranes at greater HNT loadings (Fig. 2b). This study (Govindasamy *et al.*, 2014) confirmed how the topography of fibres can play an important role when it comes to regulating cell behaviour such as cell adhesion and cell proliferation, as has also been reported by Prabhakaran *et al.* (2009). The average thickness of the electrospun samples was measured and the diameters of the individual fibres in the electrospun membranes (FE-SEM images) were
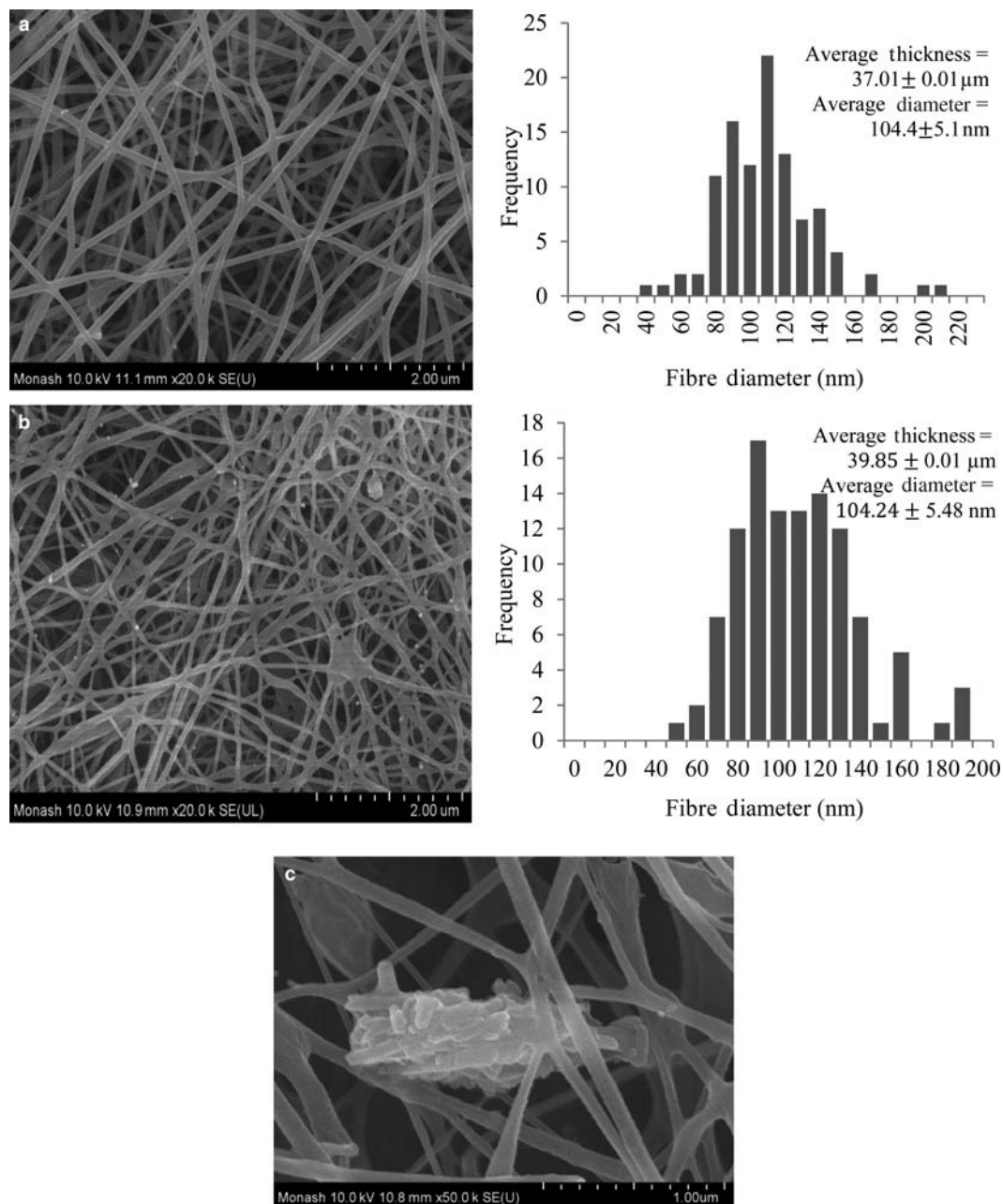
FIG. 2. Fibre-diameter measurements of electrospun chitosan/PEO with: (a) 1 wt.% of HNTs incorporated; and (b) 7 wt.% of HNTs incorporated. (c) Agglomeration of HNTs on the surface of fibres in electrospun chitosan/PEO with 7 wt/.% of HNTs incorporated.

evaluated using the *ImageJ* software by Rasband (1997–2015) and are reported in Fig. 2a,b.

