



Laporan Akhir Projek Penyelidikan Jangka Pendek

**Development of Functionalized Carbon
Nanotubes Filled Woven Glass
Fiber/Epoxy Composites for Light Weight
Structure Applications**

By

**Prof. Ir. Dr. Mariatti Jaafar @ Mustapha
Prof. Dr. Zainal Arifin Mohd. Ishak
Prof. Dr. Abdul Rahman Mohamed**

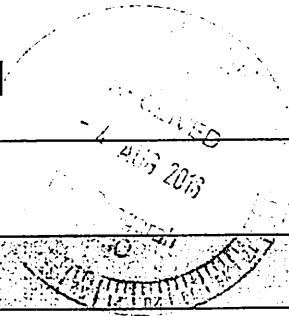
2016

Project Code :
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RU GRANT FINAL REPORT FORM

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A PROJECT DETAILS	
i	Title of Research: Development of Functionalized Carbon Nanotubes Filled Woven Glass Fiber/Epoxy Composites for Light Weight Structure Applications
ii	Account Number: 1001/PBAHAN/814153
iii	Name of Research Leader: Prof. Ir. Dr. Mariatti Jaafar
iv	Name of Co-Researcher: 1. Prof. Dr. Zainal Arifin Mohd. Ishak 2. Prof. Dr. Abdul Rahman Mohamed
v	Duration of this research: a) Start Date : 15 July 2012 b) Completion Date : 14 July 2015 c) Duration : 3 years d) Revised Date (if any) : 14 April 2016 (9 months)
B ABSTRACT OF RESEARCH	
<p>(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English. This abstract will be included in the Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)</p> <p>In the present study, composite based on multi-walled carbon nanotubes (MWCNTs), glass fiber (GF) and epoxy are fabricated by using the hand lay-up and vacuum bagging techniques. Three different methods were used to incorporate MWCNTs in GF/epoxy composites. The MWCNTs were incorporated in form of thin sheet known as buckypaper, or as particulate form by spreading or spraying onto the fabric. 3-ply and 4-ply GF/epoxy composites were used as a control. MWCNTs loadings used in spreading and spraying method are 0.4, 0.6 and 1.0 vol %. The properties of these composites were compared to the properties of control samples. It was found that 3-ply GF/epoxy with 0.6 and 1.0 vol% MWCNTs possessed density 7 and 8 % lower compared to 4-ply GF/epoxy.</p>	

Incorporation of MWCNTs in form of buckypaper has increased the flexural properties of the composites. The composite possessed 63 % and 13 % of flexural strength and flexural modulus, respectively higher compared to 3-ply GF/epoxy composites. 3-ply GF/epoxy with 0.6 vol% MWCNTs possessed the highest flexural strength which was 270 % and 219 % higher compared to 3-ply GF/epoxy and 4-ply GF/epoxy composites, respectively. 3-ply GF/epoxy with 0.6 vol% MWCNTs also exhibited the highest storage modulus and T_g . In short, this hybrid composite shows the highest performance compared to all other composites.

Dalam kajian ini, komposit berasaskan tiub nano karbon pelbagai berding (MWCNTs), gentian kaca (GF) dan epoksi telah dihasilkan dengan menggunakan teknik pelapisan tangan dan bag vakum. Tiga kaedah yang berbeza telah digunakan untuk menggabungkan MWCNTs dalam komposit GF / epoksi. MWCNTs telah dihasilkan untuk membentuk kepingan nipis dikenali sebagai 'buckypaper', atau dalam bentuk partikel dengan penyebaran atau penyemburan ke atas fabrik. Komposit GF / epoksi 3-lapis dan 4-lapis telah digunakan sebagai sampel kawalan dalam kajian ini. Pembebanan MWCNTs yang digunakan dalam kaedah penyebaran atau penyemburan adalah 0.4, 0.6 dan 1.0 % isipadu. Sifat-sifat komposit ini dibandingkan dengan sifat-sifat sampel kawalan. Keputusan menunjukkan bahawa komposit GF/epoksi 3-lapis dengan 0.6 dan 1.0 % isipadu MWCNTs memiliki ketumpatan 7 dan 8% lebih rendah berbanding komposit GF/epoksi 4-lapis. Penggunaan MWCNTs dalam bentuk 'buckypaper' telah meningkatkan sifat-sifat lenturan komposit. Komposit ini masing-masing menunjukkan peningkatan 63% dan 13% bagi kekuatan lenturan dan modulus lenturan, berbanding dengan komposit GF/epoksi 3-lapis. Komposit GF/epoksi 3-lapis dengan 0.6 % isipadu MWCNTs masing-masing menunjukkan kekuatan lenturan yang paling tinggi iaitu 270% dan 219% berbanding dengan Komposit GF/epoksi 3-lapis dan 4-lapis. Di dapati penggabungan 0.6 % isipadu MWCNT telah meningkatkan modulus simpanan dan T_g . Oleh itu komposit GF/epoksi 3-lapis dengan 0.6 % isipadu MWCNTs menunjukkan prestasi yang terbaik berbanding dengan semua bagi komposit lain yang dikaji.

C BUDGET & EXPENDITURE

i	Total Approved Budget	: RM 208,400.00
		<u>Yearly Budget Distributed</u>
		Year 1 : RM 68,500.00
		Year 2 : RM 74,000.00
		Year 3 : RM 65,900.00
	Total Expenditure	: RM 203,752.95
	Balance	: RM 4,647.05
	Percentage of Amount Spent (%)	: 98%

Please attach final account statement (eStatement) to indicate the project expenditure

ii Equipment Purchased Under Vot 35000

No.	Name of Equipment	Amount (RM)	Location	Status

5	W.A.D Wan Dalina, M.Mariatti, Z.A. Mohd Ishak, A.R. Mohamed, Effect of hybrid reinforcement of MWCNT and carbon fiber on properties of epoxy laminated composites, J. Polym Mater. Vol. 31, No. 4, 2014, 409-424 (IF=0.377)	Published
6	W.A.D. Wan Dalina, M. Mariatti, Z.A. Mohd Ishak, A.R. Mohamed, Comparison of properties of MWCNT/carbon fiber/epoxy laminated composites prepared by solvent spraying method, International Journal of Automotive and Mechanical Engineering (IJAME) 2014(10) 1901-1909 (Scopus)	Published
7	J. Ervina, M. Mariatti, S. Hamdan. Mechanical, electrical and thermal properties of multi-walled carbon nanotubes/ epoxy composites: effect of post-processing techniques and filler loading, Polymer Buletin. (IF=1.371)	Under review

b) Publications in Other Journals

No.	Publication (authors,title,journal,year,volume,pages,etc.)	Status of Publication (published/accepted/ under review)
1	Ervina Junaidi, Ong Boon Kian, Mariatti Jaafar and Sinin Hamdan. "Flexural properties for two-ply glass fiber reinforced composites with different loading of CNT/Epoxy film produced by different methods", Australian Journal of Basic and Applied Science (ISSN: 1991-8178), Special ICMMM 2014, 383-388.	Published
2	J. Ervina, M. Mariatti, S. Hamdan. Effect of Filler Loading on the Tensile Properties of Multi-walled Carbon Nanotube and Graphene Nanopowder filled Epoxy Composites. Procedia Chemistry 19 (2016) 897 – 905.	Published
3	W.A.D. W Dalina, M Mariatti, R. Ramlee, Z.A. Mohd Ishak, A.R. Mohamed, Comparison on the properties of glass fiber/MWCNT/epoxy and carbon fiber/MWCNT/epoxy composites, Advanced Materials Research 2014,858, 32-39	Published
4	W.A.D. Wan Dalina, M. Mariatti, S. H. Tan, Z.A. Mohd Ishak, A. R. Mohamed, "Fabrication and Properties of Multi-Walled Carbon Nanotubes Buckypaper", Advanced Materials Research, Vol. 1108, pp. 33-38, 2015	Published
5	W.A.D. Wan Dalina, M. Mariatti, S.H. Tan, Electrical conductivity properties of MWCNT Buckypaper/Epoxy composites: Effect of loading and pressure, Proceedings of the 23rd Scientific Conference of Microscopy Society Malaysia (SCMSM2014), AIP Conf.Proc. 1669 (2015)	Published
6	W.A.D. Wan Dalina, S. H. Tan, M. Mariatti, Properties of Fiberglass/MWCNT Buckypaper/Epoxy Laminated Composites, Procedia Chemistry, 2016 (19) 935-942	Published

c) Other Publications

(book,chapters in book,monograph,magazine,etc.)

No.	Publication (authors,title,journal,year,volume,pages,etc.)	Status of Publication (published/accepted/ under review)

d) Conference Proceeding

No.	Conference (conference name,date,place)	Title of Abstract/Article	Level (International/National)
1	NSPM2012, 3rd-5th Oct 2012, USM Engineering Campus	Properties of carbon nanotubes/Carbon fiber/epoxy laminated composites	National
2	27th Regional Conference on Solid State Science and Technology (RCSST27), Kota Kinabalu, 20-22 December 2013	Study on Multi-Walled Carbon Nanotubes Buckypaper Properties	International
3	International Conference on the Advancement of Materials and Nanotechnology 2013 (ICAMN III 2013), Penang, 19-22 November 2013	Flexural properties of Multi-Walled Carbon Nanotubes filled Carbon fiber laminated Composites	International
3	International Conference on Business, Science and Technology 2014, Hadyai, 25-26 April 2014	Flexural properties of Carbon Fiber/Multi-walled Carbon Nanotubes/Epoxy Laminated Composites	International

Please attach a full copy of the publication/proceeding listed above

iii Other Research Output/Impact From This Project
(patent, products, awards, copyright, external grant, networking, etc.)

E HUMAN CAPITAL DEVELOPMENT

a) Graduated Human Capital

Student	Nationality (No.)		Name
	National	International	
PhD	-	1	1. Zaid A Ghaleb
MSc	1		1. Boon Moon See
Undergraduate	2		1. Ong Boon Kian 2. Radziana Ramlee

b) On-going Human Capital

Student	Nationality (No.)		Name
	National	International	
PhD	2	-	1. Wan Dalina Wan Dahalan 2. Ervina Junaidi
MSc	-	-	1. 2.
Undergraduate	-	-	1. 2.

c) Others Human Capital

Student	Nationality (No.)		Name
	National	International	
Post Doctoral Fellow			1. 2.
Research Officer			1. 2.
Research Assistant	1		1. Sheril Rizal Vincent 2.
Others (.....)			1. 2.

F COMPREHENSIVE TECHNICAL REPORT

Applicants are required to prepare a comprehensive technical report explaining the project. The following format should be used (this report must be attached separately):

- Introduction
- Objectives
- Methods
- Results
- Discussion
- Conclusion and Suggestion
- Acknowledgements
- References

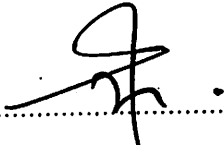
G PROBLEMS/CONSTRAINTS/CHALLENGES IF ANY

(Please provide issues arising from the project and how they were resolved)

Functionalization of multiwalled carbon nanotubes (MWCNTs) in big quantity is difficult to be carried out. Agglomeration of MWCNTs occurred after functionalization process.

H	RECOMMENDATION
	<p><i>(Please provide recommendations that can be used to improve the delivery of information, grant management, guidelines and policy, etc.)</i></p>

Project Leader's Signature:

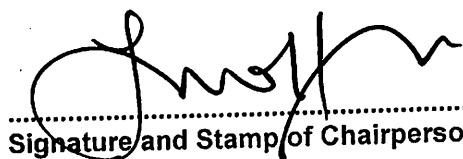


Name : **PROFESOR IR. DR. MARIATTI JAAFAR**
Timbalan Dekan
Akademik, Pelajar dan Alumni
Date : Pusat Peng. Kej. Bahan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia

28/7/16

COMMENTS, IF ANY/ENDORSEMENT BY PTJ'S RESEARCH COMMITTEE

Excellent research output. 6 ISI dan 1
Scopus cited journals have been published. The
researchers also published in 6 other journals
1 PhD and 1 MSc students have graduated
with 2 ongoing PhD candidates.



Signature and Stamp of Chairperson of PTJ's Evaluation Committee

Name :

Date :

29/7/16

PROF. MADYA DR. KHAIRUNISAK ABDUL RAZAK
Timbalan Dekan
Penyelidikan, Siswazah dan Jaringan
Pusat Peng. Kej. Bahan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia



Signature and Stamp of Dean/ Director of PTJ

Name :

Date :

29/7/16

PROF. MADYA DR. KHAIRUNISAK ABDUL RAZAK
Timbalan Dekan
Penyelidikan, Siswazah dan Jaringan
Pusat Peng. Kej. Bahan & Sumber Mineral
Kampus Kejuruteraan
Universiti Sains Malaysia

RU GRANT FINAL REPORT CHECKLIST

Please use this checklist to self-assess your report before submitting to RCMO.
Checklist should accompany the report.

NO.	ITEM	PLEASE CHECK (✓)		
		PI	JKPTJ	RCMO
1	Completed Final Report Form	✓		
2	Project Financial Account Statement (e-Statement)	✓		
3	Asset/Inventory Return Form (<i>Borang Penyerahan Aset/Inventori</i>)			
4	A copy of the publications/proceedings listed in Section D(ii) (Research Output)	✓		
5	Comprehensive Technical Report	✓		
6	Other supporting documents, if any			
7	Project Leader's Signature	✓		
8	Endorsement of PTJ's Evaluation Committee	✓		
9	Endorsement of Dean/ Director of PTJ's	✓		

UserCode: SHALYDAH / USMKCTLIVE / PBAHAN

Program Code: Votebook9100

Current Program : Votebook (Header)

Current Date : 28/07/2016 8:43:21 AM

Version: 15.124, Last Updated at 01/07/2016

DB: 13.00, 9/18/2010 VB: 13.01, 3/14/2011

Switch Language : English / Malay

Wildcard : eg. Like 100%, Like 10%1, Like %1

Element 1:

Element 2:

Element 4:

Element 5:

Year:

Detail	Excel	Budget Rule	Budget Control	Account Description	Budget Account Code	Roll over	Budget	Cash Received	Advanced	Commit	Actual	Available	Percentage
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		46	T	SubTotal		38,168.25	0.00	0.00	0.00	0.00	11,474.40	26,693.85	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.221.0.PBAHAN.814153	11,668.48	0.00	0.00	0.00	0.00	6,823.12	4,845.36	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.223.0.PBAHAN.814153	-42.30	0.00	0.00	0.00	0.00	3.20	-45.50	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.224.0.PBAHAN.814153	3,000.00	0.00	0.00	0.00	0.00	0.00	3,000.00	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.226.0.PBAHAN.814153	0.00	0.00	0.00	0.00	231.00	6,421.62	-6,652.62	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.227.0.PBAHAN.814153	17,254.94	0.00	0.00	0.00	0.00	11,289.53	5,965.41	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.228.0.PBAHAN.814153	7,330.00	0.00	0.00	0.00	0.00	2,100.00	5,230.00	0.00%
Detail	Excel	47	T	Projek Kumpulan Wang Uni Penyelidikan	1001.229.0.PBAHAN.814153	-8,116.68	0.00	0.00	0.00	0.00	24,891.44	-33,008.12	0.00%
		47	T	SubTotal		31,094.44	0.00	0.00	0.00	231.00	51,528.91	-20,665.47	0.00%
Detail	Excel	48	T	Projek Kumpulan Wang Uni Penyelidikan	1001.335.0.PBAHAN.814153	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00%
		48	T	SubTotal		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00%
Detail	Excel	50	T	Projek Kumpulan Wang Uni Penyelidikan	1001.552.0.PBAHAN.814153	0.00	0.00	0.00	0.00	13.86	1,367.47	-1,381.33	0.00%
		50	T	SubTotal		0.00	0.00	0.00	0.00	13.86	1,367.47	-1,381.33	0.00%
		9999		GrandTotal		69,262.69	0.00	0.00	0.00	244.86	64,370.78	4,647.05	0.00%

Development of Functionalized Carbon Nanotubes Filled Woven Glass Fiber/Epoxy Composites for Light Weight Structure Applications

Abstract

In the present study, multi-walled carbon nanotubes (MWCNTs), glass fiber (GF) and epoxy are fabricated by using the hand lay-up and vacuum bagging techniques. Three different methods were used to incorporate MWCNTs in GF/epoxy composites. The MWCNTs were incorporated in form of thin sheet known as buckypaper, or as particulate form by spreading or spraying onto the fabric. 3-ply and 4-ply GF/epoxy composites were used as a control. MWCNTs loadings used in spreading and spraying method are 0.4, 0.6 and 1.0 vol %. The properties of these composites were compared with the properties of control samples. It was found that 3-ply GF/epoxy with 0.6 and 1.0 vol% MWCNTs possessed density 7 and 8 % lower compared to 4-ply GF/epoxy. Incorporation of MWCNTs in form of buckypaper has increased the flexural properties of the composites. The composite possessed 63 % and 13 % of flexural strength and flexural modulus, respectively higher compared to 3-ply GF/epoxy composites. 3-ply GF/epoxy with 0.6 vol% MWCNTs possessed the highest flexural strength which was 270 % and 219 % higher compare to 3-ply GF/epoxy and 4-ply GF/epoxy composites, respectively. 3-ply GF/epoxy with 0.6 vol% MWCNTs also exhibited the highest storage modulus and T_g . In short, this hybrid composite shows the highers compared to all of the other composites.

Introduction

Incorporations of carbon nanotubes (CNTs) in composites such as glass fibers and carbon fibers are not new and proven to have ability to increase the performance of the composites. Thanks to the magnificent characteristics of the CNTs such as outstanding mechanical and thermal properties (Rigueur *et al.*, 2010; Zhang and Jiang, 2012), electrical as well as damping properties (Zhang and Jiang, 2012) and others. However, due to CNTs high aspect ratio (Böger *et al.*, 2010; Ma *et al.*, 2010) they tends to accumulates and form in bundles and ropes in the matrix. Therefore special mechanism or treatments are necessary to overcome the agglomerations problem hence optimize the exploitation of the superb properties of the CNTs.

In this study, MWCNTs were incorporated in 3-ply woven GF/epoxy composites through three different means. In the first method, the MWCNTs in form of buckypapers (MWCNTBP) were incorporated into the composite systems. Buckypaper is a planar film made of an entangled array of CNT that is held together by van der Waals interactions at the tube-tube junctions. These CNTs' buckypapers (CNT BPs) are flexible, porous, easy to handle and can form uniform film of almost any shape and size. In this method, two different types of MWCNTBP were utilized. The MWCNTBP used were either free-standing MWCNTBP or epoxy impregnated MWCNT prior to lamination procedure. The second and third methods involved dispersion of MWCNTs in diluted ink which acted as dispersing agent. Then the mixture prepared was either spread or sprayed onto the woven GF. All of the MWCNT/woven GF/epoxy composites were prepared by hand lay-up and followed by vacuum bagging method. The properties of these composites were compared to the properties of control samples of 3GF and 4GF.

properties of these composites were compared to the properties of control samples of 3GF and 4GF.

The aims of this research are to study the effect of partial replacement of GF with MWCNTs on the mechanical properties and weight reduction of MWCNT/woven GF/ epoxy composites. Besides that the effect of MWCNTs incorporation method on the properties of epoxy/woven GF composites can be determined. Characterization procedures performed allows the investigation on the damage mechanism in MWCNT/woven GF/epoxy composites in comparison with woven GF/ epoxy composites.

Materials

Multi-walled carbon nanotubes (MWCNT) with average outer diameter of $10 \text{ nm} \pm 1 \text{ nm}$ and $1 - 10 \text{ nm}$ length was purchased from Usains Holding, Universiti Sains Malaysia. The MWCNT with 80 % purity was synthesized by catalytic chemical vapor deposition process. MWCNT buckypapers which were initially prepared from vacuum filtration method. Woven glass fiber (GF) with 600 gm^{-2} of linear density used was purchased from Changshu Dongyu Insulated compound Materials, Co., Ltd, China. Commercial Chinese ink was used as MWCNT dispersing agent. Epoxy resin DER 332 as well as Polyetheramine D230 (hardener) were purchased from Penchem Technologies Sdn. Bhd. Deionized water was utilized through the study.

Methodology

In this study, the composite laminates were fabricated by hand lay-up and vacuum bagging method. Samples of MWCNT/woven GF/epoxy composites produced from different MWCNTs loading as well as MWCNTs dispersion methods. The samples fabricated were compared to control samples of 3-ply GF/epoxy and 4-ply GF/epoxy. The formulation of samples and sample loading fabricated are shown in the Table 1.

Table 1: Experimental design parameter.

No.	Sample	No. of GF Layer	CNT dispersion Method		CNTs (vol %)	Sample's Name
1.	Woven GF/Epoxy (control)	3	-		-	3GF
2.	Woven GF/Epoxy (control)	4	-		-	4GF
3.	MWCNT/woven GF/Epoxy	3	MWCNT buckypaper	MWCNTBP	2.8	CNTBP
4.		3		MWCNTBP/epoxy	2.8	CNTBPE
5.	MWCNT/woven GF/Epoxy	3	Spreading		0.4	CNT0.4
6.		3			0.6	CNT0.6
7.		3			1.0	CNT1.0
8.	MWCNT/woven GF/Epoxy	3	Spraying		0.4	CNT0.4S
9.		3			0.6	CNT0.6S
10.		3			1.0	CNT1.0S

Preparation GF/Epoxy Composites Laminates

Control sample of 3-ply woven GF/epoxy composite (refer as 3GF) which consists of 60 vol % fiberglass and 40 vol % epoxy resin was prepared by vacuum banging technique. The epoxy was mixed thoroughly with polyetheramine (hardener) at ratio 100:32. The predetermined amount of epoxy resin and hardener were mixed together. Adequate amount of epoxy was spread on the transparency sheet's surface. One ply of GF was laid on top of the epoxy layer. The roller was rolled over on the top of the fabric to ensure that the fabric was evenly wet by the epoxy resin. The procedure was repeated for the second and third layer of GF. After spreading the final layer of epoxy resin, a perforated plastic was placed on top of the layer followed by breather ply and vacuum bag. The sample was then consolidated by vacuum bagging for about 40 minutes. The consolidated GF/epoxy composite was left overnight curing. The sample was then cured at 60 °C for 2 hours and procured at 125 °C for 3 hours. Same procedures were implemented to produce another control sample of 4-ply woven GF/epoxy composite (refer as 4GF).

Preparation of MWCNT Buckypaper/woven GF/Epoxy Composites Laminates

In preparation of MWCNT reinforced woven GF/epoxy composites, two layers of MWCNTBP have been alternately inserted in between GF. In this composite, the epoxy resin was fixed at 40 vol %. However, two different types of MWCNTBP have been used. The sample incorporated with MWCNTBP is refers as CNTBP. Another sample was fabricated by incorporating epoxy impregnated MWCN BP (MWCNTBP/epoxy) and this sample is refers as CNTBPE.

In fabrication of CNTBP composites, adequate amount of epoxy was spread evenly on top of the transparency sheet. Then GF was laid on top of the resin. Roller was used to roll-over the GF so that the GF was laid flat and the resin could wet the GF uniformly. Same processes were repeated for each layer. The GF and MWCNT BP were alternately laid on top of the resin. The final layer of GF was then spread with epoxy resin and then the sample was then consolidated via vacuum bagging. The curing and post-curing were performed as in fabrication of 3GF. Same procedures were implemented in fabrication of CNTBPE composites. However, out of 40 vol % of epoxy, 15 vol % of epoxy was impregnated through the 2 pieces of MWCNTBP to produce (MWCNTBP/epoxy). The epoxy impregnated MWCNTBP were left in room temperature about 24 hrs to cure. Then the fabrication of CNTBPE composite was performed as mentioned in fabrication of CNTBP composites. Figure 1 shows the schematic diagram of the fabrication procedure for CNTBPE and CNTBP samples.

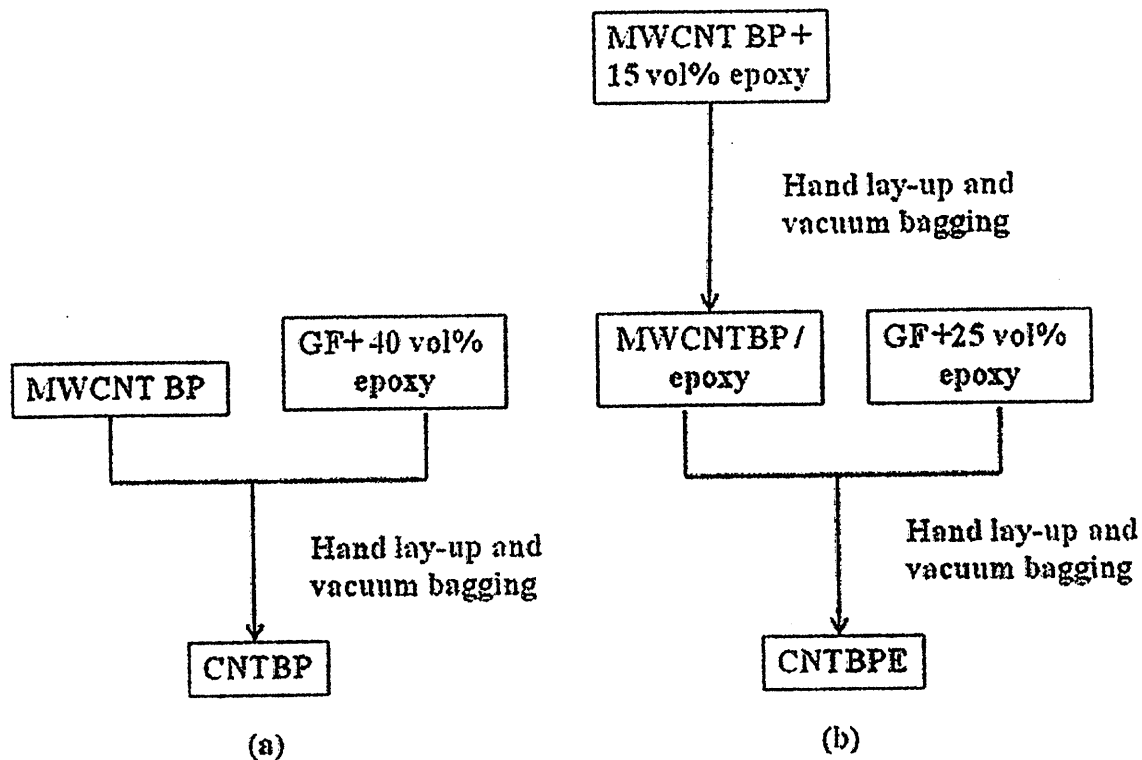


Figure 1. Schematic diagram of the fabrication procedure for CNTBP and CNTBPE samples.

Preparation of MWCNT/GF/Epoxy Composites Laminates by Spreading and Spraying Method

In preparation of 0.4CNT composites, the predetermined amount MWCNT was dispersed in diluted ink solution consists of 2.56 vol % of ink and 60 ml of deionized water. The mixture was then stirred thoroughly using a glass rod followed by agitation processing using ultrasonic probe for 30 minutes. The prepared mixture was then spread evenly on 2 pieces of fabrics. The spreading of mixture was performed at one side of the fabric only. The fabrics spread with MWCNT/ink were left to dry for about 2 hours.

The stacking of the dried GF was performed by hand lay-up and vacuum bagging in the same manner as discussed in the preparation of GF/epoxy laminated composites. The first and third layer used the fabric spread with MWCNT. The surface with MWCNT for each layer was laid so that they were facing the fabric without MWCNT. The sample was then consolidated, cured and post-cured in the same manner the GF/epoxy composite was fabricated. Same procedures were repeated in fabrication of 0.6CNT and 1.0CNT composites.

Fabrications of composites by spraying method also were performed as mention in fabrication of sample spreading method. Somehow in this method, the MWCNTs were not spread but sprayed onto the fabric. Figure 2 shows the diagram of stacking procedure for MWCNT/GF/epoxy composites which the MWCNTs were dispersed by spreading method.

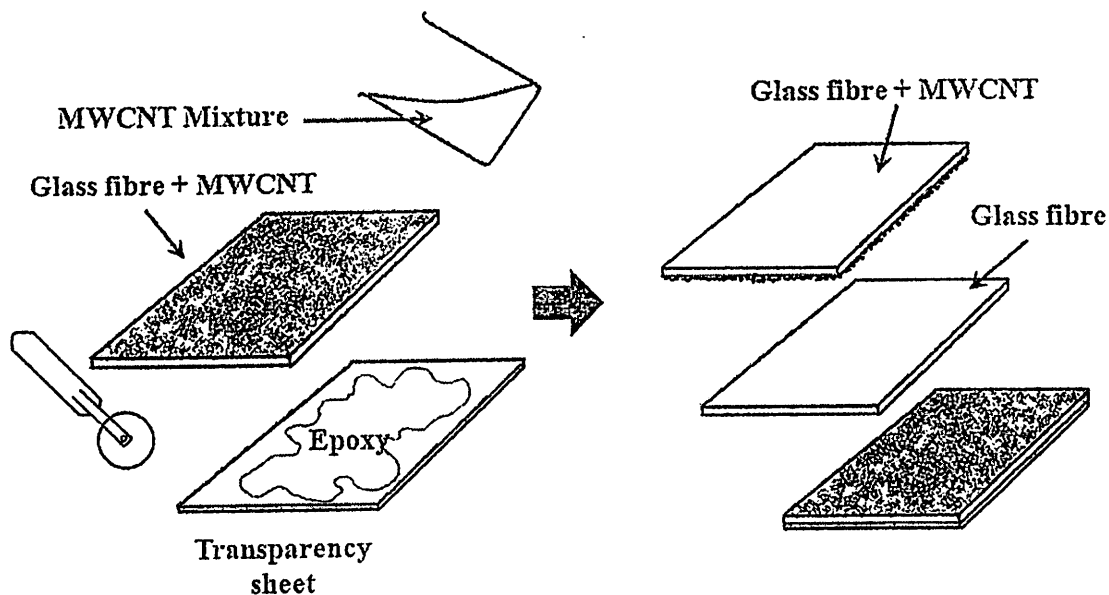


Figure 2. The diagram of stacking procedure for MWCNT/GF/ epoxy composites which the MWCNTs were dispersed by spreading method.

Characterization

The actual density of the sample was measured according to ASTM D792. In this method, the densities of five specimens were obtained by applying Archimedes's Principle. The average density of the sample was then calculated. To determine the void content of the composites, theoretical density of the composites were calculated based on rule of mixture. The difference between the theoretical densities compared to actual densities (ASTM D792) was calculated. The ratio of the difference between the actual density and the theoretical density, to the theoretical density is referred as void content.

The flexural properties of the samples were determined according to ASTM D3039. Ten specimens with dimension of 60 mm x 13 mm x t mm were tested by using INSTRON 5982 aided with Bluehill 2 software. The span of each specimen is fixed at 34 mm so that the ratio of span-to-depth ratio was more than 16:1. The flexural test was performed with cross head speed of set at 2 mm/min.

Dynamic mechanical analysis was performed by utilizing Mettler Toledo DMA 861 analyzer. Bending mode was selected. Solid samples with dimension 50 mm x 1 mm x thickness rectangular bars were tested at increasing temperature from room temperature to 150 °C with heating rate of 5 °C/min. The oscillatory sine-wave stress was applied at frequency of 1 Hz, while force amplitude was set at 1 N with displacement amplitude of 10 µm. Liquid nitrogen was used to cool down the system.

The fractured surfaces of the composite samples were observed using scanning electron microscopy (SEM). The 'stick-on tape' test was performed by sticking a piece of cellophane tape onto the surface of GF spread or sprayed with MWCNTs. To ensure that same forces have been applied while placing the cellophane tape onto the fabric, a piece of metal block was placed onto the fabric attached with cellophane tape for about 5 minutes. Then the cellophane tape was detached from the fabric. The more MWCNTs attached onto the cellophane tape, the more loosely bonded the MWCNTs onto the fabric.

Results and Discussion

Effect of incorporating MWCNT Buckypaper in woven GF/epoxy composites

In this method, MWCNT has been incorporated in the woven GF composites in form thin sheet known as buckypaper. The properties of the composites prepared were compared to the properties 4GF and 3 GF composites. The properties of the composites fabricated are discussed in the next sub-section below.

Density and void content

Table 2 summarized the density and void contents of the composites. The density of 3GF and 4 GF are expected to be similar as both composite systems consist of 60 vol % of fiber reinforcement and 40 vol % of epoxy resin. However, insignificant attenuation of the 3GF sample is observed and found to be due to the presence of slightly higher void content in 3GF composites. Incorporation of MWCNT in form of buckypaper in the composite systems caused reduction in the density of the composites and estimated to be about 1.97gcm^{-3} . Somehow, it seems that the density of the composites incorporated with MWCNT buckypaper possessed significantly lower density compared to the estimated value. 3GFCNTBP exhibited the lower density compared to 3GFCNTBPE even though they are expected to possessed similar density value. Higher void content in GFCNTBP might be due to the failure of epoxy impregnation through the MWCNTBP during the fabrication process. The presence of voids which normally exists between the laminates may affect the performance of the composites.

Table 2. Density and void content of the composites.

Composite Samples	Density (g/cm^3)	Void Content (%)
3GF	1.992	0.599
4 GF	1.987	0.872
CNTBP	1.737	11.895
CNTBPE	1.760	10.729

Flexural properties of the composites

Figure 3 illustrates the flexural strength and modulus of the composites. 4GF composites possessed 15.35 % flexural strength higher compared to 3GF. This expected increment is definitely due to the increment of the number of ply of woven glass fiber in the composites. Both CNTBP and CNTBPE exhibited flexural strength of 19 and 63 %, respectively higher than 3GF. Besides, the flexural modulus of both composites was found to be higher up to 13 % compared to the flexural modulus of 3GF. Such increment was definitely due to the incorporation of MWCNTs. MWCNTs provide a better load transfer from epoxy towards the GF reinforcement, hence promoting even forces distribution throughout the whole composite system (Kim *et al.*, 2009; Godara *et al.*, 2010).

Comparison made between the CNTBP and CNTBPE showed that CNTBP possessed lower flexural strength. The reduction in the flexural strength of CNTBP was probably due to inefficient epoxy impregnation through the MWCNTBP during vacuum bagging process hence creating voids. The voids in the composites hinder uniform stress distribution from the brittle matrix toward the strong fiber reinforcements. The presence of voids in between the laminates created weak bonding between the fibers or fillers thus attenuated the strength and stiffness of the composites (Karger-Kocsis *et al.*, 2015). Besides that, inefficient epoxy impregnation

created regions with weak buckypaper-matrix interface. As the CNTBP composites were made of free-standing MWCNTBP, the weakly bonded MWCNTs inside the buckypaper created weak regions in the composites. Therefore, CNTBP possessed lower flexural strength compared to CNTBPE. Evidences regarding the facts discussed above are proven by observation via SEM.

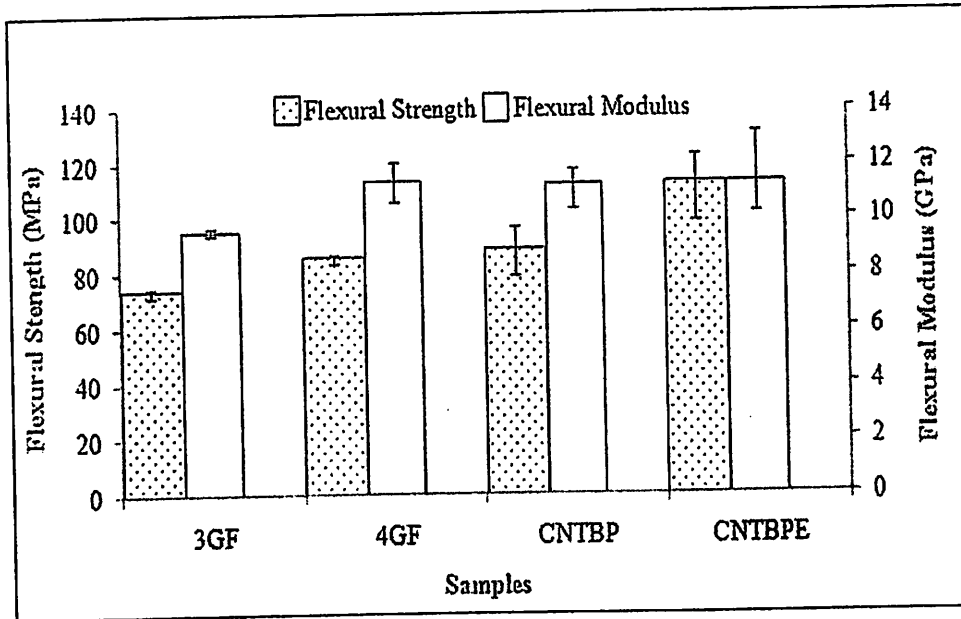


Figure 3. Flexural strength and flexural modulus of 3GF, 4GF and composites incorporated with MWCNTBP(Dalina *et al.*, 2016).

Figure 4 illustrates the fracture surface of the CNTP composite samples. Based on Figure 4 (a) and (b), it seems breakage of the fiber in the composite was due to the load applied onto the composite. Crack that occurred at the fiber glass further propagated along the fiber-matrix interface region (Figure 4 (d)). The crack then continues to propagate along the epoxy-MWCNTBP interface thus resulting failure in the composite system. As the MWCNTs in the buckypaper were weakly bonded together, the stress distributed in the buckypaper caused it to break as shown in Figure 4 (c).

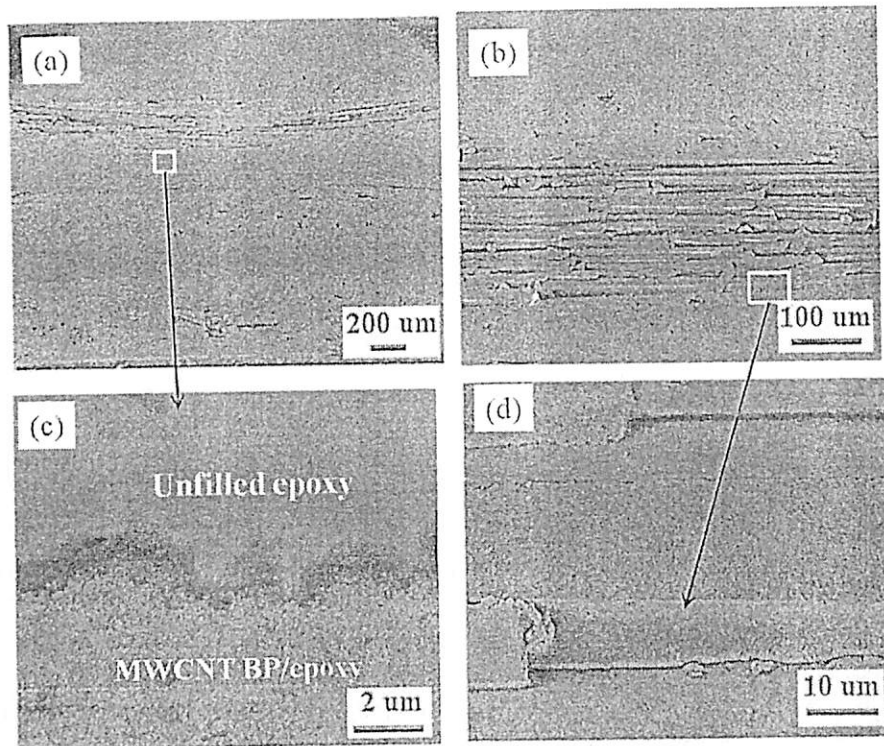


Figure 5. Fracture surface of CNTBPE sample; (a) overall fracture surface at 25 x magnification; (b) fiber broken in the composite at 100 x magnification; (c) failure in the matrix-MWCNTBP/epoxy interface at 5K x magnification; (d) cracks in the fiber propagated along the fiber-matrix interface at 1K x magnification (Dalina *et al.*, 2016).

Figure 6 illustrates the stress-strain curves of the 3GF, 4GF and composites incorporated with MWCNTBP. Based on Figure 6, it is observed that 4GF composite was stiffer than 3GF though both composites consist of 60 vol % of fiber reinforcement and 40 vol % of epoxy matrix. 3GF composite was found to be more flexible due to the reduction in the thickness of the composites compared to 4GF. The flexibility of the laminated composites are indirectly proportional to the thickness of the laminates (Dalina *et al.*, 2016). On the other hand, both composites incorporated with MWCNTBP showed similar trends as 3GF composites. However, CNTBP composite seems to be the most flexible compared to the other composites samples. The specific strength and specific modulus of the composites were shown in Table 3. Based on Table 3, it is found that CNTBPE composites possessed the highest specific strength and specific modulus compared to the other composites samples due its lower density but high flexural strength (Okubo *et al.*, 2004).

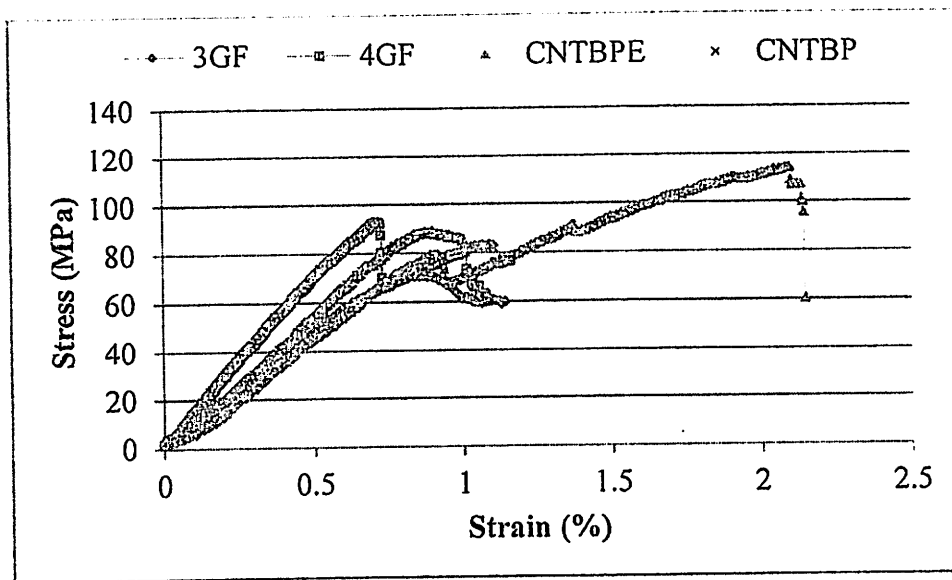


Fig. 6. Stress-strain curve of 3GF and 4GF and hybrid composites of CNTBP and CBTBPE (Dalina *et al.*, 2016).

Table 3. Specific strength and specific modulus of composites samples (Dalina *et al.*, 2016).

Composite Samples	Specific Strength (MPa/gcm ⁻³)	Specific Modulus (GPa/gcm ⁻³)
3GF	37.23	4.97
4 GF	42.89	5.67
CNTBP	50.84	6.42
CNTBPE	68.42	6.43

Dynamic mechanical analysis of the composites

Figure 7 illustrates the storage modulus of the composites with or without MWCNTs. generally, it seems that the storage modulus of those composites decreased with temperature. Reduction in the storage modulus was due to the softening of the epoxy matrix at elevated temperature prior reaching its constant modulus after the glass transition temperature, T_g (Dalina *et al.*, 2014). The storage modulus values are corresponding to the flexural modulus value (measured by static test). Composites incorporated with buckypaper (CNTBP and CNTBPE) possessed higher storage modulus compared to 3GF and 4GF. CNTBP and CNTBPE

possessed storage modulus of 46 and 59 %, respectively higher compared to 4GF. This showed that incorporation of the MWCNTs in the composites aided in increment of the storage modulus of the composites.

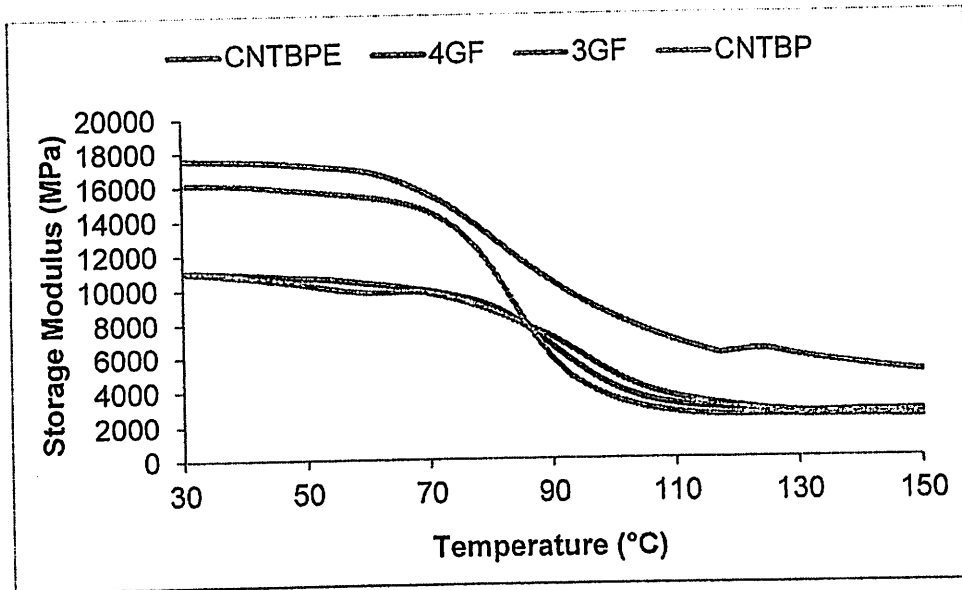


Fig. 7. Storage modulus of 3GF, 4GF, CNTBP and CBTBPE composites.

Figure 8 depicts the variations of the loss modulus of the composites as a function of the temperature. Loss modulus indicates the amount of energy dissipated as heat by the composites (Rwawiire *et al.*, 2014). Generally, the loss modulus increased with increasing temperature until reaching T_g , where the loss modulus rapidly fall. Both CNTBP and CNTBPE composites demonstrated peaks with distinct amplitude compared to 3GF and 4GF. Such phenomenon might be associated with more complex structural relaxation behavior of the composites incorporated with the MWCNTs (Margem *et al.*, 2010). Comparing composites with MWCNTs to 3GF and 4GF, it seems that the peaks of the loss modulus are displaced at lower temperature. According to Margemet *al.*, displacements of the loss modulus at lower temperature are associated with the increment in the epoxy chains flexibility. CNTBP and CNTBPE possessed higher peak value compared to 3GF and 4GF.

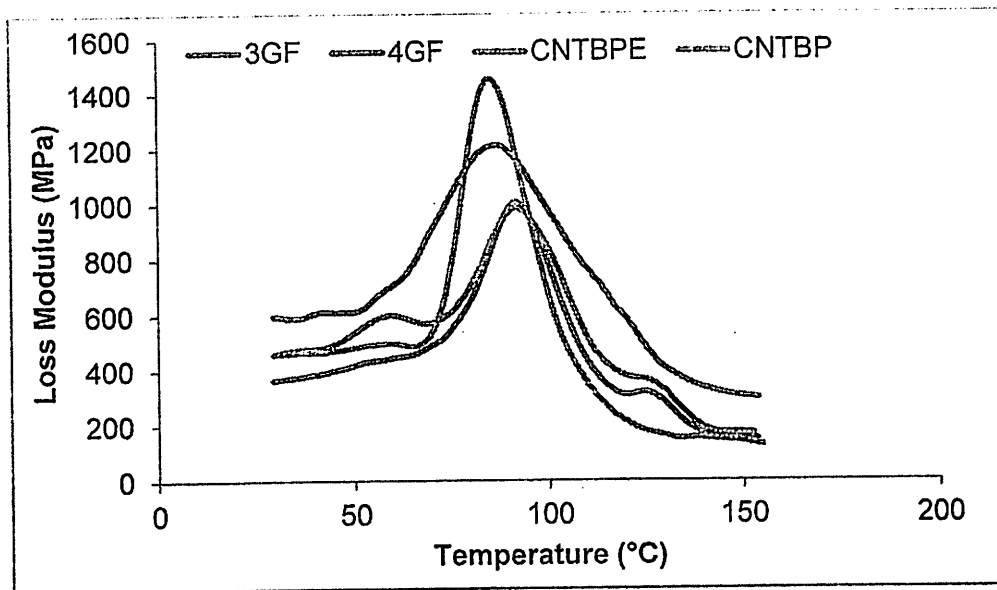


Figure 8. The variations of the loss modulus of the composites as a function of the temperature.

