Halloysite nanotubes as a novel nanofiller for polymer nanocomposites

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Introduction

Polymer clay nanocomposites have been widely investigated by various researchers (Giannelis, 1996; Alexandre and Dubois, 2000; Bhattacharya and Bhowmick, 2008). The nanocomposites with nanosized clay particles obtained by dispersion, were reported to exhibit high mechanical properties, enhanced thermal stability, improved gas barrier properties, high flame retardency, decreased solvent uptake as well as increased chemical and shape memory properties. Recently, halloysites have been characterized by many researchers for use as fillers for polymer materials and containers for drug delivery applications (Churchman and Theng, 1984; Levis and Deasy, 2002; Joussein et al., 2005; Joussein et al., 2007; Ismail et al., 2009). HNT is a kind of aluminosilicate clay ($Al_2Si_2O_5(OH)_4$ H_2O with 1:1 layer) with hollow micro and nanotubular structure, and is mined from natural deposits in countries such as China, New Zealand, America, Brazil and France. Recently Du et al. (2006) reported that HNTs have typical dimensions of, 10–50 nm in outer diameter, 5–20 nm in inner diameter with 2–40 µm in length. Halloysite, a 1:1 clay mineral chemically similar to kaolinite shows tubular morphology but also spherical, platy and semi rolled forms (Churchman and Theng, 1984; Joussein et al., 2005). HNTs have been widely used during recent years to reinforce polymer matrices such as epoxy resins (Deng et al., 2008), polypropylene (Ning et al., 2007), polyamide (Marney et al., 2008) and styrene rubber (Guo et al., 2008). In addition, HNTs are far less expensive than CNTs and can be mined from deposits as a raw material. In our previous work (Ismail et al., 2008; Ismail et al., 2009; Pasbakhsh et al., 2009b, 2009a; Pasbakhsh et al., 2010) we have studied the effect of the HNT loading on the properties of EPDM nanocomposites and found a very uniform dispersion of HNTs within the EPDM even at high HNT loading (30-100 phr).

Halloysite nanotubes

The HNTs, (ultrafine grade) were contributed by Imerys Tableware Asia Limited, New Zealand, with brightness of 98.9% as measured by a Minolta CR300 using D65 light source. The elemental composition of HNTs is as follows (wt %): SiO_2, 49; Al_2O_3, 34.8; Fe_2O_3, 0.35; TiO_2, 0.12; Na_2O, 0.25; MgO, 0.15.

Results and discussion

The peak at 12.187° 2θ corresponds to a (001) basal spacing of 0.725 nm (Fig. 1). The basal reflections are broad and this is attributed to the small crystal size, the inconsistent layer spacing and the curvature of the layers. The dehydrated state was also confirmed with the presence of the (002) basal reflection at 24.918° 2θ which is equivalent to d = 3.63Å. The relatively sharp 006 diffraction peak, with d=1.48 Å at 62.427° 2θ, indicates that the halloysite is a dioctahedral mineral and this relates to the typical sheet-structure of HNTs. It is clear that most of the peaks belonged to the (7Å)-halloysite. There are two other peaks at 22.093° 2θ and 26.698° 2θ, which correspond to the presence of silica, in the forms of cristobalite and quartz, respectively.

The SEM and TEM micrographs (Fig. 2), also depicts the nanotubular structure of halloysite. HNTs have typical dimensions of 150 *nm* – 2 µm long, 20-100 nm outer diameter and 5-30 nm inner diameter. The formation of hollow nanotubes and their lumen structure will increase the potential application of the HNTs in drug delivery as a time release capsule, in polymer nanocomposites or in paints and sealants as well as all things that could benefit from their controlled release behaviour (Levis and Deasy, 2003). A novel application hence could be expected from these hollow nanotubes to prepare the new polymer nanocomposites with high thermal stability and flame retardant properties (Du et al., 2006). The morphological variability of halloysite (Fig. 3) was reported to be due to various factors including crystal structure, degree of alteration, chemical composition, and the effect of dehydration. These morphologies are listed in Table 1.

