

Modification of halloysite nanotubes with glycidyl methacrylate

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Introduction

Halloysite is a tubular or hollow cylinder shaped clay and is commonly known as halloysite nanotubes (HNTs) which has a chemical formula of $\text{Al}_2(\text{OH})_4\text{Si}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ similar to kaolinite (Joussein et al., 2005). The natural occurrence of the tubular morphology is due to a mismatch in the periodicity between the oxygen sharing tetrahedral SiO_4 sheets and adjacent octahedral AlO_6 sheets in the 1:1 layer (Yuan et al., 2008). The external surface of the HNTs contains siloxane (Si-O) groups (Du et al., 2010) while the (Al-OH) groups dominate the internal surface. Thus, the tubule lumen surface is positively charged hence promoting the loading of negative macromolecules while the outer surface which is negatively charged will prevent the adsorption of those macromolecules. In recent years, the natural HNTs have been modified for several different applications. However, since the hydrophilic nature of clay particles is incompatible for polymerization, a hydrophobic organo-modifier is required (Ying-Ling et al., 2003; Lvov et al., 2008). This study will attempt to load glycidyl methacrylate (GMA) into the lumen of Jarrahdale HNTs (J-HNTs) with the help of an active agent, toluene.

Experimental methods

Samples of Jarrahdale obtained from a laterite pallid zone near Jarrahdale, 50 km southeast of Perth, Western Australia. 1 gram of pure J-HNTs was ground and mixed with 40 ml toluene and 0.25 ml of GMA. The suspension was then ultrasonified for 30 minutes. Then, the evacuation process was carried out before the heating process. A diaphragm vacuum pump was used to extract the excess air that is believed to be trapped in the lumen of the HNTs. After that, the suspension was heated at 80 °C for 2 hours under constant stirring. Silica gel was used to remove excess air from the heating process. After centrifuge the solid phase was washed extensively with fresh toluene for six times before drying in an oven at 105 °C overnight. The BET and BJH analysis was set according to Keeling et al. (2011). For FTIR analysis approximately 0.01 grams of J-HNT powder is mixed with 0.1 gram of potassium bromide (KBr) powder to form a pellet which was analyzed over wavelengths of 650 – 4000 cm^{-1} .

Results and discussion

BET and BJH

The BJH pore size distribution (PSD) curves in Fig. 1 were extracted from the desorption data. The BET surface areas of the pure and modified J-HNTs are 47.19 and 34.25 m²/g, respectively. Decreasing the surface area of HNTs after modification confirmed the successful modification of HNTs by GMA. According to Fig.1 three peaks were found in both pure and modified samples. The third peak at 30 to 60 nm range belongs to the pore gaps between agglomerated clay particles (Forsgren et al., 2010). However, the third peak found for the modified sample is significantly lower in pore volume as compared to the pure J-HNT's. It is believed that the difference lies in the application of the ultrasound which was used during the modification process. The pore volume for the second peak (lumen) has decreased slightly (with slight change in the pore width for the lumens with higher 11 nm size) which indicated that HNTs were partially loaded by GMA (Fig.1). It was found that the modification process which was applied in this study was unlikely to lead to closing the end of the tubes by GMA. However the first peak indicated that most of the surface's pores have been covered by GMA as the volume of those pores in the range of less than 5 nm was decreased significantly.