Figure 9 illustrates the tan delta of the selective composite samples. The loss factor tan delta, which is indicated by the ratio of the loss in flexural modulus to the loss in storage modulus, represents the mechanical damping or internal friction in a viscoelastic system. The T_g of the samples were estimated based on the temperature of the peak tan delta curves. Based on the tan delta curves, CNTBP and CNTBPE possessed lower peak compared to 3GF and 4GF. Lower peak indicates the lower energy dissipation. Rwawiire *et al.* stated that weak fiber-matrix bonding interfaces are sources of crack initiation, therefore higher energy is dissipated compared to the composites with strong fiber matrix-bonding. This showed that CNTBP and CNTBP possessed stronger reinforcement-matrix interfaces compared to 3GF and 4GF. Even though incorporation of MWCNTs in the composites were expected to increase the T_g , but somehow both CNTBP and CNTBPE composites possessed lower T_g compared to 3GF and 4GF. This might be due to the presence of the unsuccessfully evaporated ethanol in the MWCNTBP which was used during fabrication of MWCNTBP. The presence of ethanol leads to plasticizing effect which loosens the network structure and thus reduces the thermal stability of the composites.

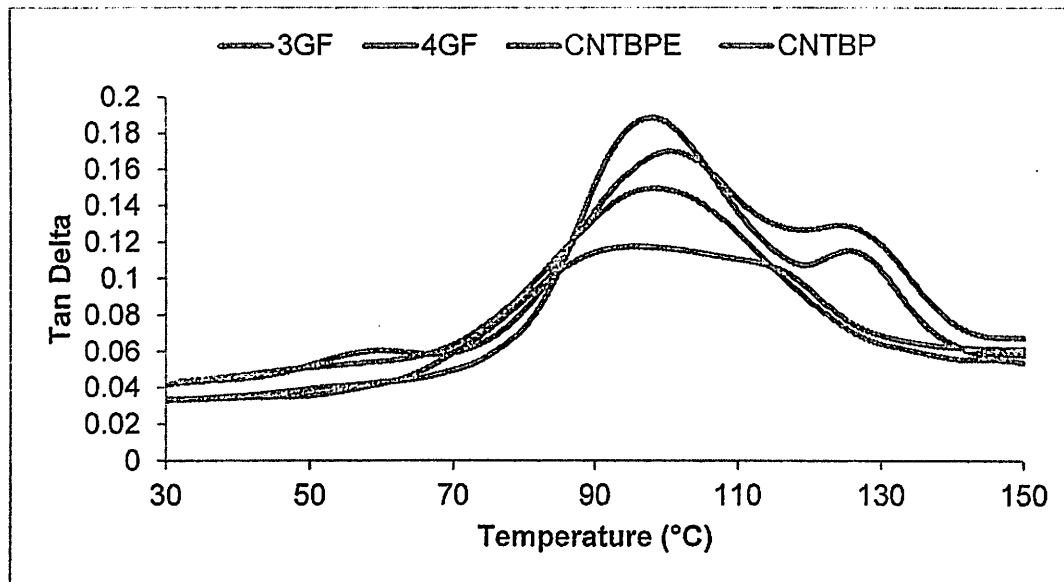


Figure 9. The tan delta of the composite samples.

Effect of MWCNT loading and incorporating method on the properties MWCNT/woven GF/epoxy composites

Density and void content

Table 4 summarized the density and void contents of the composites. As estimated, incorporation of lower density of MWCNTs in the composite systems caused reduction in the density of the composites. Basically, both methods either spreading or spraying demonstrates similar trends in changes of densities with increasing MWCNTs loading. The densities of the composites were found to be increased with increasing filler loading. Similar phenomenon was observed by Gajendran and Saraswathy, and Ogaswara et al. (Dalina *et al.*, 2014). CNT0.6 and CNT1.0s possessed density 7 and 8 % lower compared to 4GF. However the densities of the composites samples of CNT0.6 and CNT1.0S were contradicted to such observation. The density of the CNT1.0 composites was reduced while the density of CNT1.0S maintained at 1.838gcm^{-3} . The contradiction occurred can be explained by the presence of voids in the composites. Incorporation MWCNTs at higher filler loading can lead to agglomeration problem which eventually caused the formation of the void in the composites.

Table 4. The densities and void contents of the composites.

Composite Samples	Density (g/cm^3)	Void Content (%)
3GF	1.992	0.599
4 GF	1.987	0.872
CNT0.4	1.852	3.407
CNT0.6	1.855	3.107
CNT1.0	1.842	3.561
CNT0.4S	1.827	4.578
CNT0.6S	1.838	4.137
CNT1.0S	1.838	3.889

Bar chart in Figure 10 shows the variations of the flexural strength of the composites against the temperature. Basically it seems that the incorporation of the MWCNTs in the composites regardless the methods used has granted the composites with better flexural strength compared to 3GF and 4GF. Addition of 0.4 vol % of MWCNTs by spreading method (CNT0.4) has increased the flexural strength compared to 3GF and 4GF. As the filler loading was increased to 0.6 vol % (CNT0.6), the flexural strength has increased to 270 % and 219% compare to 3GF and 4GF, respectively. However, further addition of MWCNTs (1.0 vol %) resulted attenuation of the flexural strength which is about 32 % lower compared to CNT0.6 composites.

The addition of 0.4 vol % MWCNTs in the composite has increased the flexural strength compared to 3GF. Somehow the amount of MWCNTs incorporated was insufficient to strengthen the fiber-matrix interface (Dalina *et al.*, 2014). The highest flexural obtained by CNT0.6 composite proved that amount of 0.6 vol % of MWCNTs was the optimum MWCNTs loading in the fabrication of MWCNT/woven GF/epoxy composites by spreading method. Other than acting as a dispersing agent, the presence of glue in the ink aided the attachment of the MWCNTs onto the woven GF. This factual can be proven by 'stick-on tape' tests which were done to observe the attachment of the MWCNTs on the woven fibers.

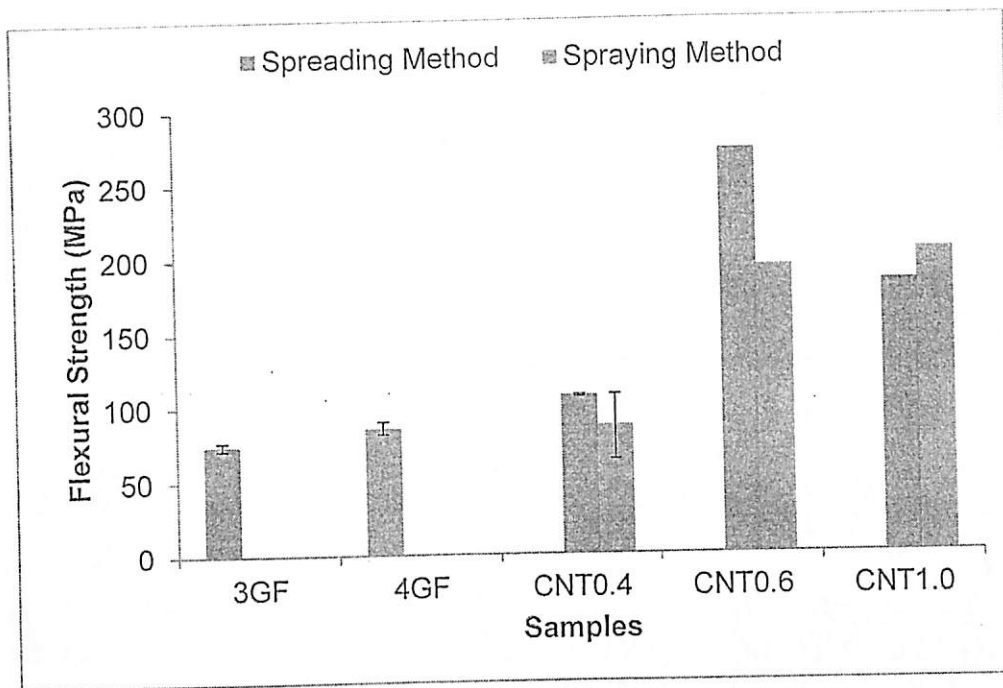


Figure 10. Variations of the flexural strength of the composites against the temperature.

Figure 11 demonstrates the surface of the cellophane tapes after being detached from the woven GF spread with ink, MWCNTs and MWCNT dispersed in ink. Dark stains that attached on the cellophane tape (Figure 11 (a)) show the presence of carbon black in the ink. Dispersion of MWCNTs only in deionized water caused the MWCNTs to be loose attached to the woven GF. As a result, more MWCNTs were found stick onto the cellophane tape in the detachment test as shown in Figure 11 (b). However, in the test performed onto the surface spread with MWCNTs dispersed in deionized water with the help of ink, less MWCNTs were found attached on the cellophane tape as illustrated in Figure 11 (c). This proven that the ink implemented in this research not only acting as dispersing agent but also helped to strongly attached the MWCNTs on the surface of the GF.

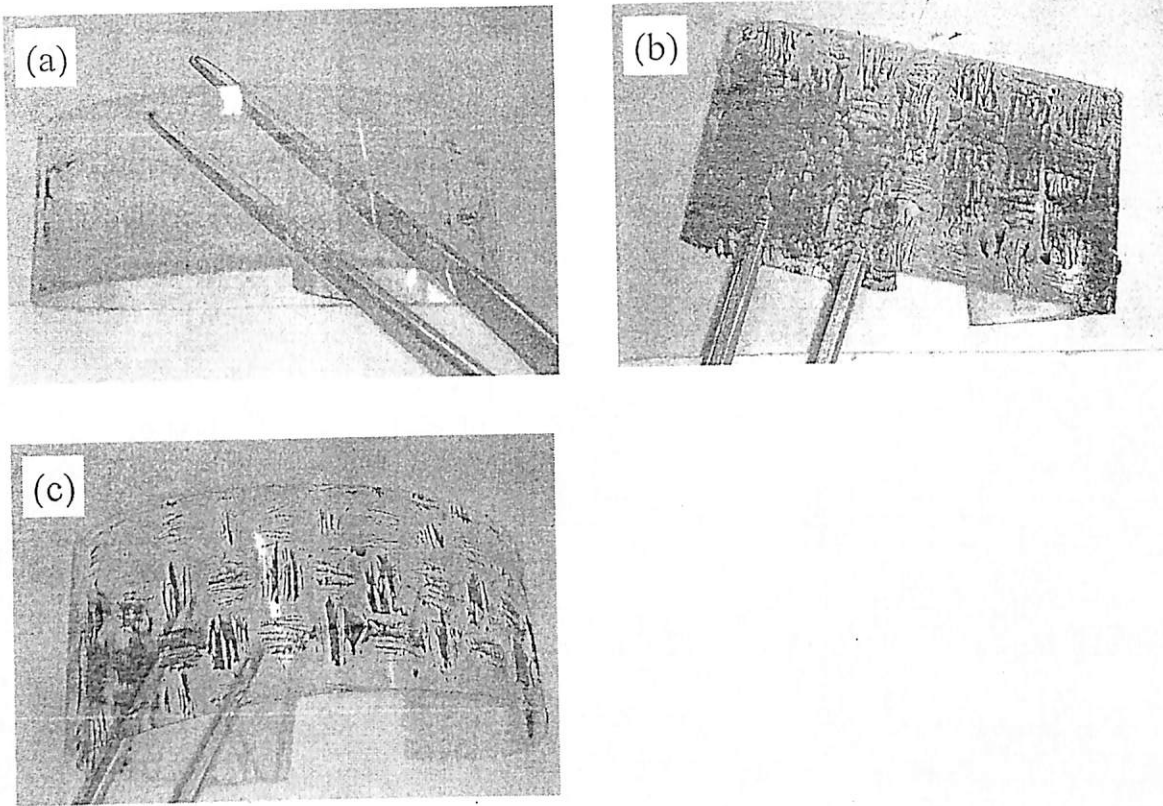


Figure 11. The surface of the cellophane tapes after being detached from the woven GF; (a) spread with ink; (b) MWCNTs dispersed in deionized water; (c) MWCNT dispersed in water with ink as dispersing agent.

At higher filler loading (CNT1.0), the MWCNTs have higher tendency to agglomerate. Agglomerations of MWCNTs prevent the maximum exploitation of the MWCNTs characteristics in the composites. Agglomerations not only prevent the uniform load transfer in the composites but also lead to improper epoxy impregnation. Different from spreading method, the flexural strength of the composites prepared by spraying method continued to increase with the increasing of filler loading. CNT1.0S exhibited the highest flexural strength compared to the other composite samples prepared by the same method. CNT1.0S possessed flexural strength of 176% and 139% higher compared to 3GF and 4GF. Somehow, the flexural strength of CNT1.0S was still lower compared to CNT0.6. The reason behind this phenomenon was probably due to inability to control the spraying process. Some of the MWCNTs might be loss in the environment or trapped in the spraying equipment.

As the spraying procedure made used of the air compressor, the MWCNTs sprayed not only attached on the surface of the woven fabric. The higher pressure acting on the nozzle sprayer caused the MWCNTs to be penetrated in between the warp, weft and even on the opposite surface of the woven GF. Therefore the amount of MWCNTs implemented even at 1.0vol % of filler loading was still insufficient to improve the flexural strength of the composites to achieve the highest performance. Figure 12 shows the surface of the woven GF being either

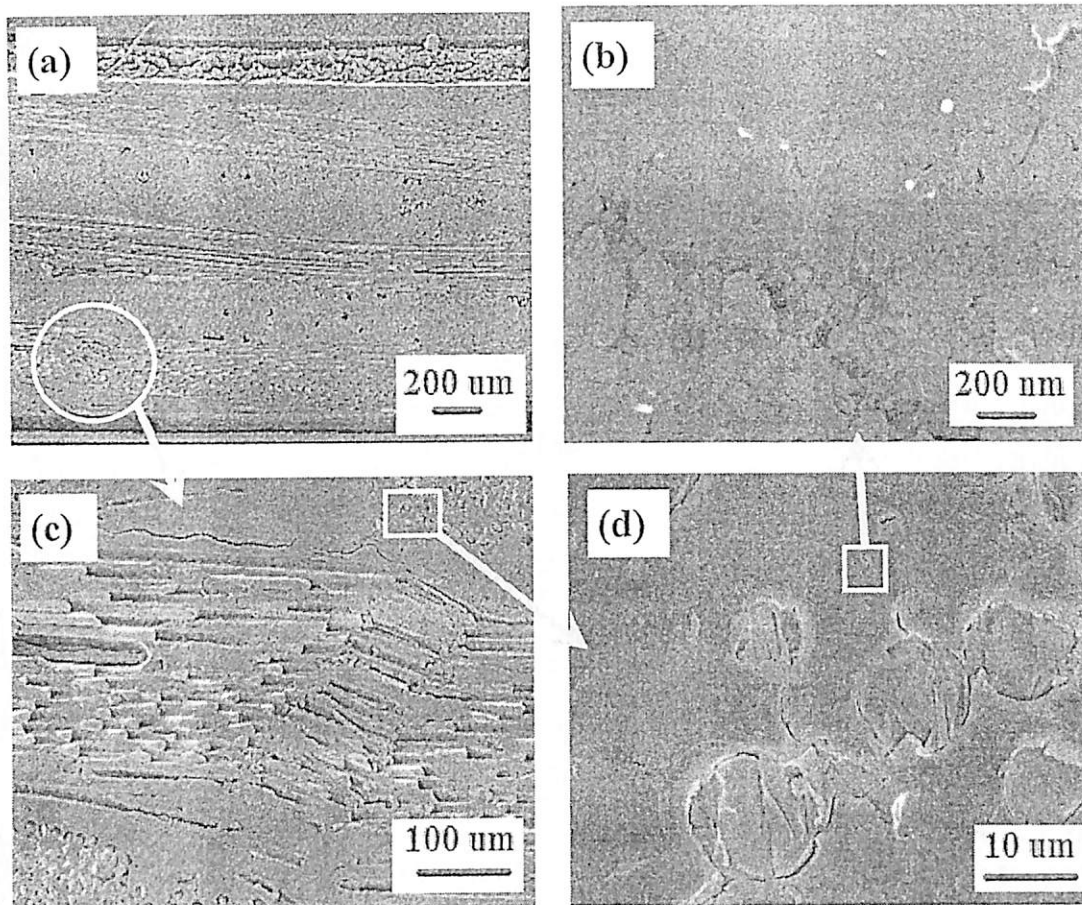


Figure 13. The fractured surfaces of CNT0.6 composite; (a) overall fracture surface at 25 x magnification; (b) failure in the matrix-MWCNT interface at 30K x magnification; (c) fiber broken in the composite at 100 x magnification; (d) rough cracks in the GF at 1K x magnification.

Figure 14 illustrates the micrographs of fractured surfaces CNT0.6S composites. Based on Figure 14 (b) and (d), it can be said that incorporation of 0.6 vol % of MWCNTs by spraying method produced CNT0.6S composite with strong fiber-matrix bonding as well as good filler-matrix interface. However due to insufficient of MWCNTs loading, the epoxy matrix and GF fiber were unable to withstand the load thus caused the fiber to break catastrophically (Figure 14 (b)). Figure 15 shows micrographs of fractured surfaces CNT1.0S composites. There was no evidence of broken fiber in the CNT1.0S composite. Again short MWCNTs surrounded by epoxy and rough cracks that occurred in the fiber proven that good filler-matrix interface as well as strong fiber-matrix bonding existed in the composites (Figure 15 (a) and (b)).

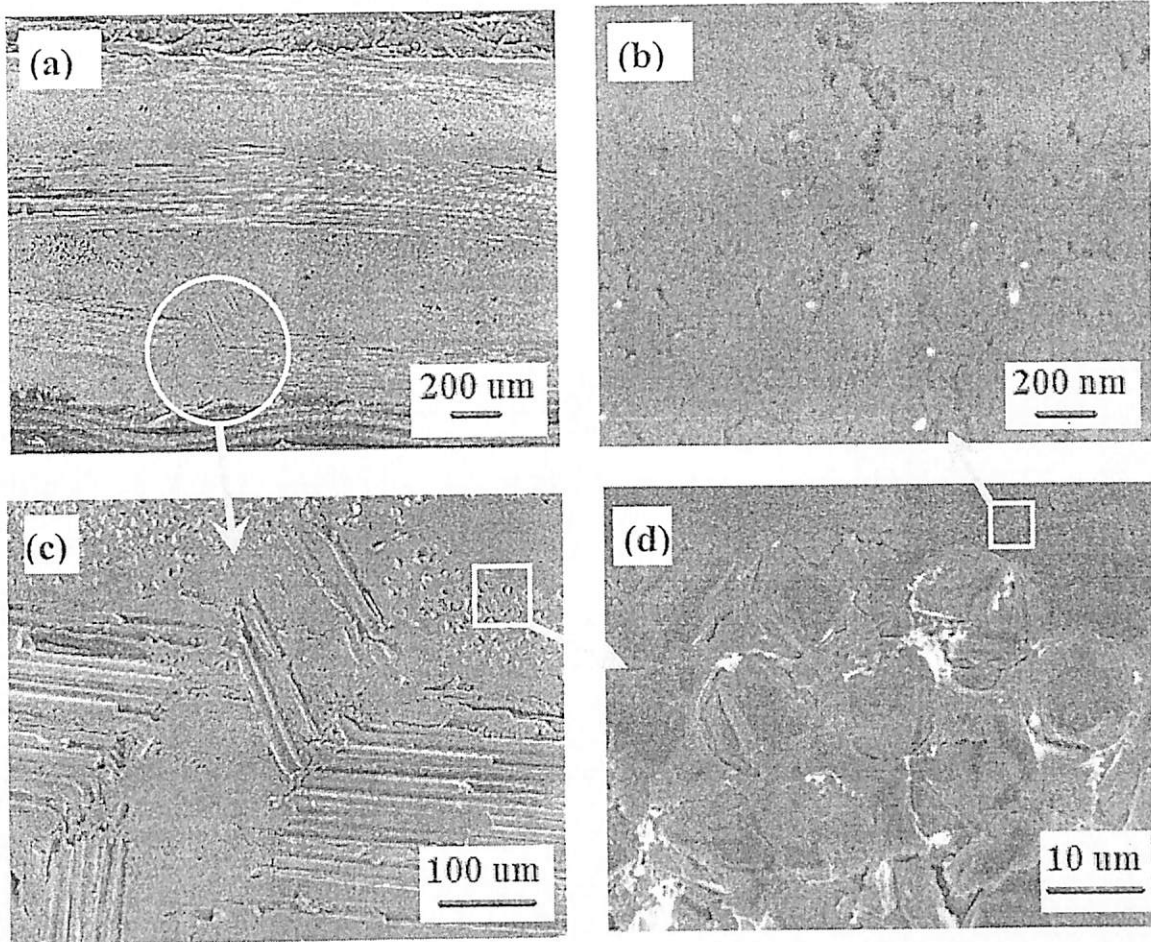


Figure 14. The fractured surfaces of CNT0.6S composite; (a) overall fracture surface at 25 x magnification; (b) failure in the matrix-MWCNT interface at 30K x magnification; (c) fiber broken in the composite at 100 x magnification; (d) rough cracks in the GF at 1K x magnification.

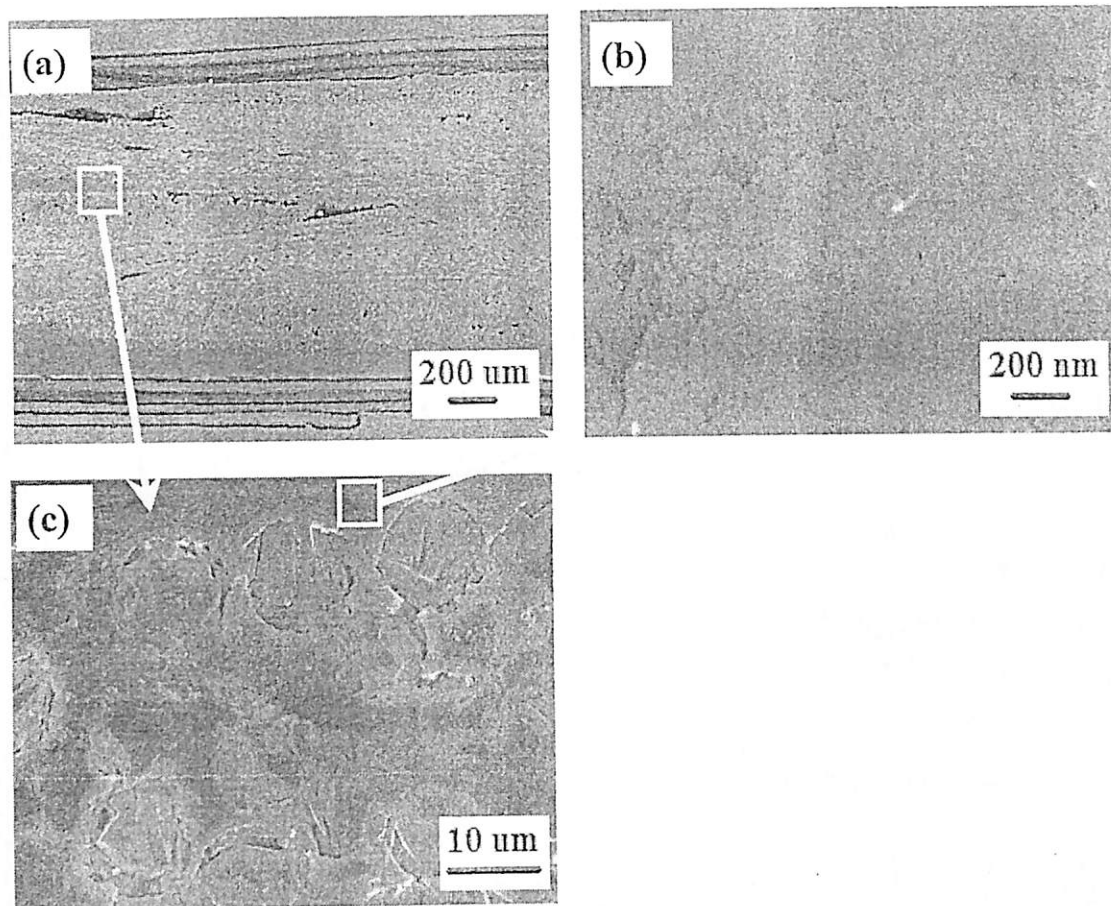


Figure 15. The fractured surfaces of CNT1.0S composite; (a) overall fracture surface at 25 x magnification; (b) failure in the matrix-MWCNT interface at 30K x magnification; (c) rough cracks in the GF at 1K x magnification.

Figure 16 shows the variations of the flexural modulus of the composites against the temperature. Generally, similar trend of changes in the composite samples prepared by either spreading or spraying. The flexural modulus of CNT0.4 is 4 % higher than 3GF but about 10 % lower compared to 4GF. Addition of 0.6 vol % MWCNTs in the composites (CNT0.6) has increased the flexural modulus up to 16 % compared to 4GF. However, the flexural modulus dropping at higher filler loading (CNT1.0) and this was due to the presence of MWCNTs agglomerations in the composites. The presence of the agglomerations were proven by observing the surface of the GF spread with MWCNT via SEM as shown in Figure 17. On the other hand, composites which MWCNTs were dispersed onto the GF by spraying method demonstrated continuous increment of the flexural modulus. CNT1.0S composite possessed the highest flexural modulus compared to the other composites. This composite exhibited flexural modulus about 23 % compared to 4GF.

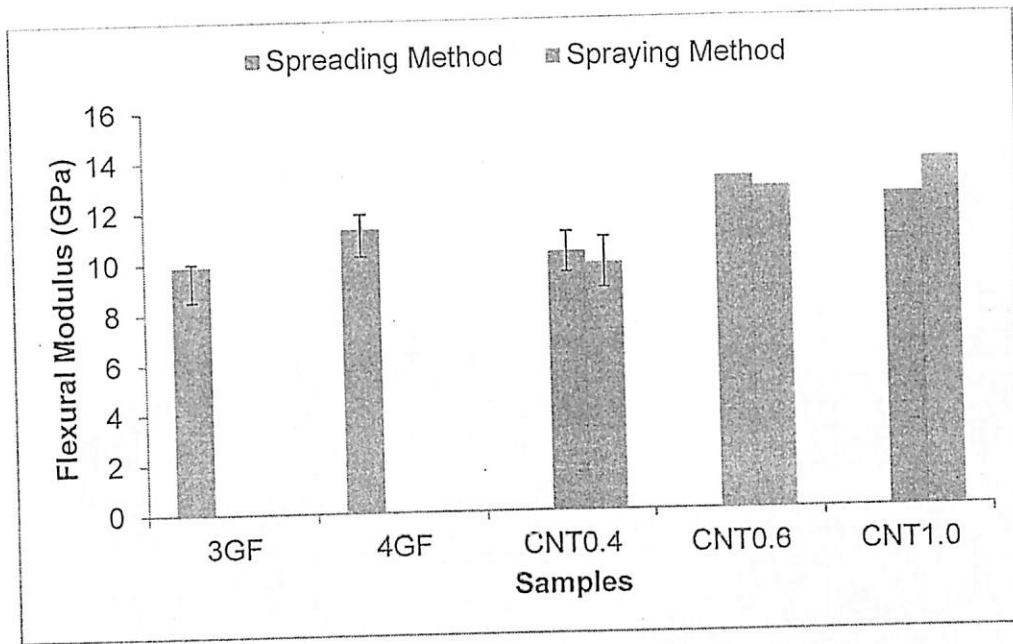


Figure 16. Variations of the flexural modulus of the composites against the temperature.

Figure 17 shows the micrographs of GF surface spread with ink, fabric of CNT0.6 and CNT1.0. Figure 17 (a) is an image of fabric with ink which was used as control sample in this observation. The carbon black existed in the ink appeared to white spheres attached on the fabric. In Figure 17 (a) and (b) the thread-like structures were the MWCNTs whereas the white round spheres were the carbon black. MWCNTs agglomerations were observed in Figure 17(c) and the presence of such agglomerations in the composites probably reduced the flexural performance of the composites.

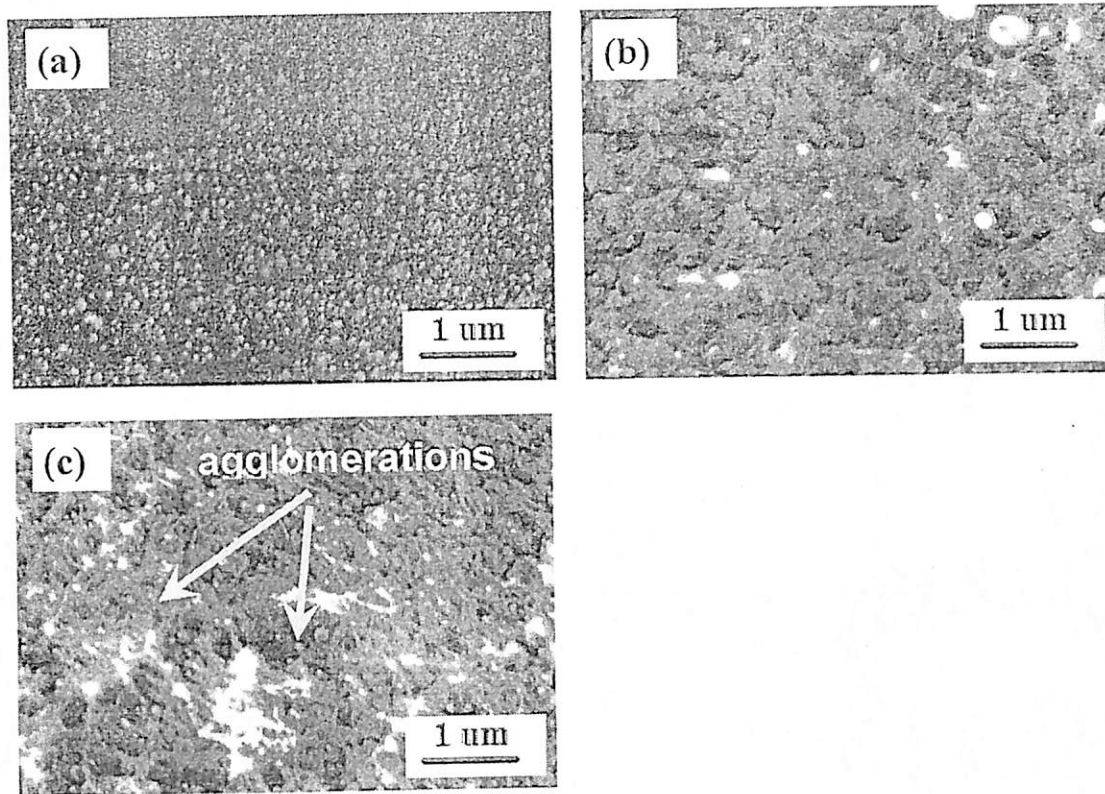


Figure 17. The micrographs of GF surface spread with ink and woven GF used in fabrication of CNT0.6 and CNT1.0 at 10K x magnification; (a) ink only; (b) CNT0.6; (c) CNT1.0.

Dynamic mechanical analysis of the composites (DMA)

DMA were only performed on selected samples namely 3GF, 4GF, CNT0.4, CNT0.6 and CNT0.6S. Figure 18 illustrates the storage modulus of 3GF, 4GF, CNT0.4, CNT0.6 and CNT0.6S. Basically the storage modulus of the samples decreased with temperature. Basically it seems that incorporation of the MWCNTs regardless the methods of MWCNTs dispersion, resulted a significant improvement in the storage modulus of the composites. The storage modulus of CNT0.4 and CNT0.6S were found to be almost similar. CNT0.6 the highest storage modulus which was about 24% higher compared 4GF whereas CNT0.6S exhibited about 19 % storage modulus compared to 4GF.

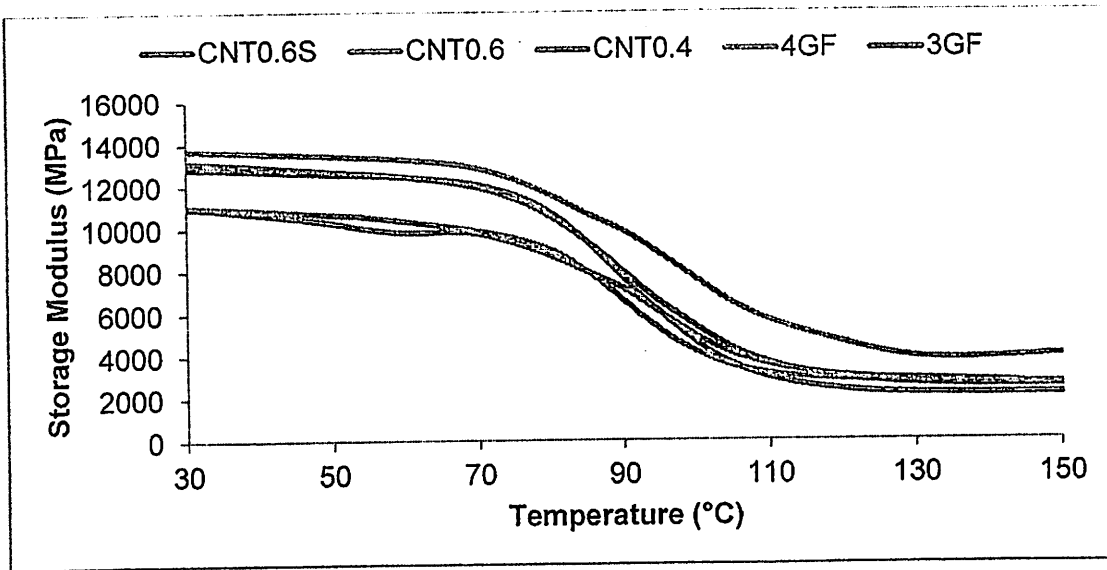


Figure 18. Storage modulus of 3GF, 4GF, CNT0.4, CNT0.6 and CNT0.6S composites.

Figure 19 depicts the variations of the loss modulus of the composites as a function of the temperature. Generally all the composites incorporated with MWCNTs demonstrated higher peaks amplitude compared to 3GF and 4GF. CNT0.6 possessed the highest peak value compared to 3GF and 4GF.

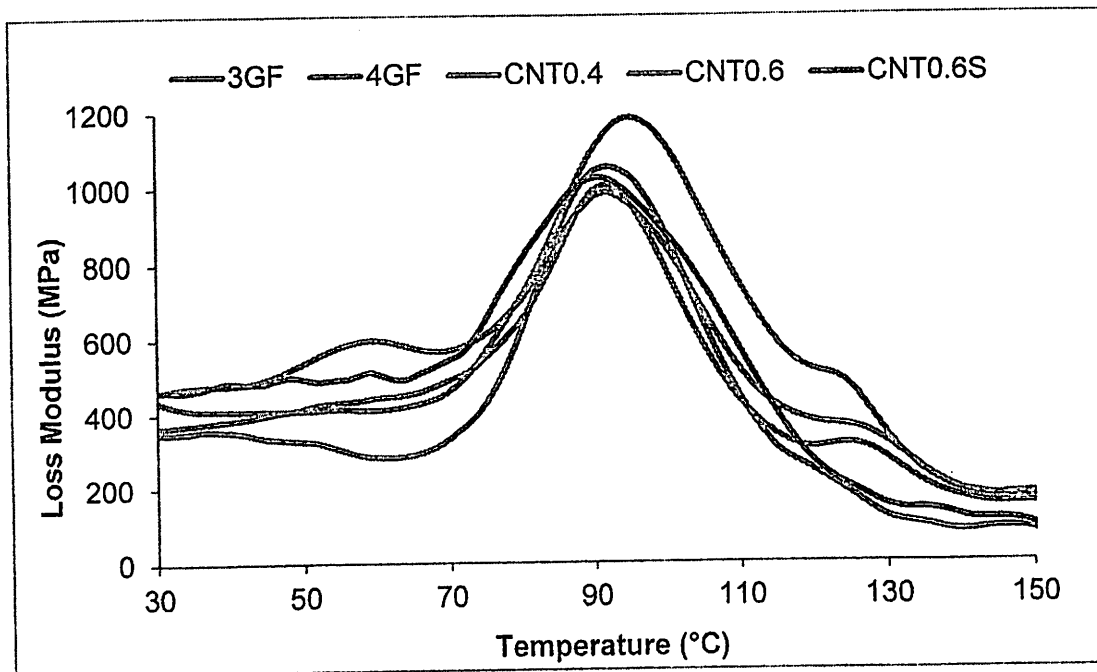


Figure 19. Loss modulus of 3GF, 4GF, CNT0.4, CNT0.6 and CNT0.6S composites.

this composite was the highest compared to CNTBP, 3GF and 4GF somehow the T_g of the composite was affected plasticizing effect of the buckypaper.

- 3) Filler loading affect the flexural performance as well as the thermo-mechanical performance of the composites. At lower filler loading (CNT0.4) the MWCNTs was insufficient to increase the flexural properties up to the optimum performance. On the other hand, excessive filler loading caused agglomerations hence attenuated the performance of the composites.
- 4) CNT0.6 possessed the highest flexural strength which was 270 % and 219% higher compare to 3GF and 4GF, respectively. However, the flexural modulus of CNT0.6 was 5 % lower compared to CNT1.0S. Besides, CNT0.6 exhibited the highest storage modulus and based on the DMA observation, the incorporation of 0.6 vol % of filler loading has increased the T_g , of CNT0.6 higher than 3GF and 4GF.
- 5) Comparing incorporation method of MWNCTs either in particulate or thin sheet (MWCNTBP) forms, it is found that incorporation of MWCNTs in particulate form was more efficient. This method allows the usage of the MWNCTS in nanoscale. Implementation of MWCNTBP only allows the exploitation of the MWCNTs at microscale. Besides, the usage of MWCNTBP was not cost efficient as fabrication of MWCNTBP required high cost.
- 6) Based on all of the observations performed, the usage of MWCNTs in the composites systems enables achievement of weight reduction in the composites. CNT0.6 is concluded to be the best MWCNT/woven GF/epoxy composites with the best performance compared to all of the other composites.

Acknowledgements

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Properties of Glass Fiber-Carbon Nanotube (CNT)/ Epoxy Composites

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ABSTRACT

A vacuum bagging method was used in this study to produce epoxy/glass fiber laminated composites with carbon nanotube (CNT) and CNT/flame-retardant fillers. The tensile properties, density, and burning rate of the laminated composites consisting of glass fiber and CNT (0.5, 1.0, and 1.5 vol%) were investigated and analyzed. The addition of CNT to four-ply glass fiber/epoxy increased tensile strength and Young's modulus. However, addition of CNT to four-ply glass fiber/epoxy reduced elongation at break and density compared with the control sample and higher CNT loading (1.5 vol%) resulted in filler agglomeration and reduced tensile properties. The epoxy/glass fiber composites exhibited better tensile properties with the addition of the hybrid flame-retardant fillers, ammonium polyphosphate (APP)/CNT compared with NP-120/CNT. However, NP-120/CNT showed a better burning rate than APP/CNT. In summary, the CNT-filled epoxy/glass fiber composite was found to exhibit higher tensile properties and burning rate than the hybrid flame-retardant system.

KEYWORDS: carbon nanotubes, glass fiber, epoxy, composite laminates, hybrid fillers.

1. INTRODUCTION

The composite industry has been rapidly developing since the 1940s. Composites made

of high-performance fiber are widely used for structural purposes in the transportation industry; these types of fiber include glass fiber and carbon fiber embedded in a compliant

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polymeric resin, such as epoxy and unsaturated polyester^[1]. Important properties in structural applications include being lightweight, and having high specific stiffness and strength, dimensional stability, adequate electrical properties, and excellent corrosion resistance^[1, 2]. Glass fibers are currently the most extensively used reinforcement materials for thermosetting composites because of their low cost, availability, and reliability^[3]. Epoxy resin is the most commonly used matrix for advanced composites because of its superior thermal, mechanical, and electrical properties; dimensional stability; and chemical resistance^[4-6]. However, the widespread use of epoxy resin is constrained because of its inherent brittleness, delamination, and limited fracture toughness^[5].

Incorporating epoxy matrices with nano-sized organic and inorganic particles, such as carbon nanotubes (CNTs), carbon nanofibers, nanoclays, and metal oxide particles, produces a new material with enhanced properties^[7-10]. Epoxy matrices in glass-fiber composites have been commonly modified with nanofillers to improve their mechanical properties. An extremely high specific surface area is one of the most attractive characteristics of nano-sized particles because it facilitates the production of a great amount of interphase in a composite^[7]. Therefore, a strong interaction may exist between the fillers and the matrix even at low nano-filler loading conditions. In principle, any material can be produced to have nano-scale shape and size, but no particle has gained as much attention as CNTs^[7]. These materials exhibit an exceptionally high aspect ratio and low density, as well as high strength and

stiffness^[7, 10], making them potential candidates for reinforcing polymeric materials.

Epoxy resins are flammable because of their organic nature. Poor flame resistance is a major setback in using epoxy resins for structural applications^[6]. Therefore, flame-retardant fillers are often used as a necessary additive in glass fiber-reinforced epoxy composites to overcome the aforementioned problem. A common fabrication method is the physical blending of flame-retardant fillers in the polymer or, alternatively, the flame retardant may be chemically bonded with the polymer backbone⁸. The use of CNTs as flame-retardant fillers has been reported. The stability of the polymer can be improved effectively by the free-radical scavenging effect of CNTs. Hence, the flame-retardant behavior of CNTs gives the material an added advantage as filler for composite materials for structural applications.

In this study, we investigated the effect of CNT content (0.5, 1.0, and 1.5 vol%) on the properties glass fiber/epoxy laminated composites. This study aims to compare the properties of glass fiber-CNT/epoxy system with those of glass fiber epoxy system. The effect of the hybrid flame-retardant fillers with CNT in the aforementioned composites was likewise determined. Two types of flame-retardant fillers, namely, ammonium polyphosphate (APP) and a newly developed halogen-free intumescent with the trade name NP-120, were combined with CNT and added into the four-ply glass fiber/epoxy laminated composites. Comparisons between the properties of these two hybrid systems (APP/CNT and NP-120/CNT) in glass fiber/epoxy laminated composites were subsequently carried out.

EXPERIMENTAL

Materials

Multiwalled carbon nanotubes (MWCNTs) used in this study were locally synthesized by a group of researchers from the Universiti Sains Malaysia. MWCNTs with high purity (99.8%), and with a nearly uniform diameter average of 6.2 ± 0.5 nm (mean \pm standard deviation), were synthesized over a magnesia-supported Co-Mo bimetallic catalyst through catalytic chemical vapor deposition¹¹. Flame retardants Budit 3159 intumescent APP and NP-120 were supplied by Brightech Supplies (M) Sdn. Bhd and Topchem Technology Co. Ltd., respectively. APP has a mean particle size (d50) of 5.1 μ m with a density of 1.90 g/cm³. NP-120 has a mean particle size of 1.8 μ m with a density of 1.2 g/cm³. Epoxy D.E.R. 332 and polyetheramine supplied by Penchem Technologies Sdn were used as resin and curing agent, respectively. Woven type-E glass fibers purchased from Saint-Gobain Ltd with a

linear density of 200 g/m² were used to reinforce the polymer composites.

Methodology

The epoxy was ultrasonicated with the filler for approximately 30 min using a Hielscher UP200S Ultrasonicator at 24 kHz and 50% amplitude. The curing agent was added into the mixture, which was ultrasonicated for another 10 min. The resin was applied layer by layer onto the woven glass fibers prior to vacuum bagging. The composite was cured at room temperature for 24 h and then postcured at 100°C for 1 h, followed by 125°C for 3 h. Figure 1 shows the schematic of the methodology used in preparing the five-ply epoxy/glass fiber laminate, which was used as the control. The amount of CNT filler loading was varied from 0.5% to 1.5% to study the effect of CNT filler loading in four-ply epoxy/glass fiber laminates. The total amount of flame retardant and CNT used was fixed at 1%; for example, 0.25 A and 0.75 C refer

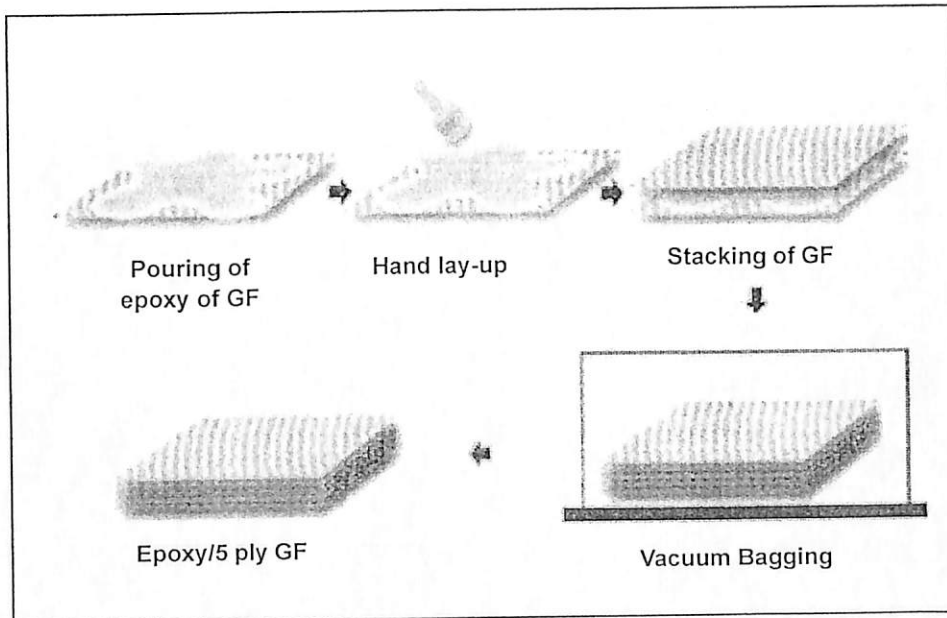


Fig. 1. Methodology for preparation of 5-ply glass fiber/epoxy laminates.

to 0.25% APP and 0.75% CNT, respectively, for the study of hybrid flame-retardant fillers in epoxy/glass fiber laminates. Three different ratios of flame retardant and CNT hybrid systems were used for comparison. Table 1 summarizes the sample designation used in the study.

TABLE 1. Sampel designation and content of glass fiber, epoxy and fillers in glass fiber/epoxy laminates

Sample labeling	Layer of Glass Fiber (vol %)	Glass Fiber (vol %)	Epoxy (vol %)	Flame retardant filler (APP)	Flame retardant filler (NP-120) (vol %)	CNT (vol %)
Epoxy	0	0	100	0	0	0
5 GF	5	62.3	37.7	0	0	0
4 GF 0.5 C	4	54.1	45.4	0	0	0.5
4 GF 1.0 C	4	53.4	45.6	0	0	1.1
4 GF 1.5 C	4	53.2	45.2	0	0	1.6
0.25 A 0.75 C	4	53.9	45.1	0.2	0	0.8
0.5 A 0.5 C	4	53.4	45.6	0.4	0	0.5
0.75 A 0.25 C	4	53.6	45.5	0.7	0	0.3
0.25 N 0.75 C	4	53.4	45.2	0	0.6	0.8
0.5 N 0.5 C	4	53.0	45.3	0	1.3	0.5
0.75 N 0.25 C	4	53.5	44.4	0	1.8	0.3

Characterization

Density

Density was measured by using a gravity balance, Precisa 8000. Five specimens measuring 10 mm × 10 mm were used, and the average density was calculated.

Tensile Test

A tensile test was conducted using Instron 3366 with a gauge length of 50 mm and a speed of 50 mm/min according to ASTM D 638-98. Samples were cut into pieces measuring 150 mm × 20 mm using a band saw.

Thermogravimetric Analysis

The decomposition behavior and thermal stability of

the composite samples were characterized using thermogravimetric analysis (TGA) (Pyris 6, Perkin Elmer). Samples weighing 10 mg to 15 mg were inserted into the pan. Testing was conducted from room temperature up to 600°C at a heating rate of 10°C/min under nitrogen environment.

Flammability Test

The rate of burning was determined by a flammability test, in accordance with the ASTM D 635 method. The composite sheet was cut into bar-shaped test specimens measuring 125 mm³ × 13 mm³ × 3 mm³. At least 10 specimens were prepared for each composition and composite system. Gauge length was fixed at 25 mm, and the average rate of burning was reported in mm per min.

Fracture Surface Characterization

The SEM machine model FESEM Zeiss SUPRA 35VP was used for flame-retardant particle and fracture surface characterizations.

RESULTS AND DISCUSSION

Effect of CNT loading

The density of glass fiber/epoxy laminated composites with the addition of different CNT contents is shown in Figure 2. As expected, density was observed to have increased by approximately 20% when the five-ply glass fiber was added into the epoxy matrix. The density

of the unfilled epoxy was noted to be 1.17 g/cm³. The density of the glass fiber laminate was reduced by approximately 14% when one layer of the glass fiber laminate was replaced by 0.5% CNT filler. An increasing trend was observed when the amount of CNT filler loading was increased from 0.5% to 1.5%. However, the density of the glass fiber laminate with 0.5% CNT is 9% higher than that of epoxy resin. The increasing trend in density with the addition of glass fiber laminate and CNT is expected because the density of glass fiber and CNT are about 2.54 g/cm³ and 1.4 g/cm³, respectively.

