

The Role of Halloysite's Surface Area and Aspect Ratio on Tensile Properties of Ethylene Propylene Diene Monomer Nanocomposites

Pooria Pasbakhsh, Rangika T. De Silva, Vahdat Vahedi, Hanafi Ismail

Abstract—The influence of three different types of halloysite nanotubes (HNTs) with different dimensions, namely as camel lake (CLA), Jarrahdale (JA) and Matauri Bay (MB), on their reinforcing ability of ethylene propylene diene monomer (EPDM) were investigated by varying the HNTs loading (from 0-15 phr). Mechanical properties of the nanocomposites improved with addition of all three HNTs, but CLA based nanocomposites exhibited a significant enhancement compared to the other HNTs. For instance, tensile properties of EPDM nanocomposites increased by 120%, 256% and 340% for MB, JA and CLA, respectively, with addition of 15 phr of HNTs. This could be due to the higher aspect ratio and higher surface area of CLA compared to others. Scanning electron microscopy (SEM) of nanocomposites at 15 phr of HNT loadings showed low amounts of pulled-out nanotubes which confirmed the presence of more embedded nanotubes inside the EPDM matrix, as well as aggregates within the fracture surface of EPDM/HNT nanocomposites.

Keywords—Aspect ratio, Halloysite nanotubes (HNTs), Mechanical properties, Rubber/clay nanocomposites.

I. INTRODUCTION

PRESENTLY a wide range of industries in materials engineering are challenging to produce novel materials with unique mechanical properties and thermal stability. In the field of products associated with rubbers, material science is rapidly pursuing materials that exhibit superior thermal and tensile properties. Ethylene propylene diene monomer (EPDM) is widely used in electrical, textile and automobile industries due to its good processability; however, its ability to be used in engineering applications has been to some extent limited due to its poor mechanical properties [1]. Therefore to improve its mechanical properties and extend its applications a number of extensive and through studies on toughening and strengthening of EPDM with fillers have been made in the last 20 years [2]. EPDM based nanocomposites have been also studied extensively to broaden the applications of EPDM.

Different types of fillers such as carbon nanotubes (CNTs), montmorillonite (MMT) and carbon black have been used to reinforce EPDM and increase its mechanical and thermal properties [3]. But due to the problems associate with these fillers such as high cost, complex modification procedure, environmental issues and low reinforcing performance, finding better reinforcing fillers like natural nanotubes (e.g. halloysite nanotubes, HNTs) has been a matter of interest for many researchers in the past 10 years [4].

HNTs were first discovered by Berthier in 1826, and they are natural aluminosilicates ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$) with nano tubular structures. Typically, the length of HNTs varies from 100 to 5000 nm, with an external diameter of 20-200 nm and internal diameter of 10-70 nm [4]. HNTs have remarkable unique properties such as good biodegradability, tubular structure, large aspect ratio, and high surface area [5]. Due to these outstanding properties, recently, HNTs have been used successfully as nano-fillers in many occasions in order to reinforce the mechanical and thermal properties of polymers [6]. It has been reported by Pasbakhsh et al. [4] that various halloysites have different properties depending to their geographical and geological environments. These properties can be varied in terms of the halloysite content (ranged from 84 to 98%), impurities which included of minor quartz, cristobalite, kaolinite, gibbsite, alunite, iron oxides and anatase and variation in halloysite morphology. These all variations can also affect the surface area and the lumen size. In this study, three different types of HNTs (Fig. 1) have been used and the properties of those HNTs are given in Table I. HNTs which had been used in the past studies had different aspect ratios, surface areas and lumen volume, resulting in contradictory outcomes. Therefore in this study the effect of three different types of HNTs with different properties was studied to reinforce EPDM nanocomposites and the tensile and morphological properties were compared with each other.

TABLE I
PROPERTIES OF DIFFERENT TYPES OF HNTS

HNTs type	Aspect ratio	Surface Area (m^2/g)	Inner diameter (nm)	Outer diameter (nm)
Matauri Bay (MB)	12	22.10	15-70	50-200
Jarrahdale (JA)	10	47.28	10-50	30-80
Camel Lake (CLA)	18	76.63	10-25	20-70

P. Pasbakhsh is with Mechanical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, Bandar Sunway, 47500, Selangor Darul Ehsan, Malaysia (corresponding author, Tel: +60-3-55146211; Fax: +6055146207; e-mail: Pooria.Pasbakhsh@monash.edu)

R.T. De Silva and V. Vaheddi are with Mechanical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, Bandar Sunway, 47500, Selangor Darul Ehsan, Malaysia (e-mail: Rangika.desilva@monash.edu, vahdath.vahedi@monash.edu)

H. Ismail is with School of Materials and Mineral Resources Engineering, Department of Polymer Engineering, Universiti Sains Malaysia, Engineering Campus, 14,300 Nibong Tebal, Penang, Malaysia (e-mail: hanafi@eng.usm.my).

