Preparation and Characterization of Treated MWCNT-Muscovite Filled Epoxy Nanocomposites

Nur Suraya Anis Ahmad Bakhtia, Yeap Cheok Kuanga, Siti Shuhadah Md. Saleha, Hazizan Md Akila,b

aSchool of Materials and Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia.
bScience and Engineering Research Center, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Pulau Pinang, Malaysia.

Abstract

This paper presents the surface treatment of multiwalled carbon nanotube (MWCNT)/muscovite (MUS) hybrid nanomaterial. The hybrid compound was synthesized by chemical vapor deposition (CVD) using methane as the carbon precursor. Morphological characterization of treatment and pristine MWCNT-MUS hybrid was conducted using Field Emission Scanning Electron Microscope (FESEM) and X-ray diffraction (XRD). The surface treatment of MWCNT/MUS hybrid nanomaterial was successfully carried out which the basal spacing of (001) plane d(001) of MWCNT/MUS was enlarged from 21.00 Å to 27.20 Å after first stage and was further enlarged to 29.28 Å after second stage of CTAB treatment. This MCNT-MUS hybrid filler was incorporated into epoxy resin at different filler loadings (0.5, 1.0, and 1.5 wt %). Thermal properties of the treated Epoxy/MWCNT-MUS was determined to have lower properties compared to pristine Epoxy/MWCNT-MUS.

© 2016 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: MWCNT-muscovite, Hybrid Compound, Chemical vapour deposition

* Corresponding author. Tel.: 04-5996161; fax: 04-5941011.
E-mail address: hazizan@usm.my
1. Introduction

Recently, hybrid filler for polymer nanocomposites increased attention due to their unusual property combinations and unique design for advanced applications such as aerospace, automotive, electronics and biotechnology. This is due to their improvement in mechanical, solvent resistance, fire retardant and thermal properties of the composites. Natural materials such as clay based mineral, lignocellulosic fibers and chrysotile were highlighted to be one of the possible materials uses to overcome the environmentally problem. Carbon nanotubes (CNT) are commonly used as one of the potential combination to fabricate the hybrid filler as they have excellent properties with high thermal conductivity, excellent electrical capacity and good thermal stability. However, it was difficult to fabricate CNT-based composites as they are tend to agglomerate among themselves and entangled with strong van der Waals interaction. Previous researcher had demonstrated the interfacial strength between the filler and matrix by growing the CNT onto surface of alumina, carbon fibers and clay.

In the present work, the MWCNT-MUS hybrid filler was synthesized by chemical vapor deposition (CVD). Surface treatment is propose on the surface of the MWCNT-MUS hybrid filler to improve the performance of epoxy nanocomposites by produces homogeneous dispersion of CNT in the epoxy matrix. Furthermore, the treatment was carried out to improve the interfacial reaction between filler and matrix. The effect of surface treatment on the MWCNT-MUS filler were analyzed by morphological and thermal stability.

2. Experimental

2.1 Preparation of MWCNT-MUS Hybrid Filler

MWCNT-MUS hybrid filler was synthesized by chemical vapour deposition (CVD). The CNT were grown on the muscovite particles using nickel as the catalyst. The catalyst was prepared using precipitate method by precipitating the nickel nitrate and muscovite powder with the present of water in NaOH solution. The reduction of the catalyst was performed under hydrogen at 400°C for 2 hours. Then, it was reacted in CH4/N2 mixture at 800°C for 30 minutes.

2.2 Surface Treatment of MWCNT-MUS hybrid filler

Ion exchange treatment of MWCNT/MUS hybrid filler was divided into two stages; 1) ion exchange treatment was carried out by replacing the K+ with Li+ using LiNO3 treatment and 2) Intercalated of Cetyltrimethylammonium cations (CTA+) into silicate interlayers of Li-Muscovite which the Li+ was replaced by CTA+.