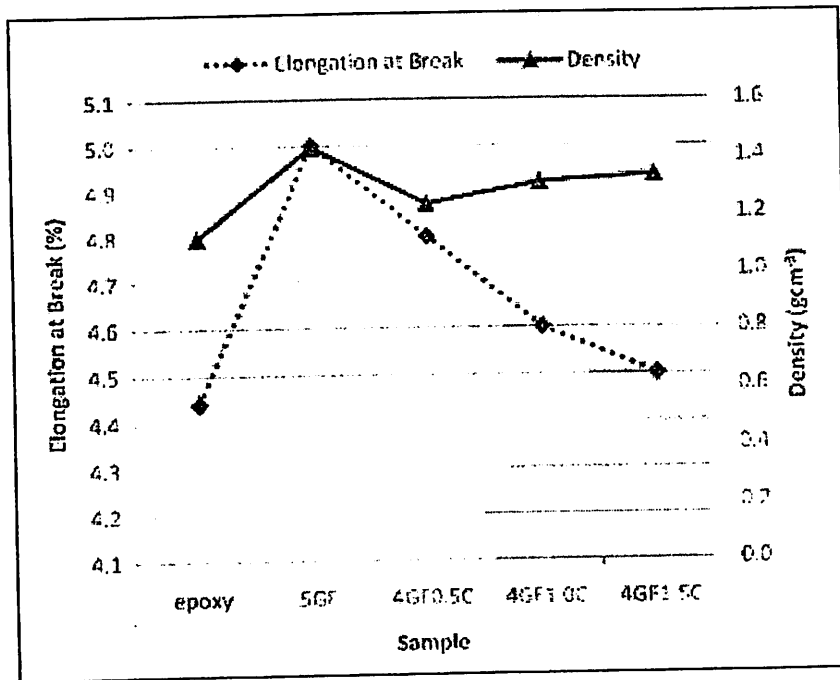


Fig. 2. Density and elongation at break of glass fiber/epoxy laminated composites with different CNT content.

Figure 2 shows the elongation at break for the glass fiber laminate. It is observed that the elongation at break increased by 15% when the five-ply glass fiber was added into the epoxy. This is due to the fact that fiber/matrix adhesion increased the ductility and toughness of the epoxy. A decrease in the elongation at break was noted with increasing CNT filler loading. The addition of CNT filler in glass fiber/epoxy laminated composites resulted in the brittleness of the composite system. This may be attributed to the reduction of the tough matrix in the system. This result is in agreement with the study by Unar et al.^[12], wherein materials with high properties, such as hardness, tensile strength, and modulus, were reported to result

in less elongation under stress. More force would be needed to stretch a hard material with high tensile strength and high modulus than a soft material with low tensile strength and low modulus.

Figure 3 shows the tensile strength and Young's modulus of the unfilled epoxy and the epoxy with different CNT filler loadings in glass fiber/epoxy laminated composites. Variations in tensile strength were observed as the CNT filler loading was increased from 0% to 1.5% (Figure 3). The tensile strength of the five-ply glass fiber laminate increased 380% compared with epoxy resin. Variations in tensile strength were observed with the addition of CNT fillers

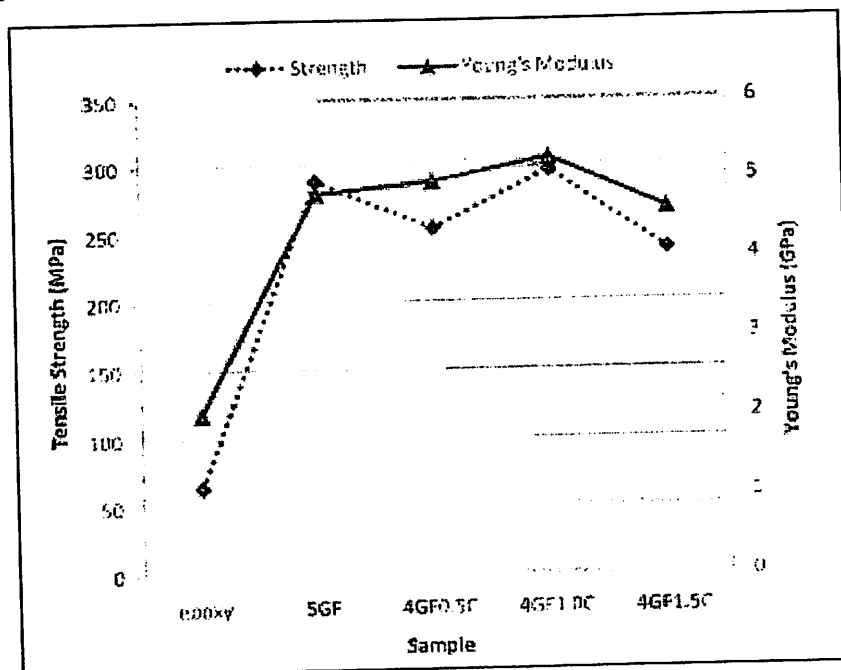


Fig. 3. Comparison of tensile strength and Young's modulus of glass fiber/epoxy laminated composites with different CNT content.

into the system. The strength of the material decreased by 14% when one layer of glass fiber was replaced with 0.5% CNT filler based on the tensile strength of the five-ply glass fiber. Tensile strength increased by 19% in the 1.0% CNT filler system compared with that of 0.5% CNT. However, a reduction in tensile strength was observed with the addition of 1.5% CNT.

The increase in tensile strength with the addition of CNT can be explained in terms of the intrinsic nature of CNT. CNT has high tensile strength and modulus, as well as a high surface area that might create a possible bonding between the resin and the reinforcement. This reduction in tensile strength at high CNT loading might be caused by the presence of a void in the composites because of the high viscosity of the CNT and epoxy mixture. This process subsequently makes it harder for the mixture to wet the fibers. Agglomeration of

nanofillers caused by the high surface area might also lower the tensile properties of the composites. The agglomeration of CNT fillers has been reported to frequently cause void formations, which reduces the mechanical properties of the glass fiber laminated composites^{9,10}. However, slightly lower tensile strength is observed in 0.5% CNT in 4-ply (4GF 0.5 C) compared to 5GF, this might be due to less reinforcement existed in 4-ply glass fiber system in comparison with 5-ply glass fiber system.

Figure 3 also shows the Young's modulus of glass fiber/epoxy laminated composites with different CNT contents. The Young's modulus was observed to increase as the CNT filler loading increased from 0.5% to 1.0%. The four-ply glass fiber with 0.5 vol% of CNT was noted to have a slightly higher modulus than the five-ply glass fiber laminate. The modulus continued

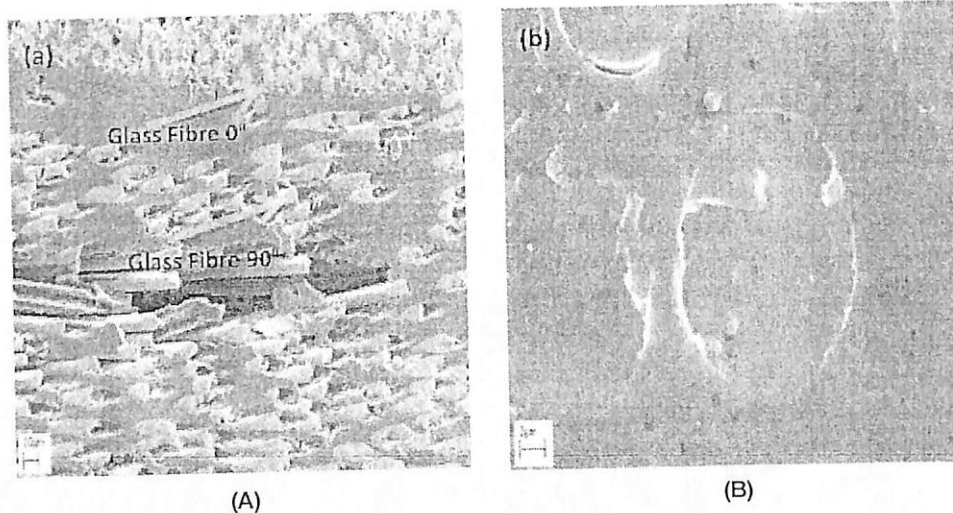


Figure 4 : SEM images of fracture surface of glass fiber laminates with 1.0 vol% CNT filler at (a) 200x and (b) 3000x magnification.

to increase when 0.5% and 1.0% CNT were added. A slight drop in trend was observed with the addition of 1.5 CNT. The presence of a void acted as a stress concentration factor and resulted in a low modulus in the 1.5% CNT system.

Figures 4 and 5 show the fracture surface of 1.0 and 1.5 CNT in glass fiber/epoxy laminates, respectively. Voids and CNT filler agglomerates were observed in Figure 5 with the addition of 1.5 CNT filler. This finding further shows that at high filler loading, the dispersion of fillers is

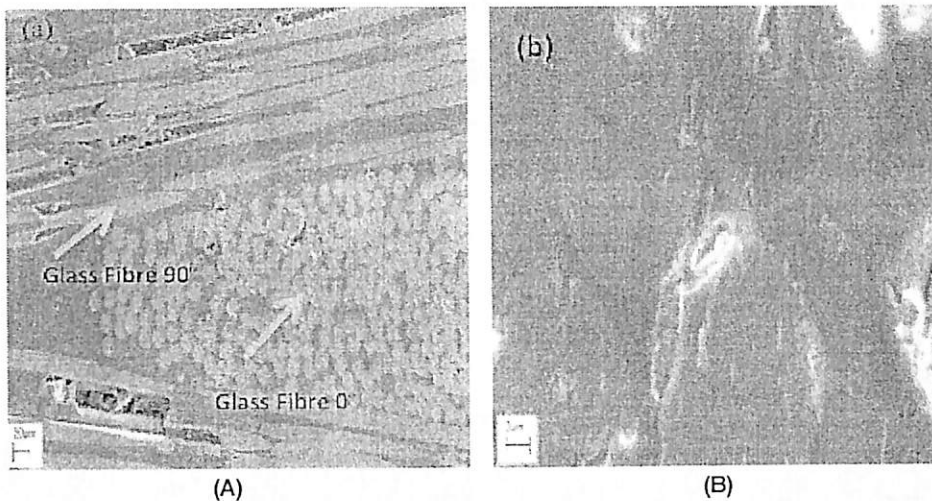


Fig. 5. SEM images of fracture surface of glass fiber laminates with 1.5vol% CNT filler at (a) 200x and (b) 3000x magnification.

poor and the agglomerates may cause the deterioration of mechanical performance of the composites.

TGA was used to determine the stability of selected samples. Epoxy resin, five-ply glass fiber/epoxy, and four-ply glass fiber/epoxy

samples with 1.0% and 1.5% filler loadings were used for comparison. Figure 6 shows the thermal stability of the glass fiber/epoxy laminated composites with different CNT contents. The results are summarized in Table 2.

TABLE 2. TGA result for the 5-ply glass fiber/epoxy composite, 4-ply glass fiber/epoxy with CNT and epoxy resin

Sample	Epoxy	5 GF	4GF 1.0C	4GF1.5 C
T _{0.5} (°C)	348	323	346	368
T _{max} (°C)	361	350	352	380

Note: T_{0.5} is the temperature corresponding to 5% weight loss
 T_{max} is the temperature at which there is the maximum rate of decomposition

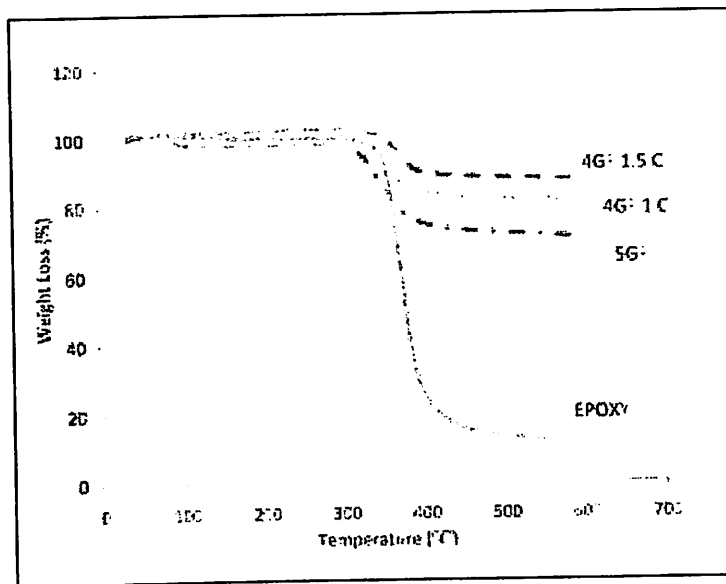


Fig. 6. TGA curve the glass fiber/ epoxy laminated composites with different CNT content.

Table 2 and Figure 6 show that incorporating CNT fillers into the epoxy matrix improved the thermal stability of glass fiber/epoxy laminated composites. Increasing the amount of CNTs enhances the thermal properties of glass fiber laminates. Figure 6 shows that only one degradation stage exists, that are from 300°C to about 450°C. The glass fiber/epoxy laminated composites decompose and form a residue or char at this stage. The weight loss of four-ply glass fiber/epoxy laminate with 1.5% CNT is only 11% at 400°C compared with that of five-ply glass fiber/epoxy laminate, which is 25%. Studies by Zhao et al.^[13] on CNT/glass fiber/epoxy composites show similar results. Polymer chain mobility was reduced when the CNT filler was added to the glass fiber/epoxy laminate^[13, 14]. The glass fiber/epoxy laminated composites becomes more rigid because part

of the volume is occupied by solid CNT filler particles. This process indicates that the CNT-filled glass fiber/epoxy laminated composites have less epoxy resin than the laminates without fillers. Incorporation of CNT has been reported to enhance the thermomechanical properties of composites, improve the glass transition temperature T_g , and decrease the coefficient of thermal expansion (CTE)^[15]. Thermal stability increases because the fillers have higher thermal stability than the epoxy resin, as reported by Litvinov et al.^[16]. Another reason is that the CNT filler possesses excellent thermal conductivity, which allows heat to be transmitted efficiently from the epoxy matrix to the CNT fillers^[17].

Figure 7 shows the comparison of the burning rates of glass fiber/epoxy laminated composites

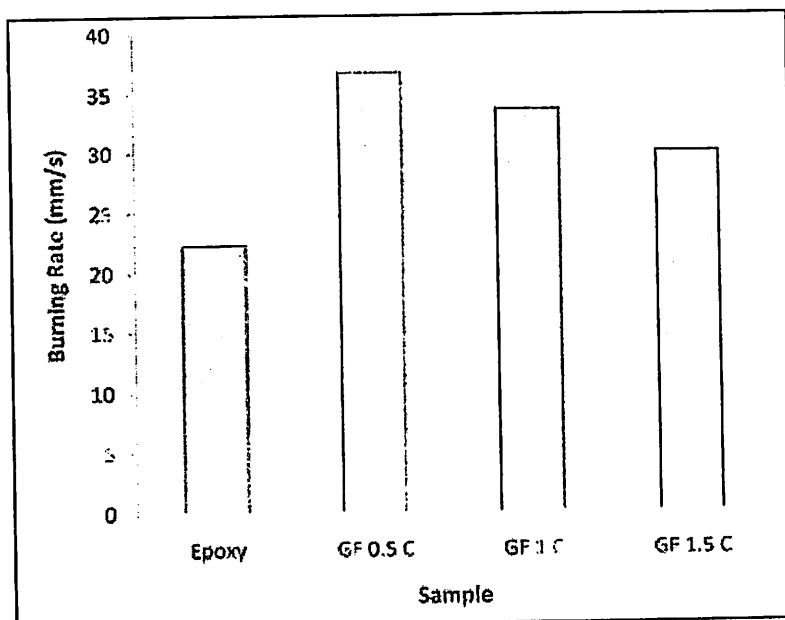
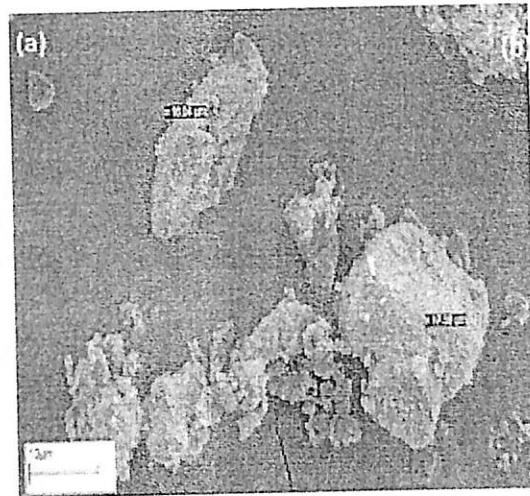


Fig. 7. Comparison of burning rate of glass fibre/ epoxy laminated composites with different CNT contents

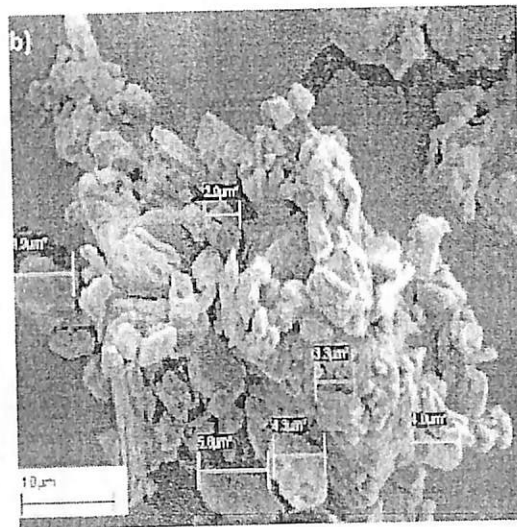
with different CNT contents. In the absence of CNT, the epoxy with glass fiber demonstrated a higher burning rate compared with the CNT-filled composite. The epoxy with 1.5% CNT filler loading exhibited a slower burning rate compared with the 0.5% and 1.0% CNT filler loading. This result is attributed to CNT acting as a flame-retardant filler to epoxy. CNTs have a high aspect ratio that enables them to percolate and to form a network at very low loading amounts of polymer matrix. This characteristic leads to the substantial enhancement of several function properties, including flame-retardant properties^[17]. Laoutid et al.^[17] reported that incorporating CNT at low loading rates can improve the flammability of a large range of polymers.

Effect of hybrid flame-retardant filler and CNT in glass fiber epoxy laminates

Two types of flame-retardant fillers, APP and NP-120, were used in this study. These fillers were hybridized with CNT and added to glass fiber/epoxy laminated composites. Figure 8 (a and b) shows the SEM micrographs of NP-120 and APP. APP size ranges from 15 nm to 20 nm as shown in Figure 8 (a). Less agglomeration can be observed in the figure, which may indirectly suggest that APP is easily dispersed in the epoxy resin compared with NP-120. NP-120 appears as a cluster of particles, indicating agglomeration of NP-120 particles. The size is noted to be 10 nm and smaller. Table 3 shows the properties of hybrid



(a)



(b)

Fig. 8. SEM micrographs of (a) APP and (b) NP-120 at 1500x magnification.

flame-retardant fillers and CNT in glass fiber/epoxy laminates.

As compared to 1% CNT, the density of hybrid flame-retardant fillers and CNT in glass fiber/epoxy is found to increase by 44% when 0.75% APP is added to the composite system (Table 3). The density is observed to increase by increments of about 31% when 0.75% of NP-120 was hybridized with CNT in the glass fiber/epoxy laminate systems. An increasing trend in density is observed when the amounts of APP and NP-120 in the laminate composites increase in both hybrid flame-retardant systems. In general, APP has a slightly higher density compared with the NP-120 composite system. This finding is attributed to the higher density of the APP filler (1.8 g/cm³) compared with that of NP-120 (1.2 g/cm³).

The trend of tensile strength decreased with the addition of APP and NP-120 flame-retardant fillers. Decreasing the amount of CNT in the system reduced the tensile strength of the hybrid filler/glass fiber/epoxy system. The

system with APP exhibited slightly higher tensile strength compared with the NP-120 system. A similar trend is observed in Young's Modulus of glass fiber/epoxy laminated composites with different CNT and flame-retardant contents. The Young's modulus value decreased by 25% when 0.75% APP was added to the composite system. In NP-120 system, addition of 0.75% NP-120 results in 29% Young's modulus reduction of the composite systems. The values continue decreasing with increasing amounts of both flame-retardant fillers,

From Table 3 it can be seen that the elongation at break of glass fiber/epoxy laminated composites decreases with decreasing amounts of CNTs and increasing amounts of flame retardant in the composite system. This finding indicates that composites become more brittle with increasing amounts of flame-retardant fillers. The fillers disturb matrix continuity, and each filler is a site of stress concentration that can act as a micro crack initiator⁽¹⁹⁾.

TABLE 3. The properties of hybrid flame retardant fillers and CNT in glass fiber/ epoxy laminate composites.

Hybrid System	Density (g/cm ³)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Elongation at break (%)	Burning Rate (mm/s)
1.0 C	1.31	280	5.2	4.30	33.63
0.25 A 0.75 C	1.55	225	4.3	4.25	31.65
0.5 A 0.5 C	1.63	180	4.2	4.21	29.18
0.75 A 0.25 C	1.89	150	3.9	4.05	26.32
0.25 N 0.75 C	1.54	220	4.2	4.15	26.59
0.5 N 0.5 C	1.64	160	4.1	4.11	22.72
0.75 N 0.25 C	1.72	149	3.7	4.04	20.19

Results of the flammability analysis assessed by linear rate of burning are presented in Table 3. Apparently, the addition of hybrid flame retardant fillers (APP/CNT and NP-120/CNT) has significant impacts on the flammability of the glass fiber/epoxy composites. These results show that burning rate is reduced after the addition of hybrid fillers APP/CNT and NP-100/CNT compared with 1% CNT in glass fiber/epoxy composites. The comparison of the burning rates of glass fiber/epoxy laminated composites with different CNT and flame-retardant contents indicates that APP has a higher burning rate compared with NP-120. According to Wu et al.^[19] and K.K. Baljinder et al.^[20], due to the presence of phosphate groups in APP, it decomposes at relatively lower temperature to form heat-resistant char which can retard the decomposition rate of the epoxy resin. NP-120/CNT composites reduce their burning rate by the formation of carbon foam layers, which protects the polymer through heat-insulating effect, this reduces further the oxygen access and thereby reducing the rate of burning of the system. In general, the burning rate was found to decrease with decreasing amounts of CNT in the composite system.

CONCLUSIONS

The following conclusions can be drawn based on the tests and observations performed:

1. The addition of 0.5 vol% to 1.0 vol% CNT to the four-ply system increases modulus and strength, and reduces the density of the composites compared with the five-ply system.
2. The addition of high amounts of CNT filler loading leads to agglomeration and an

increase in the viscosity of the epoxy matrix. This phenomenon, in turn, leads to poor adhesion and wetting among the glass fiber, CNT, and epoxy; thus reducing the properties of the composites.

3. The most suitable amount of filler loading that can be added to the epoxy resin in a hybrid system is 1% because agglomeration of fillers will occur at higher loading, thereby reducing tensile properties.
4. The addition of APP and NP-120 as flame retardants reduces the burning rate. The hybrid NP-120/CNT is much more effective in reducing burning rate than the APP/CNT. However, the addition of APP and NP-120 reduces tensile properties and increases the density of the composites.

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Properties of graphene nanopowder and multi-walled carbon nanotube-filled epoxy thin-film nanocomposites for electronic applications: The effect of sonication time and filler loading

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ABSTRACT

Graphene nanopowder (GNP) and multi-walled carbon nanotube (MWCNT)-filled epoxy thin-film composites were fabricated using ultrasonication and the spin coating technique. The effect of sonication time (10, 20 and 30 min) and GNP loading (0.05–1 vol%) on the tensile and electrical properties of GNP/epoxy thin-film composites was investigated. The addition of GNP decreased the material's tensile strength and modulus. However, among the tested samples, the GNP/epoxy composites produced using 20 min of sonication time had a slightly higher tensile strength and modulus, with a lower electrical percolation threshold volume fraction. The effect of sonication time was supported by morphological analysis, which showed an improvement in GNP dispersion with increased sonication time. However, GNP deformation was observed after a long sonication time. The GNP/epoxy composites at different filler loadings showed higher electrical properties but slightly lower tensile properties compared with the MWCNT/epoxy composites fabricated using 20 min of sonication time.

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1. Introduction

The development of packaging and interconnect technologies has been driven by the increasing functionality of semiconductor devices and higher end-user expectations seen in recent years [1]. The need for low prices and power and small sizes has driven the development of small, thin plastic packages, chip-on-board and direct-chip-attach technologies, and fine-line substrates. The demand for higher miniaturization, function integration, and reliability has influenced almost all of the materials used in such packaging and interconnect applications. Now, these materials' electrical, thermal, and mechanical properties are the most important challenges affecting their use in advanced electronics packaging [1,2].

With the phasing out of lead-bearing solders, electrically conductive adhesives (ECAs) have been identified as an environmentally friendly alternative to tin/lead (Sn/Pb) solders in electronics packaging applications. In particular, the requirements of fine-pitch and high-performance interconnects in advanced packaging have caused nanoconductive adhesives to become increasingly important owing to their special electrical, mechanical, optical, magnetic, and chemical properties. Incorporating nanotechnology into ECA systems not only enables ultra-fine-pitch capability but

also enhances the systems' electrical properties by reducing the percolation threshold and improving electrical conductivity [2].

ECAs consist mainly of polymer resins (such as epoxy, silicone, polyurethane, and polyimide) and conductive metallic fillers (such as silver, gold, and copper) [3]. Polymer resins provide mechanical strength between the component and substrate, whereas conductive fillers provide electrical conductivity. Epoxy is an important class of thermoset polymer used as a matrix in electronic applications due to its ease of processing, high tensile strength and modulus, low shrinkage under treatment, low price, and good resistance to heat, moisture, and chemicals [4]. Silver is widely used as a filler in ECA applications because of its high electrical conductivity, and, unlike many other metals, silver oxides are conductive [5]. However, high silver loading in the range of 70–90 wt% is required for insulator–conductor transition in ECAs, and high filler loading will result in better electrical conductivity, but decrease the mechanical strength of the polymer matrix [6].

Extensive research has been conducted in recent years on material and process improvements for ECAs and on advances in nanoconductive adhesives containing nanofillers such as nanoparticles, nanowires, or carbon nanotubes and nanomonolayer graphenes [2,7,8]. Different nanocarbon forms, such as single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs, respectively), graphite oxide, and graphene nanoplatelets, have been used as nanofillers with a wide range of polymers, leading to improvements in the composites' mechanical and electrical properties

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[7–9]. Graphene has remarkable properties, such as an electrical conductivity of up to 6000 S/m and good tensile properties, with a Young's modulus of 1000 GPa and tensile strength of 130 GPa. SWCNTs possess an electrical conductivity of approximately 100 S/m, a Young's modulus of 1000–1200 GPa and tensile strength of 100 GPa, while MWCNTs are reported to have an electrical conductivity of approximately 1850 S/cm and a Young's modulus and tensile strength of 270–950 GPa and 200 GPa, respectively [10–14].

Graphene has attracted considerable attention for its high electrical conductivity and superior mechanical properties. However, given its high surface-to-mass ratio, graphene's molecular scale forces and aggregation become defects that cause the deterioration of a final nanocomposite's properties. Considering that the known nanofillers are difficult to disperse uniformly in a polymer matrix, numerous methods have been used for the uniform dispersal of nanoparticles into different matrices, including mechanical mixing, ultrasonication, planetary shear mixing, and in situ polymerization in the presence of nanoparticles [8,15].

Among the different available techniques, ultrasonication has represented a promising approach for achieving a good state of nanoparticle dispersion in laboratory-scale quantities [16]. Liao et al. [17] have investigated the dispersion process of SWCNTs in an epoxy resin matrix, with results indicating that the sonication method is effective in improving SWCNT dispersion and enhancing the mechanical properties of SWCNT/epoxy nanocomposites. Faiella et al. [18] have studied the electrical percolation behavior of MWCNT/epoxy composites produced using the sonication method as a dispersion process, and have found that the percolation threshold increases with increasing sonication time. Taurozzi et al. [19] have reported that the amount of energy (E) delivered to a suspension depends not only on the applied power (P) but also on the total time (t) that the suspension is subjected to the ultrasonic treatment: $E = P \times t$. Thus, different dispersion states will be obtained if the materials have been prepared at the same power and using different sonication times. In other words, the input energy influences the dispersion of fillers in suspension during the sonication process. According to Shokrieh et al. [20], high nanofiller content requires extra sonication time to improve the dispersion of filler in the matrix.

The sonication process has commonly been used to disperse CNT in an epoxy matrix, but no studies have been performed to investigate the effect of sonication duration on graphene-filled epoxy composites. Therefore, the goal of this study was to investigate the effects of sonication time and graphene nanopowder (GNP) loading on the tensile and electrical properties of epoxy

thin-film nanocomposites. The GNP/epoxy nanocomposites were prepared using different sonication times ranging from 10 min to 30 min. These GNP/epoxy composites were then compared with MWCNT/epoxy nanocomposites produced with a sonication time of 20 min.

2. Experimental methods

2.1. Materials

An epoxy resin called D.E.R.TM 332, a chemical product made by the DOW Chemical Company, was used as a matrix in this study. The material was supplied by Penchem Technologies Sdn. Bhd, and its chemical name is bisphenol-A diglycidylether (DGEBA). DGEBA has a density of 1.16 g/cm³ at 25 °C. Polyetheramine D230 with a density of 0.946 g/cm³ was supplied by BASF Corporation (Florham Park, NJ, USA) and used as a curing agent. Two types of nanofillers were used, GNP and MWCNT. The GNP product, 0544DX, was supplied by Skyspring Nanomaterials, Inc., and the manufacturer claims that it has a surface area of 50–80 m²/g with a purity of 99.5%. The GNP consisted of flat particles with an average particle diameter of 15 μm and thickness of 5–10 nm. The MWCNTs were supplied by researchers from the School of Chemical Engineering at the Universiti Sains Malaysia and had a surface area of 93.86 m²/g with a purity of 99.8%, average outer diameter of 6.2 nm ± 0.5 nm and length of 5–50 nm. The MWCNTs were synthesized over a magnesia-supported Co–Mo bimetallic catalyst through the catalytic chemical vapor deposition of methane [21]. Both fillers (GNP and MWCNTs) were used as supplied, without any functionalization process.

2.2. Fabrication of epoxy thin-film composites

The GNP and MWCNT nanofiller loadings in the epoxy resin varied between 0.05 vol% and 1 vol%. The epoxy resin and GNP mixtures were sonicated for different durations (10, 20, and 30 min) at room temperature. In this study, sonication parameters such as power, time, frequency, probe diameter, resin container volume, resin viscosity and structure, resin temperature during the sonication process, distance between the probe and container, and filler type and dimensions were fixed, while only sonication time was varied and evaluated. The epoxy resin and MWCNT mixtures were sonicated for 20 min. Both mixtures (GNP/epoxy and MWCNT/epoxy) were subsequently vacuumed for approximately 60 min at room temperature to further remove bubbles. A curing agent was added at a ratio of 100:32 by weight (epoxy: curing agent)

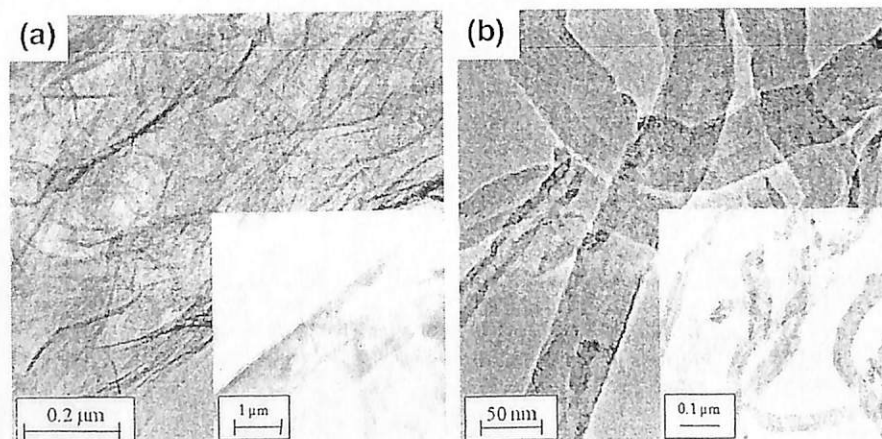


Fig. 1. TEM image of (a) GNP and (b) MWCNTs.

and the mixture was sonicated for another 10 min in an ice bath. The mixture was kept in a vacuum oven for 30 min at room temperature, after which it was spin coated using a Desk-Top Precision Spin Coater model G3P-12. Spinning speeds of 900 rpm to 12,000 rpm were used on all the epoxy systems for 60 s. The film was then left on the stationary substrate for 3 min before curing at room temperature for 24 h, after which it was post-cured at 80 °C for 2 h to produce films with thicknesses of 30–70 μm .

2.3. Characterization technique

A transmission electron microscope (TEM) model Philips CM12 was used to observe the morphology of the GNP and MWCNT nanofillers. The tensile properties of the epoxy thin-film composites were determined using an Instron 3366 according to the ASTM D882-02 standard test method at a crosshead speed of 1 mm/min. For each tensile sample, five strip specimens with a width of 10 mm and length of 150 mm were prepared and used for measurement. The fracture surfaces on the tensile specimens were examined using a field emission scanning electron microscope (FE-SEM Zeiss SUPRA 35VP) at an acceleration voltage of 10 kV. All specimens were vacuum coated with gold prior to examination to avoid charging. The epoxy thin-film composites were tested to measure their electrical conductivity using a Gwinstek LCR 817 meter at a voltage of 1 V and frequency of 1 kHz. A square-shaped thin film with a dimension of 30 \times 30 mm was prepared and used for the measurement.

3. Results and discussion

3.1. Particulate filler characterization

Two types of nanofillers, GNP and MWCNTs, were used in this study. Fig. 1 shows TEM images of the GNP and MWCNTs. The TEM image in Fig. 1(a) shows that the as-received GNP particles are superimposed on top of each other and look wrinkled in a manner similar to crumpled thin paper, indicating that the GNP formed clusters or aggregates [8]. In addition, the TEM insert image in Fig. 1(a) shows that the single layer of GNP has a flaky shape and a relatively smooth planar structure with large dimensions (4.1 $\mu\text{m} \times$ 1.3 μm). The TEM image in Fig. 1(b) shows the MWCNTs, with an average length of a few hundred microns and diameters in the range of 5–50 nm. The TEM insert image in Fig. 1(b) shows that the MWCNTs are randomly organized and aggregated owing to inter-molecular Van der Waals interaction to form entanglements in certain areas [16].

3.2. Tensile properties

Fig. 2 shows the average tensile strength, tensile modulus, and elongation at breaks in the unfilled epoxy and epoxy thin-film composites with GNP and MWCNT nanofillers at different filler loadings and sonication times. Fig. 2(a) and (b) show that the addition of GNP resulted in a decrease in both tensile strength and tensile modulus. This decrease was attributed to an aggregation of GNP that resulted in a deterioration of the final nanocomposite's tensile properties. The decrease in the epoxy's tensile strength and tensile modulus with the addition of nanofillers, specifically graphene, has been reported in previous works [22,23]. The reinforcement effects of nanofiller in a polymeric matrix are theoretically governed not only by filler content within the hosting system but also by filler dispersion, filler-matrix adhesion, particle dimensions, and voids [16,24]. Fig. 2(c) shows that increases in the GNP loading caused the epoxy thin-film composite to become more brittle, resulting in a decrease in the elongation at break.

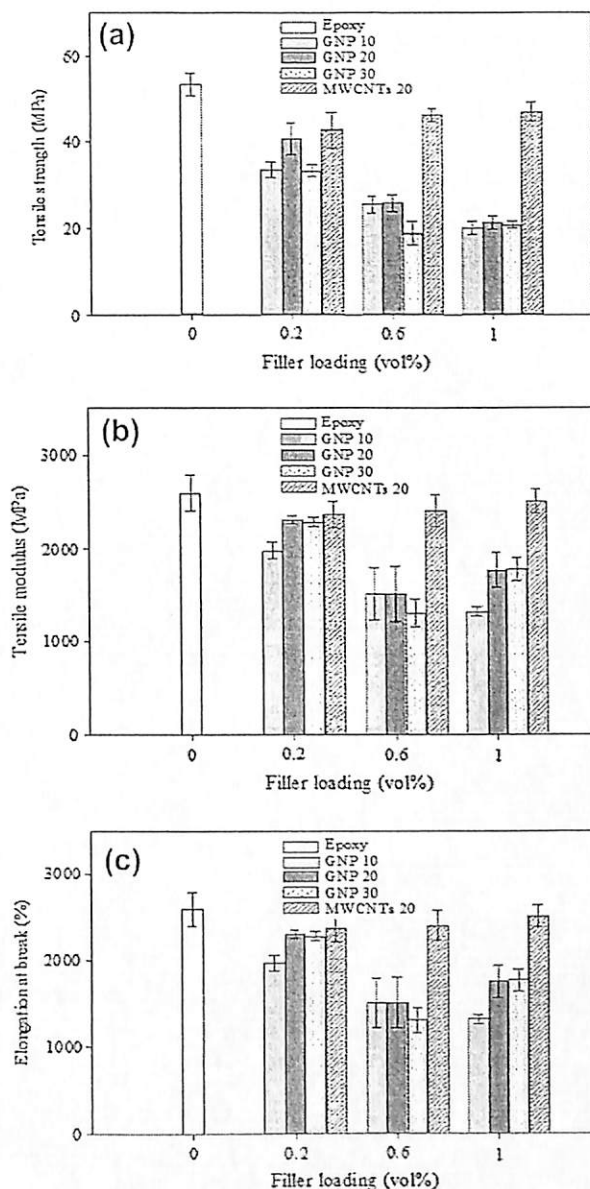


Fig. 2. Tensile properties of unfilled epoxy and epoxy thin film with different fillers loading and sonication time: (a) tensile strength, (b) tensile modulus and (c) elongation at break.

However, a slight enhancement in both the tensile strength and tensile modulus could be observed in all of the GNP/epoxy thin-film composites sonicated for 20 min compared to the GNP/epoxy thin-film composites sonicated for 10 and 30 min. Sonication for 10 min was found to be insufficient for good GNP dispersion. This result was in agreement with the findings reported by Taurozzi et al. [19] on the low input energy required for shorter sonication times. Meanwhile, the longer sonication times could cause GNP damage. These two conflicting mechanisms may have explained why the GNP/epoxy thin-film composites with identical filler loadings displayed different tensile properties at different sonication times. In a previous study on the effect of sonication time on the mechanical properties of MWCNT-filled epoxy resin [24], the tensile strength of 0.5% MWCNT loading has been shown to increase when the sonication time is increased from 0.5 h to 2 h. A further increase in sonication time results in a deterioration in the tensile strength owing to possible filler damage caused by the long sonication time.

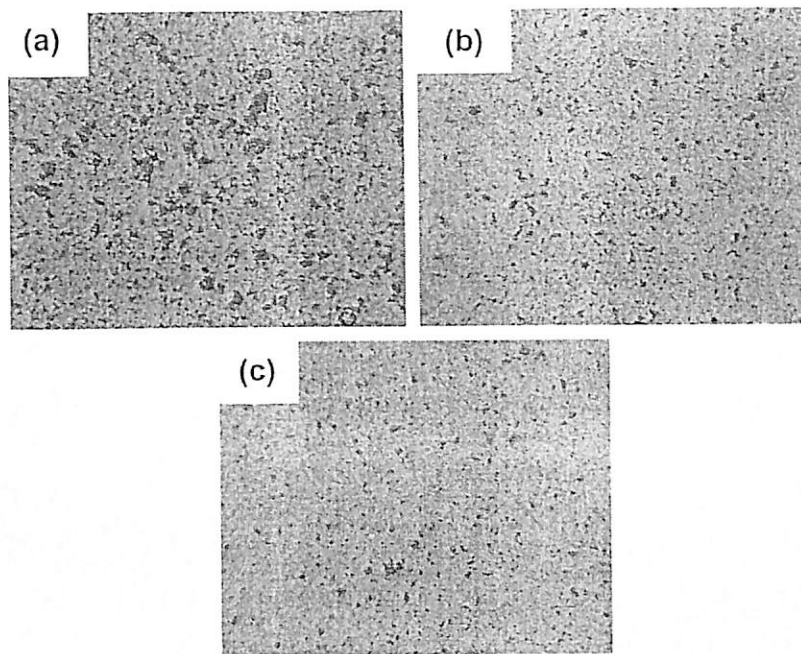


Fig. 3. Optical microscope of 0.2 vol% of GNP filled epoxy thin film composites: (a) GNP 10 min, (b) GNP 20 min and (c) GNP 30 min (at magnification of 45 \times).

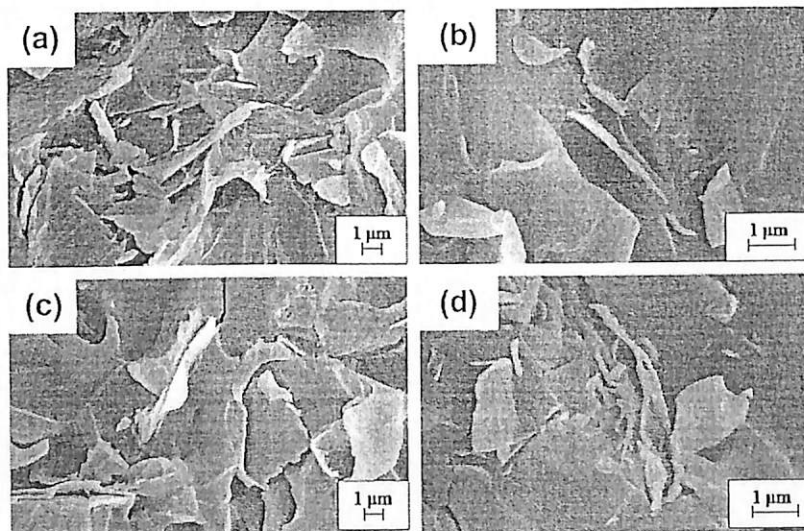


Fig. 4. SEM images on tensile fracture surface of 1 vol% of GNP/epoxy composites produced at 20 min sonication time (at magnification of 500 lx for a, c and 1000 lx for b, d).

A comparison between the GNP/epoxy and MWCNT/epoxy thin-film composites sonicated for 20 min indicated that both the tensile strength and tensile modulus of the former system decreased with the addition of nanofiller. In contrast, all of the MWCNT/epoxy thin films sonicated for 20 min showed higher tensile strengths and tensile moduli than the GNP/epoxy thin-film composites at the same filler loadings. For example, MWCNT additions of 0.6 and 1 vol% displayed lower tensile strengths and tensile moduli than unfilled epoxy thin films, but had better properties than the GNP/epoxy thin-film composites. In general, the mechanical properties of the nanofiller in a polymeric matrix are governed not only by their content within the host system but also by the level of dispersion within the final nanocomposite, aspect ratio and filler shape, functional groups and the interaction between the

filler and matrix [16]. In GNP/epoxy composites, the GNP's aggregation or networking may become a defect, causing a deterioration of the tensile properties in the final nanocomposite. This observation has been attributed to the fact that two-dimensional GNP can more easily aggregate than MWCNTs owing to its larger surface areas and plane-to-plane contact areas. Thus, the Van der Waals attraction forces between adjacent GNP particles may be stronger than those between MWCNTs, making the latter easier to disperse than the former [8].

3.3. Morphological analysis

For the morphological study, 0.2 vol% GNP samples at three different sonication times were investigated under an optical

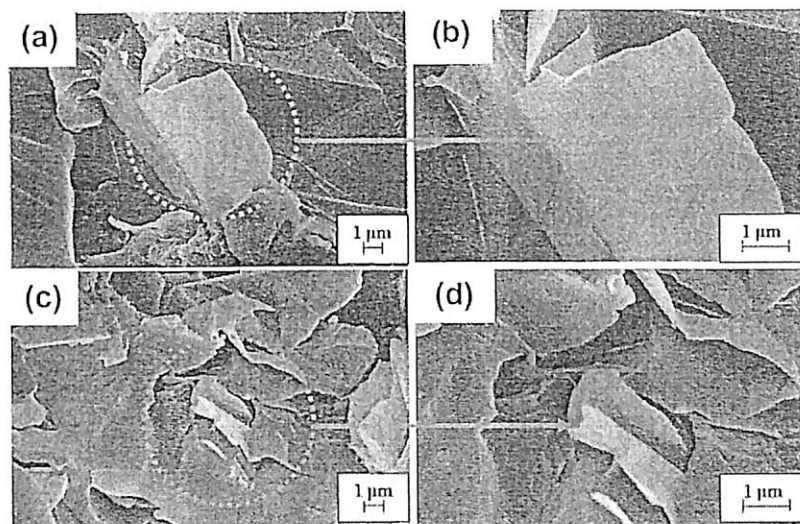


Fig. 5. SEM images on tensile fracture surface of 1 vol% of GNP/epoxy composites produced at 30 min sonication time (at magnification of 500 kx for a, c and 1000 kx for b, d). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

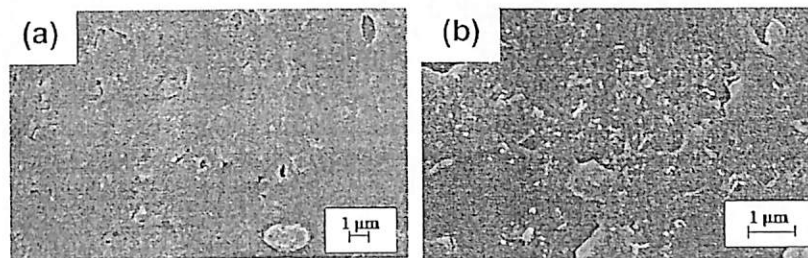


Fig. 6. SEM images on tensile fracture surface of 1 vol% of MWCNTs/epoxy composites produced at 20 min sonication time (at magnification of 500 kx for a, and 1000 kx for b).

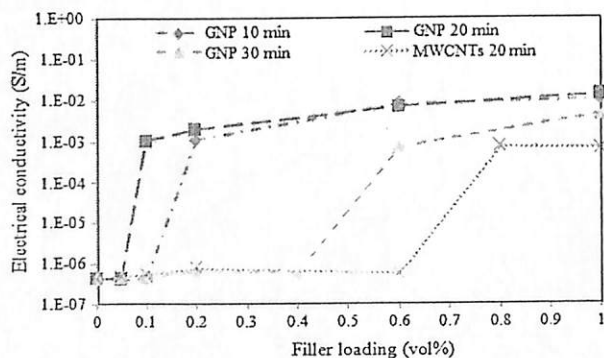


Fig. 7. Electrical conductivity of epoxy thin film with different fillers loading and sonication time. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

microscope to identify the dispersion of GNP in the epoxy matrix. Fig. 3 shows that the GNP dispersion was affected by sonication time. The black and gray regions in the micrograph indicate the GNP and epoxy matrix, respectively. As shown in Fig. 3(a), the GNP filler loadings sonicated at 10 min were poorly dispersed, as evidenced by the aggregation and clustering of the fillers. This observation supported the decrease in composite tensile strength and modulus after sonication for 10 min. According to the rule of mixture, tensile properties are expected to increase with the addition of filler. However, both the tensile strength and modulus de-

creased due to a reduction in the effective aspect ratio and micron-sized cluster formation [16].

The GNP dispersion improved and became more homogenous as sonication time increased, as shown by the smaller aggregation sizes and clustering in the samples sonicated for 20 min. This observation explained the slight improvement in tensile properties (Fig. 2). When the sonication time was increased to 30 min, the GNP dispersion became more homogenous, and aggregation and clustering were found to decrease. However, the tensile properties deteriorated at 30 min of sonication (Fig. 2). A longer sonication time generally has a positive effect on dispersibility. However, according to previous works [24,25], nanofiller damage has become apparent as a result of longer sonication times. This observation was supported by the SEM micrographs of the tensile fracture surface shown in Figs. 4 and 5. These figures show SEM images of the 1 vol.% GNP/epoxy composites produced at sonication times of 20 and 30 min, respectively. Based on Fig. 4(a–d), the GNP layer still existed, with a flaky shape and large dimensions, after 20 min of sonication time. However, Fig. 5(a–d) shows that after 30 min of sonication, the GNP deformed (wrinkling and crimping) and lost its large dimensions, although some of the GNP was apt to roll up into a tube structure with a larger diameter than that of the MWCNTs. This condition resulted in a lower aspect ratio, causing the deterioration of the material's tensile properties. This finding was in agreement with that of Du and his co-researchers [8], who have reported that graphene's two-dimensional structure is difficult to maintain. Such deformation has been attributed to the structure of graphene, which is very thin, like a piece of paper, making it very flexible and easily deformed.