II. MATERIALS AND METHODS

A. Materials

Three different types of halloysite nanotubes (HNTs) were supplied by Imerys Tableware Asia Limited, New Zealand (here as MB), Camel Lake site, on the western margin of the Eucla Basin in southern Australia (here as CLA) and Jarrahdale (Western Australia) was taken from the lower pallid zone of a deeply weathered profile in dolerite, exposed in a railway cutting near Jarrahdale (here as JA). Zinc oxide, stearic acid, sulphur, tetramethyl thiuram disulfide (TMTD) and 2-mercapto benzothiazole (MBT) were all obtained from Bayer (M) Ltd and used as received.

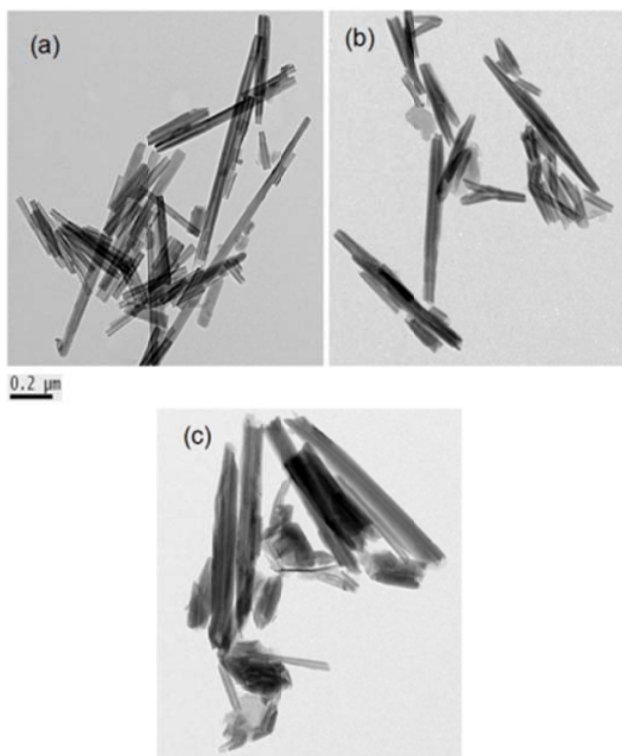


Fig. 1 TEM micrographs of pure halloysites (a) CLA, (b) JA, (d) MB

B. Preparation of Nanocomposites

The compounding of EPDM, HNTs and other ingredients such as zinc oxide, stearic acid, MBT, TMTD and sulphur was done on a laboratory-sized (160 mm 320 mm) two roll mill, model XK-160. The curing times (t_{90}) of the compounds were obtained by using a Monsanto Moving Die Rheometer (MDR 2000) at 150°C. The compounds were subsequently compression molded at 150°C, based on the respective t_{90} values. The composition of the samples is according to Ismail et al. [1].

C. Characterization

Tensile testing was carried out with compression molded sheets having a thickness of about 2 mm were punched to prepare the dumb-bell shaped specimens for tensile testing. Tensile testing was conducted following ISO 37 using a

universal tensile testing machine (Instron 3366) at room temperature (25±2°C) and a crosshead speed of 500 mm/min. Tensile strength, elastic modulus and elongation at break (E_b) were recorded. The elastic modulus was compared with the Halpin-Tsai analytical model at different aspect ratios (10, 12 and 18); where the density of the matrix and HNTs were considered to be 0.86 and 2.5 g/cm³, and modulus of EPDM and HNTs to be 1 and 140 GPa

Transmission electron micrographs of the pure halloysite samples were obtained at 200 kV using a Philips CM200 TEM. The morphologies of tensile fracture surfaces of EPDM/HNT nanocomposites were observed under an FE-SEM at low voltage and STEM mode (30 kV). Before SEM imaging, the nanocomposites were coated with a thin layer of Pd-Au, to prevent electrostatic charging during evaluation. To observe the EPDM/HNT nanocomposites under the STEM mode, ultra-thin specimens were prepared using a cryogenic ultra-microtome Leica-Reichert Supernova.