2.3 Characterization of Pristine and treated MWCNT-MUS hybrid filler

The morphologies of pristine and treated MWCNT-MUS hybrid filler were analysed using Field Emission Scanning Electron Microscope (FESEM-Leo Supra 35VP). The morphologies of pristine MWCNT-MUS hybrid filler were carried out using High Resolution Transmission Electron Microscopy (HRTEM), Model Philip TECNAI 20. The dispersion state of the MWCNT-MUS particles before and after treatment was evaluated using X-Ray Diffraction (XRD) measurement using Siemens D5000 at 40 kV. The basal spacing was calculated using the Bragg’s Law:

\[ n\lambda = 2d \sin \theta \]  

(1)

Where,

\( n \) = an integer determined by the order given
\( \lambda \) = the wavelength of x-ray and moving electrons, protons and neutrons
\( d \) = the spacing between the planes in the atomic lattice
\( \theta \) = the angle between the incident ray and the scattering plane.
2.4 Fabrication of MWCNT-MUS/Epoxy Nanocomposites

MWCNT-MUS filled epoxy nanocomposites was prepared using Qsonica Sonicators to disperse the treated and pristine MWCNT-MUS within the epoxy resin at different filler loading; 0.5, 1.0, 1.5 wt% (as shown in Table 1). Then, the trimethylhexane-thylenediamine (TMD) curing agent was added to the resin with the ratio of 6:10 to the epoxy resin. The mixture then was degassed in a vacuum for 30 minutes to remove air and poured into silicon mould. The mixture was cured at 120°C for 1 hour.

| Sample                  | Pristine MWCNT-MUS | Treated MWCNT-MUS |
|-------------------------|--------------------|-------------------|
| Epoxy                   | -                  | -                 |
| 0.5 wt% MWCNT-MUS/Epoxy | 0.5                | -                 |
| 1.0 wt% MWCNT-MUS/Epoxy | 1.0                | -                 |
| 1.5 wt% MWCNT-MUS/Epoxy | 1.5                | -                 |
| 0.5 wt% MWCNT-MUS/Epoxy | -                  | 0.5               |
| 1.0 wt% MWCNT-MUS/Epoxy | -                  | 1.0               |
| 1.5 wt% MWCNT-MUS/Epoxy | -                  | 1.5               |

2.5 Characterization of Pristine and Treatment MWCNT-MUS/Epoxy nanocomposites

Thermogravimetric analysis (TGA) was carried out to determine changes in weight in relation to the temperature with controlled atmosphere. Amount of the corresponding residue and quantitative description of the material thermal stability was also determined. Both of pristine and treated MWCNT-MUS/Epoxy were tested by heating the samples from 40°C to 600°C with rate 10°C/min.

3. Result and discussion

From Fig. 1a and 1b, it is shows that the CNT was successfully synthesized by chemical vapor deposition (CVD). It is observe that the CNT was growth on the muscovite particle with random direction. Fig.1c and 1d shows the morphologies of treated MWCNT-MUS hybrid filler. From Fig. 1c, it can be seen clearly that the MWCNT-MUS start split into a small particle size. The CNT partially damage and become shorter compared to the pristine CNT as shown in Fig. 1d. Fig. 2 shows the HRTEM morphologies of pristine MWCNT-MUS hybrid filler. The wire like hollow structures with multi layered wall confirm that the CNT is multiwalled carbon nanotube (MWCNT). Olek M. has reported the multiwall carbon nanotubes (MWCNT) with diameter 10-200 nm can be produced by chemical vapor deposition6.

Fig. 3a, b and c shows the morphological structure of pristine MWCNT-MUS, Li MWCNT-MUS and CTA MWCNT-MUS respectively. The spacing of the sample was calculated using Bragg’s law equation. It was determined that the spacing of (001) plane was enlarged from 21.00Å after first stage of LiNO3 treatment (Li-MWCNT-MUS was form) and was further enlarged to 29.28Å after second stage which form CTA-MWCNT-MUS. Similar trend increment was reported in previous study by Yu et al7. After the LiNO3 treatment, the muscovite particles become hydrophilic and provides ion exchange capacity to the muscovite. Most of the K+ and Li+ in the interlayer space of muscovite were replace by Li+ ions. The spacing of (001) plane was further enlarged when the Li-MWCNT-MUS undergo cation exchange intercalation by larger alkyl chain of CTA+ cations which could allow the intercalation of organic cations. The surface of the MWCNT-MUS then become hydrophobic and can be use as catalyst, reinforcement component in polymer-based composites and adsorbents of contaminants in water8. With the increasing in the basal spacing of the silicate layer, the penetration process of the polymer molecules in these layer. Thus, it will give good distribution of fillers particle.
Fig. 1. FESEM images pristine MWCNT-MUS hybrid filler at a) 5 kv, b) 30 kv magnification and treated MWCNT-MUS hybrid filler at c) 5 kv, d) 30 kv magnification.