Fig. 6(a and b) shows the tensile fracture surface of the 1 vol% MWCNT/epoxy sonicated for 20 min. The MWCNTs are homogeneously dispersed and covered by epoxy, indicating the existence of good interfacial interaction between the epoxy matrix and MWCNTs, resulting in better tensile properties in the MWCNT/epoxy thin-film composites (as shown in Fig. 2) compared to those of the GNP/epoxy thin-film composites.

3.4. Electrical conductivity

The results of the electrical conductivity measurements made for unfilled epoxy, GNP/epoxy and MWCNT/epoxy thin-film composites at different filler loadings and sonication times are presented in Fig. 7. The unfilled epoxy thin film is an insulator that exhibits a low electrical conductivity of approximately 4.32×10^{-7} S/m. When GNP was added to epoxy resin, the electrical conductivity of the epoxy thin film increased. The percolation phenomenon was observed at critical loading, and the results showed that different sonication times affected the percolation threshold volume fraction and electrical conductivity values. The morphology of the conductive fillers in the polymer matrix is known to significantly affect the formation of a continuous conductive network and the electrical properties of polymer composites. Moreover, other factors such as filler type, filler volume fraction and distribution, and filler-matrix interaction have also been found to influence the electrical conductivity of polymer composites [8,26].

As shown in Fig. 7, the GNP/epoxy thin films produced with 20 min of sonication demonstrated a percolation threshold of approximately 0.1 vol% of the GNP. The electrical conductivity of the 0.1 vol% GNP thin film shot up from 4.32×10^{-7} to 1.02×10^{-3} S/m. The GNP/epoxy thin film produced with 20 min of sonication had a lower percolation threshold value than that sonicated for 10 min, which exhibited a percolation threshold of approximately 0.2 vol% owing to good GNP distribution, which efficiently increased the utilization ratio in forming a conducting network at a lower filler loading, as shown earlier in Fig. 3(b). The GNP/epoxy thin-film composite produced with 10 min of sonication had a percolation threshold of 0.2 vol% owing to the GNP aggregation and clustering, as shown in Fig. 3(a).

The GNP/epoxy thin films produced with 30 min of sonication exhibited a percolation threshold of approximately 0.6 vol% as a result of the GNP deformation that occurred during the long sonication time. GNP can roll into a tube-like structure that usually has a larger diameter than that of MWCNT, resulting in a lower aspect ratio and increasing the percolation threshold volume fraction [8]. In addition, fracturing of the GNP during the sonication process subsequently reduces its area, which reduces the conductive path inside the matrix [27]. This reduction might also have increased the percolation threshold of the GNP/epoxy sonicated for 30 min. The percolation threshold of the MWCNT/epoxy thin-film composites sonicated for 20 min was observed after 0.8 vol% MWCNT loading, and showed an electrical conductivity value lower than that of

any GNP/epoxy thin-film composite. The results on the material electrical properties demonstrated that GNPs were more effective electrical conductivity enhancers than MWCNTs. These results were in agreement with previous work by Xie et al. [28].

Table 1 shows a comparison of the electrical conductivities obtained in the current study and previous works [4,27,29–31]. The material types (filler and matrix), processing method, solvent used for sonication process, and electrical properties (critical filler loading or percolation threshold and maximum electrical conductivities) are specified in the table (as far as the information is available in the publications). Notably, most previous studies have reported the addition of filler in wt%. In the present study, 0.1 and 0.6 vol% (for GNP) and 0.8 and 1 vol% (for MWCNT) were equivalent to 0.19, 1.16, 0.96 and 1.2 wt%, respectively. The table shows that the maximum electrical conductivity of GNP/epoxy is 6×10^{-3} S/m, which is higher than those reported by previous works [4,27]. The comparison showed that the GNP/epoxy composites used in the present study exhibit higher electrical conductivities and lower percolation thresholds than those reported in the literature [27]. However, the MWCNT/epoxy composites in the present study had lower electrical conductivities than the other MWCNT/polymer systems reported in previous works [29,30]. It should be reiterated that the electrical conductivity of a conductive adhesive is governed by many factors, such as processing method, the filler loading and the purity, curing conditions and the conductivity of the matrix itself.

4. Conclusions

This study investigated the effect of sonication time and filler loading on the tensile and electrical properties of a GNP-filled epoxy composite. The results indicated that the GNP/epoxy composite sonicated for 20 min showed a slightly improved tensile strength and tensile modulus compared to those sonicated for 10 and 30 min. A low percolation threshold value (0.1 vol%) was observed after 20 min of sonication time, and optical microscope observation showed improved GNP dispersion with increasing sonication time. However, morphological observation performed using an SEM showed that the GNP tended to deform and roll up after long sonication times (30 min). This observation could have explained the observed drop in tensile properties and increase in percolation threshold volume fraction to 0.2 vol%. Compared to a MWCNT/epoxy composite prepared with 20 min of sonication time, the specimens containing 0.2 vol% of GNP/epoxy had a higher electrical conductivity and slightly lower tensile strength and tensile modulus compared to those of the MWCNT/epoxy composites.

Acknowledgments

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Table 1
Comparison on the electrical property of different types of electrically conductive adhesives systems.

Filler/matrix	Processing method	Critical filler loading (vol%/wt%)	Solution	Maximum electrical conductivity (S/m)	References
GNP/epoxy	Sonicated	0.1 vol%* @ 20 min	–	6×10^{-3} @ 0.6 vol%*	Current study
MWCNTs/epoxy	Sonicated	0.8 vol%* @ 20 min	–	7×10^{-4} @ 1 vol%*	Current study
GNP/epoxy	Sonicated, stirred	1 wt%	Chloroform	9×10^{-4} @ 3 wt%	[27]
GNP/epoxy	Sonicated, stirred	1 wt%	Tetrahydrofuran	5×10^{-4} @ 3 wt%	[27]
GNP/epoxy	Sonicated, stirred	0.08 vol%	Dimethylformamide	1×10^{-5} @ 0.13 vol%	[4]
MWCNTs/epoxy	Sonicated, stirred	0.03 wt%	Acetone	5×10^{-1} @ 0.15 wt%	[29]
MWCNTs/epoxy	Sonicated	0.1 wt%	Acetone	2×10^{-1} @ 1 wt%	[30]
MWCNTs/epoxy	Sonicated, stirred	5 wt%	Acetone	2×10^{-5} @ 20 wt%	[31]

* 0.1 and 0.6 vol% (for GNP); 0.8 and 1 vol% (for MWCNT) are equivalent to 0.19, 1.16, 0.96 and 1.2 wt% respectively.

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Optimization of magnetic and dielectric properties of surface-treated magnetite-filled epoxy composites by factorial design



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ABSTRACT

The effect of surface modification parameters such as 3-aminopropyl triethoxysilane (3APTES) coupling agent concentration (5, 10, and 20 wt%) and treatment duration (3, 5, and 7 h) were studied using design of experiment (DOE) approach. A quadratic model was developed based on response surface analysis. Analysis of variance (ANOVA), R-squared (R-Sq), and normal plot of residuals were applied to determine the accuracy of the models. Multiple responses were simultaneously analyzed by optimization. Magnetic and dielectric properties were used as composite system responses. Solution 1 with 16.66 wt% silane and 7 h treatment time was selected for optimum response. Confirmation study showed that predicted response values match the experimental results.

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1. Introduction

Ferrite polymer-based composites with high permeability, high dielectric constant, and low dielectric loss are gaining attention in various areas such as embedded passive magnetic component, coils, and on-chip electromagnetic shielding applications. The dielectric and magnetic behavior of these ferrite-based polymer composites must be properly understood [1–3]. During ferrite polymer preparation, ferrite particles tend to agglomerate because of strong magnetic particle interactions [4–6]. Inhomogeneous ferrite in the polymer generally leads to the formation of defects in the composite, which affects the quality and performance of the magnetic devices. Surface treatment of ferrite fillers with a coupling agent in the polymer matrix improves matrix filler dispersion and enhances the compatibility of the ferrite fillers and matrix.

A number of parameters during the surface functionalization affect the surface treatment, including coupling agent type and concentration as well as treatment time [7]. All these parameters have not been studied simultaneously and are assumed to have no effect on one another [8–10]. These experiments are considered as single factor experimentation and are referred to as one-factor-at-a-time or OFAT. OFAT is a method of designing experiments where each factor is tested sequentially with all other factors held constant [11]. However, OFAT was found to be inefficient and inadequate in providing valid information. The information obtained often does not justify the resources expended [8].

Design of experiment (DOE), also known as experimental design, is a method commonly used to statistically evaluate the effect of one or more variables on an output through experimental runs [12]. DOE has been applied extensively, especially in the field of science and engineering [13,14]. DOE enables scientists to optimize and predict the possible output based on parameter settings. DOE is an experiment-based modeling whereby a systematic approach is used during experimental planning, data collection, and data analysis. Thus, DOE is far superior to the OFAT approach. DOE is used mainly because it shows the relationship between parameters and responses, providing significant information and better explanation than the OFAT method. In addition, DOE saves time and cost because the number of runs is determined before the actual experiment [15].

In the present study, DOE was utilized to optimize the surface modification condition of magnetite-filled epoxy thin film composite properties. Analysis of variance (ANOVA), R-squared (R-Sq), and normal plot of residuals were applied to determine the accuracy of the models. Optimization was used for simultaneous multiple response analysis. The responses used were the magnetic and dielectric properties of magnetite-filled epoxy thin film composites.

2. Experimental

2.1. Materials

Magnetite (Fe_3O_4) was purchased from Sigma-Aldrich. Magnetite has a density of 4.95 g/ml, a particle size of less than 100 nm, and a molecular weight of 231.53 g/mol. Epoxy resin based on bisphenol-A-epichlorohydrin (DER™ 332) was used as a resin with

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an epoxide equivalent weight of 182 g/eq. to 192 g/eq. and a density of 1.66 g/ml. Polyetheramine PEA (D230) with a density of 0.946 g/ml was used as a curing agent.

2.2. Surface modification of magnetite filler

In this study, magnetite fillers were treated with silane coupling agent at different concentrations (5, 10, and 20 wt%) and treatment time (3, 5, and 7 h). Magnetite fillers were added in an ethanol solution and ultrasonicated for 10 min for dispersion. Ethanol solution was prepared by diluting ethanol with deionized water with a ratio of 95:5. Then, a weighed amount of silane was added into the suspension. Formic acid was added into the mixture until pH 4 was achieved. The mixture was then stirred for 10 min to obtain homogeneity. Subsequently, the mixture was continuously stirred at 60 °C for 3, 5 and 7 h treatment time. Then, the silane-treated magnetite was washed with water followed by ethanol. The modified magnetite was then dried in an oven at 60 °C for 12 h.

2.3. Preparation of treated magnetite-filled epoxy polymer composites

Approximately 20 ml chloroform, as dispersion medium, was added to the weighed particles. The mixture was stirred in an ice-water bath for 10 min using an ultrasonic stirrer (UP 200S, Hielscher) to break up large aggregates. Next, DER™ 332 was added to the suspension at a specific weight percentage basis and ultrasonically stirred for 15 min. The solution was placed and dried in a vacuum oven at 45 °C for 30 min to remove the excess chloroform. Then, curing agent PEA (D230) with a resin-to-hardener ratio of 100:32 was added to the mixture and mixed quickly for 3 min to ensure even filler distribution. To remove bubbles, the mixture was subjected to vacuum for 15 min at room temperature. The mixture was then deposited onto a transparency and spin coated at 250 rpm for 30 s, followed by 500 rpm for 30 s and 750 rpm for 60 s. The composite films were then cured at 80 °C for 2 h.

2.4. Characterization

A vibrating sample magnetometer was used to evaluate the room temperature magnetic parameter of the polymer composites

Table 1
Factors and levels of experiments.

Levels	Low	Medium	High
Factors	(-1)	0	(+)
Amount of silane (%)	5	10	20
Treatment duration (h)	3	5	7

with an applied field range of -20 kOe to 20 kOe. Dielectric properties of the polymer composites were measured over the range of 10⁶ Hz to 10⁹ Hz using Hewlett Packard 4291B impedance analyzer. Factorial designs of 3² were constructed with two factors and three levels. The identified factors were silane amount and treatment time. The factor levels are shown in Table 1. The full factorial design with single replicate involved nine random runs. For the experimental analysis, the design matrix was created by using Design Expert 6.0.6 as shown in Table 1.

3. Results and discussions

The objective of DOE is to determine the optimal values of the two numerical factors, silane amount and treatment duration, and optimize the actual response. The actual optimized responses are saturation magnetization, dielectric constant, and dielectric loss. The experimental results are summarized in Table 2, and these data were used as input into the DOE software for analysis.

3.1. Analysis and model fitting for the responses

Multiple regression analysis was applied to develop the mathematical model or statistical equation for the desired response as a function of variable. Data obtained from the experimental technique were fitted into the mathematical model (Eq. (1)):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i < j} \beta_{ij} X_i X_j + \epsilon \quad (1)$$

where Y is the response (dependent variable), and x_i and x_j are the factors (independent variables). β₀ is the model constant, β_i is the linear coefficient, β_{ii} is the quadratic coefficient, β_{ij} is the interaction coefficient between x_i and x_j, and ε is the standard error.

To understand the impact of various control factors on the response of experimental data, ANOVA was used to determine the significant factors. Meanwhile, the adequacy of the developed models can be verified through regression analysis and normality.

3.1.1. ANOVA

The purpose of ANOVA is to determine the factors and their interactions that significantly affect the process. Tables 3–5 summarize the results of ANOVA for saturation magnetization, dielectric constant, and dielectric loss, respectively. The "Model F-value" of 22.44 for saturation magnetization, as shown in Table 3, shows that the model is significant and only a 0.04% chance exists that a "Model F-value" this large could occur due to noise. P value represents the significance level, whether suitable or unsuitable. Values of "Prob > F" less than 0.05 indicates that the model is significant. Such a condition is desirable, indicating that the terms in the model has significant effect on the response (saturation magnetization).

Table 2
Experimental design and actual responses of saturation magnetization, dielectric constant, and dielectric loss.

Run no.	Variables		Actual responses		
	Silane amount (wt%)	Treatment duration (h)	Saturation magnetization (emu/g)	Dielectric constant (at 1 GHz)	Dielectric loss (at 1 GHz)
1	10	5	15.81	2.07	0.033
2	20	7	17.46	2.42	0.042
3	20	5	14.72	2.15	0.035
4	20	3	14.21	1.91	0.028
5	10	3	14.25	1.89	0.027
6	10	7	17.80	2.38	0.040
7	5	7	15.98	2.26	0.038
8	5	3	14.21	1.88	0.026
9	5	5	14.59	2.00	0.032

Table 3
ANOVA for saturation magnetization.

Source	Sum of squares	DF	Mean square	F-value	Prob > F	Contribution
Model	15.98	5	3.2	22.44	0.0004	Significant
A	0.43	1	0.43	3.03	0.1252	
B	13.1	1	13.1	91.95	< 0.0001	
A ²	2.65	1	2.65	18.62	0.0035	
B ²	0.82	1	0.82	5.75	0.0476	
AB	0.35	1	0.35	2.47	0.1598	
Residual	1	7	0.14			
Cor total	16.98	12				

Table 4
ANOVA for dielectric constant.

Source	Sum of squares	DF	Mean square	F-value	Prob > F	Contribution
Model	0.35	5	0.07	165.3	< 0.0001	Significant
A	0.019	1	0.019	45.8	0.0003	
B	0.32	1	0.32	762.14	< 0.0001	
A ²	2.04E-03	1	2.04E-03	4.85	0.0636	
B ²	7.19E-03	1	7.19E-03	17.1	0.0044	
AB	3.47E-03	1	3.47E-03	8.25	0.0239	
Residual	2.95E-03	7	4.20E-03			
Cor total	0.35	12				

Table 5
ANOVA for dielectric loss.

Source	Sum of squares	DF	Mean square	F-value	Prob > F	Contribution
Model	2.795E-04	5	5.59E-05	92.47	0.0001	Significant
A	2.017E-05	1	2.02E-05	33.36	0.0007	
B	2.532E-04	1	2.53E-04	418.85	< 0.0001	
A ²	5.462E-07	1	5.46E-07	0.90	0.3735	
B ²	3.686E-06	1	3.69E-06	6.10	0.0429	
AB	9.643E-07	1	9.64E-07	1.60	0.274	
Residual	4.231E-06	7	6.04E-07			
Cor total	2.837E-04	12				

Meanwhile, the "Model F-value" of 165.30 for dielectric constant, as shown in Table 4, implies that the model is significant. The chance that a "Model F-value" this large could occur due to noise is at 0.01%. The values of "Prob > F" shown in Table 4 are less than 0.05, which indicate that the model is desirable. Table 5 shows that the "Model-F value" of 92.47 is significant for dielectric loss. The chance that a "Model-F value" this large could occur due to noise is at 0.01%.

3.1.2. Response surface regression analysis

Response surface method was used to examine the relationship between a response and a set of quantitative variables or factors. In the present work, the surface modification parameters silane amount and treatment duration with respect to the magnetic and dielectric properties of the magnetite-filled epoxy thin film composites were analyzed through response surface regression. The response surface regression data for saturation magnetization, dielectric constant, and dielectric loss are shown in Tables 6–8.

The quantity R^2 (R-Sq), also called the coefficient of determination, is used to assess the adequacy of the developed regression model. Table 6 shows that the R^2 of the model for saturation

Table 6
Response surface regression for saturation magnetization.

Term	Coef	SE coef	T	P
Constant	14.0024	2.72674	5.1352	0.014
Silane amount	0.3925	0.22724	1.72737	0.183
Treatment duration	-1.1017	1.0127	-1.08785	0.356
Silane amount × silane amount	-0.0182	0.00801	-2.26566	0.108
Treatment duration × treatment duration	0.1604	0.09836	1.63088	0.201
Silane amount × treatment duration	0.0194	0.01821	1.06674	0.364
Summary of model				
S=0.556419	R-Sq=94.42%		R-Sq (adj)=85.11%	
Press=11.0392	R-Sq (pred)=33.64%			

Table 7
Response surface regression for dielectric constant.

Term	Coef	SE Coef	T	P
Constant	1.7425	0.141645	12.3019	0.001
Silane amount	0.01402	0.011804	1.188	0.320
Treatment duration	-0.02417	0.052606	-0.4594	0.677
Silane amount × silane amount	-0.00064	0.000416	-1.5482	0.219
Treatment duration × treatment duration	0.01167	0.005110	2.2833	0.107
Silane amount × treatment duration	0.00193	0.000946	2.0384	0.134
Summary of model				
S=0.0289041	R-Sq=99.28%		R-Sq (adj)=98.08%	
Press=0.0319028	R-Sq (pred)=90.82%			

Table 8
Response surface regression for dielectric loss.

Term	Coef	SE coef	T	P
Constant	0.0188333	0.0034422	5.47132	0.012
Silane amount	0.0004726	0.0002869	1.64755	0.198
Treatment duration	0.0007917	0.0012784	0.61926	0.58
Silane amount × silane amount	-0.0000156	0.0000101	-1.53773	0.222
Treatment duration × treatment duration	0.0002083	0.0001242	1.6778	0.192
Silane amount × treatment duration	0.0000321	0.000023	1.39801	0.257
Summary of model				
S=0.000702415	R-Sq=99.47%		R-Sq (adj)=95.58%	
Press=0.0000172542	R-Sq (pred)=93.78%			

magnetization is 94.4%, showing that a correlation higher than 90% exists between the predicted and actual values. Similarly, the regression analyses for dielectric constant and dielectric loss are presented in Tables 7 and 8, respectively. The R^2 of the model for dielectric constant and dielectric loss are 99.3% and 99.5%, respectively.

3.1.3. Normal probability plot of the residuals

Normal probability plot is a graphical technique for normality testing to assess whether or not a data set is approximately normally distributed. Normal plots show residuals versus expected data. The plotted residuals show normal distribution; the data points form an approximately straight line. The farther the points from the line, the greater the indication of departure from normality. In practice, for balanced or nearly balanced designs,

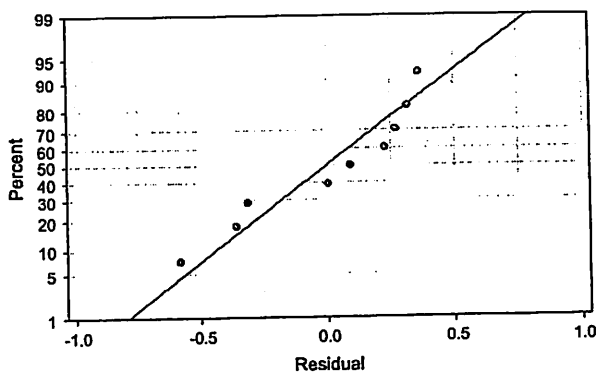


Fig. 1. Normal probability plot for saturation magnetization.

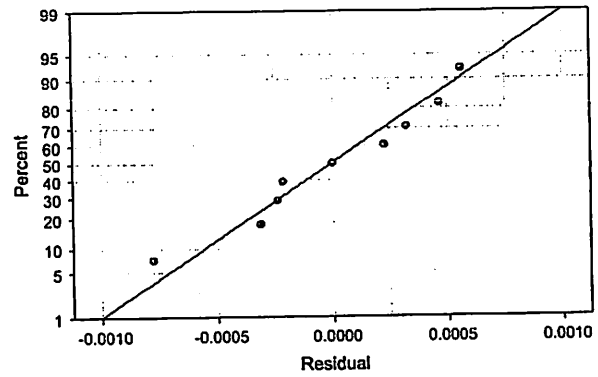


Fig. 3. Normal probability plot for dielectric loss.

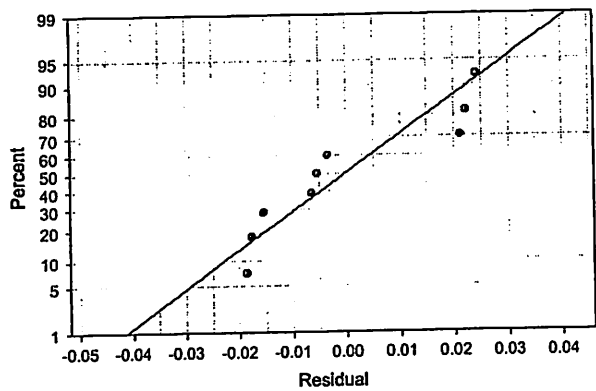


Fig. 2. Normal probability plot for dielectric constant.

moderate departures from normality do not obviously affect the results. Figs. 1–3 show the normal probability plot for saturation magnetization, dielectric constant, and dielectric loss, respectively. In the current work, the residuals are roughly plotted along a straight line for each response, implying no evidence of non-normality or unidentified variables.

Fig. 4(a and b) shows the individual 3D and surface counter plot for saturation magnetization response. The plots show that as treatment duration increases with silane increase up to a certain amount, there is an increase in the saturation magnetization. Magnetite-filled epoxy thin film composites with saturation magnetization higher than 17.36 emu/g can be achieved with a treatment duration longer than 6 h and a silane amount higher than 14.50 wt%.

The 3D and surface counter plots for dielectric constant response are shown in Fig. 5(a and b). Dielectric constants higher than 2.34 can be obtained by increasing the silane amount and treatment duration. Approximately 16 wt% of silane and 7 h of treatment duration may produce magnetite-filled epoxy composite thin film composites with high dielectric constant.

Meanwhile, Fig. 6(a and b) shows the 3D and surface counter plots for dielectric loss response. As shown in Fig. 6, the low dielectric property loss can be obtained by reducing silane amount and treatment duration. Magnetite-filled epoxy composites with dielectric loss less than 0.04 can be produced by setting silane amount treatment and duration to approximately 12.50 wt% and 7 h, respectively.

3.2. Optimization

Given that the optimization of the multiple responses is required, the simultaneous optimal condition for the multiple

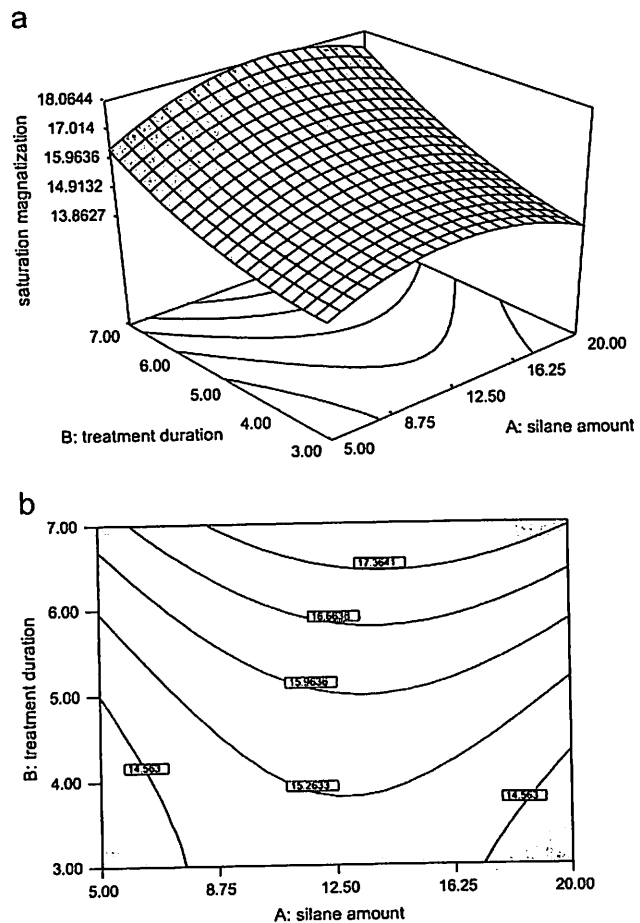


Fig. 4. Response surface (a) 3D plots and (b) contour plots for saturation magnetization.

responses must be determined. To obtain the optimal response, the numerical approach in Design Expert was used to find the solution and desirability for the composite. The solution is a combination of factor settings to achieve the desired properties (responses). To obtain acceptable responses, the ranges and the targets of the response must be identified. In this study, ferrite-filled epoxy thin film composites with high saturation magnetization, high dielectric constant, and low dielectric loss are desirable. Therefore, the goal for saturation magnetization and dielectric constant is set to “maximize”, whereas the goal for dielectric loss is set to “in a range”, where dielectric loss value between 0.026 and 0.042 is acceptable.

Three solutions with predicted response optimizations are shown in Table 9. Solutions are sorted based on desirability and on how well the specified goals are met. The closer the goal achievement, the higher the desirability number. Table 9 shows that the individual desirability for all the solutions is 1. This means that predicted responses are closest to the target requirements. Among the three solutions, solution 1 was selected because it produces ferrite-filled epoxy thin film composites with higher saturation magnetization response and dielectric constant with acceptable dielectric loss properties. Thus, solution 1 with 16.66 wt% silane amount and 7 h of treatment was chosen for its optimum electromagnetic properties.

3.3. Confirmation of test results

Silane-modified magnetite-filled epoxy composite was prepared based on the optimal settings obtained from solution 1. The experimental results of magnetic and dielectric properties of the silane-treated magnetite-filled epoxy thin film composite, which was obtained based on the optimum processing condition, are shown in Figs. 7 and 8, respectively. Experimental results show a saturation magnetization value of 17.93 emu/g, and the dielectric constant and dielectric loss at 1 GHz are 2.42 and 0.041, respectively.

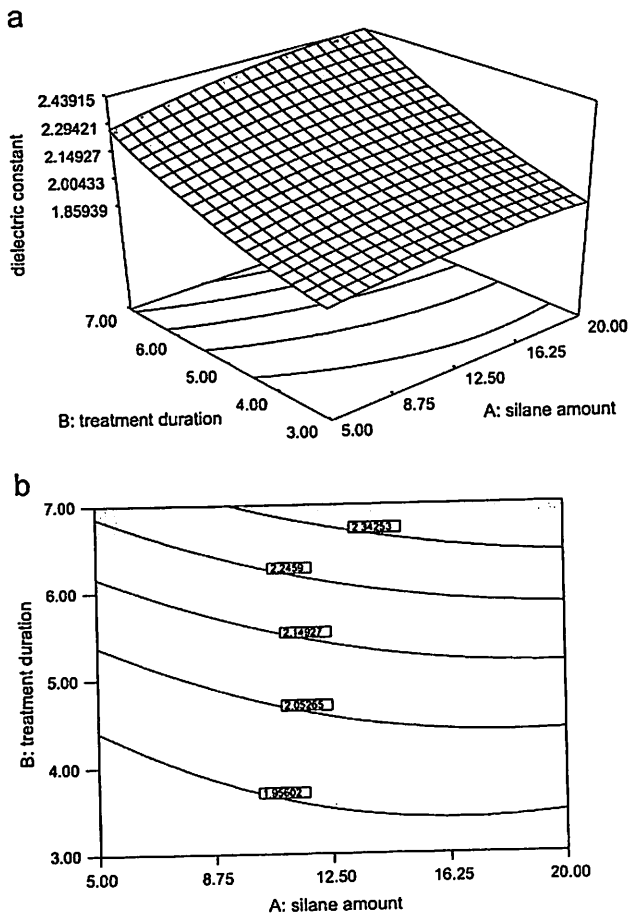


Fig. 5. Response surface (a) 3D plots and (b) contour plots for dielectric constant.

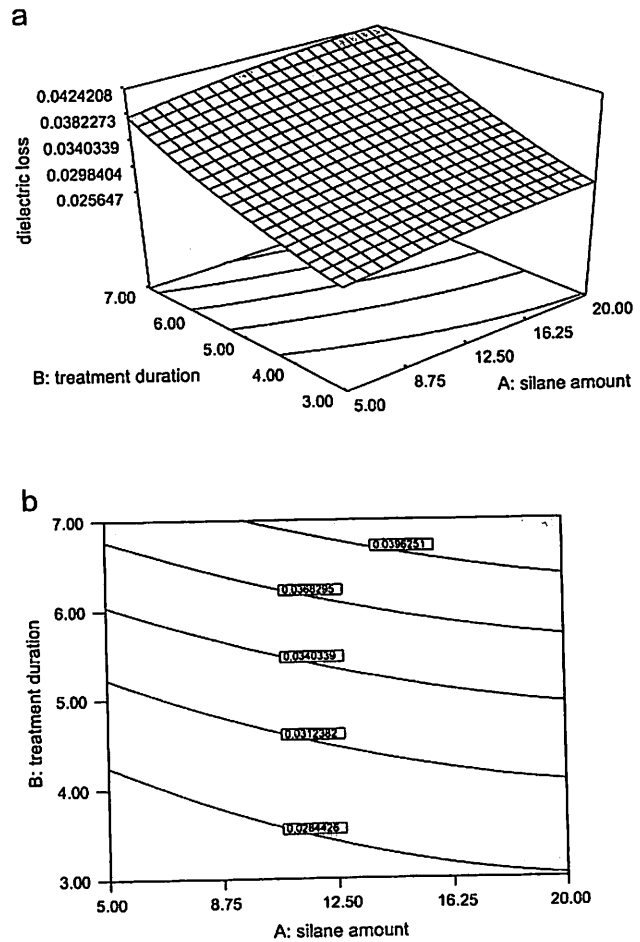


Fig. 6. Response surface (a) 3D plots and (b) contour plots for dielectric loss.

Table 9
Response optimization of multiple responses.

Name	Goal	Lower limit	Upper limit	Lower weight	Upper weight	Importance
Silane amount	is in range	5	20	1	1	3
Treatment time	is in range	3	7	1	1	3
Saturation magnetization	maximize	14.21	17.80	1	1	3
Dielectric constant	maximize	1.88	2.42	1	1	3
Dielectric loss	is in range	0.026	0.042	1	1	3
Solution	Silane amount	Treatment time	Saturation magnetization	Dielectric constant	Dielectric loss	Desirability
1	16.66	7.00	17.96	2.42	0.0417	1
2	17.10	6.99	17.89	2.42	0.0418	1
3	16.87	6.98	17.91	2.42	0.0417	1

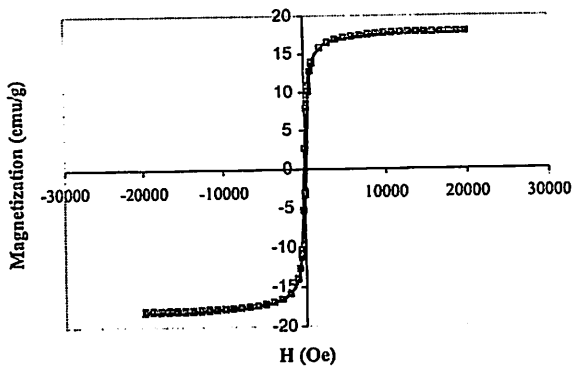


Fig. 7. Experimental values of saturation magnetization of modified magnetite-filled epoxy thin film composite.

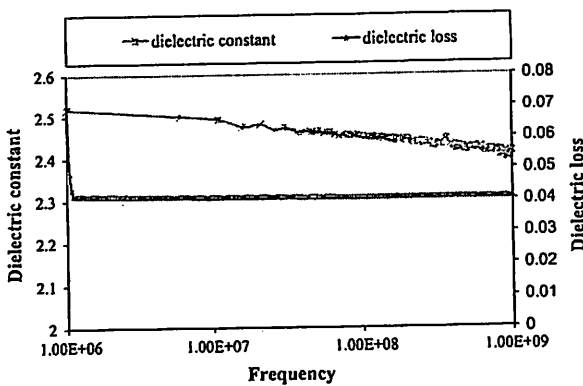


Fig. 8. Experimental values of dielectric constant and dielectric loss of modified magnetite-filled epoxy thin film composite.

Table 10
Comparison of predicted and experimental values of saturation magnetization, dielectric constant, and dielectric loss of the surface-treated magnetite-filled epoxy composite.

Response	Predicted	Experimental
Saturation magnetization (emu/g)	17.96	17.93
Dielectric constant at 1 GHz	2.42	2.42
Dielectric loss at 1 GHz	0.042	0.041

To confirm the statistical data, the predicted values based on solution 1 were compared with experimentally obtained values. The predicted and experimental values of the magnetic and dielectric properties are presented in Table 10. The predicted values of all responses have good agreement with the experimental results.

4. Conclusions

The effect of process parameters such as silane concentration (5, 10, and 20 wt%) and treatment duration (3, 5, and 7 h) on the

magnetic and dielectric properties of magnetite-filled epoxy composite were investigated using DOE. The 3^2 experimental designs were constructed with two factors and three levels, which involved nine runs. Based on response surface analysis, a quadratic model was developed. ANOVA, R-Sq, and normal plot of residuals were applied to determine the accuracy of the models. Based on optimization response, solution 1 with 16.66 wt% silane and 7 h treatment time was selected for optimum desired response. The confirmation of the testing result showed that the predicted response values match the experimental results.

Acknowledgments

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Magnetic, dielectric and thermal stability of Ni–Zn ferrite-epoxy composite thin films for electronic applications

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ABSTRACT

The fabrication of flexible epoxy thin film composites was investigated in this study. Neat epoxy with a resin-to-hardener ratio of 100:32 exhibits higher tensile properties and thermal stability than neat epoxy with a resin-to-hardener ratio of 100:45. In addition, the thermal stability of epoxy composites decreased as the NiZn ferrite content in the epoxy was increased. This result could be caused by the catalytic effect of ferrite. Vibration sample magnetometer results revealed the ferrimagnetic behavior of the ferrite-filled epoxy composites. The degree of saturation magnetization of the epoxy composites increased with the addition of NiZn ferrite nanoparticles. Dielectric tests were performed at room temperature and at frequencies ranging from 10^4 Hz to 10^6 Hz. These findings indicate that the dielectric constant and the dielectric loss are dependent on the filler concentration and test frequency.

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1. Introduction

The rapid development of electronic processing, especially in wireless telecommunication, has led to an increased demand for multifunction electronic nanocomposites that fulfill the requirements of electronic devices [1,2]. Soft magnetic nanoparticles dispersed in polymer matrixes have been intensively studied because of their excellent magnetic and electrical properties [3]. Ferrite-filled composites for important applications such as radar absorbers and electromagnetic shields, have exhibited superior properties compared with their ceramic counter parts and could be widely applied in the military, industrial, and commercial fields [4–7]. NiZn ferrite has attracted a great deal of interest because of its promising electromagnetic properties, specifically, its high resistivity, high permeability, and low dielectric loss in high frequency device applications [8]. Therefore, NiZn ferrite has the potential to provide the desired magnetic and electrical properties for various engineering applications.

Epoxy resin is a promising polymer based on its high electrical resistivity, low dielectric constant, and ease of processing [1,9]. The mechanical and chemical properties of an epoxy can be tailored to meet the required values for specific applications. A ferrite-based epoxy nanocomposite thin film with flexibility, light weight, and the ability to be easily

manipulated into various shapes is highly desirable because it can fulfill the requirements, in term of properties and performance, of specific engineering applications. However, current knowledge on epoxy thin films remains limited because such films are still rigid and brittle [10]. These rigid epoxy thin films provide good thermal properties and mechanical strength, but they can only be positioned in two dimensions [11]. Flexible electronic materials that can be folded and bent in three dimensions are gaining acceptance because flexible substrates can reduce the possibility of failure during mechanical bending by absorbing internal stresses generated during the process [11]. Therefore, these flexible materials will increase the reliability of thin films in roll-to-roll processing, reducing manufacturing costs. In order to contribute to the production of a flexible epoxy thin film, we investigate the resin-to-hardener ratio (stoichiometry) as a parameter to be considered during manufacturing. Note that the term 'stoichiometric ratio' refers to a formulation with equal initial concentrations of epoxy groups and amine hydrogen.

Several studies have performed characterization of ferrite-based polymer nanocomposites. However, to the best of our knowledge, there are few works concerning flexible NiZn ferrite-filled epoxy polymer composites. In the present study, the influence of varied stoichiometry, which is achieved by changing the resin-to-hardener ratio, on the polymer composite was evaluated. Moreover, the effect of NiZn filler loading was also explored. The thermal, magnetic, and dielectric properties of epoxy matrix composites embedded with 0–8 vol% of NiZn ferrite particles were investigated.

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2. Experimental

2.1. Materials

A commercial epoxy based on bisphenol-A-epichlorohydrin (EPON™ resin 8281; Hexion Specialty Chemical, USA) was used as a resin with an epoxy equivalent of 188 g/eq. Polyetheramine PEA (Baxxodur™ EC301; BASF Corporation), with an equivalent weight of 61 g/eq. and a density of 0.948 g/cm³ was used as a curing agent. NiZn ferrite (Sigma-Aldrich) was used as a source of ferrite with a particle size of less than 100 nm, a density of 2.81 g/cm³ at 298 K, and a molecular weight of 411.46 g/mol.

2.2. Preparation of epoxy thin film

Two formulations were used to prepare a flexible epoxy film: a stoichiometric formulation with an epoxy-to-hardener ratio of 100:32 and a non-stoichiometric formulation with an epoxy-to-hardener ratio of 100:45, corresponding to 32 and 45 amine parts per 100 epoxy resin parts in weight, respectively. Mixtures were vacuumed to remove all trapped bubbles before the spin-coating process. Next, the epoxy mixtures were deposited on a transparency and were spin-coated at a rate of 1000 rpm for 30 s followed by a second spin-up at 1500 rpm for 120 s. Composite films were subsequently cured at 80 °C for 2 h. The thickness of the epoxy thin film produced from this spin coating process was approximately 30–50 μm.

2.3. Preparation of NiZn ferrite-filled epoxy polymer composites

NiZn ferrite nanoparticles were dispersed in a chloroform solution at a weight ratio of 3:1 and were ultrasonically stirred in an ice-water bath for about 10 min. Next, EPON 8281 was added to the particle suspension at a specific weight percentage basis and mechanically stirred for 5 min. The solution was placed in an ultrasonication bath for 10 min and dried in a vacuum oven at 45 °C for 0.5 h to remove the chloroform. The PEA curing agent (at the proper amount corresponding to the resin/hardener ratio) was added immediately and mixed quickly for 3 min to ensure even distribution. Mixtures were then deposited onto a transparency and spin-coated at 1000 rpm for 30 s followed by a second spin-up at 1500 rpm for 120 s. Composite films were subsequently cured at 80 °C for 2 h. For the dielectric test, the mixtures were vacuumed, and they were poured into 1-mm thick silicone rubber molds and cured at 80 °C for 2 h. Two series of specimens with epoxy-to-hardener ratios of 100:32 and 100:45, which were designated composite I and composite II, respectively, were produced.

2.4. Characterization

The tensile properties of the neat epoxy thin film were measured by the Instron 3366 instrument. The thermal stability of the polymers and the composite materials was determined by thermo-gravimetric analysis (TGA) using a Pyris™ TGA. Measurements were obtained at a heating rate of 10 °C/min from 30–600 °C in a nitrogen atmosphere. A vibrating sample magnetometer (VSM) was used to evaluate the room temperature magnetic parameter of the polymer composites with an applied field of $-20 \text{ kOe} \leq H \leq 20 \text{ kOe}$. The samples were covered with aluminum foil and were placed on the sample holder with Teflon tape. The dielectric constant and dielectric loss of the polymer composites were measured using an Agilent 4284A LCR meter in the frequency range of 10⁴–10⁶ Hz at room temperature.

3. Results and discussions

3.1. Tensile properties

Tensile testing was carried out to determine the elastic modulus, tensile strength, and elongation at break of the epoxy thin films. The samples were in the shape of dumbbell as required by ASTM D638-03. The stress–strain curves for each ratio, 100:32 and 100:45, were plotted in Fig. 1. This figure indicates that the stress–strain curve increases to a maximum drop off abruptly after fracture. The values of the elastic modulus, tensile strength and elongation at break are presented in Table 1. It is observed that the elastic modulus and tensile strength of the thin film with an epoxy-to-hardener ratio of 100:32 are higher than those of the film with an epoxy-to-hardener ratio of 100:45. However, the samples with ratios of 100:32 and 100:45 show similar elongation at break with values of 58.2% and 58.8%, respectively.

3.2. Thermo-gravimetric analysis

The TGA and derivative curves of the NiZn ferrite-filled epoxy composites with filler loading varying from 0 vol% to 8 vol% are presented in Fig. 2. Fig. 2a and b shows the TGA and derivative curves for the epoxy-to-hardener ratios of 100:32 (composite I) and 100:45 (composite II), respectively. The curve reveals a single-step degradation process for all composites. Table 2 shows variations in the 5% weight loss temperature ($T_{5\%}$) and the onset temperature (T_{onset}) of polymer composites I and II at different filler loading. Neat epoxy resin with non-stoichiometric matrix formulation (composite II) showed slightly lower T_{onset} and $T_{5\%}$ than did neat epoxy resin with stoichiometric matrix formulation (composite I). According to Calventus et al. [12], in stoichiometric resin, all amine groups react with all epoxide groups, thereby forming a network of interconnected rings consisting of two or three epoxide chains that react with the corresponding amine group. For the non-stoichiometric epoxy resin, the presence of an excess amine group increased the number of un-reacted amine

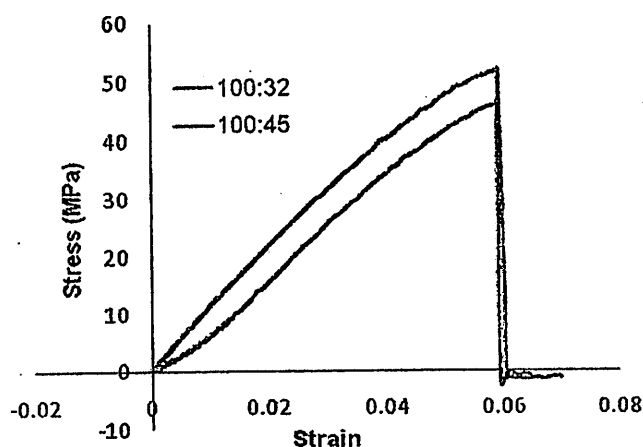


Fig. 1. Stress–strain curve of different epoxy-to-hardener ratio.

Table 1
Tensile properties of thin film with different of epoxy-to-hardener ratios.

Epoxy:hardener	100:32	100:45
Elastic modulus (MPa)	1021.9	937.9
Tensile strength (MPa)	55.8	44.4
Elongation at break (%)	58.2	58.8

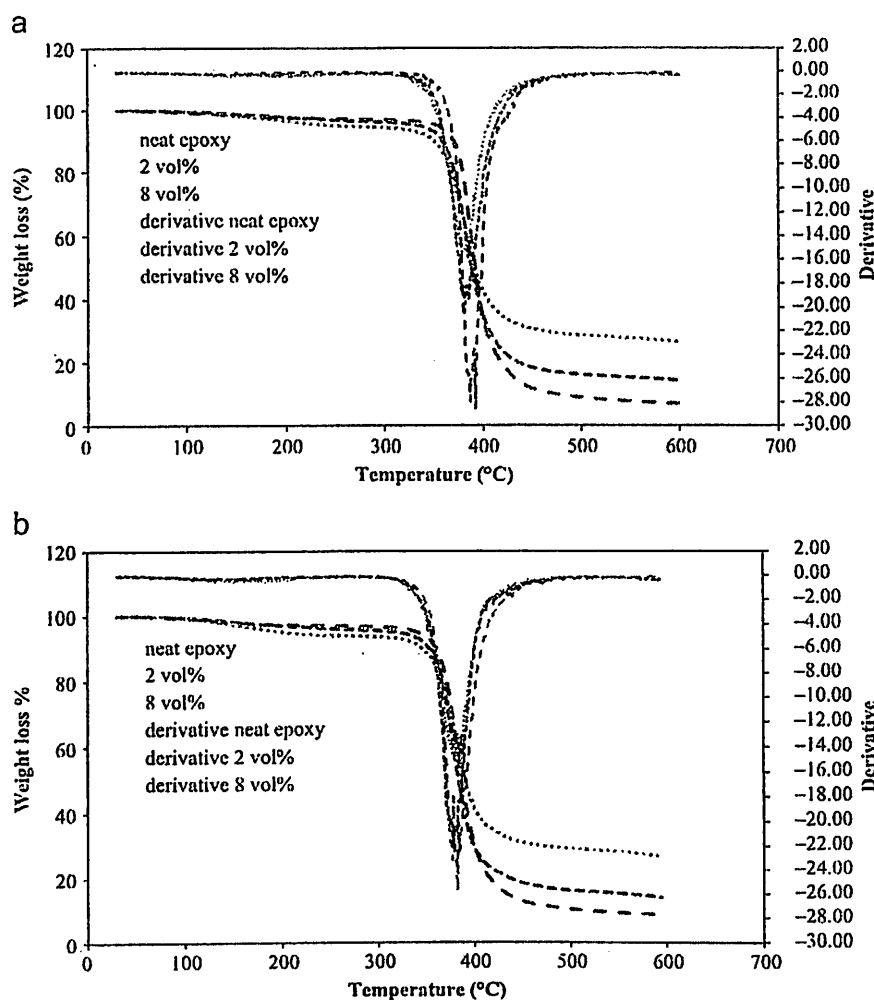


Fig. 2. TGA curves for (a) composite I and (b) composite II.

Table 2
TGA of NiZn ferrite-filled epoxy composite with varying filler loading.

System	NiZn ferrite loading (vol%)	Initial degradation temperature $T_{5\%}$ (°C)	Onset degradation temperature T_{onset} (°C)	Weight of residual (%)
Composite I	0	353	346	6.1
	2	333	339	10.8
	8	259	336	21.4
Composite II	0	341	338	8.6
	2	322	331	14
	8	206	325	26.7

groups, thereby influencing the thermal stability of the non-stoichiometric composite. In addition, T_{onset} and $T_{5\%}$ for the NiZn ferrite-filled polymer composite I was higher than that of the NiZn ferrite-filled epoxy composite II. Thus, the reduced thermal stability of the non-stoichiometric epoxy resin is probably a result of the excess of hardener, which degrades at a low temperature. A similar observation was reported by Laza et al. [13], who observed that increased amounts of hardener lowered the initial thermal decomposition temperature of epoxy.

Furthermore, 8 vol% NiZn ferrite-filled epoxy composite I exhibited lower T_{onset} and $T_{5\%}$ relative to 2 vol% NiZn ferrite-filled epoxy composite I. Similar behavior was observed in composite II

when comparing T_{onset} and $T_{5\%}$ of the 2 vol% and 8 vol% NiZn ferrite-filled epoxy composites. According to previous studies [14–17], metallic compounds could serve as catalysts to degrade the epoxy matrix. Therefore, the ability of the NiZn ferrite filler to facilitate thermal degradation of the polymer composite at the initial stage might be attributed to this catalytic effect. Conversely, the char yields of the composite were higher than those of the neat epoxy. The weight of the residuals in the neat epoxy can be attributed to carbon char, which remains as a black residue. The char yield increased with the filler content because NiZn ferrite has a higher decomposition temperature than epoxy resin. We observed that all composites were stable and that no substantial weight loss occurred at operating temperatures of up to 100 °C. Therefore, it is recommended that normal device operating temperatures should not exceed 100 °C.