Chitosan/HNT scaffolds have been fabricated using a combination of solution-casting and freeze-drying techniques for tissue-engineering applications (Liu *et al.*, 2013b). Chitosan scaffolds with HNTs exhibited significant enhanced compressive strength and thermal stability compared to those of pure chitosan scaffolds,

but the nanocomposites led to reduced water uptake and increased density. Moreover, the cell-culture studies revealed that chitosan/HNT nanocomposites were cytocompatible even when the HNT content was 80%. Drug-loaded HNTs which incorporated biopolymer-based scaffolding nanocomposites such as poly-caprolactone/gelatine have also been fabricated by an electrospinning technique for sustained antimicrobial protection (Xue *et al.*, 2015). As reported, these drug-loaded HNT nanocomposite membranes have a smaller initial drug burst and increased release time, compared to those of conventional electrospun fibre-based drug-delivery systems.

Poly (lactic acid)/HNT nanocomposites for active food-packaging applications

A number of studies have reported the ability of HNTs to reinforce Poly (lactic acid) (PLA) (Murariu *et al.*, 2012; Liu *et al.*, 2013a; De Silva *et al.*, 2014b,c). For instance, tensile strength and the elastic modulus of PLA nanocomposites with 5 wt.% of HNTs improved by 43% and 58%, respectively, compared to those of pure PLA (De Silva *et al.*, 2014b). These improvements in mechanical properties were due to stronger hydrogen bonding between the end hydroxyl groups of PLA and outer-surface siloxane groups of HNTs. However, the dispersion of HNTs with PLA beyond 5 wt.% was not effective (De Silva *et al.*, 2014a). PLA/HNT active-packaging films have been fabricated using an antimicrobial agent, ZnO (De Silva *et al.*, 2015). As reported, incorporation of ZnO into PLA leads to excellent antimicrobial properties and poor thermo-mechanical properties. De Silva *et al.* (2015) overcame this limitation by using HNTs as nanocontainers to carry ZnO within the PLA matrix, where the inner and outer walls of the HNTs were deposited with ZnO. The PLA nanocomposites with ZnO-deposited HNTs (ZnO-HNTs) led to simultaneous improvements in the mechanical and antimicrobial properties. Tensile strength and elastic modulus improved by 30% and 65%, respectively, with the addition of ZnO-HNTs compared to that of pure PLA films. Antimicrobial tests revealed that the PLA nanocomposites with ZnO-HNTs act against two types of bacteria (*Escherichia coli* and *Staphylococcus aureus*), where the bacteria count reduced by 99% after incorporation of ZnO-HNTs (Fig. 1c). This study also revealed that HNTs alone do not have any innate antimicrobial ability and the antimicrobial activity depends on the amount of ZnO

deposited on HNTs as well as the time, *i.e.* microbial exposure time to ZnO-HNTs.

Instrumented impact properties of epoxy/HTN nanocomposites

The toughening effects of HNTs in brittle polymer matrixes, *e.g.* epoxy resin, have been reported previously (Deng *et al.*, 2009; Tang *et al.*, 2011). To provide further insight into the details and mechanisms of the effects of nanotubes on the high-speed fracture toughness of polymers, the impact behaviour of epoxy nanocomposites reinforced with unmodified and modified HNTs at different loadings was investigated by instrumented impact tests. Instrumented impact analysis showed that incorporation of modified or unmodified HNTs did not affect the crack-initiation stage of impact fracture. However, their incorporation impeded the propagation of cracks and dramatically increased the crack-propagation energy. The force required for crack propagation was increased considerably by incorporation of modified HNT nanocomposites to be even larger than that of crack initiation; this is important to maintain the structural integrity of the nanocomposites after crack initiation (Vahedi & Pasbakhsh, 2014b).

Studies of the fracture mechanisms showed that the behaviour of the polymer matrix, which can be adjusted by compound formulations such as curing agents and plasticizers, plays an important role in determining the toughening effect of HNTs (Vahedi *et al.*, 2015). Although 4,4′-diaminodiphenylmethane (MDA)-cured HNTs had enhanced impact resistance from the HNTs, incorporation of HNTs in diethylene-triamine (DETA)-cured epoxy decreased the impact resistance which is attributed to the shear yielding behaviour of DETA-cured epoxy matrix. Moreover, the type of HNT was found to be remarkably influential on the properties of the epoxy/HNT nanocomposites. Halloysite nanotubes with a larger aspect ratio and more uniform tubes confer much stronger toughening compared to those with a small aspect ratio and less uniformity (Vahedi *et al.*, 2015). However, the shorter length of HNTs compared to other nanotubes like carbon nanotubes (CNTs) can be an obstacle to their further toughening.