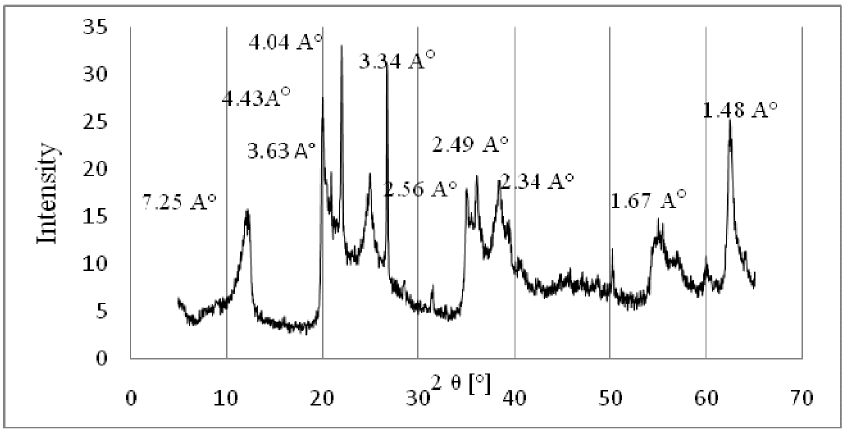

Fig. 1. XRD pattern of halloysite nanotubes.

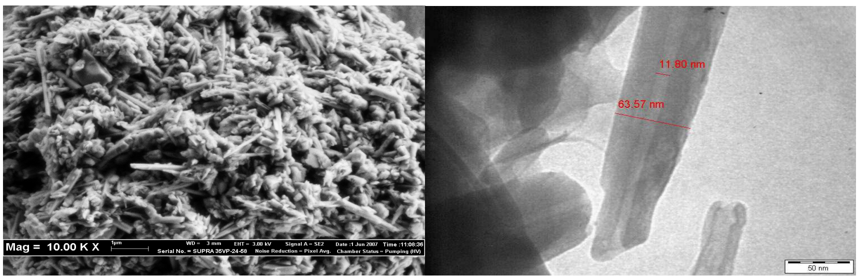

Fig. 2. SEM and TEM images of halloysite nanotubes.

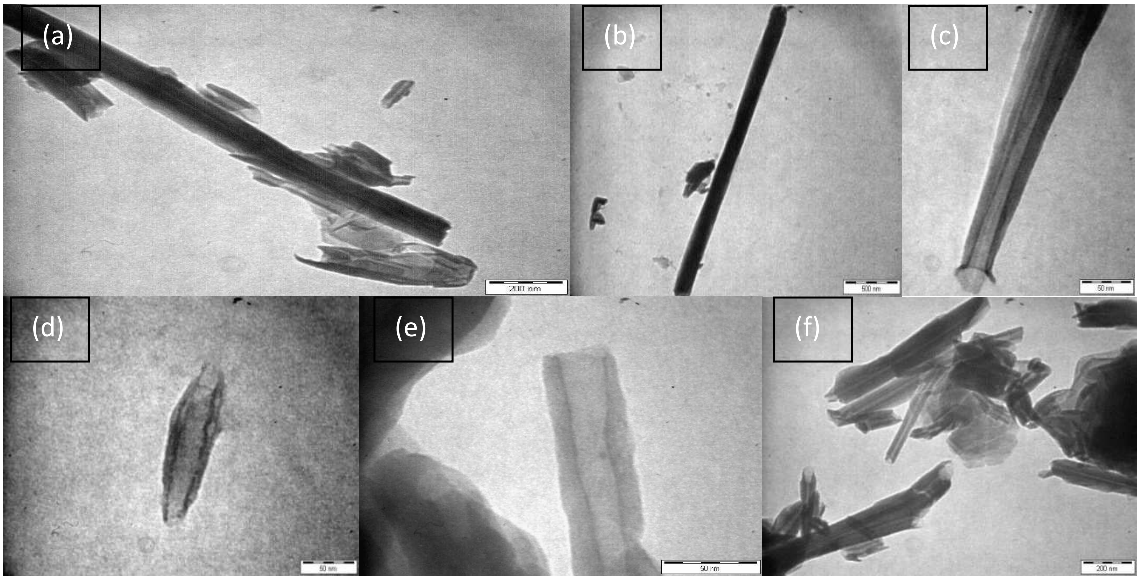

Fig. 3. Various shapes of HNTs observed by TEM.