3.3. Effect of NiZn ferrite loading on the properties of the epoxy composite thin film

3.3.1. Magnetic properties

Discussion of the magnetic properties of the epoxy composites will be based on the results of composite I because the results of the tensile and TGA analysis indicated that an epoxy-to-hardener ratio of 100:32 produced an epoxy thin film with thermal stability superior to that of composite II. The magnetic properties of the NiZn ferrite-filled epoxy composites were explained using the M -

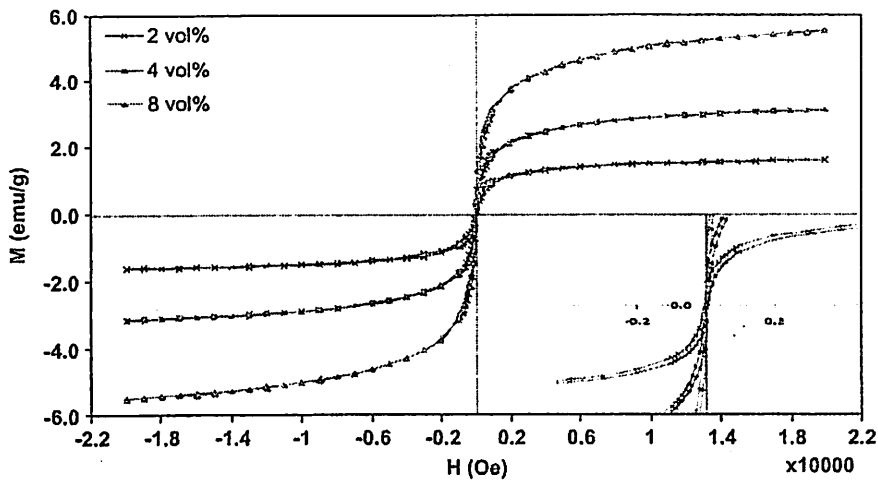


Fig. 3. M - H curves of epoxy composites I. The inset shows the enlarged hysteresis loops at low applied field.

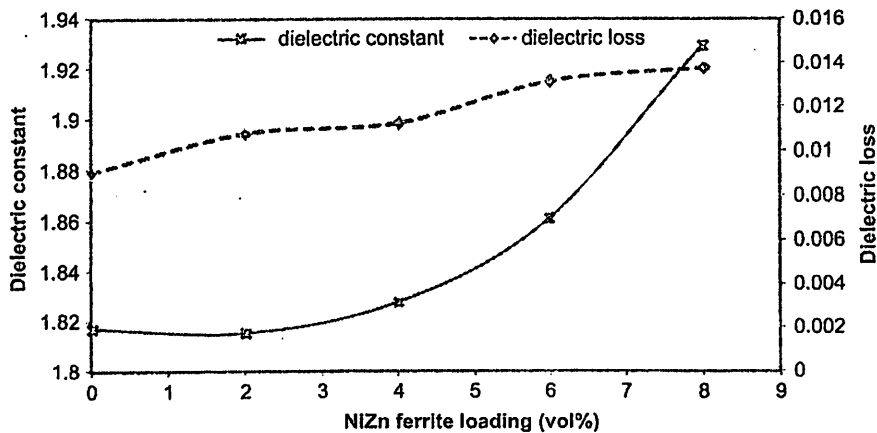


Fig. 4. Variation of dielectric constant and dielectric loss as a function of ferrite loading in NiZn ferrite-filled epoxy composite I at 10^6 Hz.

H curve in Fig. 3. In all cases, a notably small value of coercive force is observed with negligible retentivity, which indicates the ferrimagnetic nature of the material [4,18]. The room temperature saturation magnetization (M_s) of the NiZn ferrite-filled polymer composites increased with higher filler loading at an external field of 22 kOe. M_s of the 2 vol% ferrite-filled polymer composite was found to be 1.6 emu/g. When the volume fraction of ferrite was increased to 8%, the M_s value increased drastically to 5.5 emu/g. According to the equation $M_s = \phi m_s$, M_s is related to the volume fraction of particles (ϕ) and the saturation moment of a single particle (m_s) [19]. A similar observation was reported by Agarwal et al. [20] in which the value of the saturation magnetization increased with increasing iron oxide loading. Therefore, the saturation magnetization of the NiZn ferrite-filled epoxy composite depends mainly on the volume fraction of magnetic ferrite filler. The magnetization measurement indicated that NiZn ferrite-filled epoxy composite can serve as a typical EMI suppressor in the frequency range of 10^4 – 10^6 Hz.

3.3.2. Dielectric properties

Fig. 4 shows the variations of dielectric constant and dielectric loss at 10^6 Hz as a function of the filler loading. The dielectric constant and dielectric loss increased from 1.817 to 1.948 and 0.009 to 0.042, respectively, as the filler loading increased from

0 vol% to 8 vol%. Thus, the dielectric constant and dielectric loss were found to be dependent on the volume fraction of the filler component. Elevation of the dielectric constant can be attributed to interfacial polarization. This phenomenon occurs in heterogeneous systems consisting of phases with different dielectric constants in which the accumulation of charges at the interfaces is responsible for the conductivity [21,22]. Heterogeneity increased as the NiZn ferrite loading in the epoxy was increased. Greater interfacial area leads to greater average polarization, which consequently increases the dielectric constant. Similarly, the dielectric loss increased when the filler loading in the composite was increased from 0 vol% to 8 vol%. As the NiZn ferrite filler loading was increased, the number of dipoles available also increased, and dipolar polarization resulted in an enhancement of the dielectric properties of the composites [23].

The room temperature dielectric constant of the neat epoxy and NiZn ferrite-filled epoxy composites with different filler loading is presented as a function of frequency in Fig. 5. Higher values of the dielectric constant were obtained at lower frequency. This correlation can be attributed to the low resistivity of ferrite, which generates electric charge transference [1]. In general, the dielectric constant decreased with increasing frequency with slight variation. The decrease in the dielectric constant with frequency can be ascribed to the inability of the interfacial dipoles to orient themselves in the direction of the time-varied external

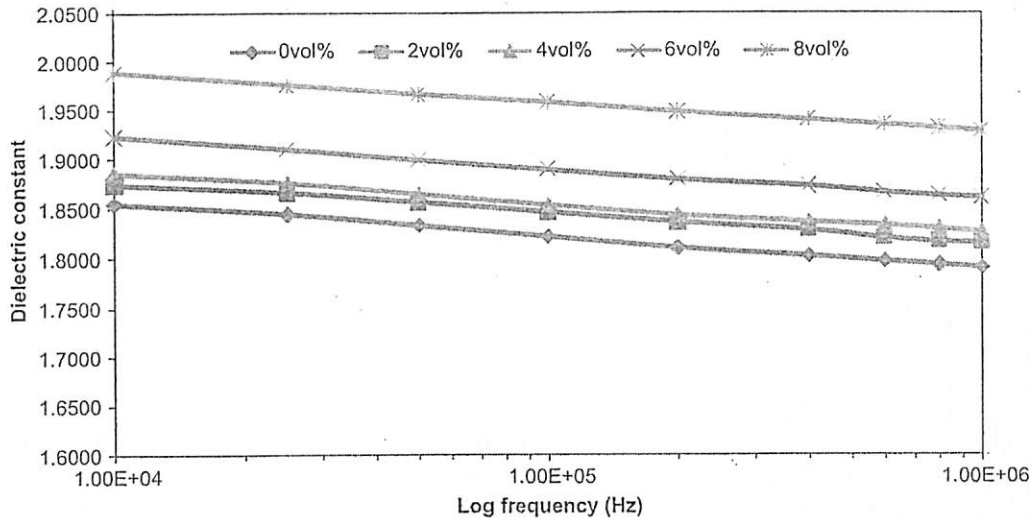


Fig. 5. Variation of dielectric constant of NiZn ferrite-filled epoxy composite I at frequency ranging from 10^4 Hz to 10^6 Hz.

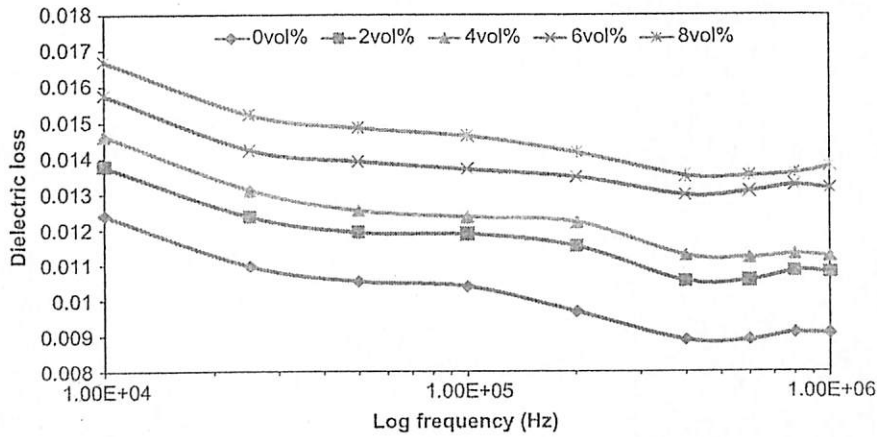


Fig. 6. Variation of dielectric loss of NiZn ferrite-filled epoxy composite I at frequency ranging from 10^4 Hz to 10^6 Hz.

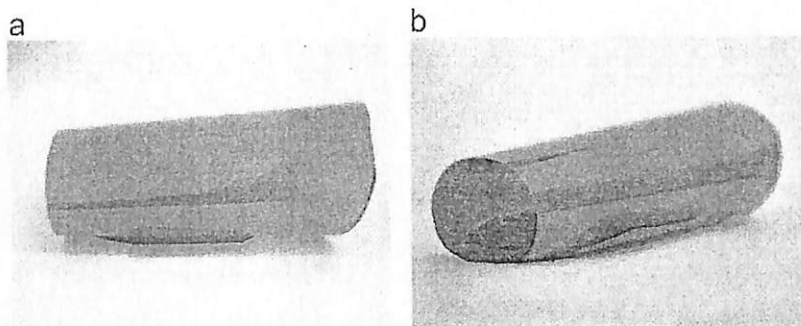


Fig. 7. (a) Top and (b) side view of 8 vol% NiZn ferrite-filled epoxy composite I.

applied field [21]. In addition, the slight reduction in the dielectric constant indicates the absence of resonant phenomena at these frequencies [8].

Fig. 6 demonstrates the dielectric loss of the neat epoxy and NiZn ferrite-filled epoxy composites as a function of frequency. It is observed that the dielectric loss of the samples was decreased as the frequency was increased from 10^4 Hz to 10^6 Hz. The trend

observed can be ascribed to dipole polarization. At low frequency, dipolar molecules have enough time to orient themselves to the external applied field. As the frequency is increased, the dipoles have less time to orient in the direction of the applied field. Therefore, as the frequency was further increased from 10^4 Hz to 10^6 Hz, the dipole polarization was reduced, and hence the dielectric loss dropped accordingly [21]. It was observed that

the dielectric loss of the samples is low at 10^6 Hz, which satisfies the need for a low loss value in practical engineering applications.

The top and side views of the fabricated flexible epoxy thin film with 8 vol% NiZn ferrite-filled epoxy are shown in Fig. 7a and b. It is observed that the addition of 8 vol% NiZn ferrite in epoxy produced a flexible film that can be bent to 360° . In other words, it can be noted that the flexibility of the film, which is determined by the ability of the epoxy film to be bent to 360° , is maintained with the addition of high filler loading.

4. Conclusion

Two sets of composites with different epoxy-to-hardener ratios (100:32 and 100:45) were fabricated and studied in order to produce flexible epoxy thin films. The tensile results revealed that the elastic modulus and tensile strength of the neat epoxy thin film with a stoichiometric matrix formulation are higher than those of the non-stoichiometric matrix formulation. However, it is observed that both the stoichiometric and non-stoichiometric formulations show similar elongation at break. The thermal stability of the stoichiometric epoxy resin was found to be better than that of the non-stoichiometric epoxy resin. Epoxy composite filled with 8 vol% of NiZn ferrite exhibited lower T_{onset} and $T_{5\%}$ followed by the 2 vol% epoxy composite and the neat epoxy resin, due to the catalytic effect of the filler. The VSM results revealed that the saturation magnetization M_s of the epoxy composites increased with increase in NiZn ferrite loading. A notably small value of coercivity and negligible retentivity was observed, indicating the ferrimagnetic nature of the material. The dielectric constant and dielectric loss of the composites increased with increase in filler loading because of interfacial and dipolar polarization.

Acknowledgments

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Effect of Hybrid Reinforcement of MWCNT and Carbon Fiber on Properties of Epoxy Laminated Composites

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ABSTRACT

The properties of carbon fiber/epoxy laminates were investigated after incorporating multi-walled carbon nanotubes (MWCNT) with different volume percentages. Addition of MWCNT in 4-ply Carbon fiber CF results in lower density and burning rate compared to control samples (5CF and 4CF). CF with 1 vol% of MWCNT prepared through the ethanol spraying method exhibited 134% and 75% higher flexural strength than the control samples of 4CF and 5CF, respectively. The composite laminates with 1 vol% MWCNT prepared through the ethanol spraying method showed better thermal and mechanical properties compared with the other composite samples.

KEYWORDS: Carbon fiber, Multi-walled carbon nanotubes, Polymer-matrix composite, Mechanical properties, Thermal properties.

INTRODUCTION

Carbon fiber reinforced epoxy composites are widely used in engineering applications because of their low densities, light weight, remarkable strength, and stiffness. Compared with steel and

aluminum, carbon fiber reinforced epoxy materials have greater strength-to-weight and stiffness-to-weight ratios and exhibit excellent fatigue resistance^[1, 2]. The application of the epoxy matrix in the composite allows the transfer of loads between fibers. However, epoxy

is known as a brittle material. Thus, improving its toughness improves the mechanical properties of the composites.

Application of nanofillers in fiber reinforced polymers are getting acceptance due to its ability to enhance mechanical properties of the composites. Different types of nanofillers have been used in previous works such as carbon nanotubes (CNTs), carbon nanofibers (CNFs), fumed silica and others^[4]. CNTs are gaining popularity judging from their remarkable flexibility, low mass density and large aspect ratio (typically > 1000)^[3-6]. Therefore, the incorporation of CNT into the matrix is expected to improve the mechanical, thermal, and electrical properties^[5-7] that grant the composite unique properties. However, the fabrication of these composites is restricted by the agglomeration of CNTs^[8], which is due to the strong intertube van der Waals forces [8] that also cause the CNTs to form into bundles and ropes in the matrix^[9]. The effective dispersion of CNTs in the composite system is important because the agglomeration of CNTs limits the load transfer process from the matrix to the CNTs^[9].

The solution mixing method is commonly used to fabricate polymer nanocomposites^[4, 6]. However, higher loading of nanofillers is impossible due to the high viscosity of the polymer matrix. Therefore, the solution spraying method was used in this study to improve the dispersion of CNT.

This study aims to produce hybrid laminated composites of carbon fiber (CF)/ epoxy with multi-walled carbon nanotubes (MWCNT) in the composite system. The effects of the different methods of MWCNT dispersion and the different

MWCNT volume percentages (vol%) on the properties of CF/epoxy composites were investigated. The 4-ply CF/MWCNT/epoxy composites were fabricated using the hand lay-up technique, followed by the vacuum bagging technique. The density, flexural, thermogravimetry analysis, dynamic mechanical analysis and burning rate of the fabricated 4-ply composite laminates were compared with the properties of the control samples of unfilled epoxy and the 5-ply CF/epoxy composite laminates.

EXPERIMENTAL

Materials

Carbon fabric type 5-harness satin weave with identical warp and fills yarns of 6000 multifilament continuous tow was used as reinforcement. The fabric with linear density of 369.58 g/m² was supplied by Fibre Glast Developments Corporation, Brookville, Ohio. The D.E.NTM 431 epoxy novolac resin was manufactured by Dow Chemical Company. The curing agent Baxxodor® EC301 (Polyetheramine D230) was manufactured by BASF (Malaysia) Sendirian Berhad. Both epoxy resin and curing agent were supplied by Penchem Technologies Sendirian Berhad. Mixture of resin and curing agent of 100 to 32 weight ratios, were used in the study. The MWCNTs used in this study were synthesized by a group of researchers from the Universiti Sains Malaysia. The highly pure MWCNTs (99.8%), with nearly uniform diameter average of 6.2 nm \pm 0.5 nm, were synthesized over magnesia-supported Co-Mo bimetallic catalysts through catalytic chemical vapor deposition^[12]. Ethanol (95%) was used as dispersing agents in the solvent spraying method.

Composite laminate fabrication

Preparation of control sample

A 5-ply CF/epoxy (5CF) sample was prepared by using 5 pieces of fabric with a dimension of 180 mm \times 210 mm. The ratio of CF to epoxy matrix was fixed at 60 vol % to 40 vol %. The predetermined mixture of epoxy and curing agent (100:32 ratios by weight) was ultrasonicated. The composite laminate was prepared via hand lay-up

technique, followed by consolidation for about 1 hr using the vacuum bagging technique. The fabricated sample was left overnight to cure, and then subjected to a post-curing process where the sample was heated at a temperature of 100 °C for 1 h and at 125 °C for 3 h. A 4-ply CF/epoxy composite laminates sample (4CF) was also prepared using a similar procedure. The ratio of CF to epoxy in 4CF was also fixed at 60 vol % to 40 vol %.

Preparation of 4-ply CF/MWCNT/epoxy via solution mixing method

Four pieces of CF with a dimension of 180 mmx 210 mm were used in the fabrication of 4-ply CF/epoxy incorporated with MWCNT. The MWCNT used in the

laminated composites were varied from 0.5 to 1.5 vol %.

In this solution mixing method, MWCNT fillers were directly mixed with 40 vol % of epoxy matrix prior to laminating procedure. The predetermined amount of MWCNT was ultrasonicated with epoxy for 30 min in cold bath followed by addition of the curing agent and ultrasonicated again for 10 min. Fabrication method as discussed in previous section was applied to prepare the composite laminates. Figure 1(a) shows the solution mixing method used in this study. Here, the 4-ply and 5-ply CF/epoxy laminates were referred to as 4CF and 5CF, respectively. Composites with 0.5, 1, and 1.5 vol % of MWCNT were referred to as 4CF0.5S, 4CF1.0S, and 4CF1.5S, respectively.

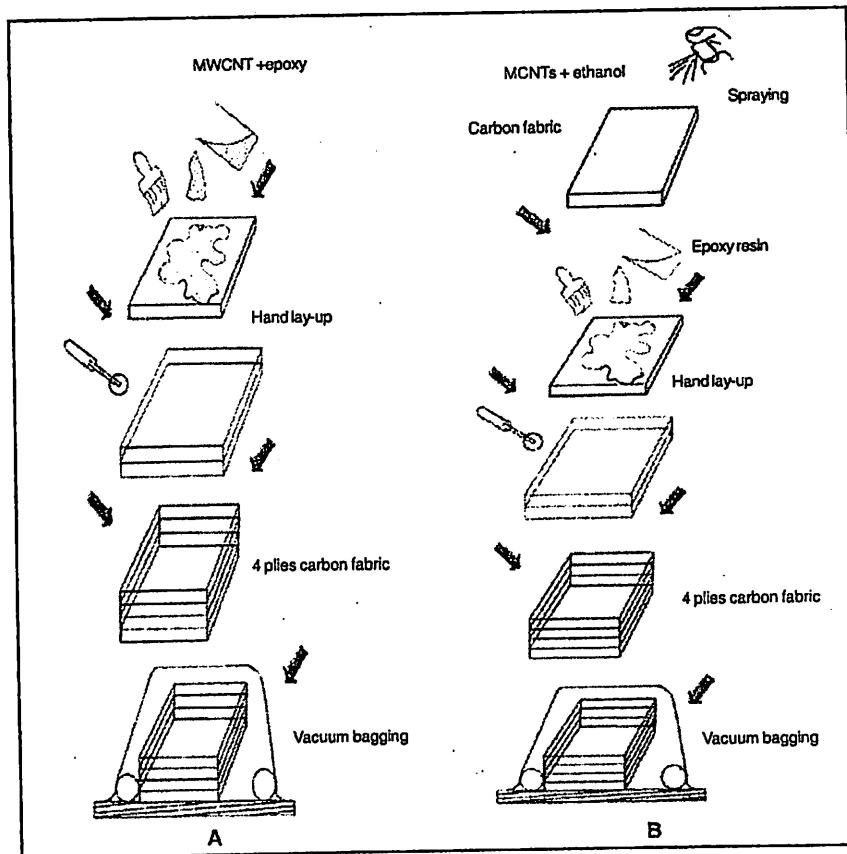


Figure 1: (a) solution mixing method and (b) solvent spraying method used in preparation of CF/MWCNT/epoxy composite laminates.

Preparation of 4-ply CF/CNT/epoxy via solvent spraying method

Same dimension of CF as well as same amount of epoxy and curing agent as in Section 2.2.1 were utilized in this study. However, the predetermined weight of MWCNT was first dispersed in ethanol and ultrasonicated in cold bath for 30 min prior to hand lay-up process. For 0.5 vol % MWCNT concentration, the MWCNT was dispersed into 30 ml of ethanol, while 1.0 and 1.5 vol % of MWCNT were dispersed into 60 and 90 ml of ethanol, respectively. The solution was then sprayed onto the surface of 4 pieces of CF until all the MWCNT was consumed. The sprayed fabrics were left at room temperature for about 4 hours to allow evaporation of the ethanol. Same fabrication method has been used to prepare the composite laminates. Figure 1(b) shows the solvent spraying method used in this. Composites with 0.5, 1, and 1.5 vol % of MWCNT prepared by solvent spraying method were referred to as 4CF0.5E, 4CF1.0E, and 4CF1.5E, respectively.

Specimen configuration and test method

The density of the composite samples was measured based on Archimedes' Principle using a gravity balance, Precisa 8000. Six samples with the dimension 10 mm × 10 mm were used in the test; the average density was calculated. The flexural properties of the composites were measured using INSTRON 5982, set according to ASTM D-790, with a cross-head rate of 2 mm/min. At least 5 specimens were tested. Specimens with dimension of 80 mm long × 17 mm wide × 2 mm thickness with 40 mm support span were loaded under three-point bending until failure [13]. The thermal stability of the samples was measured through thermogravimetry analysis (TGA) using a Mettler Toledo, TGA/DSC Star[®] System Analyzer. A small piece of the selective sample was weighed and heated in a nitrogen environment from ambient temperature to 600 °C at a heating rate of 10 °C per min. Raw fabric samples sprayed with MWCNT and cross section of flexural samples were observed under a scanning electron microscope (SEM), FESEM/Zeiss Supra 35 VP.

Dynamic mechanical analysis (DMA) was carried out using a Mettler Toledo DMA 861 Analyzer. A selected sample with a dimension of 50 mm × 10 mm × thickness

was tested at dual cantilever mode from ambient temperature to 150 °C at a heating rate of 5 °C/min. Oscillatory sine-wave stress was applied at a frequency of 1 Hz. Force amplitude was set at 1 N, with a displacement amplitude of 25 μm. Liquid nitrogen was used to cool down the system [14]. A rate of burning test was carried out according to ASTM D 635 [15] to investigate the linear rate of burning of the samples. Specimens with the dimension of 125 mm × 13 mm × thickness were burned horizontally. The timer was set after the flame reached a mark that was 25 mm away from the end of the specimens. The time taken for the specimens to be extinguished was recorded, the length exposed to the flame was measured, and the burning rate was then calculated.

RESULTS AND DISCUSSION

Density

Figure 2 shows the densities of the epoxy, 5-ply CF/epoxy (5CF), 4-ply CF/epoxy (4CF) and 4-ply CF samples with addition of different MWCNT vol % through different dispersion methods. As expected, the density of 4CF is 12% lower than that of 5CF samples. 4-ply composite samples incorporated with MWCNT also show lower density compared with that of 5CF samples. Although MWCNT was incorporated through different dispersion methods, the densities of the samples with similar MWCNT loadings were almost equal. Compared with the 5CF sample, the density of the sample with 0.5 vol % MWCNT was reduced by about 7%, whereas those with 1 vol % and 1.5 vol % of MWCNT loading was reduced by and 6% and 3%, respectively. The reduction in density was due to the decreasing number of CF ply in the 4CF compared with 5CF composite samples. Meanwhile, the density of the 4-ply CF/MWCNT/epoxy samples increased with the increasing MWCNT loading compared

to 4CF. Modest increment of the density of the 4CF0.5, 4CF1.0 and 4CF1.5 composites is due to the increasing amount of MWCNT in the composite laminates. In general, it is observed that the densities of 4-ply CF/epoxy incorporated with MWCNT composites are still lower than that of 5CF composites. The same observation was also reported by Gajendran and Saraswathy⁽¹⁶⁾ in their study on polyaniline-carbon nanotubes

(PANI-CNT) composites. They observed that the density of PANI-CNT composites increased when CNT loading was added in the PANI-CNT system through the solution mixing method. Ogaswara et al.⁽¹⁷⁾ also reported the increasing density trend of aligned multi-walled carbon nanotubes/epoxy composites with the increasing volume fraction of MWCNT.

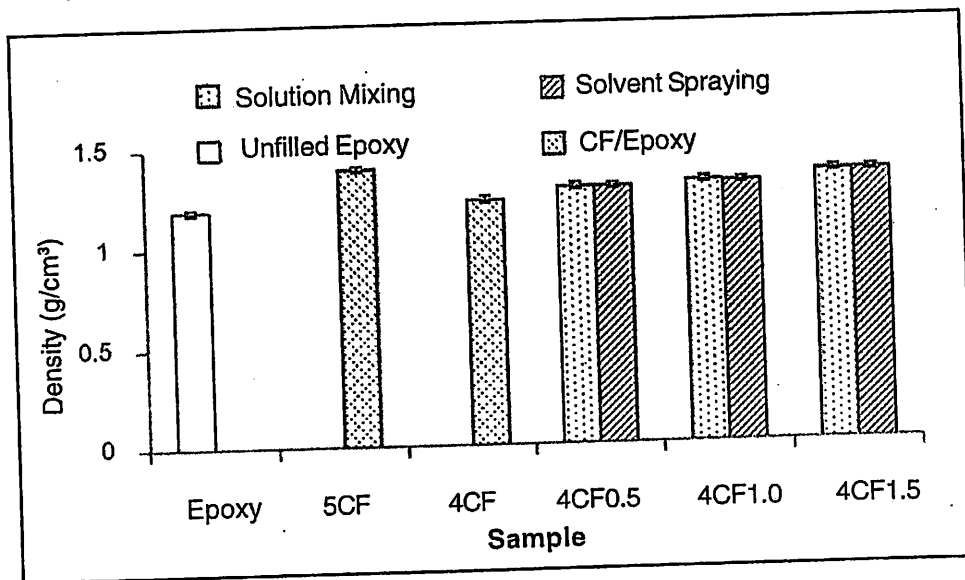


Figure 2: Density of epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

Flexural test

Figure 3 shows the flexural strength of the unfilled epoxy, 5CF, 4CF and 4-ply CF/epoxy composites incorporated with MWCNT. Based on Figure 3, it is observed that 4-ply CF/MWCNT/epoxy composite samples prepared by solution mixing method and solvent spraying method showed higher flexural strength compared to that of 4CF composite samples.

The samples incorporated with 1 vol % of MWCNT prepared via solution mixing method (4CF1.0S) exhibited an increment of 80% in flexural strength compared to 4CF. The samples incorporated with 0.5 vol % of MWCNT (4CF0.5S), have lower flexural strength compared with the samples with 1.0 vol % (4CF1.0S). At lower filler loading, MWCNT are homogeneously dispersed in the epoxy with the aid of ultrasonication. However insufficient

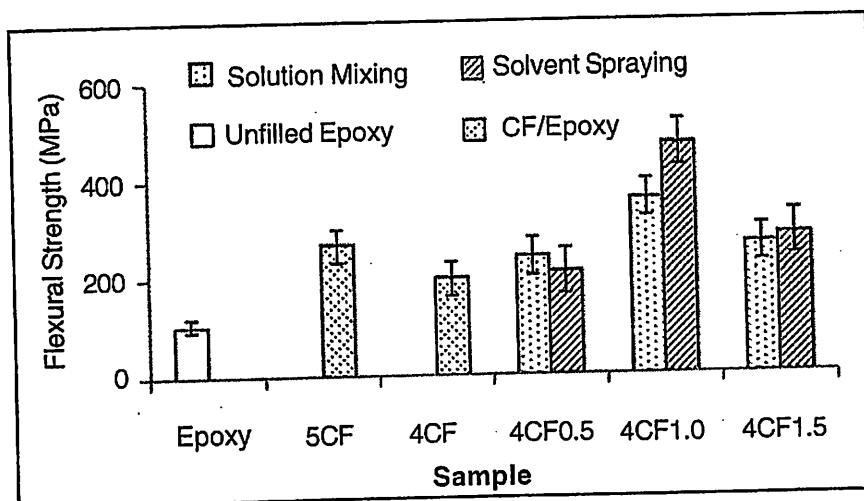


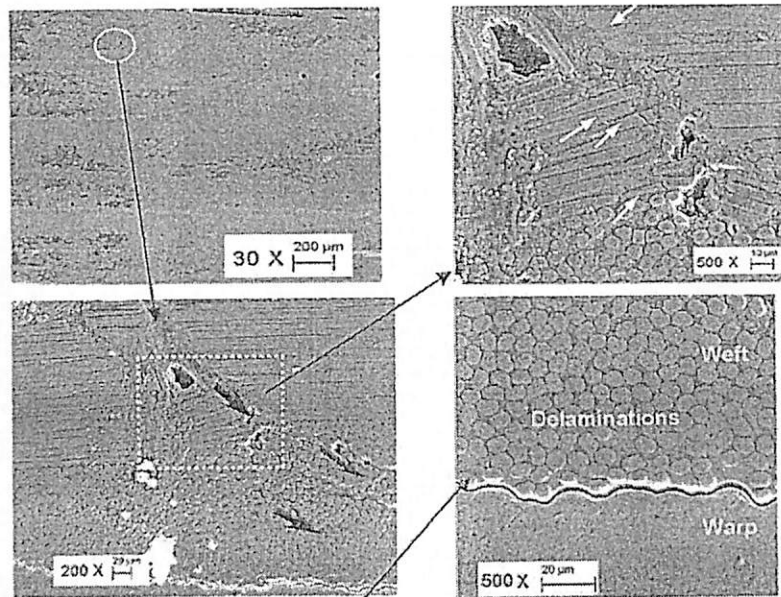
Figure 3: Flexural strength of epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

amount of MWCNT loaded into the composites is unable to strengthen the fiber/matrix interface. Meanwhile, higher loading of MWCNT (1.5 vol %) into the epoxy as found in samples of 4CF1.5S caused the viscosity of the epoxy to increase [7], thereby leading to improper wetting of the CF by the epoxy. Furthermore at higher filler loading, the ultrasonication technique was unable to disentangle the pristine MWCNT bundles and agglomerates in the epoxy. High concentration of agglomerated MWCNT in the epoxy lead to poor dispersion of MWCNT onto the CF thus results in the reduction of flexural strength.

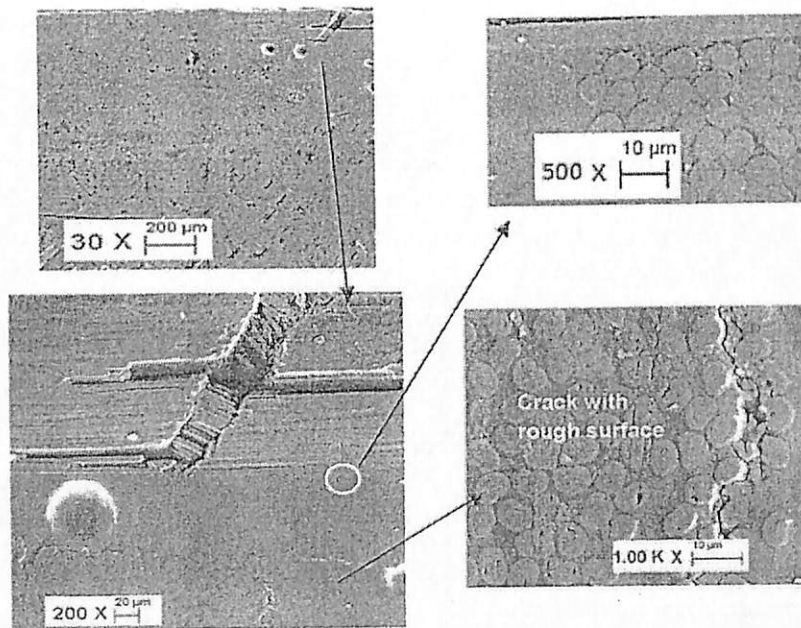
Figure 4 shows SEM micrographs of cross section of flexural fracture surface of 4CF samples. Generally, crack was observed to propagate from top layer across the warp (0°) to weft (90°) fibers during the flexural testing. Force exerted onto the 4CF composites during flexural test caused carbon fiber to break

catastrophically. Direction of the crack propagation is showed by the black arrows while microcracks existed in the fiber are showed by the white arrows. Therefore based on the observations gained from Figure 4 (a), it shows that failures that existed in the composites were transferred by the epoxy to the carbon fiber and finally throughout the whole composites. Smooth crack that found in the composite propagates along the surface between the warp and weft lead to delaminations. Such cracks indicate brittle failure^[7] occurred in the composites.

Different scenarios were observed in the composite incorporated with 1.0 vol % of MWCNT prepared via solution mixing method. Lower crack density existed in the 4CF1.0S composites compared to that of the 4CF composites indicates that the 4CF1.0S composites are less damaged than 4CF composites. Even though forces that applied



(a)



(b)

Figure 4: SEM micrographs of cross section of flexural fracture surface of samples; (a) 4CF; (b) 4CF1.0S.

to the composite structures caused the fiber to break, however the presence of MWCNT in the matrix prevents such cracks to propagate throughout the matrix. The MWCNT provides efficient bonding between the fiber and the matrix as observed in Figure 4 (b). Rough cracks presence in the fiber indicates strong fiber-matrix bonding.

The samples prepared by solvent spraying method showed an increase in flexural strength

from 5% to 75% compared to 4CF samples, respectively. MWCNTs fillers were attached on the CF surface by spraying method. As the epoxy introduced onto the fabric via the hand lay-up technique followed by consolidation process, the amount of epoxy is sufficient enough to infuse into the MWCNT and thus form bonding between the epoxy, CF and MWCNT. Spraying method is able to solve the problem with high viscosity of epoxy resin with addition

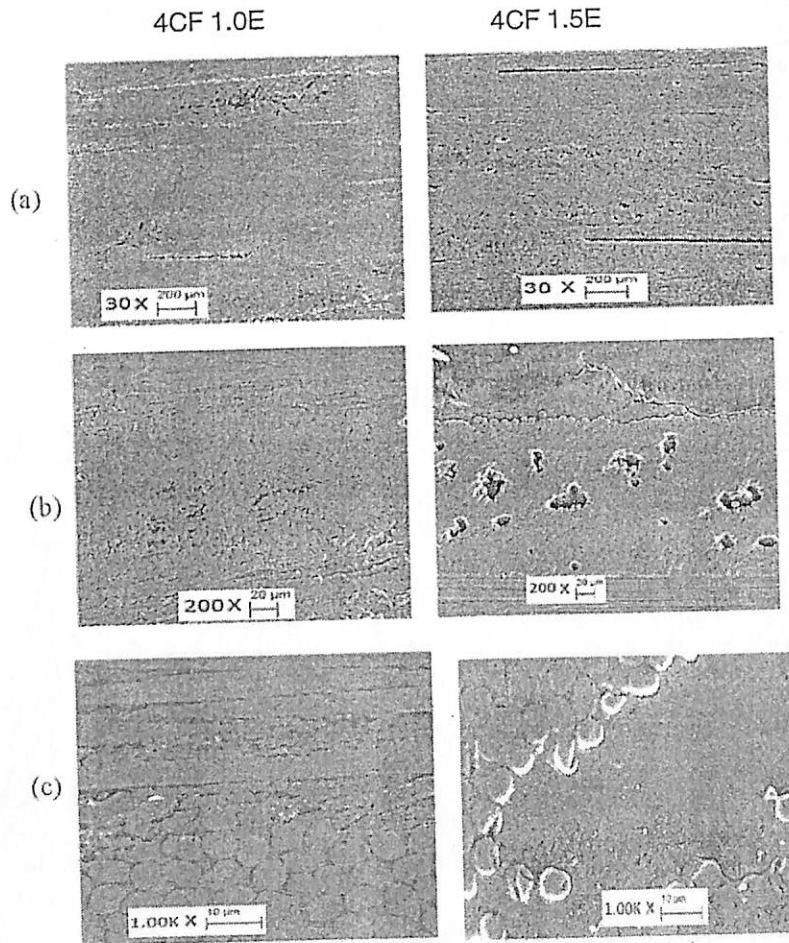


Figure 5: SEM micrographs of cross section of flexural fracture surface of composites samples prepared by solvent spraying method.

of MWCNT in solution mixing method. The addition of 1 vol % of MWCNT in sample 4CF1.0E exhibited the most significant increment in flexural strength (134%) in comparison with 4CF sample. However, higher loading of MWCNT (1.5 vol %) as found in samples of 4CF1.5E results in the reduction of flexural strength.

Figure 5 shows the fracture surface images of the 4CF composites incorporated with 1.0 and 1.5 vol % of MWCNT prepared by solvent spraying method. Composite with 1.0 vol% of MWCNT prepared by solvent spraying method (Figure 5 (a)) shows the epoxy has successfully wet the CF reinforcement as found in sample

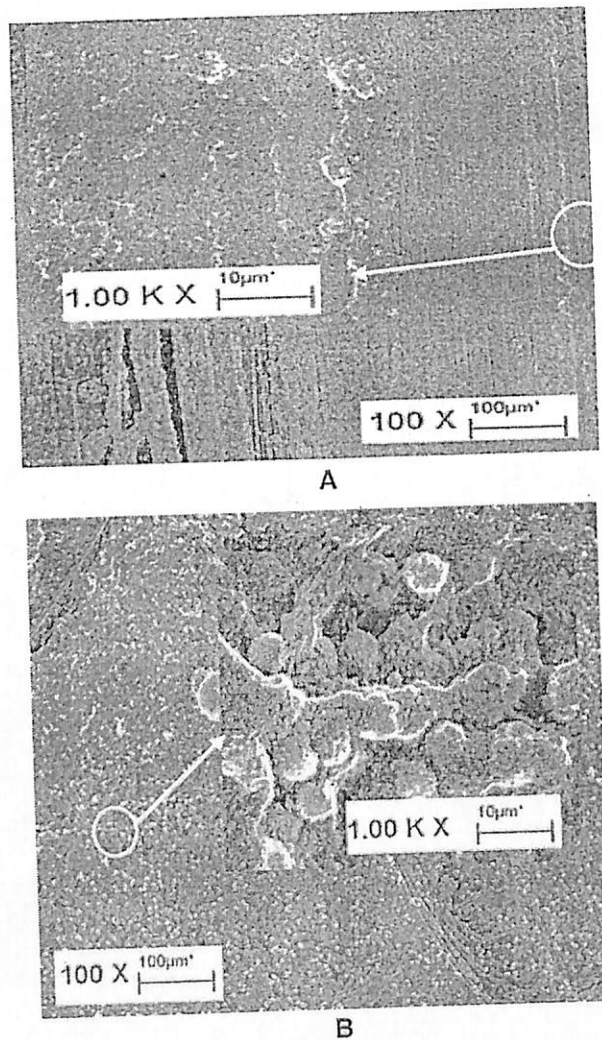


Figure 6: SEM micrographs of CF sprayed with MWCNT dispersed in ethanol at different filler loading; (a) 1.0 vol%; and (b): 1.5 vol%.

with 1.0 vol% prepared by solution matrix in Figure 4 (b). However, incorporation of 1.0 vol % of MWCNT via solvent spraying method has successfully formed a stronger fiber-matrix bonding compared to that of 4CF1.0S composites. It is found that the fiber reinforcements appear to be less damaged during the flexural testing. Besides, the MWCNT aid in preventing the crack found on the reinforcement from propagating towards the neighboring fiber reinforcements. This shows that the MWCNT play an important role in hindering the formation and development of transverse crack in the composites⁷.

Spraying higher filler loading of MWCNT onto the CF caused the increased amount of MWCNT attached onto the fabrics. As the epoxy introduced into the fabric, the epoxy was unable to infuse into the MWCNT efficiently thus lead to improper wetting of the epoxy matrix onto the CF. The improper wetting of epoxy on sample 4CF 1.5E can be observed in Figure 5

(a). As the fiber/matrix are weakly bonded due to improper wetting, thus the 4CF1.5E composites are found to experience damaged with more cracks during flexural test compared to 4CF1.0S and 4CF1.0E composites. Hindering effect of MWCNT on cracks propagation seems to be less successful as shown in Figure 5 (b) and (c). The main factor that initiates such behavior is probably due to MWCNT agglomeration. Figure 6 shows the SEM micrographs of CF sprayed with MWCNT at different filler loading. It is obviously shown that agglomeration occur on carbon fiber sprayed with 1.5 vol % of MWCNT (Figure 6 (b)) compared to that of 1.0 vol % MWCNT (Figure 6(a)). MWCNT agglomerations that occurred on the fabric caused difficulties for the epoxy to infuse into the MWCNT towards the CF to form a strong fiber-matrix bonding.

Figure 7 demonstrates changes in flexural modulus which is corresponded to the changes in the flexural strength. The same phenomenon

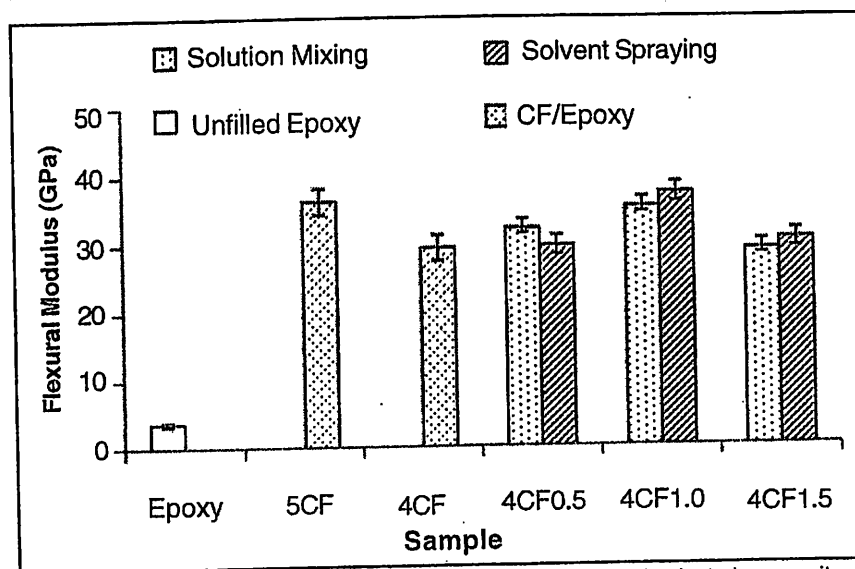


Figure 7: Flexural modulus of epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

was observed with regard to flexural modulus, where samples with MWCNT loading possessed higher modulus compared with the 4CF samples. The sample with 1 vol % of MWCNT prepared through the solvent spraying method (4CF1.0E) exhibited the highest modulus, which was 27% higher than 4CF composite samples comparison with that of 20% for the samples prepared through the solution mixing method. Based from Figures 3 and 7, it can be observed that incorporation of 1 vol % of MWCNT via solution mixing and solvent spraying method produced composites with 34% and 75% flexural modulus higher than 5CF, respectively. The modulus value increased when the amount of MWCNT loading was increased. However, as expected the addition of 1.5 vol % of MWCNT reduced the modulus, which may be due to the agglomeration of MWCNT.

Thermogravimetry Analysis (TGA)

Figure 8 shows the curves and the result of TGA for the control and the composite laminate samples with the addition of MWCNT dispersed through different methods. The TGA curves in Figure 8 show single-step degradation. The epoxy starts to decompose at a temperature around 330°C, which was lower compared to a previous study [18]. 5CF demonstrated slightly higher thermal stability compared with other types of composite laminates. This is due to higher carbon fiber loading (5-ply) compared to other composite laminates (4-ply). From the TGA curves, it is found that decomposition temperature of 4CF0.5S and 4CF1.5S composites are almost equal to the unfilled epoxy. This phenomenon occurs probably due to decomposition of the epoxy matrix in the

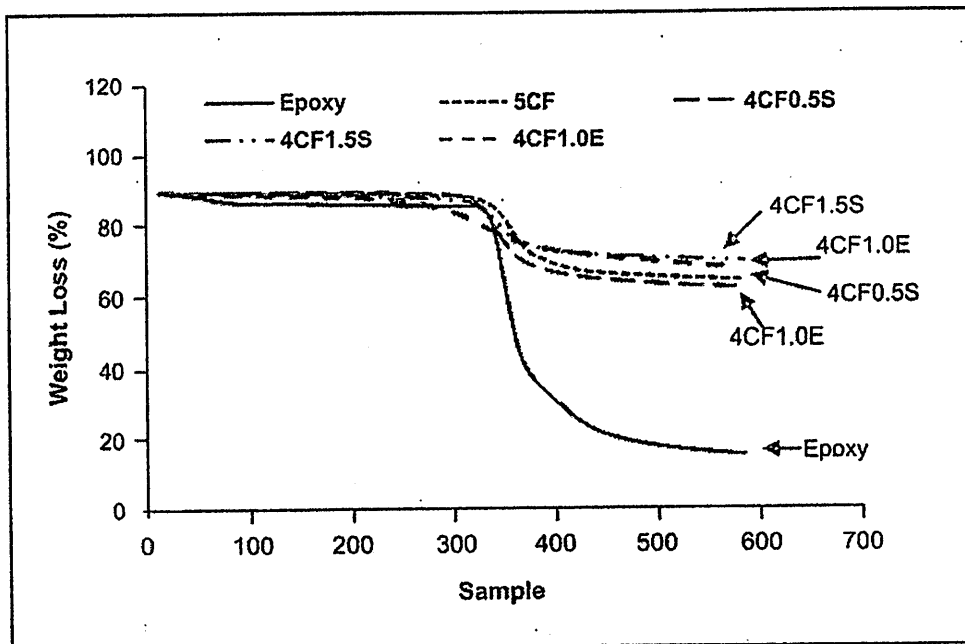


Figure 8: TGA curves of epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

sample. However sample of 4CF1.0E started to decompose at lower temperature. The presence of the unsuccessfully evaporated ethanol in the laminated composite bring to plasticizing effect which loosen the network structure and thus reduce the thermal stability of the composite laminates^[19].

Comparing 4CF0.5S and 4CF1.5S, it is observed that the sample with 1.5 vol % MWCNT (4CF1.5S) had higher thermal stability than the sample with 1 vol % MWCNT. This result shows that as MWCNT loading increases, thermal stability also increases. This finding is supported by Ogaswara et al. [17]. The structured network layer acting as a shield re-emits much of the incident radiation back into the gas phase, thereby decreasing the degradation rate [20]. Solution mixing produced slightly higher thermal stability compared to solvent spraying method. The residue of the composite samples varied

between 75% and 80% at 390°C, whereas the residue of the epoxy was 25% at 400°C.