Fig. 2. HRTEM images of pristine MWCNT-MUS hybrid filler
Fig. 3. X-Ray diffractogram of (a) MWCNT-MUS, (b) Li-MWCNT-MUS, (c) CTA-MWCNT-MUS

Fig. 4a shows the thermal degradation properties of 0.5 wt%, 1.0 wt%, and 1.5 wt% of MWCNT-MUS filled epoxy. Weight loss from 100°C to 350°C was attributed to the dehydration of samples meanwhile weight loss from 350°C to 600°C attributed to the depolymerisation and oxidative decomposition of MWCNT-MUS. From Fig. 4, it was clearly shown that the thermal stability of epoxy decreased with increasing percentage of MWCNT-MUS filler loading in epoxy composite. Weight residual of epoxy filled with 0.5wt% of MWCNT-MUS shows the highest value with 17.35% as compared to epoxy filled 1.0wt% of MWCNT-MUS and 1.5wt% of MWCNT-MUS which shows value of 16.19% and 15.30% respectively. From previous study by Valera-Zaragoza et al., low filler loading of organoclay incorporated into polymer matrix tend to retard thermal degradation as compared to high organoclay filler loading. Fig. 4b shows the weight residual of 0.5 wt%, 1.0 wt% and 1.5 wt% of MWCNT-MUS filled epoxy as a function of temperature. At 200°C-370°C was attributed to desorption of water and 370-600°C that was attributed to depolymerisation and oxidative decomposition of composites. The weight residual at 600°C of epoxy filled with treated MWCNT-MUS was decreased from 15.81 % to 12.80% with increasing of filler loading. This indicates that 0.5wt% MWCNT-MUS/Epoxy have better thermal stability as compared to epoxy filled with higher weight percentage of same fillers. Theoretically, the epoxy filled treatment MWCNT-MUS should have better improvement of thermal properties compared to pristine MWCNT-MUS/Epoxy as the treatment MWCNT-MUS can dispersed well in the matrix with strong interfacial bonding between the matrix and filler. This preventing the crack formation. Thus, the heat will distribute more evenly in the nanocomposites and delay organic epoxy to evaporate. Sidique et al. has reported that the thermal stability of a polymer was improved by incorporating small amounts of layer silicate (organoclay). Thus the organoclay will make the path longer for the polymer to decompose thermally and the degradation of epoxy filled treatment MWCNT-MUS could be reduced. However, in this study, the thermal properties of treated MWCNT-MUS/Epoxy show lower thermal stability compared to pristine MWCNT-MUS/Epoxy. This is may be due to low char yield within the silicate layer of muscovite causes less efficiency of silicate layers to decompose in faster rate. Generally, muscovite is a layered of tetrahedral-octahedral silicate sheet. By intercalated the lithium nitrate and CTAB into muscovite, the d-spacing of MWCNT-MUS was increased which expected to generate higher amount of exfoliated layers and lead to retard the degradation. Both of the pristine and treated MWCNT-MUS contain silicate layers which indicate the nano clay to retard degradation. But, as the MWCNT-MUS was treat using Li and CTAB, the structure of the carbon nanotubes was affected as the carbon nanotubes partially damage and become
shorter. As a consequence, the nanolayer affects the thermal characteristics when it is incorporated within the epoxy nanocomposites. Thermogravimetric analysis results are presented in Table 2.

![Thermogravimetric (TGA) analysis of MWCNT-MUS/Epoxy with 0.5 wt%, 1.0 wt% and 1.5 wt% filler loading](image)

Fig. 4. (a) Thermogravimetric (TGA) analysis of MWCNT-MUS/Epoxy with 0.5 wt%, 1.0 wt% and 1.5 wt% filler loading (b) Thermogravimetric (TGA) analysis of treated MWCNT-MUS/Epoxy with 0.5 wt%, 1.0 wt% and 1.5 wt% filler loading

![Thermogravimetric (TGA) analysis of neat epoxy, 0.5 wt% treated MWCNT-MUS/Epoxy, and 0.5 wt% of MWCNT-MUS/Epoxy](image)