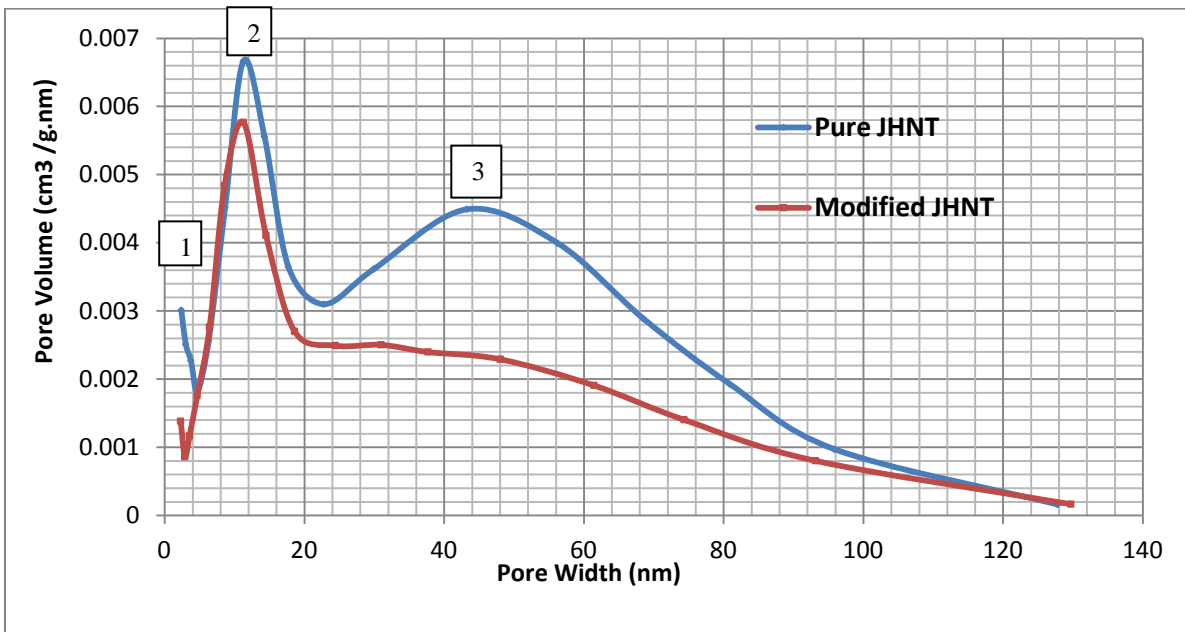


Fig 1. N₂ desorption analysis of pore volume versus pore width of pure and GMA-modified HNTs.

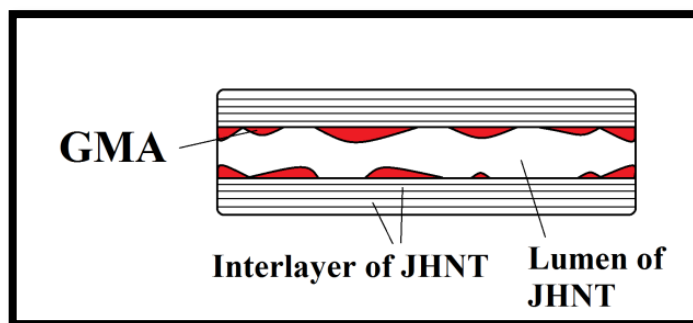


Fig.2. The partial loading of GMA in the lumen diameter of HNTs.

FTIR analysis

Justification of the extent of modification of the J-HNTs can be further reinforced by the FTIR results (Fig.3). Decreasing the intensity of the 909 cm^{-1} peak of modified HNTs is due to the disappearance of the GMA's oxirane ring which has added to the OH peak of the halloysite that is also found in the 909 cm^{-1} peak (Ying-Ling et al., 2003). Moreover, the strong absorbance at peaks that are found from $3700 - 3200\text{ cm}^{-1}$ include contributions from the additional OH generated from the modification reaction as well. In addition, the peak at 1263 cm^{-1} (Yuan et al., 2008) has increased due to the additional C-H_3 groups that belong to the GMA as seen in Fig. 4.

Fig.4 is a representation of the GMA and J-HNT's cross-linked network, showing the possible grafting mechanism of GMA occurred on the aluminol (Al-OH) groups. According to this scheme GMA reacted with Al-OH groups through the reactive oxirane ring (Ying-Ling et al., 2003). With attention to the study by Hirotsu, (2006) the hydrogen atoms that are found in the inner aluminol groups are exchanged to the GMA's oxirane ring to form a hydrogen bond between the oxide that produces a hydroxyl molecule in order to free up the carbon link of the GMA which then performs a covalent bond with the unstable oxide atom at the surface of the JHNTs (Ying-Ling et al., 2003). These reactions not only introduce a newly bonded hydroxyl group ($-\text{OH}$) at the GMA's chain, but also produce a new aluminoxy (Al-O-CH_2-) group between the HNT and GMA. Hence, beside modification of the Si-O groups at the surface of HNTs with GMA, one may suggest that possible partial grating of GMA into the HNT's lumen occurred.