Dynamic Mechanical Analysis (DMA)

Figure 9 shows the storage modulus of the selective composite samples (with and without MWCNT) and unfilled epoxy. It is shown that the storage modulus decreased with temperature because of the softening of epoxy resin at elevated temperature before finally reaching a constant modulus value after the glass transition temperature, T_g . The values of the storage modulus correspond to the values of the flexural modulus (measured by static test). The 5CF composite laminate sample had lower storage modulus compared with the 4-ply CF/MWCNT/epoxy composite laminates prepared by solution mixing method and the solvent spraying method. The incorporation of 1 vol % of MWCNT through the solvent spraying method (4CF1.0E) resulted in the significant

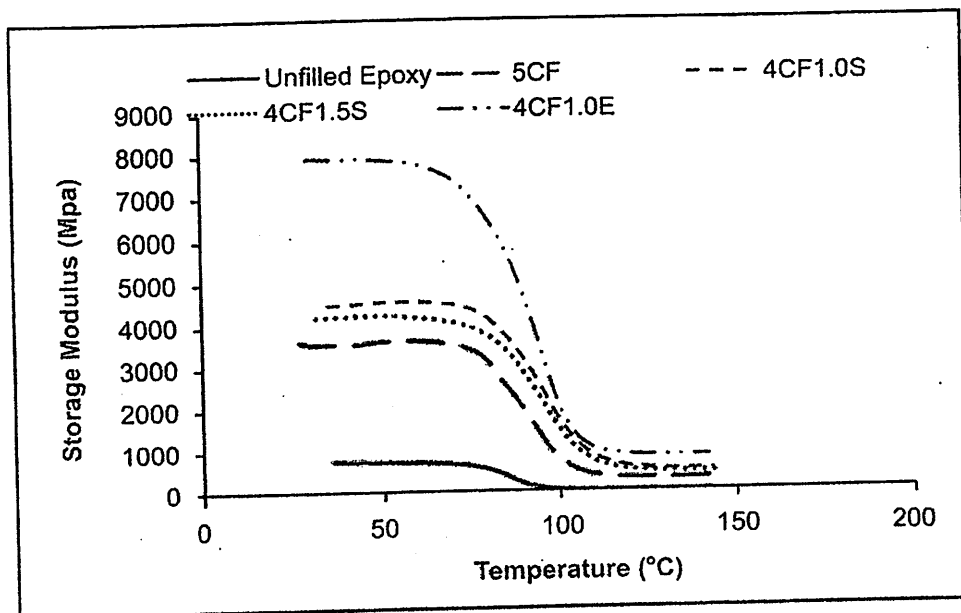


Figure 9: Storage modulus epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

increment of the storage modulus by 119.5%. This result proves that the addition of MWCNT in the composites increases the storage modulus [21]. Higher loading of MWCNT (1.5 vol %) results in the reduction in storage modulus, which is in accordance with the micrograph in Figure 6. This occurrence may be due to the fact that higher MWCNT loading leads to poor MWCNT dispersion, causing the agglomeration of MWCNT. The agglomeration of MWCNTs results in weak matrix-fiber interfacial interactions^[22].

Figure 10 shows the tan delta of the selective composite samples (with and without MWCNT) and the unfilled epoxy. The loss factor tan delta, which is indicated by the ratio of the loss in flexural modulus to the loss in storage modulus, represents mechanical damping or internal

friction in a viscoelastic system. The tan delta peak for the unfilled epoxy was high compared with the peak for the composite samples. The incorporation of carbon fiber and carbon nanotubes in the composites increased the free volume, which serves as the segmental motion in the composite systems, thereby lowering the tan delta values. The presence of free volume may be due to gas entrapment during the composite fabrication process as well as the exposure of some fractured microspheres during the stirring process. T_g was estimated based on the peak temperature of the peak tan delta curves. Figure 10 shows that samples with added MWCNT have higher T_g compared with the control sample (5CF). As illustrated by the curves, the sample prepared through the solution mixing method with higher MWCNT

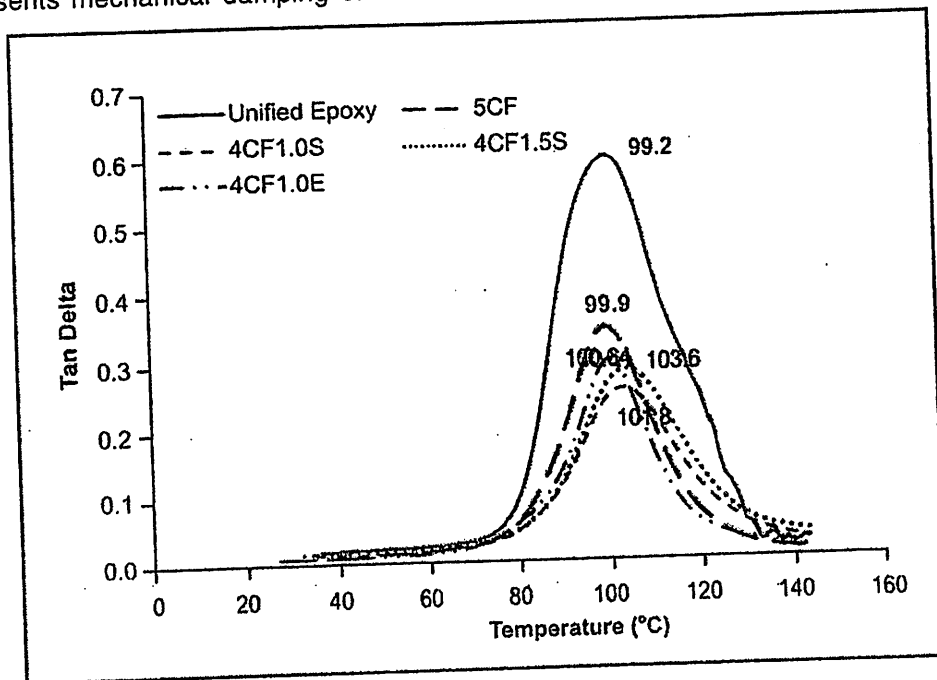


Figure 10: Tan delta of epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

loading has higher T_g compared to the sample with lower MWCNT loading prepared using the same method. T_g increased as the vol% of MWCNT incorporated in the composites increases because of the strong epoxy-MWCNT interaction that slows down the diffusion of small molecules in the resin matrix, thereby resulting in higher T_g [23].

Burning Rate

In the burning rate test, unfilled epoxy samples burned at with higher burning rate and the flame reached 100 mm mark. Meanwhile for all of the composite samples, the flame merely passes the 25 mm marks and continues to burn for a few millimeters before distinguished. From the tested composite samples, it was found that

only the epoxy matrix burned during the burning rate test, not the reinforcement materials. Figure 11 shows the burning rate of the control samples and the 4CF composite laminates prepared through different methods. The burning rate increases 4% when the number of ply reduced from 5-ply to 4-ply. The graph illustrates that the burning rate decreases as the vol% of MWCNT loading increases. Compared with the 5CF samples, the burning rate of the 4CF samples was reduced by 9%, 16%, and 20% with the addition of 0.5, 1, and 1.5 vol% of MWCNT respectively, regardless of the dispersion method. This phenomenon occurred due to the high aspect ratio that MWCNT percolates to form a network at very low loading instances in the polymer matrix; thereby

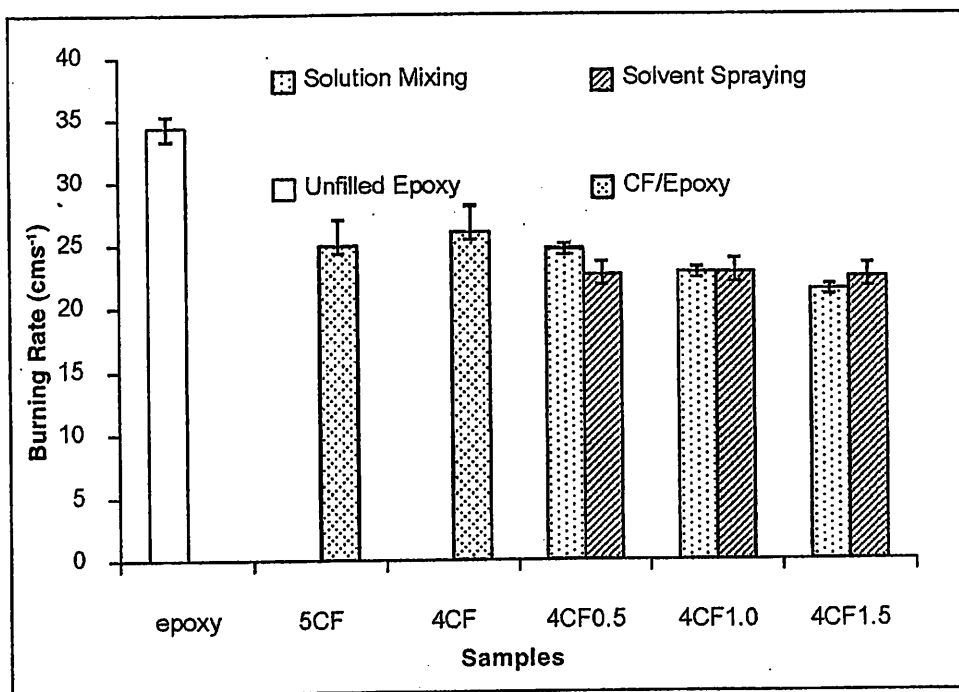


Figure 11: Burning rate of epoxy, 5CF, 4CF and 4-ply CF/MWCNT/epoxy laminated composite samples prepared by solution mixing and solvent spraying method.

resulting in the substantial enhancement of several function properties, including flame retardant properties [20]. Carbon nanotubes can act as protective layers. A carbon nanotube protective layer serves as a heat shield for the virgin polymer below the layer. The formation of such network-structured protective layer during burning is essential for the vast reduction in the heat release rate [24]. The protective layer limits the transfer of volatile gas and oxygen, significantly decreasing the production of decomposition gases. Furthermore, the fuel gas was physically separated from the oxygen and prevented the combustion from being sustained [20].

CONCLUSION

Based on the several tests performed throughout the study, the 4CF samples exhibited lower density compared with 5CF, regardless the MWCNT loadings and dispersion methods. Comparing to 5CF composite laminates, the four-ply carbon fiber samples with 1 vol% MWCNT prepared through solvent spraying method using ethanol (4CF1.0E) showed the highest flexural strength and storage modulus than the other samples. The 4CF samples incorporated with MWCNT have lower burning rate compared with the 5CF. The burning rate of the composite laminate samples was reduced with higher MWCNT loading. This study revealed that 1 vol% addition of MWCNT produces composite laminates with better mechanical and thermal properties compared with the other samples. The 4CF1.0 composite laminates with 1 vol% MWCNT loading prepared through the ethanol spraying method (4CF1.0E) possess higher mechanical and thermal stability compared with the other samples of 4-ply system as well 5-ply CF composites.

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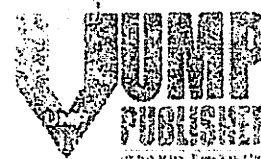
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COMPARISON OF PROPERTIES OF MWCNT/CARBON FIBRE/ EPOXY LAMINATED COMPOSITES PREPARED BY SOLVENT SPRAYING METHOD

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ABSTRACT

The incorporation of multi-walled carbon nanotubes (MWCNT) in laminated composites is believed to improve the mechanical and thermal properties of the composites. However, the nature of the MWCNT, which tend to agglomerate and form into ropes, restricts their dispersion in the composites. MWCNT-filled carbon fibre laminated composite was fabricated via hand lay-up followed by the vacuum bagging technique. MWCNT at different loadings of 0.5 to 1.0 vol% was dispersed by a solvent spraying method with two different dispersing agents, namely ethanol and Triton X-100. The flexural and thermal properties of the hybrid laminated composites were investigated. The CF laminated composites filled with 1.0 vol% of MWCNT dispersed in ethanol possessed better mechanical properties than other hybrid CF composites.

Keywords: Carbon fiber; multi-walled carbon nanotubes; flexural properties; thermogravimetry analysis

INTRODUCTION

Owing to their remarkable mechanical properties as well as low densities, carbon fibre reinforced epoxy composites are extensively chosen for use in engineering applications [1-4]. On the other hand, very active research on CNT over the last decades has revealed the remarkable flexibility of CNTs, their low mass density and large aspect ratio (typically > 1000) [5, 6]. The success of carbon nanotubes (CNT) in improving the toughness properties of polymer has attracted increasing interest in their use as an additional reinforcement material in laminated composites [7]. Though incorporation of CNTs has been reported to improve the toughness of composites, the fabrication of these laminated composites is constrained by the agglomeration of CNTs [8]. CNTs have a high tendency to form into bundles and ropes in the matrix due to their strong inter tube van der Waals forces [8, 9]. The CNTs agglomeration limits the load transfer process from the matrix to the CNTs; therefore the effective dispersion of CNTs in the matrix is vital [8]. In order to improve CNTs dispersion on the reinforcement, a solvent

spraying method [2] was chosen, by which the CNTs were sprayed onto the fabric prior to hand lay-up. This study intends to fabricate hybrid laminated composites of carbon fibre (CF)/ epoxy incorporated with multi-walled carbon nanotubes (MWCNT) in the composite system by using the hand lay-up technique, followed by the vacuum bagging technique. The effects of the type of dispersing agents and filler loadings on the flexural and thermal properties of laminated composites were investigated.

EXPERIMENTAL

Materials

Carbon fabric type 5-harness satin weave with identical warp and fills yarns of 6000 multi-filament continuous tow was used as reinforcement. The fabric with a linear density of 369.58 g/m² was supplied by Fibre Glast Corporation. The D.E.N. 431 epoxy novolac resin and Polyetheramine D230 (supplied by Penchem Industries Sdn. Bhd.) were used as a matrix and curing agent, respectively. A resin and a curing agent, with a ratio of 100 to 32, were used in the study[10]. The MWCNTs used in this study were synthesized by a group of researchers from the Universiti Sains Malaysia. The highly pure MWCNTs (99.8%), with nearly uniform diameter average of 6.2 nm ± 0.5 nm (mean ± standard deviation), were synthesized over magnesia-supported Co-Mo bimetallic catalysts through catalytic chemical vapour deposition [11]. Ethanol and octyl phenol ethoxylate or Triton X – 100 (TX-100) at a concentration of 1% were used as dispersing agents.

Methodology

A control sample of 4-ply CF/epoxy (4CF) was prepared using 4 pieces of CF with similar dimensions. The fabric was first weighed to determine the amount of epoxy matrix needed. The amount of epoxy matrix was fixed at 40 vol%. The predetermined epoxy resin was mixed with curing agent at a ratio of 100:32. The fabrics were then stacked together by applying the hand lay-up technique followed by the vacuum bagging method. The laminated composite was consolidated for 1 hour, then left overnight to cure before being subjected to a curing and post-curing process at 100 °C (1 hr) and 125 °C (3 hrs), respectively. The same procedures were repeated in preparing 5-ply CF/epoxy laminated composite (5CF). MWCNT-filled laminated composites were prepared by first incorporating MWCNT into the composites by the spraying method prior to the hand lay-up and vacuum bagging technique. The predetermined mass of MWCNT (0.5 vol%) was first ultrasonicated in 30 ml of ethanol in a cold bath for about 30 minutes. The prepared mixture was then sprayed onto 4 pieces of CF with the same dimensions. The fabrics were then left to dry at room temperature for about 4 hours to allow evaporation of ethanol. The dried fabrics were stacked up together with 40 vol% of epoxy matrix. The vacuum bagging, curing and post-curing process were carried out as mentioned previously. Samples with 1.0 and 1.5 vol % of MWCNT were dispersed in 60 and 90 ml of ethanol respectively. The same procedure was applied to prepare samples which used TX-100 as dispersing agent. The sample designations are shown in Table 1.

Table 1. Sample designations.

No.	Sample	No. of CF layers	Epoxy (vol %)	CF (vol %)	CNTs (vol %)
1.	Epoxy	-	100	-	-
2.	4CF	4	40	60	-
3.	5CF	5	40	60	-
4.	4CNT E0.5	4	40	59.5	0.5
5.	4CNT E1.0	4	40	59.0	1.0
6.	4CNT E1.5	4	40	58.5	1.5
7.	4CNT T0.5	4	40	59.5	0.5
8.	4CNT T1.0	4	40	59.0	1.0
9.	4CNT T1.5	4	40	58.5	1.5

Characterization

The flexural properties of 5 composites samples were tested according to ASTM D-790 using an INSTRON 5982. The specimens with dimensions 80 mm long \times 17 mm wide \times 2 mm thick with a 40 mm support span were loaded under three-point bending at a cross-head rate of 2 mm/min until failure [10]. The density of 6 composite samples with dimensions of 10 mm \times 10 mm was measured using a gravity balance, Precisa 8000, based on Archimedes' Principle. The average density was calculated [10]. Raw fabric samples sprayed with MWCNT were observed under a scanning electron microscope (SEM), FESEM/Zeiss Supra 35 VP. The thermal stability of the samples was measured through thermogravimetry analysis (TGA) using a Mettler Toledo, TGA/DSC Star^c System Analyzer. A small piece of the selected sample was weighed and heated in a nitrogen environment from ambient temperature to 600 °C at a heating rate of 10 °C per min.

RESULTS AND DISCUSSION

Flexural Properties

Figure 1 demonstrates the flexural strength and modulus of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites. As expected, the flexural strength of 4CF was 25% lower than 5CF. This is due to the reduction of the fibre reinforcement that is present in the composite system. It is observed that composites prepared by solvent spraying with TX-100 possessed lower flexural strength than either 4CF or 5CF. The drop in the flexural strength might be due to the nature of the Triton X, which caused the surface between the carbon fabrics to become slippery [12-14]. Conversely, composites prepared by spraying with ethanol show improvements in flexural strength compared to 4CF. In comparison with 5CF, composites incorporated with 0.5 vol% MWCNT exhibit a flexural strength 5% higher than 4CF but 22% lower than 5CF. This observation shows that incorporation of 0.5 vol% MWCNT increases the flexural strength of 4-ply CF. However, the amount of MWCNT used was insufficient to increase the flexural strength compared to that of 5-ply CF. Incorporation of 1.0 vol% of MWCNT recorded the most significant improvement in flexural strength compared to both 4CF and 5CF. These hybrid composites exhibit flexural strength that is 135% and 75% higher than 4CF and 5CF, respectively. On the other hand, addition of a higher

filler loading of MWCNT (1.5 vol%) caused a drop in the flexural strength compared to samples incorporated with 1.0 vol% MWCNT. This drop in flexural strength might be due to agglomeration of the MWCNT, which is observed in the SEM micrographs in Figure 2. Figure 2 shows micrographs of CF sprayed with 1.0 and 1.5 vol% of MWCNT dispersed by ethanol and TX-100 respectively. From Figure 2(a) – (d), it is proven that the higher filler loading caused MWCNT to agglomerate and thus reduced the flexural modulus. On the other hand, it is found that MWCNT dispersed in TX-100 also shows agglomeration at the higher filler loading.

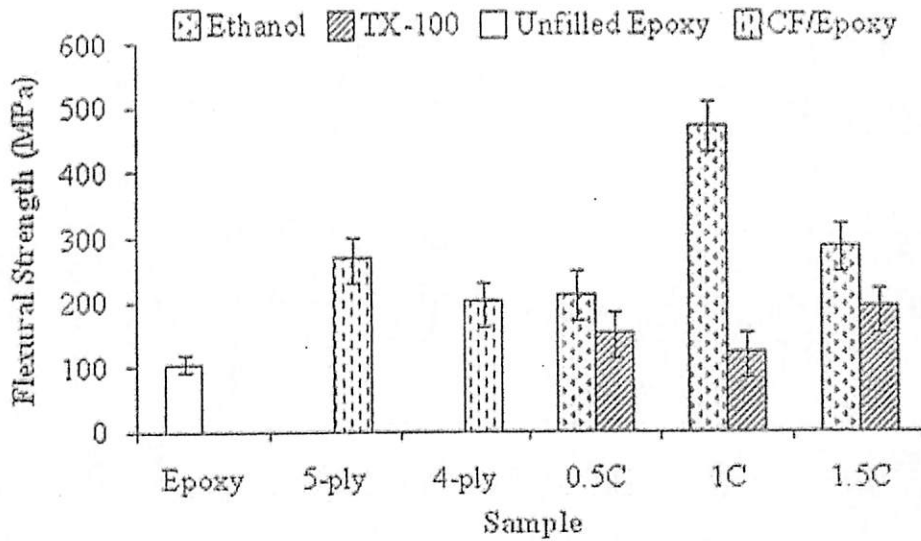


Figure 1. Flexural strength of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites.

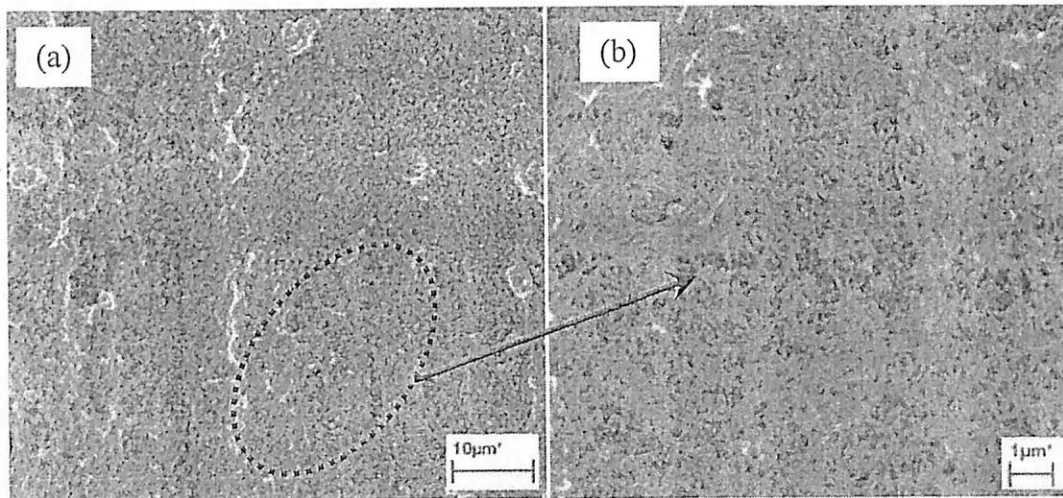


Figure 2. SEM micrographs of CF sprayed with MWCNT at different loadings using different dispersing agents: (a) and (b): 4CNT E1.0; (c) and (d): 4CNT E1.5; (e) and (f): 4CNT T1.0; (g) and (h): 4CNT T1.5.

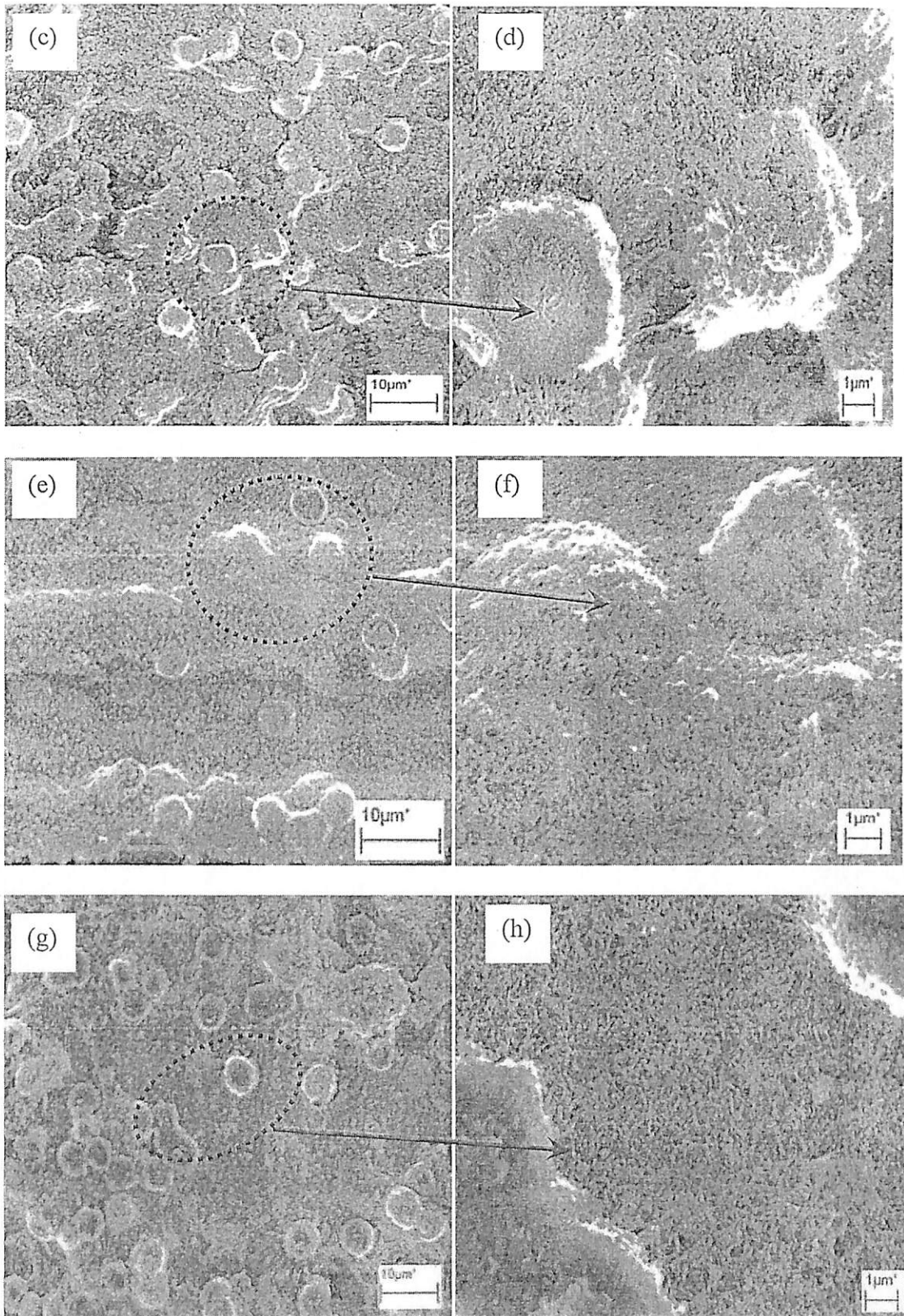


Figure 2. Continued.

Figure 3 demonstrates the flexural strength and modulus of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites. Reducing the number of CF from 5-ply to 4-ply caused a 19% reduction of flexural modulus.

Regardless of the vol% of the filler loading, composites incorporated with MWCNT dispersed by ethanol exhibit higher flexural modulus compared to 4CF. However, in comparison with 5CF, all the hybrid composite samples possessed lower flexural modulus except for composite laminates incorporated with 1.0vol% dispersed by ethanol. Comparing the hybrid samples dispersed by ethanol, it seems that the flexural modulus shows a similar trend to that for flexural strength. The flexural modulus dropped at higher filler loading (1.5 vol%). This observation is supported by the micrographs in Figure 2(a) – (d). The higher filler loading leads to agglomeration of the MWCNT and thus reduces the flexural modulus.

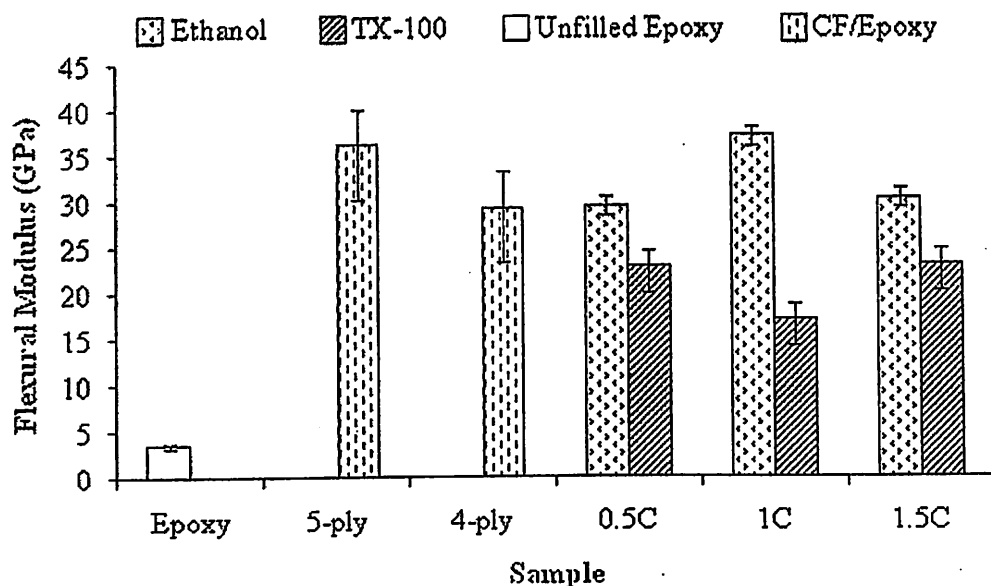


Figure 3. Flexural modulus of the unfilled epoxy, the laminated CF composites and MWCNT-filled CF laminated composites.

Density

Figure 4 shows the densities of the unfilled epoxy, CF/epoxy laminated composite samples and MWCNT-filled CF/epoxy laminated composites samples. As predicted, the density of 4CF and 4-ply MWCNT-filled CF laminated composites is lower than that of the 5CF samples. Samples incorporated with the same filler loading exhibit almost identical density regardless of the type of dispersing agent. Incorporation of MWCNT into 4-ply CF laminated composites caused the density to increase from 4 to 7 % compared to 4CF. Gajendran and Saraswathy, (2008) also reported that the density of polyaniline-carbon nanotubes composites increased when CNT loading was added in the PANI-CNT system through the solution mixing method [15]. Ogasawara, Moon [16] also reported the same trend when aligned MWCNT was incorporated into epoxy [16]. However, the densities of these laminated composites are 3 to 7 % lower in comparison with the 5-ply CF. This observation indicates that a weight reduction can be achieved in the 4CF system.

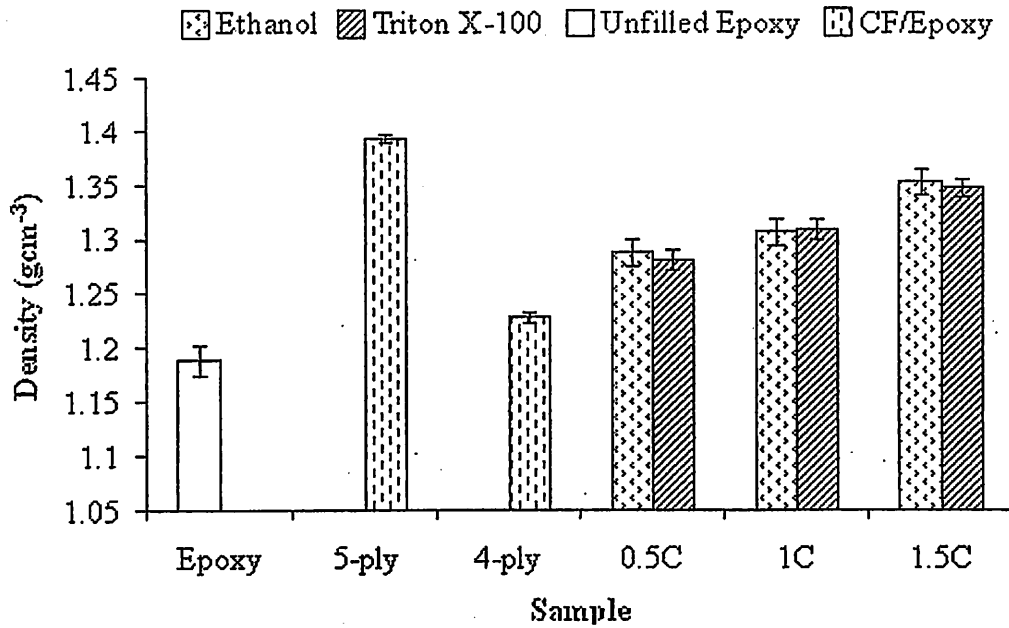


Figure 4. Density of the unfilled epoxy, CF/epoxy laminated composite samples and MWCNT-filled CF/epoxy laminated composites samples.

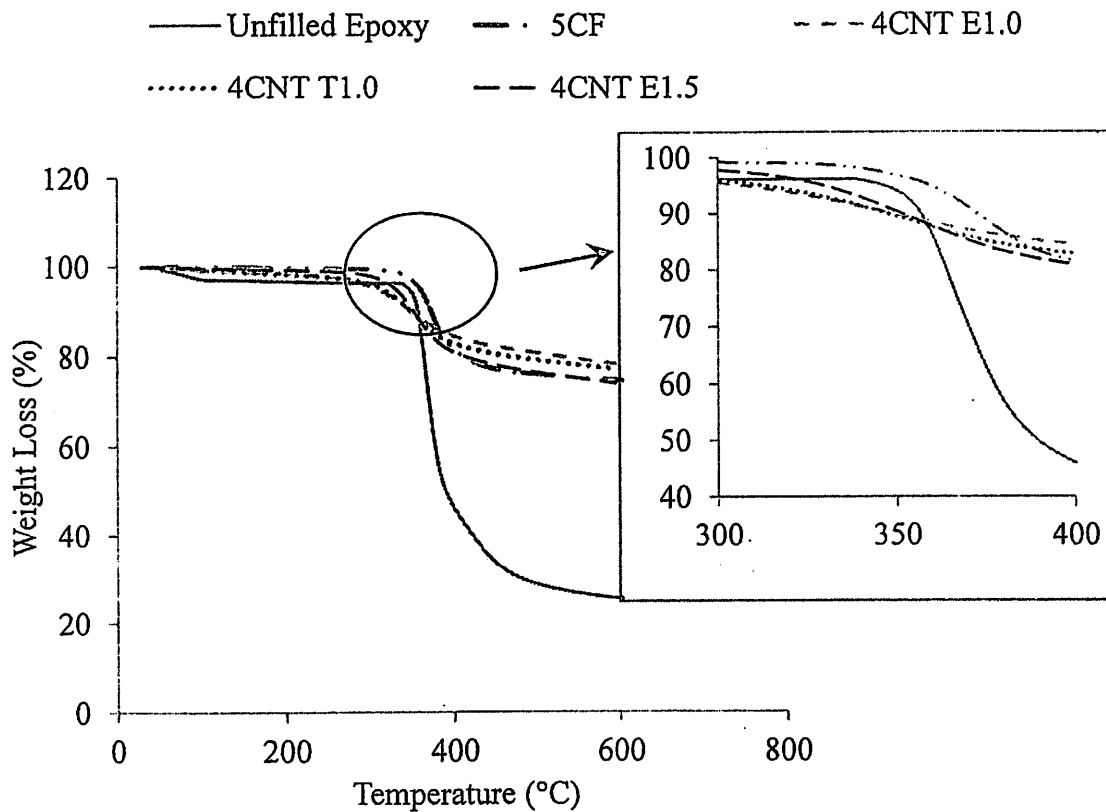


Figure 5. TGA curves of the unfilled epoxy, 5 CF and hybrid composites samples incorporated with 1.0vol% of MWCNT dispersed by ethanol and TX-100.

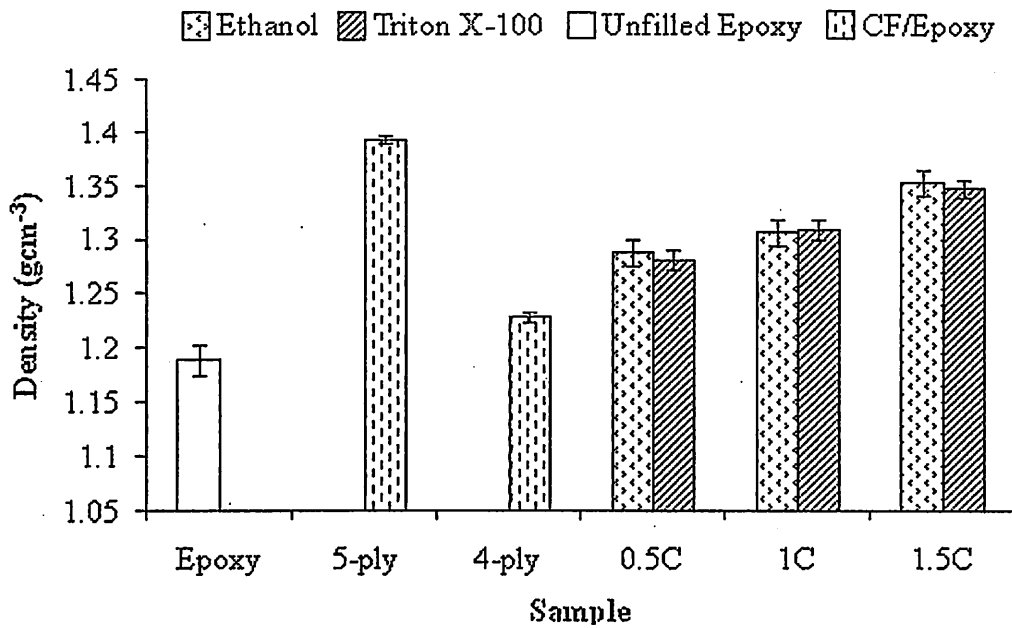


Figure 4. Density of the unfilled epoxy, CF/epoxy laminated composite samples and MWCNT-filled CF/epoxy laminated composites samples.

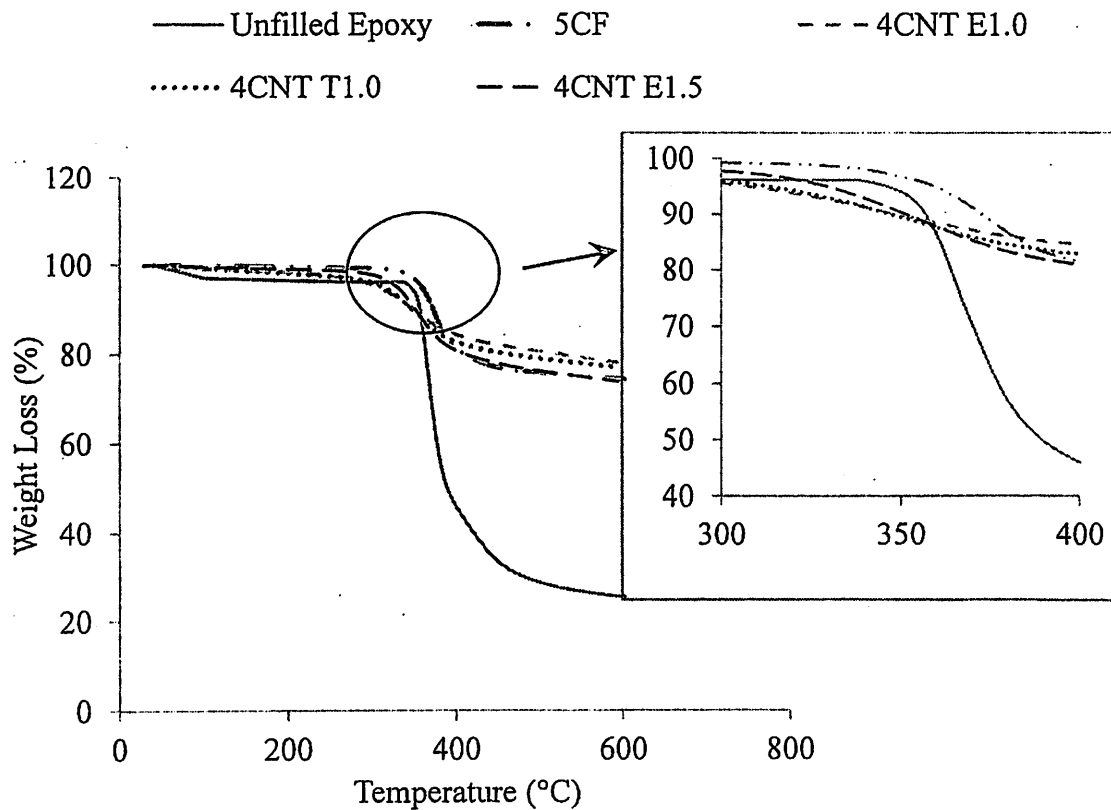


Figure 5. TGA curves of the unfilled epoxy, 5 CF and hybrid composites samples incorporated with 1.0vol% of MWCNT dispersed by ethanol and TX-100.

Thermogravimetry Analysis

Figure 5 shows the TGA curves of the unfilled epoxy, 5 CF and hybrid composites samples incorporated with 1.0vol% of MWCNT dispersed by ethanol and TX-100. The TGA curves demonstrate single-step degradation. At 330 °C, the epoxy starts to decompose. 5CF exhibits thermal stability which is slightly higher than the samples incorporated with 1 vol% of MWCNT. On the other hand, it is observed that the thermal stability of composites incorporated with 1.0 vol% MWCNT dispersed by ethanol is almost identical to the composites filled with 1.0vol% MWCNT dispersed by TX-100. Comparing composites CF with MWCNT dispersed with ethanol, it is found that the thermal stability increases with the increasing filler loading. This observation is also in agreement with the observation reported by [16]. The presence of MWCNT produces a structured network layer which acts as a shield that re-emits much of the incident radiation back into the gas phase, thereby decreasing the degradation rate [17].

CONCLUSIONS

Different types of dispersing agent affect the dispersion of MWCNT differently and thus affect the flexural and thermal properties of the laminated composites incorporated with MWCNT. On the other hand, the amount of filler loading also affects the flexural and thermal properties in different ways. A higher filler loading may lead to agglomeration of the MWCNT and thus have a negative impact on the mechanical properties, whereas the thermal properties of the composites increase with increasing filler loading. From the study, it can be concluded that 4-ply CF laminated composites incorporated with 1.0 vol% of MWCNT dispersed in ethanol exhibit better flexural properties compared to 5-ply CF. Judging from the discussion, we can conclude that the fabrication of light-weight hybrid composites with better mechanical properties is possible.

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Polymer Bulletin

Mechanical, electrical and thermal properties of multi-walled carbon nanotubes/epoxy composites: effect of post-processing techniques and filler loading

--Manuscript Draft--

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Section/Category:	Polymer Engineering
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Abstract:	<p>In this study, MWCNT/epoxy composites were fabricated via combination of ultrasonication with two post-processing techniques namely, casting and hot-pressing respectively. The effect of these two post processing techniques and MWCNT loading ranging from 0 to 1.0 vol% on the mechanical, electrical and thermal properties of MWCNT/epoxy composites were investigated. The addition of MWCNT in epoxy reduced the tensile strength and tensile modulus of the MWCNT/epoxy composites compared to unfilled epoxy. However, the MWCNT/epoxy composites prepared by hot-pressing technique improved the tensile strength and tensile modulus at 0.4 vol% MWCNT loading as confirmed by morphological analysis. The DMA properties of MWCNT/epoxy composites prepared by both post-processing techniques shows no significant change in storage modulus and Tg values. The increment of MWCNT loading increased the electrical and thermal properties of MWCNT/epoxy composites with slightly higher via hot-pressing technique. These findings indicate that different post-processing techniques and filler loading govern the properties of MWCNT/epoxy composites.</p>
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Flexural properties for two-ply Glass Fiber Reinforced composites with different loading of CNT/Epoxy film Produced by different Methods

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ABSTRACT

Background: Composite materials reinforced by glass fibers are widely used in various applications ranging from aerospace to sporting goods due to their remarkable properties including high strength to weight ratio and high modulus to weight ratio. However, the addition of nanoparticles as reinforcement shows promising results for properties enhancements. Unique properties of nanoparticles such as carbon nanotubes (CNTs) make them potential candidates for many applications from mechanical enhancements to electrical and thermal conductivities. **Objective:** In this work, the effect of CNTs loadings and different methods used to fabricate CNT/epoxy film on flexural properties of two-ply glass fiber reinforced composites were investigated. Various CNTs loadings ranged from 0 vol% to 2.0 vol% were used to fabricate the films by using casting and hot press methods. The films were then stacked in between 2-ply of glass fiber reinforced epoxy composite by vacuum bagging process. **Results:** The results shows that the 0.5 vol% cured CNTs/epoxy film fabricated by using hot press method demonstrated better flexural properties compared to other CNTs loadings and fabrication methods. Hot-press sample shows improvements in flexural strength and modulus which were 190.5% and 368.6% respectively followed by casting (187.2% and 360.0%) and prepreg (169.8% and 330.8%) compared to the neat glass fiber composite. However, the glass fiber reinforced composite with 2.0 vol% CNTs film shows lower improvement (72.0% and 152.7%). **Conclusion:** Casting and hot press methods were used to fabricate film and the flexural properties of two-ply glass fiber reinforced composites were investigated. The results exhibited that the flexural properties were influenced by properties of the film, methods to produce film and the adhesion between film and glass fiber mats. For future works, it is aimed to optimize film and laminates processing parameters to enhance structural properties of the fiber reinforced composites.

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INTRODUCTION

Glass fiber-reinforced plastics (GFRPs) composite are widely used in various structural applications such as aerospace, automotive, sporting goods and marine due to their remarkable properties including high strength to weight ratio and high modulus to weight ratio. Composites materials are commonly used due to their adaptability to various conditions and ease of combination with other materials in order to perform specific purposes and achieve desirable properties. However, performance of final composite depends on various parameters such as matrix materials, reinforcing fibers, fiber alignments and fiber directions.

Recent developments in fiber reinforced polymer composites shifted direction towards application of nanoparticles for properties enhancements. The addition of nanoparticles as reinforcement shows promising results for properties enhancements and thus will maximize their applications. Unique properties of nanoparticles such as carbon nanotubes (CNTs) in terms of high mechanical strength and stiffness, exceptional thermal conductivity, low density and high aspect ratio make them very good candidates for many applications from mechanical enhancements to electrical and thermal conductivities (Baughman *et al.*, 2002; Zhidong *et al.*,

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2011; Kesong *et al.*, 2014). Excellent mechanical properties of CNTs make them potential candidates as advanced filler materials for polymer composite reinforcement. In another area, combination of their conductivity and high aspect ratio were predicted to create conductive polymer with exceedingly low percolation thresholds (Kilbride *et al.*, 2002). Biercuk *et al.* (Biercuk *et al.*, 2002) reported that their massive thermal conductivity can be exploited to produce thermally conductive composites. However, it is foreseen that the most promising area of polymer using CNTs as reinforcing fillers will be more significant on mechanical enhancement (Jonathan *et al.*, 2006). Christopher *et al.* (Christopher *et al.*, 2008) have incorporated epoxy with CNTs into glass fiber polymer composites by using wet lay-up method and cured the samples by using heated platen press. It was reported that the CNTs exhibit a relatively uniform distribution in the polymer with little agglomeration and clumping. Ramlee *et al.* (Ramlee *et al.*, 2013) investigated the effect of CNT content and hybrid flame-retardant filler on the properties glass fiber/epoxy laminated composites and found out that CNT-filled epoxy/glass fiber composite exhibit higher tensile properties and burning rate than hybrid flame-retardant system. Wan Dalina *et al.* (Wan Dalina *et al.*, 2014) compared the performance of the glass fiber and carbon fiber/epoxy laminated composites. The results shows that addition of 0.5 vol% of CNT in the 4-ply system of glass fiber increases the flexural properties compared to carbon fiber laminated composite.

This study aims to investigate the effect of CNTs loadings and different methods used to fabricate CNT/epoxy film on flexural properties of two-ply glass fiber reinforced composites. Various methods have been reported in previous works to fabricate films composite such as layer by layer (LBL), casting, spin coat, electrophoretic deposition (EPD) and buckypapers (Mamedov *et al.*, 2002; Martone *et al.*, 2010; Ghaleb *et al.*, 2014; Zhang *et al.*, 2009; Wang *et al.*, 2004). CNTs loadings ranged from 0 vol% to 2.0 vol% were dispersed in epoxy system and the films were fabricated by using casting and hot press methods. The films were then stacked in between 2-ply of glass fiber reinforced epoxy composite by vacuum bagging process.

MATERIALS AND METHODS

Materials:

The materials used in this study were an epoxy resin D.E.R.TM 332 (diglycidyl ether of bisphenol-A) cured with polyetheramine D230 hardener, with weight ratio of 100:32, both supplied by Penchem Technologies Sdn. Bhd. The density of materials were 1.16 g/cm³ and 0.946 g/cm³ respectively. The multi-walled carbon nanotubes (MWCNTs) used in this study were purchased from USAINS Holding, Universiti Sains Malaysia. The MWCNTs were produced via catalytic chemical vapour deposition (CCVD) process with an average diameter and length ranged 10 ± 1 nm (mean ± standard deviation) and 1-5 µm, respectively. Sodium dodecyl sulfate (SDS) was used as the dispersant supplied by Sigma-Aldrich Corporation. The reinforcement was woven type-E glass fibers with a linear density of 200 g/m² supplied by Saint-Gobain Ltd.

Composite fabrication:

The general process of composites fabrication were divided into three stages; solution preparation, film composites fabrication and glass fiber reinforced composites fabrication. Various CNTs loadings (0 vol% to 2.0 vol%) were dispersed in acetone and dispersant, then placed in the ultrasonic bath for 30 min. The mixture was then placed in the oven at 60°C for approximately 1h to evaporate the solvent. Then, the mixtures were suspended in epoxy resin and sonicated using Hielscher UP200S Ultrasonicator at 24 kHz and 50% amplitude for 10 min at room temperature. A hardener was added at a ratio of 100:32 by weight (epoxy: hardener) and the mixture was sonicated for 10 min in an ice bath. Thereafter, the mixture was vacuumed at room temperature for 30 min to remove entrapped air. The controlled samples (neat epoxy) were prepared following the same procedure for comparison purposes.