Polyacrylonitrile/HNT membranes for use in water filtration

Polyacrylonitrile (PAN) nanofibrous membranes were fabricated using an electrospinning technique

(electrospinning parameters: flow rate = 1.4 mL/h, collector distance = 15 cm, voltage = 13–14 kV, solvent: dimethyl sulfoxide) with different HNT concentrations (1–3 wt.%) (Makaremi *et al.*, 2015). The majority of the nanofibre diameters ranged from 450 to 550 nm with an average diameter of 484 nm as confirmed by FE-SEM micrographs (Fig. 3). Nitrogen absorption-desorption tests revealed that the surface area and pore volume of the fibres increased with addition of HNTs. The tensile properties of PAN fibres increased marginally with the addition of small amounts of HNTs. The thermal stability of PAN/HNT fibrous mats was also significantly greater than that of pure PAN fibrous mats. The water-filtration efficiency of these PAN/HNTs nanofibrous mats was evaluated by filtering an oil-water feed solution. The filtration ability of these nanofibrous mats was remarkable, with an oil particle rejection rate of 99.5%; feed water turned out to be completely transparent after filtering it through the membrane (Fig. 3c). Although there was no effect of HNTs on oil-particle separation in the filtration process, negatively charged surfaces of HNTs contributed to the adsorption of heavy metal particles (Cu(II) ions) from water. For instance, Cu ion-removal efficiency of nanofibrous mats improved by 31% with the addition of 3 wt.% of HNTs. Furthermore, the rate of flux of the membranes increased with the addition of HNTs. These remarkable filtration performances illustrate a great potential of PAN/HNTs nanofibrous mats for use in effective water-filtration applications.

Nevertheless, having a well dispersed mixture of HNTs alongside and/or inserted into the nanofibres in an electrospun membrane has remained a challenge during our recent efforts in fabrication of biopolymer/HNT membranes with the electrospinning method. Figure 3a shows an individual HNT nanotube alongside a PAN nanofibre while Fig. 3c shows an agglomeration of tubes in a matrix of PAN electrospun membrane with 3 wt.% HNTs.

The role of HNTs in self-healing composites

Preparation of smart self-healing materials by incorporation of (micro) encapsulated active agents has attracted considerable attention in recent decades. The hollow lumen space of HNTs provides an opportunity to use them as nanocontainers for the facile encapsulation of healing chemicals. Loading of healing agents could be performed by vacuum infiltration. However the viscosity and size of the molecules will affect the efficiency of encapsulation.

To enhance the encapsulation of some chemicals as agents, some pre-treatment/modification should be applied to the lumen by using surfactants. The pH-, temperature-, and redox-responsive silica/polymer hybrid nanotubes developed by Li *et al.* (2013) presented a new, functional and "intelligent" nanocontainer system for corrosion-protection coatings. This proposed universal approach for the synthesis of surface-active and tube-like hybrid nanomaterials can be used to construct promising building blocks for various future applications (Li *et al.*, 2013). Self-healing anticorrosion coating was prepared by incorporation of corrosion inhibitor-loaded HNTs in industrial paints (Shchukin *et al.*, 2008; Abdullayev *et al.*, 2009, 2013). To prevent possible leakage of the loaded chemicals from the open ends of the tubes, chemical stoppers (Abdullayev *et al.*, 2009) or layer by layer deposition of polyelectrolytes (Shchukin & Möhwald, 2007) with adjustable release have been suggested. Although HNTs have been used successfully in the preparation of self-repair anticorrosion coatings (Shchukin *et al.*, 2008; Abdullayev *et al.*, 2009), they cannot yet be used in the development of self-healing structural composites. The lower loading capacity of ~10%–20% by weight (*vs.* 40%–90% in traditional polymeric microcapsules) offers the main challenge for using halloysite in such applications. Lumen enlargement of HNTs through selective alumina etching allowed the enhancement of its loading efficiency (Abdullayev *et al.*, 2012). However, the etching process could change the dispersion behaviour of HNTs in polymeric matrices and this presents a challenge for further development in this area.