III. RESULTS AND DISCUSSION

A. Tensile Properties

A considerable increment in tensile properties of the nanocomposites was observed with addition of HNTs in to EPDM matrix (Fig. 2 (a)). For instance, tensile strength (σ) increased by 120%, 256% and 340% for MB, JA and CLA, respectively with addition of 15 phr. The elastic modulus (E) followed a similar trend as the σ , where the E increased with addition of HNTs for all three types of HNTs, but more prominent results were observed in CLA (Fig. 2 (b)). The increase in E with addition of HNTs was attributed to the effect of HNTs-rubber interactions which leads to the occlusion of rubber [7]. The occlusion of the rubber is the rubber which is trapped between or within aggregates of HNTs, the perpendicular rubber inside and between the tubules which acts as part of the filler network and increases the stiffness of the EPDM/HNTs nanocomposite. The experimentally obtained E was compared with the linear Halpin-Tsai model (H-T model; derived for randomly oriented fiber composites) (Fig. 2 (b)), and it was observed that the experimental E of CLA and JA based nanocomposites is in good agreement with the H-T model, where the E increase linearly with addition of HNTs. Nevertheless, MB significantly deviate from the model results and do not exhibits a linear trend. This could be due to non-uniform structure of MB compared to JA and CLA. Comparing the different types of HNTs CLA, JA and MB, it can be stated that CLA had outperformed JA and MB at all concentrations. This trend is mainly due to the difference in aspect ratio of the HNTs. The aspect ratios of HNTs follows the order of CLA (18) > MB (12) > JA (10), where CLA exhibits the highest aspect ratio [4]. Moreover, tensile properties increased due to the high surface area of the HNTs; where the higher the surface area, the more opportunity for filler-matrix interactions. CLA exhibited the highest surface area of 77.47 (m²/g) followed by JA and MB with surface area of 44.62 (m²/g), 22.10 (m²/g), respectively [4]. The EPDM

nanocomposites reinforced by JA had higher σ and E compared to MB based nanocomposites. In this case, the difference of the aspect ratio was insignificant and the surface area played a dominant role.

The elongation at break (ϵ) has increased with addition of all types of HNTs compared to the control sample (Fig. 1 (c)). The increment is significant between MB and other two types, but the increment of ϵ within the JA and CLA is not appreciably changed. However, ϵ has increased by 100%, 149% and 164% with addition of 15Phr of MB, JA and CLA, respectively.

types of HNTs were well dispersed within the EPDM matrix (Figs. 3 and 4). CLA exhibits a clear uniform dispersion of the long and narrow nanotubes, while the JA and MB exhibits non-cylindrical particles apart from the nanotubes. These non-cylindrical particles could be attributed to the impurities (kaolinite, quartz, mica and feldspar) presented in MB and JA, which is around be 10% and 20% from the volume, respectively. These impurities could also affect the tensile properties, since the stress transformation from matrix to non-cylindrical filler is inefficient and therefore CLA gives better performance.

There are some “micro-voids” which can be seen in the micrographs of MB incorporated to EPDM nanocomposite (Fig. 2 (c); marked by arrows) and these could be due to the pulled out nanotubes during the tensile testing. This implies that the interfacial interaction between MB and EPDM is inferior to the interaction between EPDM and other two types of HNTs. This observation is in well agreement with the tensile results. Moreover, no pores can be observed (removal of the matrix parts due to the applied force during the tensile testing) in all types of HNTs reinforced EPDM and it is due to the good filler-matrix interaction and three dimensional orientations of HNTs.