Film composites with dimensions of 155 mm × 245 mm were fabricated based on three different conditions; (1) *Casting (fully cured)*. The mixtures were cast into silicon mold and cured at room temperature for 24h followed by post-cured at 80°C for 2h, (2) *Casting (prepreg)*. The mixtures were cast into silicon mold and partially cured (prepreg) at 50°C for 2h and (3) *Hot-press (fully cured)*. The mixtures were moulded into a flat steel plate and pressed using hot press GOTECH GT-7014-A at 300 psi and 80°C for 2h. The thicknesses of thin film composites produced were within ranges of 0.3-0.5mm. Glass fiber/epoxy composite laminates were fabricated by stacking up thin film composite (casting-fully cured/ casting-prepreg/hot press-fully cured) in between two-ply of glass fibers. The composite laminates were consolidated for 30 min using the vacuum bagging technique. Then, the composite laminates were cured at room temperature for 24h, followed by post cure at 80°C for 2h.

Characterisation:

The flexural properties of 2-ply glass fiber reinforced epoxy composite were performed using three-point bending tests according to the ASTM D790 standard test method at a crosshead speed of 2 mm/min (INSTRON series IX/s Automated Material Tester Version 8.25.00). Five specimens with a dimension of 50.8 mm x 12.7

mm (for sample with thickness, $t < 1.6\text{mm}$) and the span length is 25.4 mm were prepared and tested. The fracture surfaces of the thin film were examined using scanning electron microscopy (FESEM Zeiss SUPRA 35VP) at an acceleration voltage of 10kV. The samples surface were vacuum coated with a thin layer of gold palladium to provide conductive surface for testing.

RESULTS AND DISCUSSION

Flexural tests were performed to evaluate the flexural strength and modulus of the two-ply glass fiber reinforced composites. Figure 1 shows the comparison of the representative flexural stress-strain curves for two-ply glass fiber reinforced composites with different loading of CNTs/epoxy film produced by different methods. The stress-strain curves of the tested samples represents the effect of CNTs loadings on the mechanical behavior of the composites. As the CNTs loadings increased, the areas under the stress-strain curve increases. It shows that the toughness of the composites increased with the addition of CNTs. However, at 2.0 vol% CNT the areas under the curve decreases which due to the agglomeration of CNTs in epoxy film deteriorates the overall flexural properties of the composites. The addition of CNTs more than 0.5wt% was very challenging due to the massive surface area of CNTs and leads to increase in viscosity (Njuguna *et al.*, 2007). Amongst the tested samples, 0.5 vol% CNTs exhibits better performance compared to neat epoxy and 2.0 vol% CNTs. Hot press methods shows higher flexural properties followed by casting and prepregs.

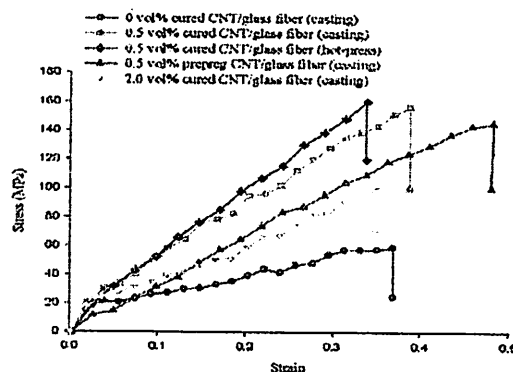


Fig. 1: Comparison of the flexural stress-strain curves for two-ply glass fiber reinforced composites with different loading of CNTs/epoxy film produced by different methods.

Table 1 and Figure 2 shows the flexural properties of two-ply glass fiber reinforced composites with different loading of CNTs/epoxy film produced by casting and hot-press methods. The results shows that the flexural properties increased consistently as the CNTs loadings increased. Similar trend was reported by the previous works (Wan Dalina *et al.*, 2014; Luen *et al.*, 2012; PC Ma *et al.*, 2007; Mora *et al.*, 2009; Breton *et al.*, 2004). The composites containing 0.5 vol% CNTs loadings exhibited maximum values in flexural strength and modulus compared to neat epoxy and 2.0 vol% CNTs loadings. Hot-press sample shows slightly higher in flexural strength and modulus ranged 156.6 ± 27.19 MPa and 79.2 ± 34.65 GPa respectively followed by composite samples prepared by casting (154.8 ± 52.03 MPa and 77.9 ± 19.40 GPa) and prepreg (145.4 ± 28.77 MPa and 72.8 ± 13.86 GPa) methods. In this work, the hot press methods shows improvements in flexural strength and modulus which are 190.5 % and 368.6% compared to the neat glass fiber composite. However, the glass fiber reinforced composite with 2.0 vol% CNTs film shows lower improvement (72.0% and 152.7%). This scenario was due to the agglomeration of CNTs in epoxy film deteriorates the overall flexural properties of the composites. For prepreg, the variation of thickness causes non-uniform stress was not been transferred uniformly in the composites and leads to lower flexural properties compared with hot press and casting samples. The thickness of prepreg was uneven due to the shrinkage of epoxy matrix during curing stages (Koran *et al.*, 1983). Tack is one of the prepreg properties that have to be monitored. The epoxy content of prepreg influences the tack and as well as the final strength of the laminate. Tack refers to the ability of a prepreg to adhere to itself or to other material surface. In many prepreg systems, the resin content of the prepreg is higher than desired in the finishing part. This improves tack and drape but the excess resin must be removed in the manufacturing process. The removal of this excess resin assists the removal of trapped air in the laminate. It is essential to remove trapped air, since voids within laminate have a negative effect on interlaminar strength (Peterson *et al.*, 1992). The defect caused by trapped air was observed in Figure 3.

Figure 4 represents the morphologies of composites containing 0 vol%, 0.5 vol% and 2 vol% CNTs loadings. Figure 4a shows the cleavage plane between two cleavage steps that were flat and smooth at different

magnifications. This indicated a typical fractography feature of brittle fracture behavior for neat epoxy. The fracture surface of the CNTs composite (Figure 4b-c) shows different fractographic features; rougher with the CNTs added into epoxy matrix, which indicates ductile deformation and smooth fracture surface suggests that it had a brittle failure mode. Additionally, the white points indicates the CNTs dispersed in the epoxy resin. The white points increases as the loadings of CNTs increased. In this work, the 0.5 vol% CNTs film shows better dispersion due to low agglomeration in the mixture. Hence, the glass fiber reinforced composite with 0.5 vol% CNTs film shows higher improvement in flexural properties as compared to the neat glass fiber composite. However, the glass fiber reinforced composite with 2.0 vol% of CNTs film gives lower improvement (72.0%) due to high agglomeration occurs in the film. From the SEM images, microvoid and void were also observed which will initiates the propagation of cracks. This scenario occurs due to the insufficient degassed application to remove entrapped air from the mixture during solution processing.

Table 1: Flexural properties of two-ply glass fiber reinforced composites with different loading of CNTs/epoxy film produced by different methods.

CNTs Loading (vol%)	Flexural Strength (MPa)	Flexural Modulus (GPa)
0 vol% cured CNT/glass fiber (casting)	53.9 ± 10.79	16.9 ± 2.07
0.5 vol% cured CNT/glass fiber (casting)	154.8 ± 52.03 (+187.2%)	77.9 ± 19.40 (+360.0%)
0.5 vol% cured CNT/glass fiber (hot-press)	156.6 ± 27.19 (+190.5%)	79.2 ± 34.65 (+368.6%)
0.5 vol% prepreg CNT/glass fiber (casting)	145.4 ± 28.77 (+169.8%)	72.8 ± 13.86 (+330.8%)
2.0 vol% cured CNT/glass fiber (casting)	92.7 ± 12.02 (+72.0%)	42.7 ± 7.38 (+152.7%)

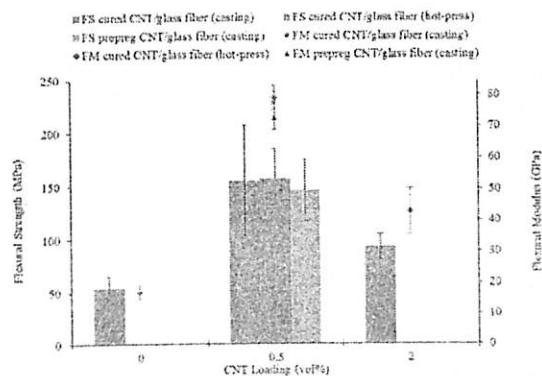


Fig. 2: The bar charts of flexural strength (FS) and modulus (FM) for two-ply glass fiber reinforced composites with different loading of CNTs/epoxy film produced by different methods.

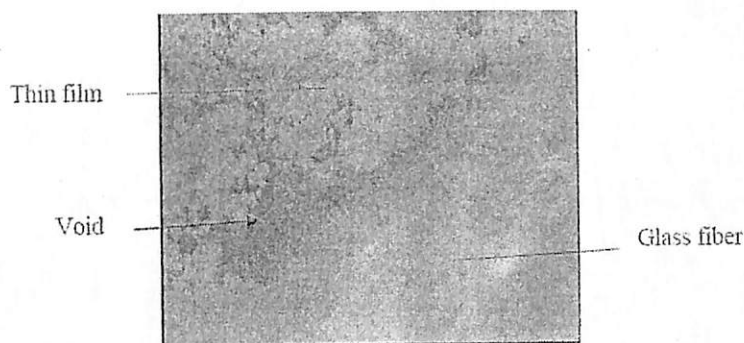


Fig. 3: Void caused by trapped air in sample prepared by preimpregnated CNTs/epoxy thin film and glass fiber mats at 45x magnification.

Conclusion:

Flexural properties for two-ply glass fiber reinforced composites with different loading of CNT/epoxy film produced by different methods were investigated. The increase of CNTs loading increases the flexural properties where 0.5 vol% exhibited better performance compared to other CNTs loadings. The flexural properties of composites are depending on the dispersion and presence of defects in the CNTs/epoxy film. Higher CNTs loading increases the tendency of agglomeration of CNTs in the epoxy system which causes poor dispersion of CNTs and creates stress concentration. Methods used to fabricate the CNTs/epoxy film will also influence the

performance of the composites. Hot-press sample shows improvements in flexural strength and modulus which were 190.5% and 368.6% respectively followed by casting (187.2% and 360.0%) and prepregs (169.8 % and 330.8%) compared to the neat glass fiber composite. However, the glass fiber reinforced composite with 2.0 vol% CNTs film shows lower improvement (72.0% and 152.7%). The results shows that the 0.5 vol% cured CNTs/glass fiber composites fabricated by using hot press method demonstrated better flexural properties. The flat surface of hot-pressed film has smaller contact areas with glass fiber and this scenario creates smaller air gaps and minimize voids after curing and hence improve the adhesion between the surface contacts.

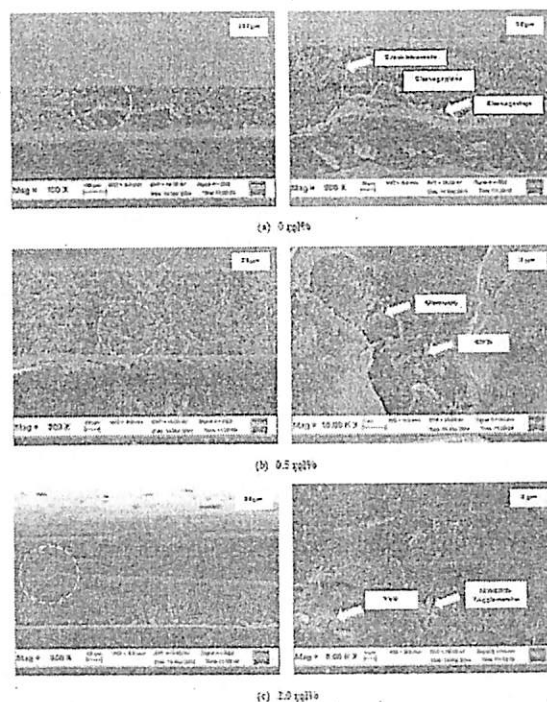


Fig. 4: SEM images of the fracture surfaces of two-ply glass fiber reinforced composites with different CNTs loadings at different magnifications: (a) 0 vol%, (b) 0.5 vol% and (c) 2.0 vol%.

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Effect of Filler Loading on the Tensile Properties of Multi-walled Carbon Nanotube and Graphene Nanopowder filled Epoxy Composites

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Abstract

At present, carbon nanotube (CNT) and graphene are attracting a great deal of attention due to their superior structural and functional properties as well as its suitability for engineering applications. In this work, multi-walled carbon nanotube (MWCNT) and graphene nanopowders (GNP) filled epoxy composites were fabricated via ultrasonication and casting method. The effect of MWCNT and GNP loadings (0-1 vol%) on tensile properties of filled epoxy composites were investigated. The experimental results prove that the strength and modulus of filler (MWCNT and GNP) filled epoxy composites are lower as compared to pristine epoxy. However, the addition of GNP at 0.8 vol% had slightly increased the composite tensile modulus which was approximately 3.4% in comparison with pristine epoxy. Thus, in general it indicates that the addition of filler (MWCNT and GNP) had reduced the mechanical properties of epoxy composites. The reason for this is due to the high aspect ratio and high van der Waals attraction of the MWCNT causes entanglement among nanotube. Subsequently, this leads to aggregations and agglomerations which limit the load transfer from the matrix to nanotubes. Similarly, agglomeration in GNP composites is due to the stacking of flaky-shaped GNP particles and the sharp edges of GNP cause cracks to initiate and resulting in lower mechanical properties.

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Keywords: Multi-walled carbon nanotube; graphene nanopowder; tensile properties

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1. Introduction

Polymer based composites filled with carbon nanofillers have been extensively investigated for the past decade¹⁻⁴. Polymers are the ideal resin materials due to their low cost, easy processing, lightweight, reproducibility and offer vital mechanical properties. Various polymers have been employed either thermoplastics or thermosetting such as epoxy (EP)^{5,6}, poly methyl methacrylate (PMMA)^{7,8}, poly vinyl alcohol (PVA)^{9,10}, polyvinyl chloride (PVC)^{11,12}, polypropylene (PP)^{13,14}, polyethylene (PE)^{15,16}, polyamide-12 (PA12)^{13,17} and polystyrene (PS)^{18,19} as matrices to prepare carbon-based fillers polymer composites. However, amongst these polymers, epoxy resin is the most frequently used for advanced composites materials as a result of their excellent thermal, mechanical and electrical properties (dimensional stability) and chemical resistance.

Many researchers have reported the promising findings of carbon-based fillers epoxy composites. Addition of carbon nanofillers such as single-walled carbon nanotube (SWCNT), multi-walled carbon nanotube (MWCNT), carbon nanofibers (CNFs), graphene and carbon black (CB) incorporated into epoxy matrix can improve structural and functional properties such as mechanical properties and electrical and thermal conductivities of polymer based composites^{4,20-22}. However, carbon nanotube (CNT) and graphene are attracting a great deal of attention due to their excellent structural and functional properties as well as its suitability for engineering applications²³⁻²⁶. To date, great progress has been made on MWCNT or GNP as fillers in the epoxy matrix^{4,24-30}. Martone et al.,²⁷ reported the effect on the bending modulus of dispersed MWCNT into an epoxy system. The results shows that the MWCNT displayed their maximum reinforcement efficiency, 1.780 TPa at very low loading 0.05% w/w. This is resulting from both the high aspect ratio and the high modulus of the filler, the optimized state of dispersion and the low filler loading which reduced the agglomeration of the MWCNT. Guo et al.²⁸ investigated the effects of MWCNT loading and surface modification on the mechanical performances and fracture morphologies of composites. It was shown that both the tensile strength and the fracture strain increased with the increase of MWCNT, while Young's modulus reduced at the same time. This is due to the addition of MWCNT could increase the toughness of the composites and through mixed-acid treatment, the outer layer of MWCNT were destroyed by oxidation. Mittal et al.²⁴ highlighted that CNT and graphene have the potential to modify properties of materials for various applications. However, the performance of MWCNT or GNP epoxy composites depends upon various factors such as types and quality of CNT, layers of graphene, length of CNT, aspect ratio, amount of CNT and graphene loading, dispersion of CNT and graphene into matrix, the choice of matrix, fillers-matrix adhesion, surface modification and etc.

This study aims to investigate the effect of MWCNT and GNP fillers and filler loading on the tensile properties of epoxy composites. Fillers with different geometric shape: one dimensional multi-walled carbon nanotubes (1-D MWCNT) and two dimensional graphene nanopowder (2-D GNP) were chosen in this study. A relatively low filler loading of 0-1 vol% were selected for the mixture solution based on suggestion from previous work^{31,32}. Sandler et al.,³¹ revealed that the randomly oriented CNT loading under 1 wt% was sufficient to achieve good dispersion and substantial mechanical improvement. The MWCNT and GNP filled epoxy composites were fabricated via ultrasonication and casting method. The preparation of mixture solution and the sonication time were based on optimized conditioned obtained in our group^{33,34}. It is important to note that the conclusions achieved in this study will be beneficial for similar composite system and the parameters that affect the performance of the composites shall be improve for mechanical enhancements.

2. Experimental methods

2.1. Materials

The materials used in this study included an epoxy resin D.E.R.TM 332 (diglycidyl ether of bisphenol-A) cured with polyetheramine D230 hardener, with weight ratio of 100:32, both supplied by Penchem Technologies Sdn. Bhd. The density of materials were 1.16 g/cm³ and 0.946 g/cm³ respectively. The fillers; MWCNTs (purchased from USAINS Holding, Universiti Sains Malaysia) have an average diameter of 10 nm ± 1 nm and length of 1-5 µm, prepared via catalytic chemical vapour deposition (CCVD) process and GNP (supplied by Skyspring Nanomaterials, Inc.) consisted of flake particles with an average particle diameter of 15 µm and thickness of 5-10 nm, were used.

2.2. Fabrication of MWCNT and GNP filled epoxy composites

Fig. 1. shows a simplified schematic diagram for the fabrication of film composites. Various MWCNT and GNP loadings between 0 vol% and 1.0 vol% were suspended in epoxy resin and sonicated using Hielscher UP200S Ultrasonicator at 24 kHz and 50% amplitude. The epoxy was ultrasonicated with filler for 20 min at room temperature and then degassing for 60 min to remove bubbles. Then, a hardener was added at a ratio of 100:32 by weight (epoxy: hardener) and the mixture was sonicated for 10 min in an ice bath. The preparation of mixture solution and the sonication time were based on optimized conditioned obtained in our group^{33,34}. Thereafter, the mixtures (MWCNT/epoxy and GNP/epoxy) were vacuumed at room temperature for 30 min to remove entrapped air. The mixture solution was cast onto coated transparency OHP film mold and flattened to uniform thickness using consolidation roller. The thickness of the film on the substrate was controlled by a spacer and the thicknesses of films produced were within ranges of 0.3-0.5mm. The film composites was cured at room temperature for 24h, followed by post cure at 80°C for 2h. The controlled samples (pristine epoxy) were prepared following the same procedure for comparison purposes.

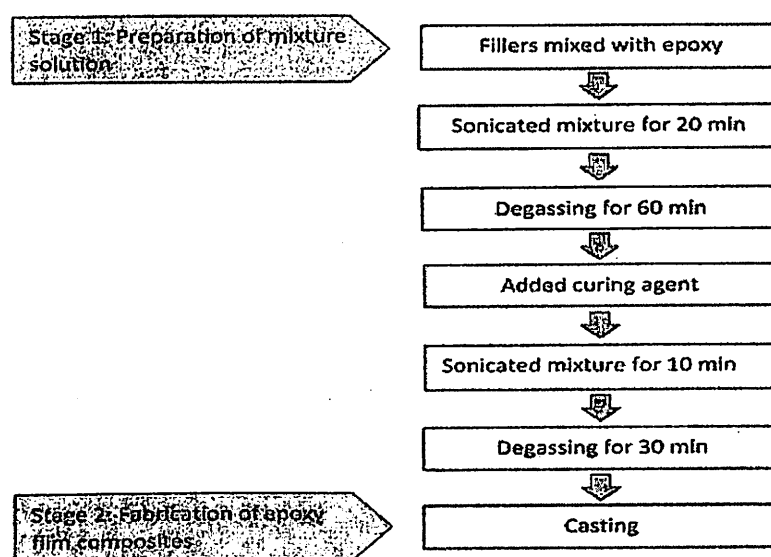


Fig. 1. Schematic of filled epoxy composites fabrication.

2.3. Characterization

The tensile properties of MWCNT and GNP filled epoxy composites were measured by an Instron 3366 mechanical testing machine according to the ASTM D882-02 standard test method at a crosshead speed of 1 mm/min. Low loading rate was chosen due to the brittle character of composites. Eight specimens with a dimension of 10 mm x 150 mm (for sample with thickness, $t < 1$ mm) were prepared and tested. Dispersion of fillers in filled epoxy composites was observed using Polarizing Microscope Meiji with image Analyser Software. The fracture surfaces of the film composites were observed by a high resolution scanning electron microscopy (FESEM Zeiss SUPRA 35VP) at an acceleration voltage of 10kV.

3. Results and discussion

3.1. Filler characterization

Two types of fillers, MWCNT and GNP, were used in this study. Fig. 2. shows SEM images of as-received filler powders namely MWCNT and GNP. Figure 2 (c) shows that MWCNT are tubular forms of carbon that can be visualized as a sheet of graphene rolled into cylindrical form and are consisting up to few hundred individual randomly oriented CNT and in the form of heavily agglomerates due to various factors such as van der Waals attraction, large surface areas and physical entanglement³. This scenario was observed for as-received MWCNT and properties inconsistently causes the performance of MWCNT filled epoxy composite to be very different even if the composites are fabricated by using a similar method and with the same epoxy resin^{29, 35}. GNP are consisting of several layers of graphene sheets and has a flaky shape which causes aggregates. Similar to MWCNT, GNP agglomerates are due to additional π - π bonding which causes the stacking of the individual graphene sheets³⁶.

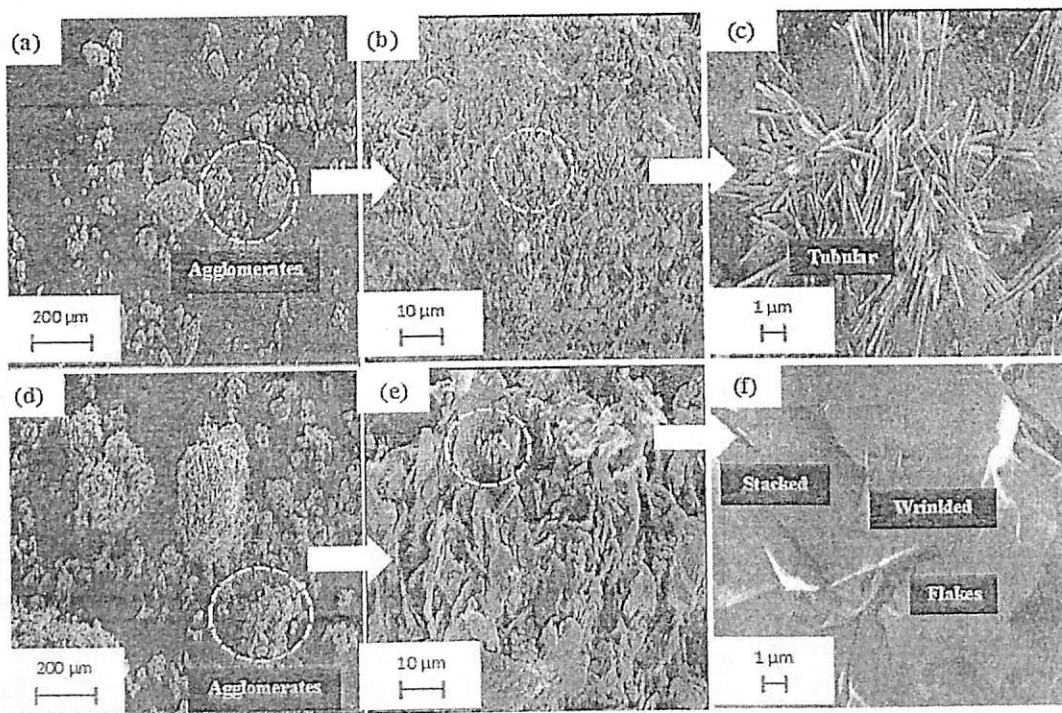


Fig. 2. SEM images of (a)-(c) MWCNT powder and (d)-(f) GNP powder (at magnification of 50x for a, d, 500x for b, e and 2.5kx for c, f).

3.2. Tensile properties

Fig. 3. shows the mechanical properties of the pristine epoxy, MWCNT and GNP filled epoxy composites at various filler loading ranged from 0 to 1vol%. Both tensile strength and tensile modulus of the filled epoxy composites decreases with increase in filler loading as shown in Fig. 3. (a) and (b). The tensile strength and tensile modulus of MWCNT filled epoxy composites were reduced by 10%-44% and 3%-19.3%, respectively. For GNP filled epoxy composite, the tensile strength were reduced by 39%-62%. However, the addition of GNP at 0.8 vol% had slightly increased the composite tensile modulus, which was approximately 3.4% in comparison with pristine epoxy. A slight improvement is explained due to the well dispersion of GNP epoxy composite and thus obeys the rule of mixtures in which any increment in filler loading will increase the modulus of the polymer composite. Similar trend was reported by the previous works^{34, 37-39}. In general, a decreased in the tensile strength and modulus are due to the agglomeration that limits the load transfer from the matrix to nanotubes, cause cracks to

initiate and propagate easily. Then, the produced cracks reduce the strength of the filled epoxy composites³⁷. The 1D structure of MWCNT has one disadvantage which is increasing viscosity as a result of increasing filler loading. This is due to entanglement among nanotubes which are caused by van der Waals attraction, high surface area and π - π bonding of the nanotubes which subsequently affect the processing. In contrast, GNP have a 2D layered structure which has higher surface area aiding better stress transfer and lower viscosity of the epoxy composite compared to MWCNT during fabrication⁴⁰. However, due to the morphology of GNP which were flaky-shaped particles and stack upon one another cause agglomeration of filler and the sharp edges of GNP cause cracks to initiate and resulting in lower mechanical properties. Elongation at break is plotted as a function of the filler loading in Fig. 3. (c). When the filler loading is increased, the amount of polymer component is decrease and hence causing the decrease in elongation at break. The elongation at break of GNP filled epoxy composites was lower than MWCNT filled epoxy composites. This is due to the fact that the epoxy composite become more brittle with the addition of flaky filler. It is known that mechanical properties is governed by various factors such filler types and their morphology and structure, filler loadings, filler qualities, filler dispersion, filler orientation (random or aligned), filler-matrix adhesion, particle dimension, voids, filler surface modification (functionalization and surfactant), fabrication method²⁷.

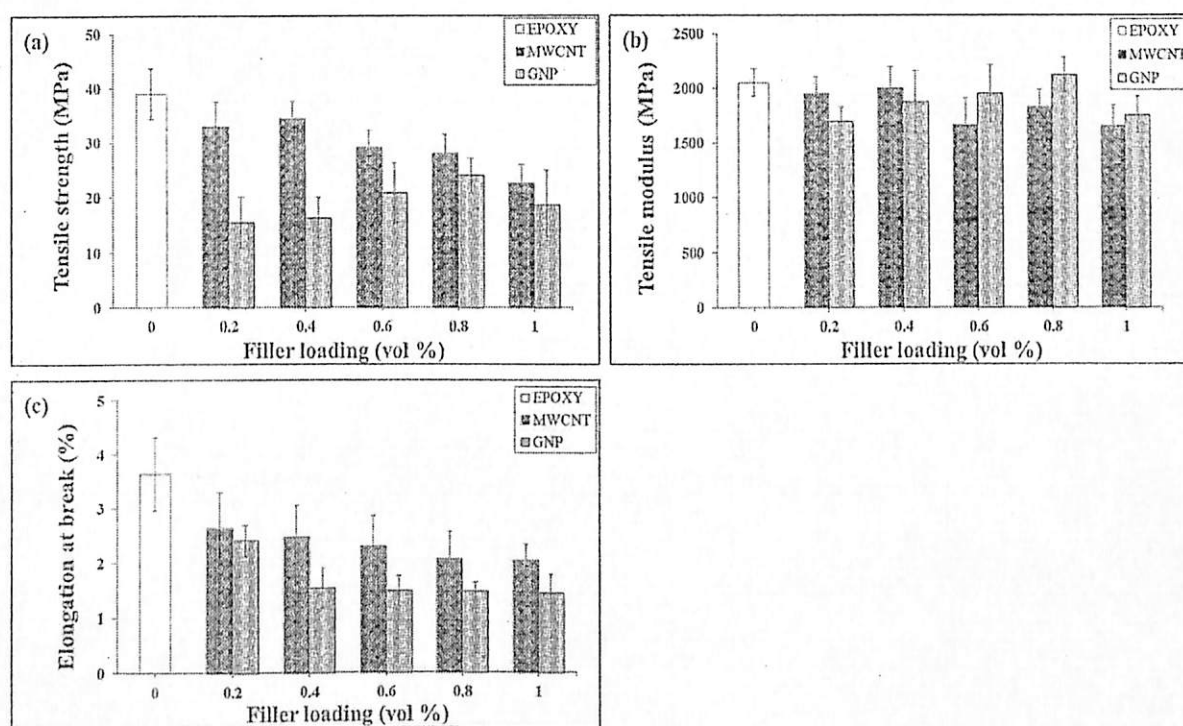


Fig. 3. Tensile properties of pristine epoxy, MWCNT and GNP/filled epoxy composites with various loading: (a) tensile strength, (b) tensile modulus and (c) elongation at break.

3.3. Morphological analysis

Morphological study of filler samples were investigated under an optical microscope to identify the dispersion state and clustering morphology of MWCNT and GNP dispersion in the epoxy matrix at fixed sonication time (20 min) with different filler loading as shown in Fig. 4. Fig. 4. (a) – (b) shows that at low MWCNT loading (0.2 vol%-0.4 vol%), samples perform homogeneous and fine particles under optical microscope. However, at higher loading (0.6 vol%-1 vol%), the samples appear not only a fine particles but the formation of the coarse particles agglomerates (Fig. 4. (c)-(e)). Similar trend was observed with the GNP filled epoxy composites but the formation of coarse particles slightly lesser as compared to MWCNT epoxy composite (Fig. 4. (f) – (j)).

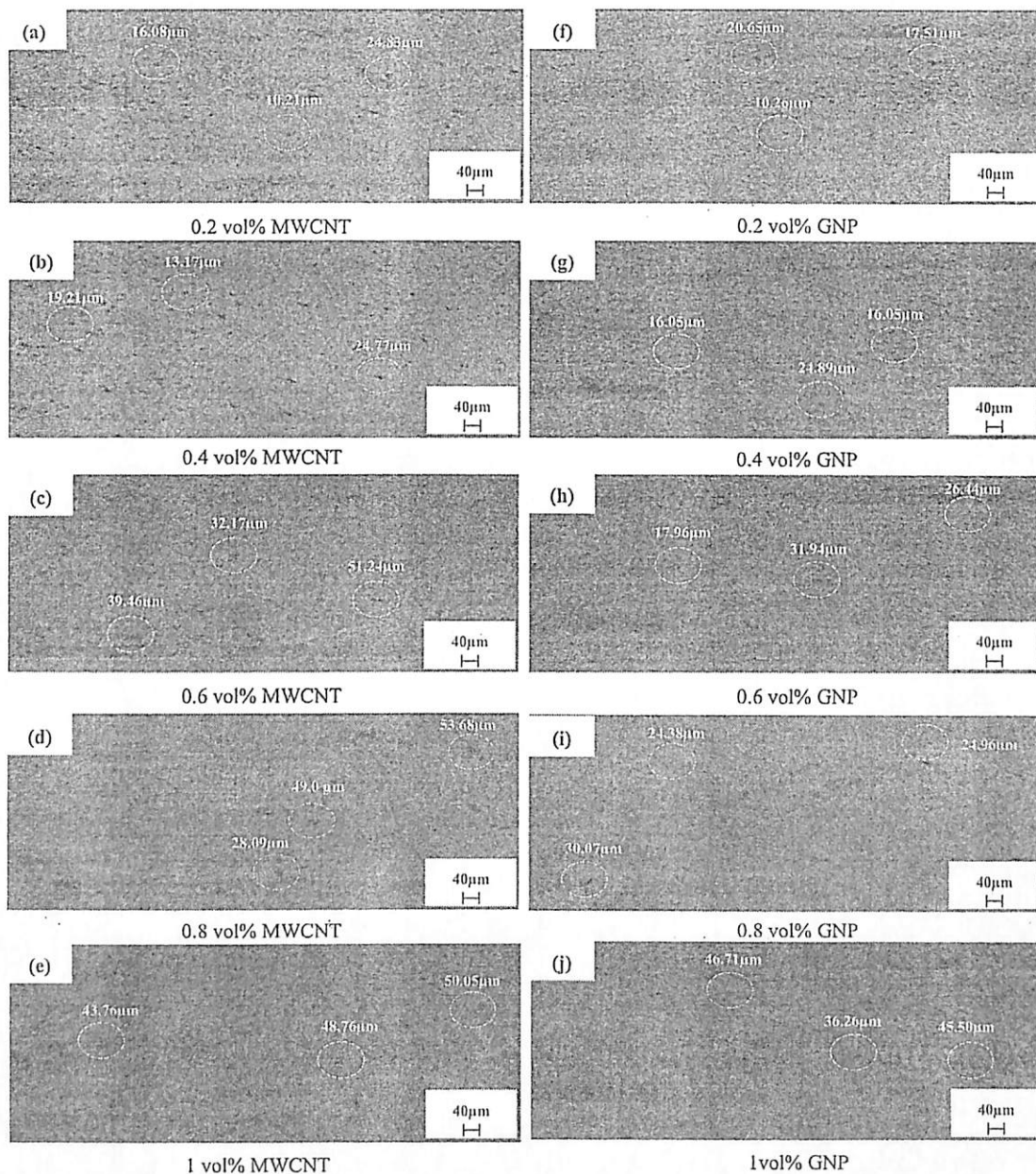


Fig. 4. Optical microscopy of (a) - (e) MWCNT filled epoxy composites and (f) - (j) GNP epoxy composites dispersion with different filler loading from 0 vol% to 1 vol% (at magnification of 40x).

Fig. 5. shows SEM micrographs of tensile fracture surfaces of pristine epoxy and filled epoxy composites with different MWCNT and GNP loading. The pristine epoxy has a smooth and mirror-like fracture surface, indicating a brittle material with low strength (Fig. 5. (a) and (b)). Thermosetting resins is well known as brittle and the addition of nanofillers induces the appearance of the fracture mechanism of crack deviation and generates many fracture rivers which grow in various planes. In contrast, the fracture surfaces of MWCNT (Fig. 5. (c)-(f)) and GNP (Fig. 5. (g)-(j)) filled epoxy composites are highly rough and the roughness increases with filler loading, indicating toughening²⁰. However, this fracture mechanism does not induce toughening effect to the MWCNT filled epoxy composites due to the weak filler-matrix interface. Composite fracture surfaces with 0.4 v% MWCNT show fewer and smaller areas with MWCNT as indicated with a square magnified box (Fig. 5. (d)), whereas in composites with

0.8 v% MWCNT indicated that there were large areas with MWCNT (Figure 5 (f)). This specifies the presence of carbon nanotubes and with the increasing content of nanotubes, the white spot increases. From the images, it shows that the MWCNT were poorly dispersed in the matrix with aggregations of MWCNT as the loading increases and there were cracks, filler-rich and resin-rich areas were observed. The agglomerates reduce reinforcing effects of the MWCNT as they are acting as defects in the resin and subsequently the poorly dispersed CNTs/epoxy composites have lower mechanical properties³⁷. Fig. 5. (h) and (j) represent the GNP loading at 0.4 v% and 0.8 v%. As shown in Fig. 5. (h), it can be clearly seen that non uniform filler dispersion occurs due to aggregated GNP with a few clusters of GNP stacked on each other and cracks are formed in the composite. The presence of cracks suggests low adhesion and poor compatibility between filler and matrix resulting in reduction in the composite properties⁴. However, for 0.8 vol% loading, it is shown that the epoxy filled composite is slightly well dispersed throughout the matrix and the GNP flakes are distributed evenly without any stacking observed. Thus, slightly improve in the composite tensile modulus.

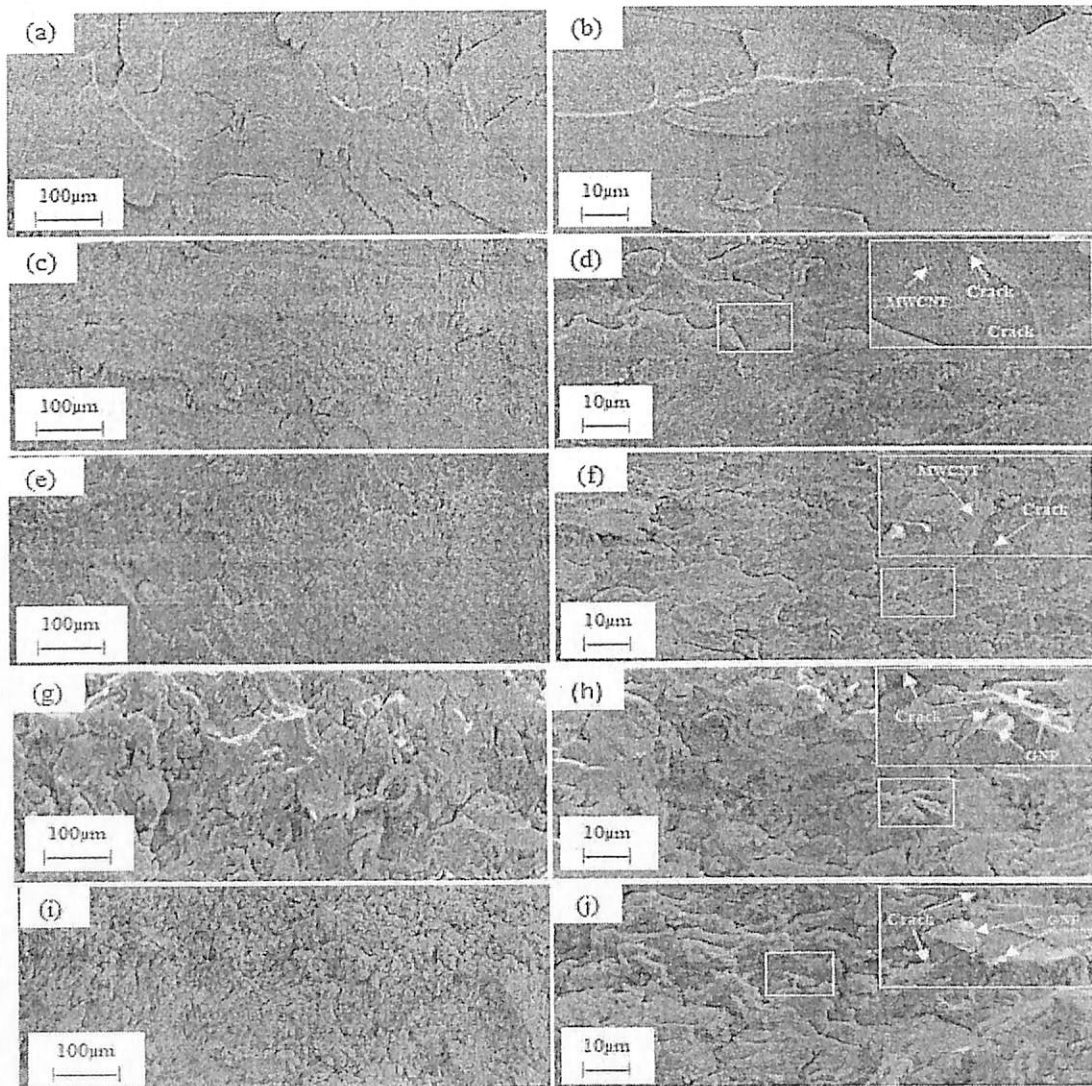


Fig. 5. SEM micrographs of fracture surfaces of (a)-(b) pristine epoxy, (c)-(d) 0.4 vol% MWCNT, (e)-(f) 0.8 vol% MWCNT, (g)-(h) 0.4 vol% GNP and (i)-(j) 0.8 vol% GNP filled epoxy composites (Left: 100x magnification and right: 500x magnification).

4. Conclusion

The effect of filler loading on tensile properties of MWCNT and GNP filled epoxy composites were investigated. Based on the experimental findings, it can be concluded that the incorporation of MWCNT and GNP in epoxy shows insignificant impact on the tensile properties of the filled epoxy composite. The incorporation of MWCNT and GNP had reduced the tensile properties of epoxy composites. The tensile strength and tensile modulus of MWCNT filled epoxy composites were reduced by 10%-44% and 3%-19.3% respectively which were related to the high aspect ratio and high van der Waals attraction of the MWCNT causes entanglement among nanotube. Whereas, for GNP filled epoxy the tensile strength were reduced by 39%-62%. The morphology of GNP which were flaky-shaped particles and stack upon one another causes agglomeration of filler and the sharp edges of GNP causes cracks to initiate and resulting in lower tensile properties. However, the addition of GNP at 0.8 vol% had slightly increased the composite tensile modulus which were approximately 3.4% in comparison with pristine epoxy. Elongation at break decreases as the filler loading increases. It was observed that the elongation at break of GNP filled epoxy composites was lower than MWCNT filled epoxy composites and this is caused by the fact that the epoxy composite become more brittle with the addition of flaky fillers.

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Comparison on the Properties of Glass Fiber/MWCNT/Epoxy and Carbon Fiber/MWCNT/Epoxy Composites

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Keywords: carbon nanotubes, composite laminates, carbon fiber, glass fiber.

ABSTRACT

A hand lay-up and vacuum bagging method was used in this study to fabricate glass fiber/epoxy laminated composites and carbon fiber/epoxy composite laminates with multi-walled carbon nanotube (MWCNT). The density, flexural properties, and burning rate of the laminated composites incorporated with different concentration of MWCNT (0.5, 1.0, and 1.5 vol%) were investigated and analyzed. Trend in the density, flexural and burning rate of glass fiber composite laminates were compared to those of carbon fiber composite laminates. Effect of MWCNT concentration on glass fiber composites properties varies from carbon fiber composite laminates. Incorporation of 0.5vol% of MWCNT has increased flexural strength by 54.4% compared to 5-ply glass fiber composite laminates. Nonetheless addition of 1vol% of MWCNT has only increased flexural strength by 34% compared to 5-ply carbon fiber laminated composites. Incorporation of MWCNT has successfully reduced the burning rate of the glass fiber composites as well as the carbon fiber laminated composites.

INTRODUCTION

Since 1940, the composite industry has been rapidly developed. High-performance fibers include glass and carbon fibers are widely used as reinforcement materials in composites for structural purposes in the transportation industry. The fibers are embedded in a compliant polymeric resin, such as epoxy and unsaturated polyester [1, 2]. In order to be used as reinforcement material for structural applications, the fibers should have high specific stiffness and strength, dimensional stability, adequate electrical properties, excellent corrosion resistance as well as being lightweight [2, 3]. Presently the most extensively used reinforcement materials for thermosetting composites are glass fibers owing to their low cost, availability, and reliability. On the hand, epoxy resin is the most frequently used as matrix for advanced composites due to its superior thermal, mechanical, and electrical properties, dimensional stability and chemical resistance. However, its inherent brittleness, delamination, and limited fracture toughness the constrained widespread use of epoxy resin.

Incorporation of nano-sized organic and inorganic particles, such as carbon nanotubes (CNTs), carbon nanofibers, nanoclays, and metal oxide particles in the epoxy matrices produces a new material with enhanced properties [4 - 8]. Epoxy matrices in glass-fiber composites have been normally modified with nanofillers to improve their mechanical properties. This is due to the fact that extremely high specific surface area of nano-sized particles facilitates the production of a great amount of interphase in a composite. Therefore, a strong interaction may exist between the fillers

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ABSTRACT

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Incorporation of nano-sized organic and inorganic particles, such as carbon nanotubes (CNTs), carbon nanofibers, nanoclays, and metal oxide particles in the epoxy matrices produces a new material with enhanced properties [4 - 8]. Epoxy matrices in glass-fiber composites have been normally modified with nanofillers to improve their mechanical properties. This is due to the fact that extremely high specific surface area of nano-sized particles facilitates the production of a great amount of interphase in a composite. Therefore, a strong interaction may exist between the fillers

and the matrix even at low nano-filler loading conditions. Theoretically, any material can be created to have nano-scale shape and size, nevertheless no particle has gained as much attention as CNTs [4]. Instead of having an exceptionally high aspect ratio and low density, these materials also possess high strength and stiffness [4, 7], consequently making those potential candidates for reinforcing polymeric materials. Furthermore, the free-radical scavenging effect of CNTs has been reported to effectively improve the stability of the polymer. Hence, the flame-retardant behavior of CNTs grants additional advantage as filler for composite materials for structural applications.

In this study, the effect of multi-walled carbon nanotubes (MWCNT) content (0.5, 1.0, and 1.5 vol%) on the properties of 4-ply glass fiber/epoxy laminated composites and carbon fiber/epoxy laminated composites have been investigated. This study aims to judge the properties of 4-ply glass fiber/MWCNT/epoxy and 4-ply carbon fiber/MWCNT/epoxy system against the 5-ply glass fiber/epoxy and 5-ply carbon fiber/epoxy system, respectively. The comparison of aforementioned composites was likewise observed.

EXPERIMENTAL

Materials

Materials used in the study were epoxy, curing agent, woven type E-glass fibers (GF), carbon fabric (CF) and MWCNT. The epoxy matrix used was and D.E.N 431 novolac resin, while curing agent used was Polyetheramine D230, respectively. Both matrix and curing agent were supplied by Penchem Industries Sdn. Bhd and they were used with ratio of 100 to 32. The reinforcement material, woven type E-glass fibers with a linear density of 200 g/m^2 was supplied by Saint-Gobain Ltd. The carbon fabric used was 5-harness satin weave with identical warp and fills yarns of 6000 multifilament continuous tow. The fabric which has linear density of 369.58 g/m^2 is commonly used for lightweight structures was supplied by Fibre Glast Corporation. On the other hand, multi-walled carbon nanotubes (MWCNTs) utilized in this study was synthesized by a group of researchers from the Universiti Sains Malaysia [8]. The highly pure MWCNTs (99.8%), with nearly uniform diameter average of $6.2 \text{ nm} \pm 0.5 \text{ nm}$ (mean \pm standard deviation), were synthesized over magnesia-supported Co-Mo bimetallic catalysts through catalytic chemical vapor deposition [9].

Methodology

Five pieces of fabric with a dimension of $180 \text{ mm} \times 120 \text{ mm}$ were utilized in fabrication of 5-ply GF/epoxy (5GF) sample. The fabric pieces were weighed to determine the weight of the epoxy. The ratio of reinforcement (fiber) to matrix (epoxy and curing agent) was fixed at 60% to 40%. Epoxy and the curing agent were mixed prior to hand lay-up procedure. The composite laminate was fabricated via hand lay-up technique and then consolidated for about 1 hour using the vacuum bagging technique. The fabricated sample was left overnight at room temperature to cure, and then subjected to a post-curing process where the sample was heated at a temperature of $100 \text{ }^\circ\text{C}$ for 1 h and then post-cured at $125 \text{ }^\circ\text{C}$ for 3 h. The same procedures were repeated in fabrication of 5-ply CF/epoxy, 4-ply GF/epoxy and 4-ply CF/epoxy composite laminates. The ratio of fiber to matrix was also fixed at 60% to 40%. An unfilled epoxy sample was also prepared as control.

4-ply GF/epoxy composite laminates incorporated with MWCNT samples were also fabricated using the same methods as that of the 5GF samples. However, the epoxy was first mixed with the nanofillers and then ultrasonicated using a Hielscher UP200S Ultrasonicator at 24 kHz and 50% amplitude for approximately 30 min. The procedure was then followed by addition of the curing agent into the mixture and ultrasonicated again for another 10 min. The hand lay-up, vacuum bagging, and post-curing processes were carried out as mentioned in the preparation of the composite control sample. The aforementioned procedures were repeated in fabrication of composites laminates with carbon fiber reinforcement. Fig. 1 (a) and (b) shows the schematic of the

methodology used in preparing the 5-ply and 4-ply GF/MWCNT/epoxy, respectively. Table 1 summarizes the sample designation used in the study.