Fig. 5. Thermogravimetric (TGA) analysis of neat epoxy, 0.5 wt% treated MWCNT-MUS/Epoxy, and 0.5 wt% of MWCNT-MUS/Epoxy

| Sample                        | $T_{\text{onset}}$ |
|-------------------------------|-------------------|
| Epoxy                         | 340.10            |
| 0.5 wt% MWCNT-MUS/Epoxy       | 374               |
| 1.0 wt% MWCNT-MUS/Epoxy       | 368.5             |
| 1.5 wt% MWCNT-MUS/Epoxy       | 362.7             |
| 0.5 wt% Treated MWCNT-MUS/Epoxy| 357.05            |
| 1.0 wt% Treated MWCNT-MUS/Epoxy| 351.4             |
| 1.5 wt% Treated MWCNT-MUS/Epoxy| 345.75            |

$T_{\text{onset}}$ denotes the decompositions temperature of the nanocomposites $T=\degree \text{C}$
4. Conclusion

MWCNT-MUS hybrid filler was successfully synthesized using chemical vapour deposition (CVD). This was proven by the Field Emission Scanning Electron Microscope (FESEM) which the micrograph shows the growth of CNT on the muscovite particle with the used of nickel as a catalyst. Surface treatment on the MWCNT-MUS hybrid filler was successfully carried out and proved by X-ray diffraction (XRD) analysis which the basal spacing of 001 plane, of MWCNT-MUS was enlarged from 21.00 Å to 27.20 Å after first stage of lithium nitrate (LiNO3) treatment to form Li-MWCNT-MUS. After second treatment by using CTAB the d (001) was further enlarged to 29.28 Å. Thermal properties of epoxy composites was improved with addition both of treatment and pristine MWCNT-MUS hybrid filler which the filler will slow the rate of thermal degradation and increased the maximum temperature $T_{\text{max}}$. Unfortunately, the treatment MWCNT-MUS/Epoxy show lower thermal properties compared to pristine MWCNT-MUS/Epoxy as the CNT partially damaged during the treatment.

Acknowledgements

This project was supported by the Research University Grant (1001/PBAHAN/814137) of University Science Malaysia (USM) for the financial assistance.

References

1. Camargo PHC, Satyanarayana KG & Wypych F. Nanocomposites: synthesis, structure, properties and new application opportunities. *Mater. Res.* 2009; 12: 1-39.
2. Kwon Y, Yim B-S, Kim J-M & Kim J. Dispersion and heat dissipation properties of functionalization carbon nanotubes in epoxy composites for electrically conductive adhesives (ECAs). *Microelectron Reliab* 2011; 51: 812-818.
3. Zhang WD, Phang IY & Liu T. Growth of carbon nanotubes on clay: Unique nanostructured filler for high-performance polymer nanocomposites. *Ad. Mater.* 2006; 18: 73-77.
4. Yan Y, Miao J, Yang Z, Xiao F-X, Yang HB, Liu HB & Yang Y. Carbon nanotube catalyst: recent advances in synthesis, characterization and applications. *Chem. Soc. Rev.* 2015; 44: 3295-3346.
5. Kudus MHA, Akil HM, Mohamad H & Loon LE. Effect of catalyst calcination temperature on the synthesis of MWCNT-alumina hybrid compound using methane decomposition method. *J. Alloys Compd.* 2011; 509: 2784-2788.
6. Olek M. Carbon nanotube composites-mechanical, electrical, and optical properties. Dr. Rer. Nat Rheinischen Friedrich-Wilhelms-Universität Bonn. Bonn 2006.
7. Yu X. The preparation and characterization of cetytrimethylammonium intercalated muscovite. *Microporous Mesoporous Mater.* 2007; 98: 70-79.
8. Feng X, Hu G, Meng X, Ding Y, Zhang S & Yang M. Influence of ethanol addition on the modification of montmorillonite by hexadecyl trimethylammonium bromide. *Appl. Clay Sci.* 2009; 45: 239-243.
9. Valera-Zaragoza M, Ramírez-Vargas E, Medellín Rodríguez FJ & Huerta-Martínez BM. Thermal stability and flammability properties of heterophasic PP-EP/EVA/organoclay nanocomposites. *Polym. Degrad. Stab.* 2006; 91: 1319-1325.
10. Siddiqui NA, Li EL, Sham M-L, Tang BZ, Gao SL, Mäder E & Kim J-K. Tensile strength of glass fibres with carbon nanotube-epoxy nanocomposites coating: effects of CNT morphology and dispersion state. *Compos Part A-Appl. S.* 2010; 41: 539-548.