Conclusions

It has been shown that functionalization and partial loading of halloysite nanotubes with the glycidyl methacrylate is achievable which will benefit the use of these natural nanotubes with self healing applications especially for the reinforced epoxy nanocomposites.

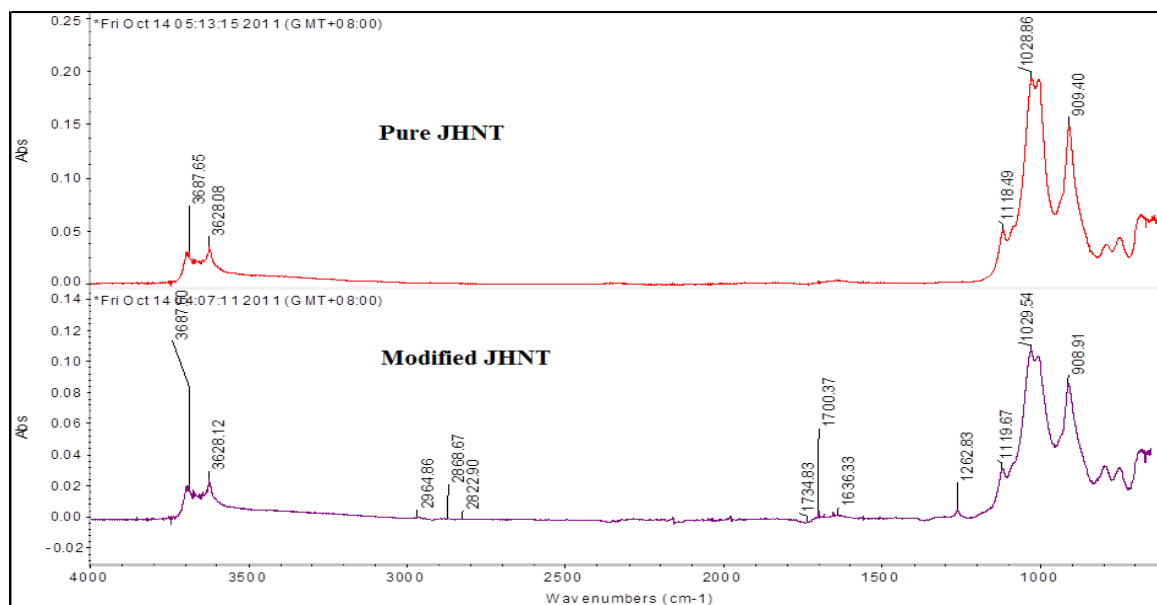


Fig 3. FTIR analysis of pure and modified J-HNTs.

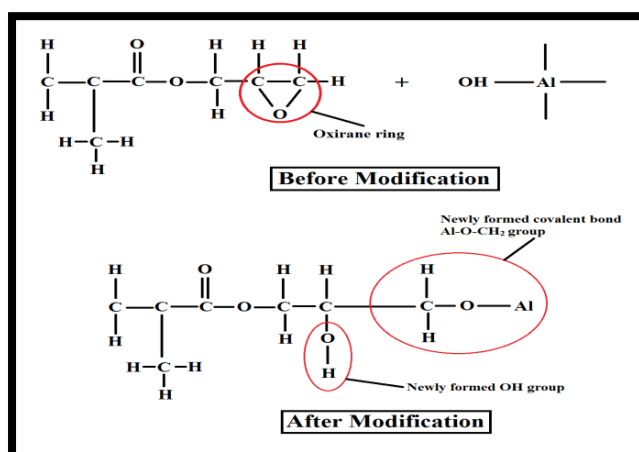


Fig.4. Possible interaction mechanism between GMA and HNTs after modification.

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