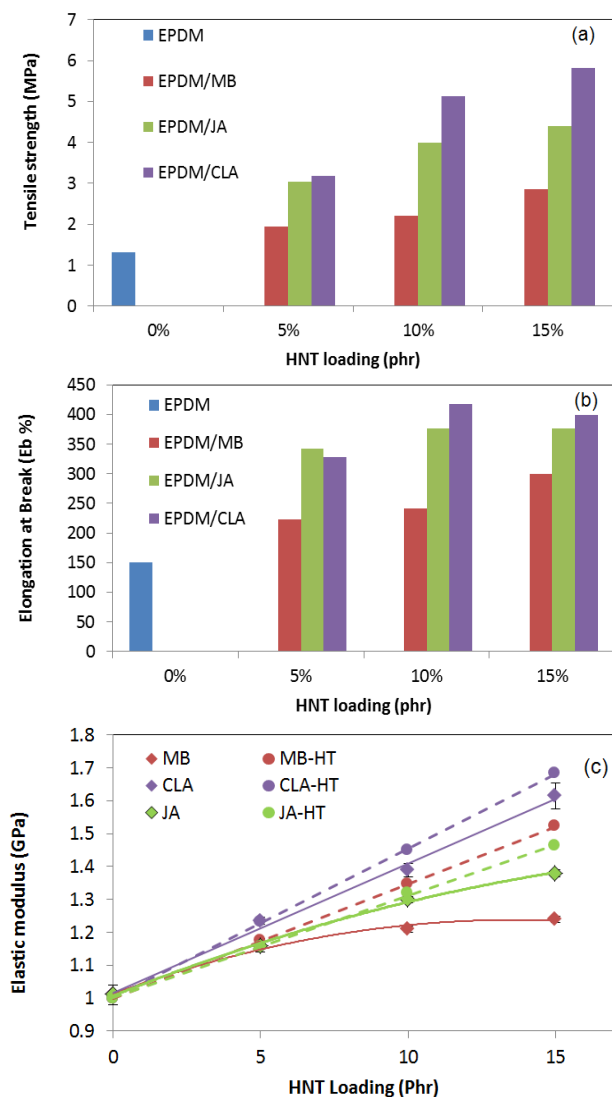
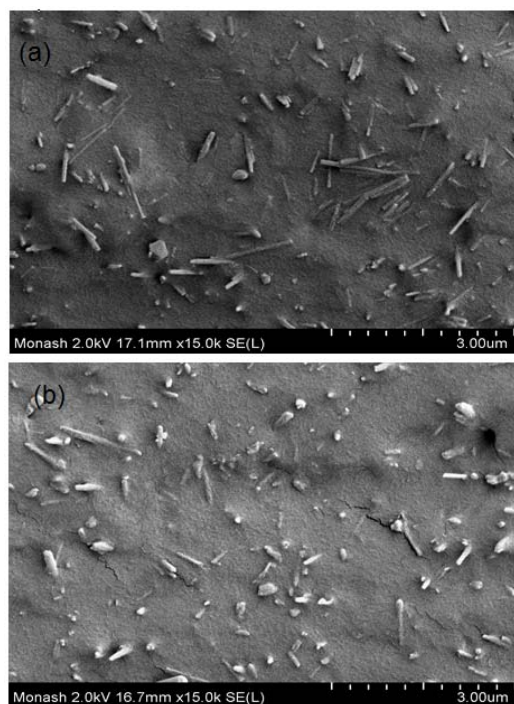
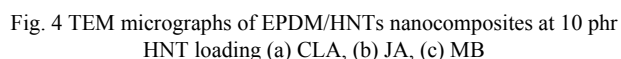
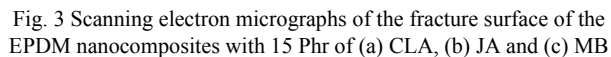


Fig. 2 Tensile properties; (a) tensile strength, and (b) elongation at break, (c) elastic modulus (both experimental (♦-) and H-T (●--) results)

B. Morphology

Fig. 1 shows the TEM micrographs of three different types of HNTs. Electron micrographs (SEM and TEM) of the fractured surface of EPDM/HNTs revealed that the all three





EPDM/HNTs nanocomposites were fabricated using two-roll mill. Herein, the influence of three different HNTs types (obtained from different mines) on the mechanical and morphological properties were studied. Addition of 15 phr of HNTs increased the tensile strength by 120%, 256% and 340% for HNTs types of MB, JA and CLA, respectively. It showed that HNTs with high aspect ratios and surface areas lead to higher mechanical properties. But when MB and JA compared, JA has slightly lower aspect ratio and high surface area, and nanocomposites with JA exhibited superior tensile properties compared to MB, showing a dominant influence of the surface area on mechanical properties. Morphological studies characterized the dispersion of HNTs. CLA showed better potential to disperse in EPDM compared to MB and JA.

- [1] H. Ismail, P. Pasbakhsh, M. A. Fauzi, A. A. Bakar. Morphological, thermal and tensile properties of halloysite nanotubes filled ethylene propylene diene monomer (EPDM) nanocomposites. *Polymer Testing*. 27(7): 841–850, 2008.
- [2] M. Du, B. Guo, D. Jia. Newly emerging applications of halloysite nanotubes: a review. *Polymer International*. 59(5): 574-582, 2010.
- [3] H. Zheng, Y. Zhang, Z. Peng, Y. Zhang. Influence of clay modification on the structure and mechanical properties of EPDM/montmorillonite nanocomposites. *Polymer Testing*. 23(2): 217-223, 2004.
- [4] P. Pasbakhsh, J. Churchman, J. Keeling. Characterisation of properties of various halloysites relevant to their use as nanotubes and microfibre fillers. *Applied Clay Science*. 74: 47-57, 2013.
- [5] X. Sun, Y. Zhang, H. Shen, N. Jia. Direct electrochemistry and electrocatalysis of horseradish peroxidase based on halloysite nanotubes/chitosan nanocomposite film. *Electrochimica Acta*. 56(2): 700-705, 2010.
- [6] A. S. Deuri, A. K. Bhowmick. Aging of EPDM rubber. *Journal of Applied Polymer Science*. 34(6):2205-2222, 1987.
- [7] Y. -W. Chang, Y. Yang, S. Ryu, C. Nah. Preparation and properties of EPDM/organomontmorillonite hybrid nanocomposites. *Polymer International*. 51(4):319-324, 2002.