Table 1. Morphologies observed by TEM images as shown in Figure 3.

Outline	Morphology	Figure
1	Tubular elongated & Uncompleted tube	Fig 3 (a)
2	Short and thin tube & Semi rolled tube	Fig 3 (a)
3	Platy form, Splitting & Double nanotube inside each other	Fig 3 (a)
4	Solid nanotubular	Fig 3 (b)
5	Curved edges	Fig 3 (c)
6	Thin and stubby form	Fig 3 (d)
7	Serrated edges	Fig 3 (e)
8	Pseudo spherical	Fig 3 (f)

The thickness of the HNTs wall is around 10-40 nm (Fig. 4). Figure 4 shows the dimensions of lumen of HNTs in EPDM/HNT nanocomposite and their walls which consisted of tens of layers. HNTs have two different interlayer surfaces; the Al-OH group is located inside the tubes while the outer surface of HNTs is covered by the siloxane group (Liu et al., 2007) (Fig. 5). The lumen space inside HNTs can be intercalated and interacts with modifiers, vulcanization ingredients and the polymers.

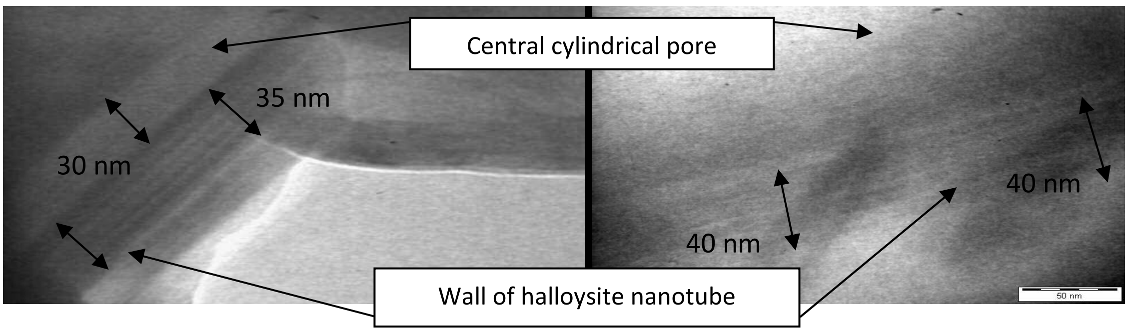

Fig. 4. TEM micrographs showing the dimensions of interlayers along the HNTs' wall and cylindrical pore inside the HNTs in EPDM/HNT nanocomposite.

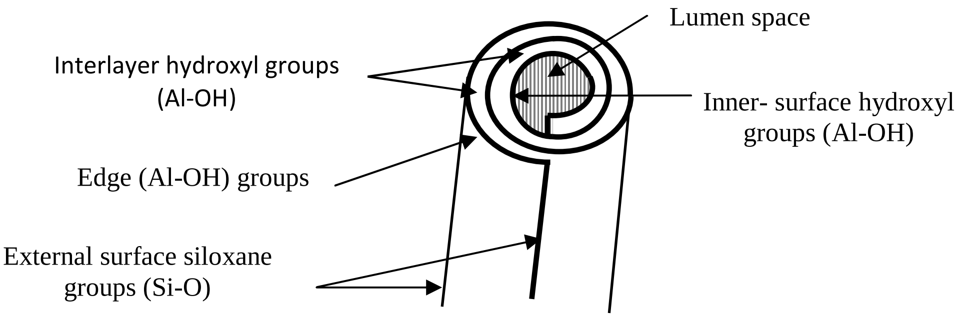

Fig. 5. Structure of a halloysite nanotube (Pasbakhsh et al., 2010).

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