HNT/alginate beads for lead adsorption

Using HNTs can enhance the mechanical performance of biopolymer beads like alginate due to a greater elastic modulus of the HNTs. The HNT/alginate nanocomposite beads have been used by Chiew *et al.* (2016) as these adsorbents incorporate the distinctive merits of both HNTs and alginate, which include a high affinity towards Pb^{2+}, strong mechanical properties and easy separation from the treated solution (Chiew *et al.*, 2016). The beads have been designed to remove Pb^{2+} from aqueous solutions by adsorption (Fig. 4). The HNT/alginate nanocomposite beads have an adsorption capacity for Pb^{2+} of 325 mg g^{-1} compared to 84 mg g^{-1} for free HNT nanotubes. The overall process was diffusion limited, well described by the shrinking core model. The HNT/alginate beads removed Pb^{2+} through ion exchange with Ca^{2+}
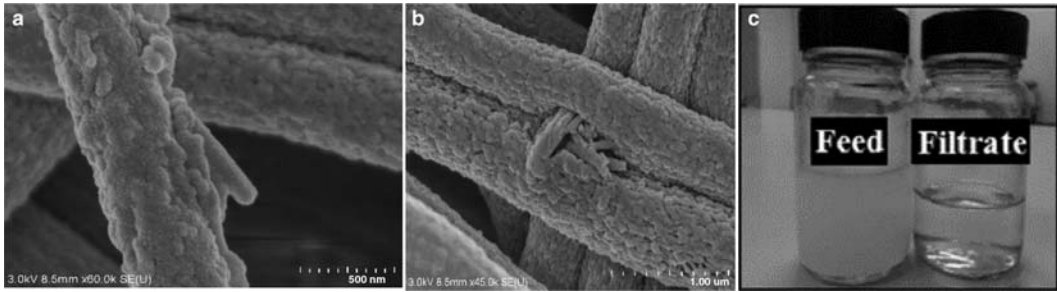
FIG. 3. (a) Halloysite nanotube alongside the PAN nanofibres; (b) agglomeration of HNTs between two PAN nanofibres and (c) solution clarity before and after filtration (reproduced from Makaremi *et al.*, 2015, with the permission of the American Chemical Society Publishing group).

followed by coordination with carboxylate groups of alginate, in addition to physisorption on HNTs.

Prospects of improvements in applications from the range of characteristics of HNTs

Often, studies of the applications of HNTs reported in the literature have used only one, or, at most two, particular HNT samples. Not all HNTs are nanotubular (Joussein *et al.,* 2005; Churchman, 2015). However, even among HNTs, it is well known that their characteristics, such as tube length and lumen diameter, vary greatly between samples of different origins (Joussein *et al.*, 2005; Pasbakhsh *et al.*, 2013). Pasbakhsh *et al.* (2013) showed that their usefulness for different broad applications, *e.g.* as additives in nanocomposites, or as carriers for active agents for their slow or focused release, required different sets of characteristics for the HNTs. For example, more uniform tubes with large surface areas are likely to

be most suitable as additives in polymer nanocomposites to enhance the mechanical properties, while long tubes are most likely to be suitable as additives/carriers, and the large volume of the lumen should provide an advantage for that particular sample as a carrier of active agents. Research is needed to compare the detailed properties of HNTs to determine which are the most suitable for each potential application.

CONCLUSIONS

HNTs as natural nanotubular materials with tube lengths from 50 to 5000 nm and lumen sizes of 5 to 70 nm have attracted much interest in the literature. In this study some recent findings and challenges of using HNTs in various applications have been reviewed. The applications included chitosan/HNTs for bone-tissue scaffolds, grafting of ZnO on HNTs for PLA antimicrobial food packaging films, self-healing, lead adsorption, water filtration and impact damage of

FIG. 4. Pb^{2+} removal/adsorption by halloysite/alginate nanocomposite beads (from Chiew *et al.*, 2016; reproduced here with the permission of Elsevier).

epoxy composites. For each of these applications it is found that modification and/or functionalization of HNTs may be helpful to create and prepare appropriate functional groups for interaction with certain types of polymers, although these modification and treatment processes can be expensive and complicated in an industrial context. In a number of studies reviewed in this work different types of HNTs have been used and it can be concluded that properties of HNTs may be changed due to their origin; certain types of HNTs showed some limitations in suitability for use in certain types of applications depending on their length, lumen volume and uniformity. For example, shorter and thinner tubes may not be suitable for increasing the impact toughness of epoxy composites while they can be useful as additives in many other applications such as anticorrosion coatings. In another example, long tubes can be more suitable for longer release times of the encapsulated drugs and carriers. In another instance, HNTs do not exert a significant antimicrobial effect on their own but that property can be added by using antibacterial materials such as zinc and silver whilst concurrently contributing to the reinforcement of the biopolymer films for use in packaging applications. An increase in the number of well characterized commercial deposits in the world would give researchers and consumers more flexibility in terms of choice of the most appropriate type of HNTs for their specific requirements. Even so, the challenge is for researchers to provide awareness of the natural variability in HNTs and how and when to take appropriate stock of it, not just from deposit to deposit but even within a deposit (through quality control).

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