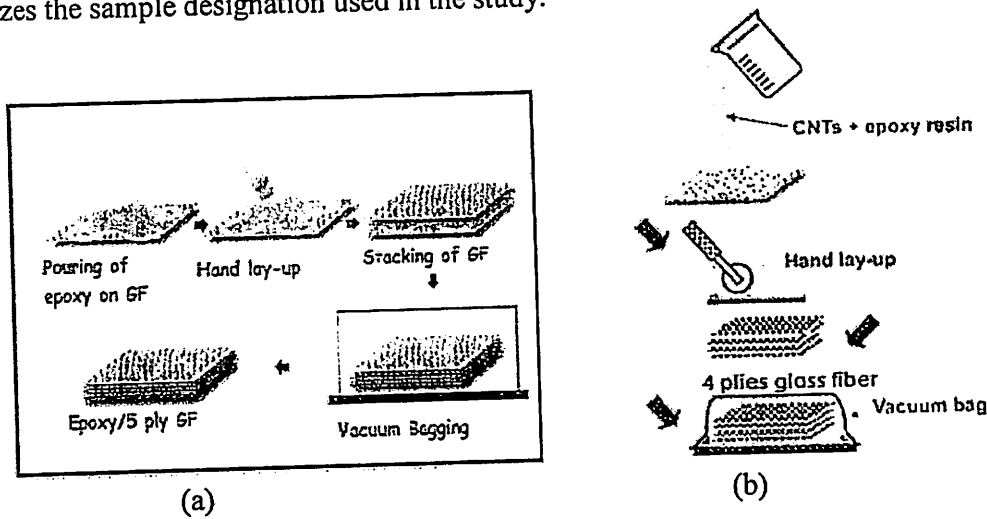


Fig. 1 (a) 5-ply GF/epoxy and (b) 4-ply GF/MWCNT/epoxy laminates [8].

TABLE 1: Sample designation and content of glass fiber (GF), carbon fiber (CF), epoxy and fillers in composite laminates

Sample labeling	Layer of Fiber	Fiber (vol %)	Epoxy (vol %)	MWCNT (vol %)
Epoxy	0	0	100	0
5 GF	5	60	40	0
4GF	4	60	40	0
4GF 0.5 C	4	54.5	45	0.5
4GF 1.0 C	4	54	45	1.0
4GF 1.5 C	4	54	44.5	1.5
5CF	5	60	40	0
4CF	4	60	40	0
4CF 0.5 C	4	54.5	45	0.5
4CF 1.0 C	4	54	45	1.0
4CF 1.5 C	4	54	44.5	1.5

Characterization

Density was measured based on Archimedes' Principle, using a gravity balance, Precisa 8000. Specimens with dimension of 10 mm × 10 mm were tested, and the average density was calculated. The flexural properties of the composites were measured using INSTRON 5982. Five samples with dimension of 80 mm × 17 mm were utilized for 3-point bending flexural test. The test was set according to ASTM D 790, with a cross-head rate of 2 mm/min. The burning rate of composite samples was determined by a flammability test, in accordance with the ASTM D 635 method. At least 10 bar-shaped test specimens measuring 125 mm × 13 mm × 3 mm with gauge length fixed at 25 mm from each composition and composite system were tested.

RESULTS AND DISCUSSION

Density

The density of unfilled epoxy, 5-ply and 4-ply composite laminates and 4-ply composite laminates with the addition of different CNT contents is shown in Fig. 2. As expected, density was observed to increase when the 5-ply and 4-ply glass fiber (GF) as well carbon fiber (CF) was added into the epoxy matrix. However their densities were reduced by approximately 14 and 8% when the glass fiber and carbon fiber layer was reduced from 5-ply to 4-ply laminates, respectively. An increasing trend was observed when the amount of CNT filler loading was increased from 0.5% to 1.5% for both fiber reinforcements. Conversely, the density of the composite laminates incorporated with CNT is lower compared to that of the 5-ply composite laminates and thus indicating that weight reduction can be achieved in 4-ply system. Ogaswara et al. [10] reported the increasing density trend of aligned multi-walled carbon nanotubes/epoxy composites with the increasing volume fraction of MWCNT. In addition, Gajendran and Saraswathy [11] also observed the same changing trend in the density in their study on polyaniline-carbon nanotubes (PANI-CNT) composites. They reported that the density of PANI-CNT composites increased when CNT was added in the PANI-CNT system through the solution mixing method. Composite laminates reinforced with glass fiber tends to have higher density compared to carbon fiber reinforced composites in the similar system as the nature of the glass fiber itself that has higher density compared to the carbon fiber.

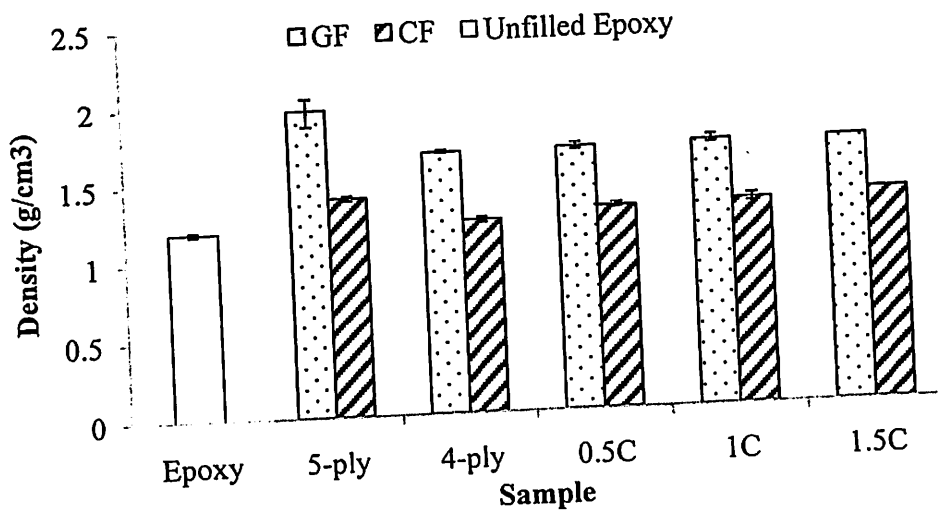


Fig. 2 Density of epoxy, 4-ply and 5-ply composite laminates and 4-ply laminated composites incorporated with different CNT content.

Flexural Properties

Fig. 3 shows the flexural strength of the unfilled epoxy, 4-ply and 5-ply composite laminates, and 4-ply composite laminates incorporated with MWCNT. The graph in Fig. 3 illustrates that sample with 5-ply GF has flexural strength 26.8% lower than the sample of CF with similar number of ply. Both samples, GF/epoxy and CF/epoxy composite laminates experienced about 25% reduction in flexural strength when the reinforcement was reduced from 5 to 4-ply. Variation of flexural strength is observed with addition of MWCNT at different concentrations. Generally, samples with either type of reinforcement showed increment in the flexural strength with addition of 0.5 of MWCNT compared to 4-ply composite laminates. Addition of 0.5 vol% of MWCNT results in enormous impact on the 4-ply composite laminates reinforced with GF. GF composite laminates incorporated

with 0.5 vol% of MWCNT has 54.4% higher flexural strength than that of 5-ply GF composite laminates. This shows that the mixture of epoxy mixed with 0.5 vol% of MWCNT increase the properties of 4-ply system. Nonetheless addition of 1.5 vol% of MWCNT results in reduction of the flexural strength. Such reduction may be attributed to agglomeration of the MWCNT. The agglomeration of MWCNT fillers has been reported to frequently caused void formations thus reduce the mechanical properties of the glass fiber laminated composites [6, 7, 12]. Incorporation of higher concentration of MWCNT in the epoxy on the other hand has increased the viscosity of mixture. This higher viscosity of the mixture subsequently intricate the wetting process of the fibers thus leads to the formation of voids in between the fabric layers. Unlike the composite laminates with GF reinforcement, laminated composites with CF and 0.5 vol% has flexural strength which is 10% lower than the flexural strength of 5-ply CF composites. This might be due to the inefficient amount of MWCNT presence in the epoxy to wet the CF layers. However, incorporation of 1 vol% of MWCNT has increased the flexural strength by 34% but reduced by 0.8% with addition of 1.5 vol% of MWCNT compared to 5-ply CF composites.

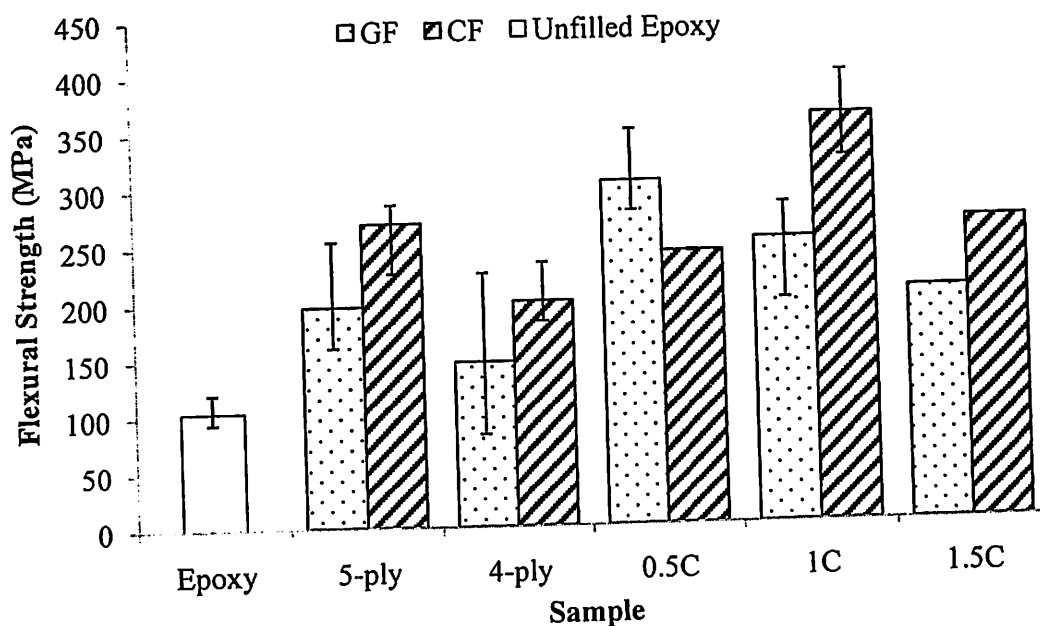


Fig. 3 Flexural strength of epoxy, 4-ply and 5-ply composite laminates and 4-ply laminated composites incorporated with different CNT content.

Fig. 4 illustrates the flexural modulus of the unfilled epoxy, GF composite laminates and CF laminated composites. Similar trend of changes in the modulus of both composite laminates incorporated with increasing MWCNT loading. Addition of 0.5 vol% of MWCNT in the GF laminated composites has increased the flexural modulus by 0.2% and 16% compared to 5-ply GF composites and 4-ply GF composite laminates, respectively. Conversely, addition of MWCNT in the CF composite laminates does not produce significant increment of flexural modulus compared to 5-ply CF composites. However, incorporation of MWCNT in the CF composite has increased flexural modulus about 20% compared to 4-ply CF composite laminates. Higher loading of MWCNT (1.5 vol%) caused reduction in the modulus, which may be due to the agglomeration of MWCNT.

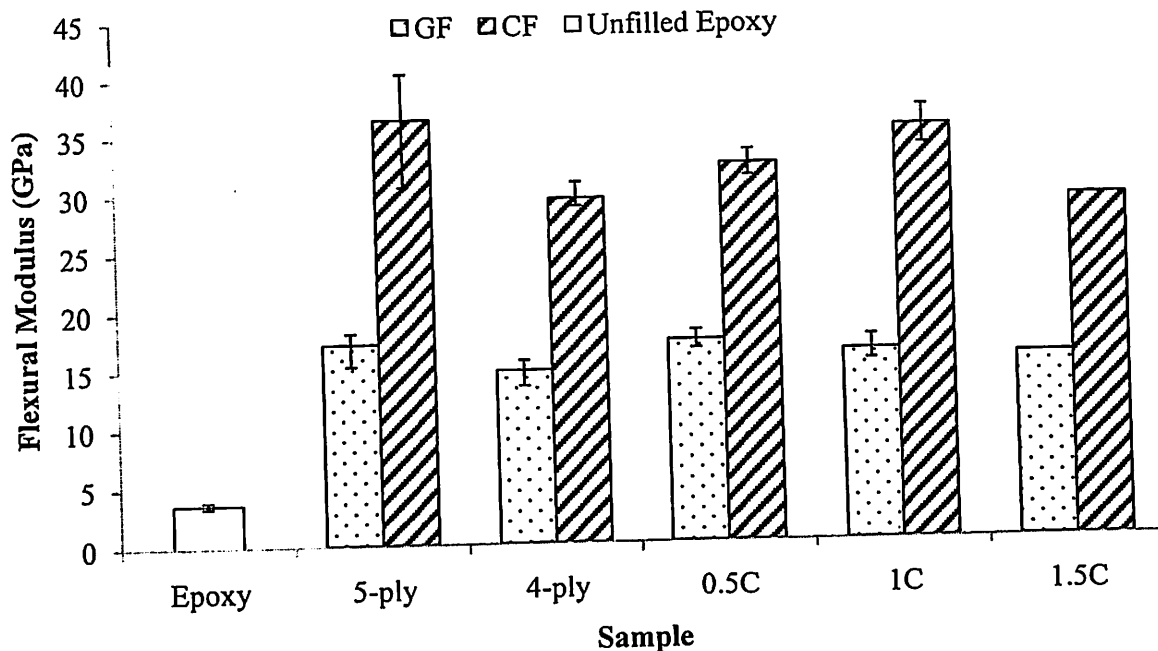


Fig. 4 Flexural modulus of epoxy, 4-ply and 5-ply composite laminates and 4-ply laminated composites incorporated with different CNT content.

Fig. 5 shows the burning rate of the unfilled epoxy, GF composite laminates and CF laminated composites. Unfilled epoxy burned completely at the highest burning rate compared to other composite samples. The epoxy burned continuously to produce char. Nonetheless, only the surface of the sample of GF and CF composite samples were burned. Composite laminates with 4-ply CF and GF have higher burning rate compared to those with 5-ply fibers. Comparing 5-ply composites to 4-ply composite laminates, burning rate of 4-ply GF and CF composites increased by 8 and 2%, respectively. However, addition of MWCNT has decreased the burning rate of those composites. Generally, it is observed that the burning rate reduced with increasing MWCNT loadings. This phenomenon occurred due to the high aspect ratio of MWCNT that percolates to form a network at very low loading instances in the polymer matrix; thereby resulting in the substantial enhancement of several functional properties, including flame retardant properties [13]. Carbon nanotubes can act as protective layers which serve as a heat shield for the virgin polymer below the layer. The formation of such network-structured protective layer during burning is essential for the vast reduction in the heat release rate [14]. The protective layer limits the transfer of volatile gas and oxygen, significantly decreasing the production of decomposition gases. Furthermore, the fuel gas was physically separated from the oxygen and prevented the combustion from being sustained [13]. From the bar graph, it is observed that carbon fiber composite laminates have lower burning rate compared to glass fiber laminated composites.

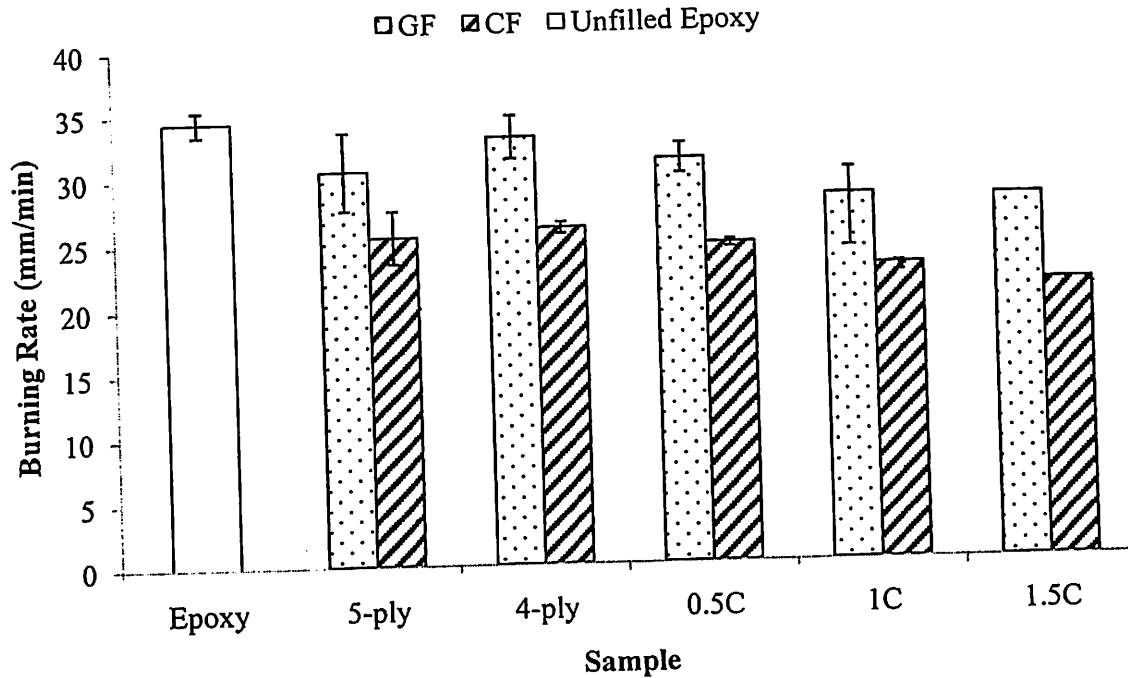


Fig. 5 Burning rate of epoxy, 4-ply and 5-ply composite laminates and 4-ply laminated composites incorporated with different MWCNT content.

CONCLUSIONS

The following conclusions drawn based on the tests and observations performed:

1. Density of the GF and CF composites laminates reduced from 5-ply to 4-ply laminates, and slightly increased with increasing MWCNT loading from 0.5 to 1.5 vol%.
2. The addition of 0.5 vol% of MWCNT in the four-ply system of GF composites increases flexural strength by 54.4% while modulus increases by only 0.17% compared to 5-ply CF composites.
3. The addition of 1.0 vol% of MWCNT in the four-ply system of CF composites increases flexural strength by 34% while modulus is 2.7% lower compared to 5-ply CF composites.
4. The addition of high loading of MWCNT filler not only increase in the viscosity of the epoxy matrix but also leads to agglomeration of the nanofillers. This phenomenon, consecutively, causes poor adhesion and wetting among the fiber, MWCNT, and epoxy; thus reducing the flexural properties of the composites.
5. Addition of 0.5 to 1.5 % of MWCNT has reduced the burning rate for both composite laminates systems.

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Fabrication and Properties of Multi-walled Carbon Nanotubes Buckypaper

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Keywords: multi-walled carbon nanotubes, buckypaper, thermal conductivity, electrical conductivity

Abstract. Free-standing carbon nanotubes (CNTs) film known as buckypaper is a method used to address dispersion problems of CNTs. Unique properties of CNTs made the CNTs buckypaper to be considered as promising reinforcement materials in development of high-performance of nanocomposites. Studies on the effects of filler loading, dispersion agents and together with the pressure on the electrical and thermal properties of the buckypaper are not much being explored. This study revealed that filler loadings, dispersing agents and vacuum pressure used played an important role in determining the properties of the fabrication of buckypaper. At 20 kPa pressure and filler loading of 100 mg, sample dispersed in TX-100 possessed the highest electrical conductivity of $6.7 \times 10^1 \text{ Sm}^{-1}$ whereas sample dispersed in ethanol exhibited the highest thermal conductivity of 0.19 WmK^{-1} .

Introduction

Laminated fiber reinforced composites has been used widely for structural materials, from transportation industries as found in light rail transit and bus to an ultra demanding sector such as aircraft components in aviation and aerospace industries [1, 2, 3]. There is an enormous diversity of fibers that have been used as reinforcing materials in the laminated composites such as glass, carbon, aramid and boron fiber, kevlar and natural fibers. Fiber reinforced polymers are gaining increasing importance in lightweight structural materials [4]. Lightweight structural promoting weight reduction thus reduced fuel consumption and emissions, enhanced aerodynamic efficiencies and lower manufacturing costs [5].

Application of nanofillers in the laminated composites has been reported to be quite encouraging [6]. Out of those nanofillers, carbon nanotubes stands out as it possessed magnificent mechanical, thermal and electrical properties. However to exploit those superb properties, the CNT has to be dispersed efficiently. There have been several ways introduced to disperse the CNT into the laminated composites namely solution mixing [7, 8], solvent spraying [1], CNT buckypaper [9, 10] and electrophoretical deposition [11].

To address CNT agglomeration problem, we decided to use multi-walled carbon nanotubes (MWCNTs) buckypaper approach to be incorporated in the glass fiber/epoxy laminated composites. This preliminary work was basically focused on the thermal and electrical properties of MWCNT buckypapers. In this study, buckypaper was fabricated by dispersing MWCNTs into two different types of solution namely Triton X-100 and ethanol then followed by filtration process. MWCNTs loading and pressure used during filtration process were being manipulated from 60 to 100 mg and 10 to 20 kPa respectively.

MWCNT loading. At pressure 10 kPa, it is found that the conductivity increased from 100 to 120 % for the MWCNT dispersed in TX-100 while sample with MWCNT dispersed in ethanol recorded 20 to 98 % increment. Similar observation was also supported by A. Aldalbahi and M. I. H. Panhius who reported that increasing the CNT mass fraction increases the electrical conductivity of the composite films regardless of CNTs used [15].

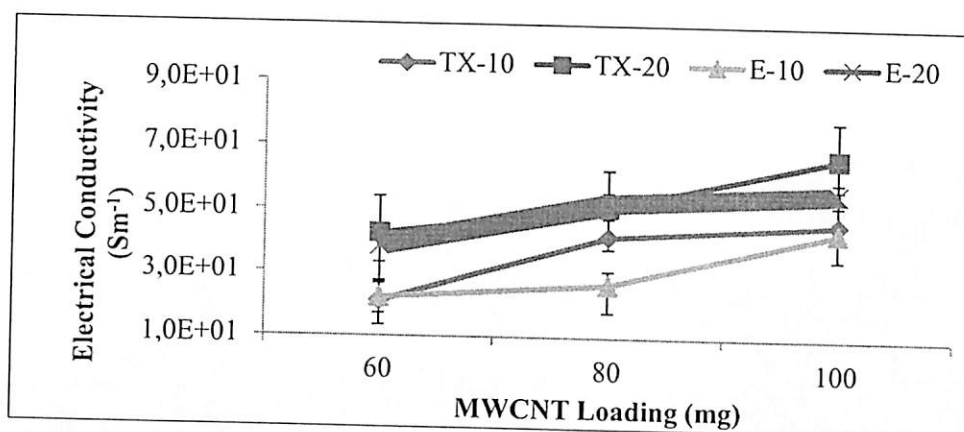


Figure 1: Electrical conductivity of MWCNT buckypapers.

At similar filler loading, the conductivity is found to be higher in sample filtered at higher pressure. Increasing the pressure from 10 kPa to 20 kPa has increased the electrical conductivity from 20 % to 100 % and 29 % to 98 % for samples dispersed in TX-100 and ethanol, respectively. The application of pressure has reported to increase the conductivity basically by enlarging the contact area between particles [16]. Table 2 summarizes the thickness and the electrical conductivity of MWCNT buckypaper samples. The table indicates that at similar MWCNT loading, sample filtered at higher pressure produced thinner thickness. This showed that the pressure aid in compressing the sample during the filtration process.

Comparing the buckypaper prepared with different dispersion solution, it can be obviously observed that sample dispersed in the surfactant, TX-100 produced buckypaper with higher electrical conductivity. Buckypaper 80TX-10 exhibited conductivity 37 % higher than the buckypaper 80E-10. This showed surfactant TX-100 dispersed the MWCNT better than the ethanol. This finding was proven with SEM images.

Table 2: Electrical conductivity properties and thickness of the MWCNT buckypapers produced using different MWCNT loading, pressure and dispersing agent.

Pressure (kPa)	MWCNT Loading (mg)	Triton X-100		Ethanol	
		Average Thickness (μm)	Average Electrical Conductivity (Sm^{-1})	Average Thickness (μm)	Average Electrical Conductivity (Sm^{-1})
10	60	110	2.1E+01	100	2.2E+01
	80	120	4.2E+01	130	2.6E+01
	100	160	4.6E+01	195	4.4E+01
20	60	100	4.3E+01	100	3.8E+01
	80	115	5.1E+01	120	5.2E+01
	100	150	6.7E+01	190	5.6E+01

Referring to Table 2, it is found that buckypapers prepared with ethanol were thicker compared to buckypaper of the same MWCNT loading and pressure prepared by TX-100. Figure 2 illustrates the cross-section of the buckypaper loaded with 100 mg MWCNT filtered at 10 kPa

prepared by using TX-100 and ethanol. Sample prepared with ethanol seems to have entangled nanotubes compared to sample prepared with TX-100. As mentioned previously, MWCNT dispersed with ethanol was first purified prior to filtration process. Purification with acid only removed carbonaceous impurities [17]. Besides, it has been reported that purification shorten, damaged and altered the natural properties of CNTs [17].

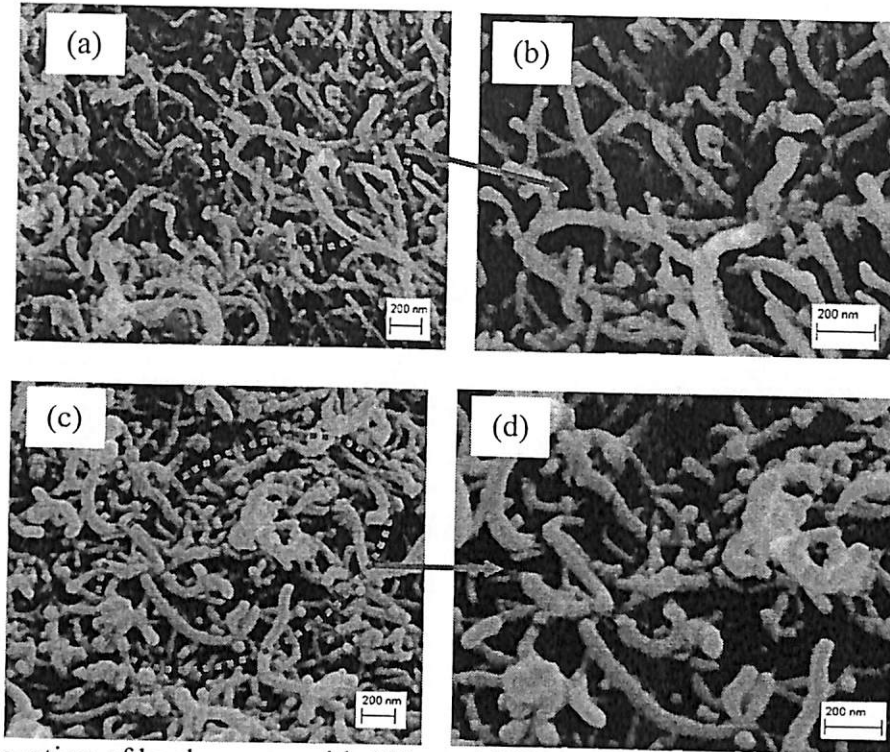


Figure 2: Cross-section of buckypaper with 100 mg MWCNT loading and filtered at 10 kPa; (a) and (b): TX-100; (c) and (d) ethanol

Figure 3 illustrates the thermal conductivity of the MWCNT buckypapers. It is observed that sample loaded with 100 mg MWCNT dispersed in ethanol and filtered at 20 kPa exhibited the highest thermal conductivity compared to other samples. Samples dispersed in different solutions showed two different patterns of changes of the thermal conductivity. The samples by which MWCNT dispersed in TX-100 showed increment with addition of 80 mg of MWCNT but the thermal conductivity dropped abruptly when the MWCNT loading increased. This might be due to the presence of pores within the buckypaper. The pores trapped the air hence affect the thermal conductivity properties. Figure 4 demonstrates the images of cross-section of the buckypaper filtered at 10 kPa, loaded with 60 and 100 mg MWCNT, respectively. From those images, it is clearly seen that sample with 100 mg MWCNT were more porous compared to sample with 60 mg.

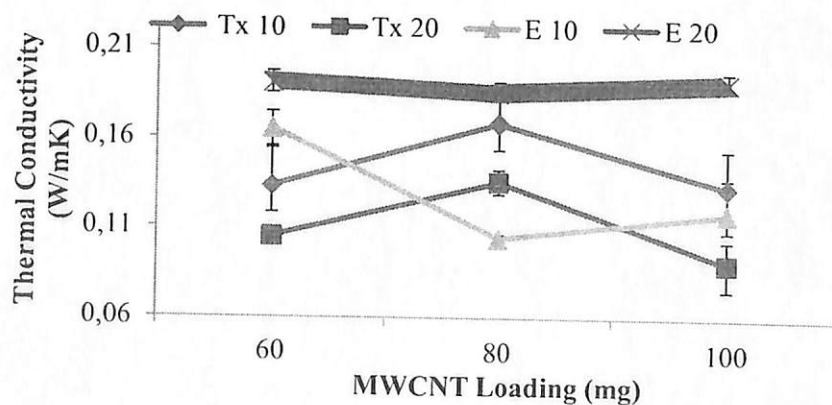


Figure 3: Thermal Conductivities of MWCNT buckypapers at different loading and pressure.

ip to main content

Electrical conductivity properties of MWCNT buckypaper and MWCNT buckypaper/epoxy composites: Effect of loading and pressure

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Abstract

Since the discoveries of the carbon nanotubes, numerous methods have been employed to take advantage of the superb mechanical and electrical properties of the carbon nanotubes in the fabrication of composites. Buckypaper has been found to be one of the suitable methods to be utilized in the production of nanocomposites with enhanced mechanical and electrical performance. In this study, buckypapers with different loading has been fabricated using filtration technique under two different pressures. Increasing loading of the carbon nanotubes caused significant reduction in the electrical conductivity of the buckypaper. It is found that pressure did not affect the electrical conductivity as much as the loading. Agglomerations are found to be the main reason of the diminution in the electrical conductivity properties of MWCNT buckypaper and MWCNT buckypaper/epoxy composites.

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Right1,Right2,Right3.

ELECTRICAL CONDUCTIVITY PROPERTIES OF MWCNT BUCKYPAPER AND MWCNT BUCKYPAPER/EPOXY COMPOSITES: EFFECT OF LOADING AND PRESSURE

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Abstract: *Since the discoveries of the carbon nanotubes, numerous methods have been employed to take advantage of the superb mechanical and electrical properties of the carbon nanotubes in the fabrication of composites. Buckypaper has been found to be one of the suitable methods to be utilized in the production of nanocomposites with enhanced mechanical and electrical performance. In this study, buckypapers with different loading has been fabricated using filtration technique under two different pressures. Increasing loading of the carbon nanotubes caused significant reduction in the electrical conductivity of the buckypaper. It is found that pressure did not affect the electrical conductivity as much as the loading. Agglomerations are found to be the main reason of the diminution in the electrical conductivity properties of MWCNT buckypaper and MWCNT buckypaper/epoxy composites.*

Keywords: MWCNT, buckypaper, thermal conductivity, electrical conductivity.

INTRODUCTION

Decades of studies revealed that carbon nanotubes (CNTs) possessed superb mechanical, electrical and thermal properties [1, 2]. Up to now, several investigations on CNT filled polymer composites as electrical conductive fillers have been performed [1, 3, 4, 5] as the CNTs possessed exceptional electric transport properties [3, 5]. The electrical conductivities are found to be depending on the formation of conducting networks in the composites [1, 5]. As a result, appropriate dispersion as well as distribution of the CNTs in the composites is mandatory in order to develop the utilization of their excellent electric transport properties.

Through the developments of research of carbon nanotubes (CNT) filled polymer matrix, several methods have been established to ensure efficient distribution and dispersion of the CNT in the matrix. Ball milling, calendering, ultrasonication and stirring and extrusion, as well as combination as those methods has been utilized to disperse the CNT in the matrix [1]. Without proper dispersion, CNTs tend to form into bundles and agglomerate due to strong intertube van der Waals forces. Therefore CNT sheet known as CNT skeleton or buckypaper has been introduced as an alternative to maximize the exploitation of magnificent mechanical, electrical and thermal properties of the CNT [2].

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Buckypaper is a planar film made of an entangled array of CNT which is held together by Van der Waals interactions at the tube-tube junctions [6, 7]. The CNT buckypaper are flexible, porous, easy to handle and can form uniform film of almost any shape and size [8]. Buckypapers preserve some of the excellent properties of CNT [9] and therefore they established promising electrical conductivity and mechanical performance [10]. They have been chosen as a practical candidate for radio frequency filters, cold-field cathode emitters, filtration devices [6], conducting composites, battery electrodes, capacitors and etc [9, 10].

CNT sheet can be produced by 2 different methods in different condition, either in solution or solid-state process [11]. Some methods have been applied to fabricate the buckypaper namely vacuum filtration [6-10, 12], casting [6], electrophoretical deposition (EPD) [13], ink-jet printing [14] and other methods. The properties of the buckypapers fabricated will depend on the fabrication technique. Filtration technique has been commonly employed in fabrication of the buckypaper. In this method, several types of appropriate organic solvents, surfactants or other chemicals are utilized in order to break the entanglement of the CNT thus forming a superior CNT dispersion [6]. The mixture will be then filtered through a filter membrane followed by drying process prior to the peeling of procedure. The buckypaper prepared by this methods are affected by several factors which are growth method and the condition of the CNT, types of medium used in CNT dispersion, technique and period of time utilized in dispersion procedure, CNT loading in the dispersion medium, vacuum pump pressure used during film depositions, as well as topology and surface condition by which the film is deposited [9].

In this study, multi-walled carbon nanotubes (MWCNT) buckypaper has been fabricated using a vacuum assisted filtration technique. MWCNT loading will affect the thickness of the buckypaper. The lower the filler loading, the thinner the buckypaper that been produced. It is found that, it is more

difficult to handle thinner buckypaper as it is more susceptible to failure. Meanwhile, fabrication of buckypaper with higher filler loading produced thicker buckypaper. Based on our preliminary study, MWCNT with different loading from 200 to 300 mg was chosen. These MWCNT powders have been dispersed in a surfactant, Triton X-100 [9] and filtered under two different vacuum pressures, 30 and 40 kPa. The effect of filler loading and pressure to the electrical conductivity of the MWCNT buckypapers and MWCNT buckypaper filled epoxy were studied.

MATERIALS AND METHOD

Materials

Multi-walled carbon nanotubes (MWCNT) utilized in this research was purchased from USAINS Holding, Universiti Sains Malaysia. The 80% purity MWCNT with average diameter of $10 \text{ nm} \pm 1 \text{ nm}$ and 1- 10 nm length was synthesized by catalytic chemical vapor deposition process. Surfactant namely Triton X-100 was purchased from Fluka. Epoxy DER 332 and hardener of Polyetheramine D230 were both purchased from Penchem Industries Sdn. Bhd. Deionized water was being utilized throughout the studies.

Preparation of MWCNT Buckypaper

MWCNT buckypaper was prepared by dispersing the predetermined amount of MWCNT in 30 ml of 1% Triton X-100 solution. The mixture was ultrasonicated in water bath using ultrasonic probe for 30 minutes. After the ultrasonication procedure, the mixture was immediately filtered through a nylon membrane filter with $0.45 \mu\text{m}$ pore diameter. During the filtration process, the pump pressure was set to 30 kPa. The MWCNT buckypaper deposited was then washed with a lot of deionized water. The filtered sample was then let to dry in the oven at 60°C for 15minutes and then peeled off. The above mentioned procedure was repeated in preparation of MWCNT buckypaper with different loading and pressure.

Infiltration of Epoxy

In the preparation of MWCNT buckypaper/epoxy samples, the predetermined amount of epoxy resin and hardener was mixed with ratio 100:32. The 30 volume percent of epoxy was infiltrated into the MWCNT buckypaper via vacuum bagging technique [7, 15] for about 1 hour. The epoxy infiltrated MWCNT buckypaper was left overnight to dry then followed by post-curing procedure in the oven for 2 hours at 80°C. Figure 1 shows epoxy infiltrated buckypaper (CNT/epoxy).

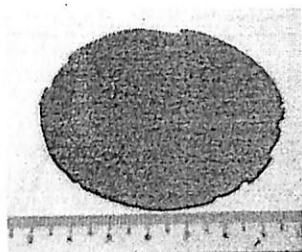


Figure 1: Epoxy infiltrated buckypaper (CNT/epoxy).

Characterizations

The electrical conductivity of the samples with diameter of 60 mm was measured by 4-point probe method [10] using Jandel Model RM3000. The detector was placed on the surface of the buckypaper and the resistivity of the sample was measured. More than 10 different spots of each samples has been utilized to measure the electrical resistance. The electrical conductivities of the samples were then calculated. In order to examine the surface morphology of the MWCNT buckypaper, optical microscope, Meiji Techno Metallurgical Microscope MT8500 Series has been utilized. The topography and surface roughness of sample with minimum size of 10 mm x 10 mm was measured by atomic force microscope (AFM), SPA 400 using silicon AFM probe with aluminum reflex coating. The measurement was made by operating in tapping mode with resonant frequency of 300 kHz at 40Nm⁻¹ force constant. The topography images were visualized with the aid of software SII Nanotechnology Nanonavi.

RESULTS AND DISCUSSION

MWCNT is known to be hydrophobic. TX-100 as is used as a dispersing agent to reduce the surface tension thus permitting uniform dispersion of MWCNT in the TX-100 solution. Adsorbing action of the TX-100 on the surface of more than one nanotube bridges the nanotubes hence allocates denser packing of buckypaper under filtration process [6]. Figure 2 shows the electrical conductivity of MWCNT buckypaper at different loading and MWCNT buckypaper/epoxy.

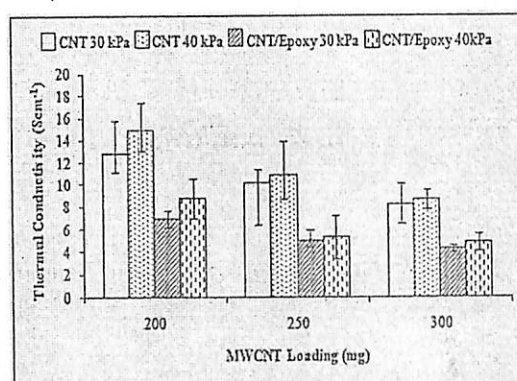


Figure 2: Electrical conductivity of MWCNT buckypaper and MWCNT buckypaper/epoxy with different MWCNT loading and pressure.

The bar graph reveals the electrical conductivity is inversely proportional to the MWCNT loading. For example, samples with 250 mg MWCNT loading filtered under 30 kPa and 40 kPa show reduction in electrical conductivity of 21% and 27%, respectively in comparison with the sample with 200 mg MWCNT loading filtered under the same pressure. Same trend on loading and pressure is observed for MWCNT buckypaper/epoxy. As expected, the conductivity of the samples infiltrated with epoxy is lower compared to the MWCNT buckypaper samples with same loading. The reduction of the electrical conductivity of MWCNT buckypaper/epoxy is mainly due to presence of epoxy resin which is known to be an electrical insulator [1].

Differ from MWCNT buckypaper/epoxy samples, the attenuation in the electrical conductivity of MWCNT buckypaper with increasing MWCNT loading is found to be

due to the agglomeration of the MWCNT. Agglomerations of the MWCNT at higher loading are confirmed by observation of the surface of the buckypaper using optical microscope. Figure 3 shows the image of the surface of MWCNT buckypaper with 2 different loading.

From Fig. 3 it can be clearly seen that agglomeration of the MWCNT which appears as small spheres structure on the surface of the sample occurs at higher filler loading. Morphology of conductive fillers has been reported to have significant effect on the formation of conductive network and the electrical properties of the composites [6]. The electrical properties of MWCNT which consists of multilayer of graphene are rather complex compared to the single-walled CNT (SWCNT). As the MWCNT in the buckypaper is randomly interconnected, therefore the agglomeration might disturb the interactions the graphene layers within the MWCNT thus disturb the current along the tube axis [1].

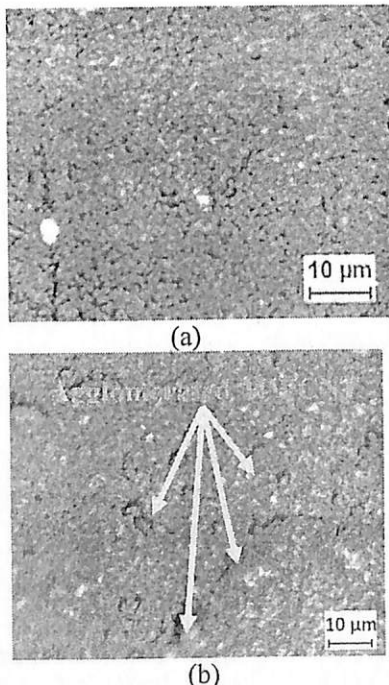


Figure 3: Image of samples filtered at 40 kPa pressure under microscope with 500 x magnifications; (a) 200 mg MWCNT loading; (b) 300 mg MWCNT loading.

As mentioned in previous section, the filtration procedures were performed at two different pressures; 30 kPa and 40 kPa. Greater pressure results in lessening filtration period. However based on the error bar of the electrical conductivity results for 200 mg to 300 mg MWCNT loading it is found that the pressure did not significantly affect the electrical properties. For example, the error bar for sample with 200 mg filtered at 30 and 40 kPa seems to be extending beyond each other. Only slight increment about 16% is observed from the sample with 200 mg MWCNT loading after increasing pressure from 30 kPa to 40 kPa. Furthermore, the average of electrical conductivity for sample with same MWCNT loading are almost equivalent especially samples with higher MWCNT loading.

The significant effect of pressure on the electrical conductivity of MWCNT buckypaper cannot be successfully examine may be due to pressure chosen in the study was in a small range. Pressure is reported as one of the factor that affects the porosity of the MWCNT buckypaper [16]. Figure 4 envisaged the topography and roughness factor (R_a) of MWCNT buckypaper with different loading filtered at different pressure measured by AFM.

Fig. 4 proven that the texture of the MWCNT buckypaper depends on preparation process [16]. Roughness factor (R_a) is defined as the ratio between the area of the topography and the nominal or geometrically projected area of the topography which also known as apparent area [17]. Comparing Fig. 4 (a) and (b), it seems that lower filtration pressure produced sample with smoother surface. Sample with 200 mg MWCNT filtered at 30 kPa pressure possessed lower roughness factor ($R_a = 54$ nm) compared to the sample with similar loading but filtered at 40 kPa. Lower roughness factor indicates lower porosity [16]. Sample filtered at 40 kPa showed higher porosity and this might be due to the higher suction pressure during filtration process.

Conversely, samples with 300 mg filler filtered at 40 kPa (Fig. 4 (c)) shows reduction

in roughness factor. Though high pressure is expected to increase the porosity of the sample, increasing filler loading allowing more filler to fill up the pores thus seal it to form surface with lower roughness. In this study, agglomeration is not able to be

captured as surface roughness by AFM due to the high roughness of the MWCNT buckypaper which forbids the AFM visualization of MWCNT bundles on the buckypaper surface [16].

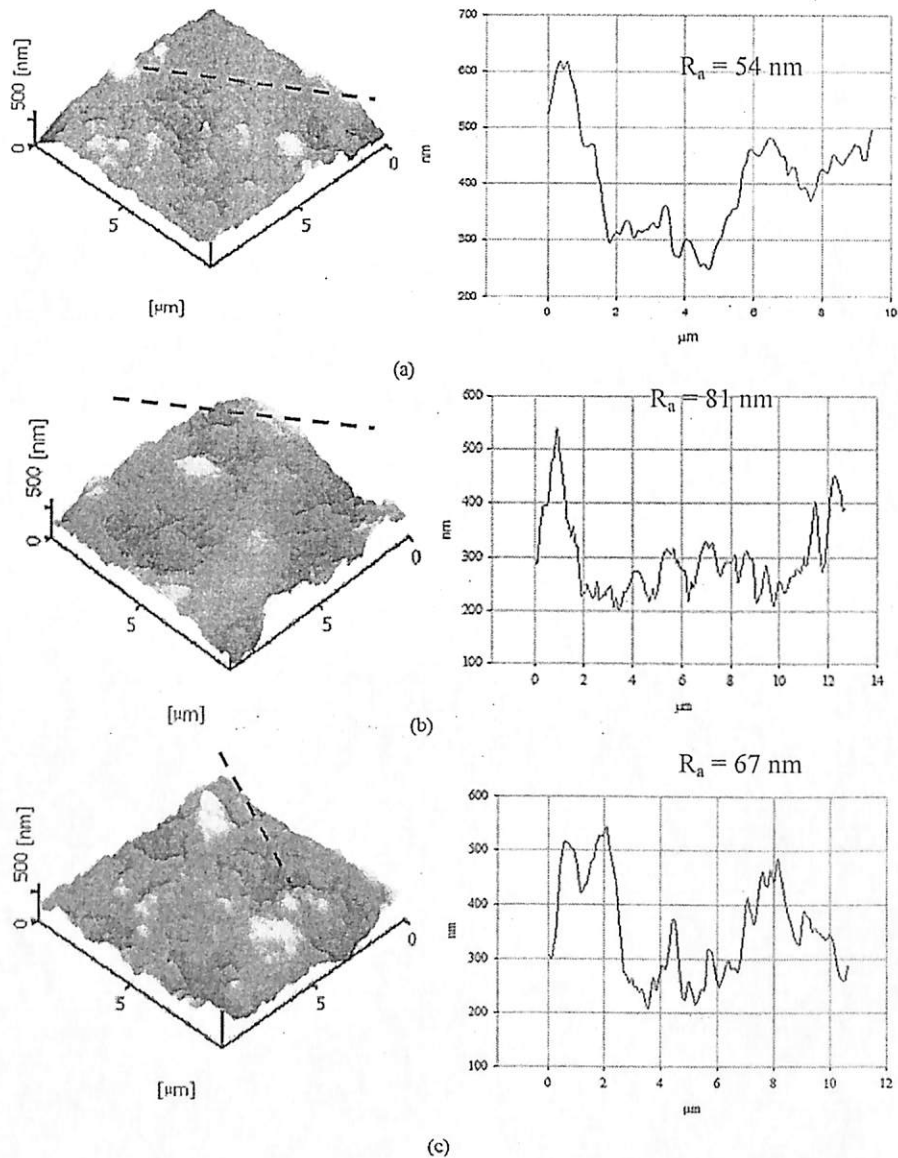


Figure 4: AFM topography and roughness factor (R_a) of MWCNT buckypaper at different filler loading and pressure; (a) and (b) MWCNT buckypaper with filler loading 200 mg filtered at 30 kPa and 40 kPa, respectively; (c) MWCNT buckypaper with 300 mg filler loading filtered at 40 kPa pressure.

Efforts have been made in embedding the MWCNT buckypaper under higher vacuum pressure (50 kPa) but it is found that greater pressure caused difficulties in peeling off the

buckypaper from the membrane consequently damaged the buckypaper. On the other hand, filtration at lower pressure < 30 kPa will prolong the filtration period.

CONCLUSION

Based from the observation, it is found that MWCNT buckypaper with lower loading (200 mg) possessed higher electrical conductivity property compared to that of the higher loading (250 mg and 300 mg). Pressure affects the filtration time and suction force to deposit the MWCNT on to the filter membrane. However, there is no significant effect of pressure between 30 kPa and 40 kPa towards the electrical properties of the MWCNT buckypaper.

ACKNOWLEDGMENTS

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5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

Properties of Fiberglass/MWCNT Buckypaper/Epoxy Laminated Composites

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Abstract

In this research, multi-walled carbon nanotubes buckypaper have been incorporated into three-ply glass fiber/epoxy laminated composites to form hybrid composites. Two different type of MWCNT buckypaper have been incorporated into glass fiber/epoxy laminated composites. The buckypaper incorporated were either in form of free-standing MWCNT buckypaper (CNTBP) or MWCNT buckypaper/epoxy (CNTBPE). The effect of the incorporation of the buckypaper in the hybrid composites have been compared to three-ply and four-ply glass fiber/epoxy laminated composites. It was found that CNTBPE sample exhibits 50 % and 30 % higher flexural strength compared to three-ply glass fiber composite and four-ply glass fiber composite, respectively. Specific strength and specific modulus of the CNTBPE samples reached up to $64.03 \text{ MPa/gcm}^{-3}$ and $6.43 \text{ GPa/gcm}^{-3}$, respectively. The specific strength and modulus of CNTBPE is 70 and 30 %, respectively higher compared to 3GF. This showed that incorporation of MWCNTBP/epoxy in the glass fiber composite system promotes the fabrication of lightweight structures with better flexural strength properties.

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Keywords: multi-walled carbon nanotubes; buckypaper, flexural properties

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1. Introduction

Lightweight structures have become necessities for vehicles industry as an effort to reduce energy consumption¹. Polymer matrix composites (PMC) have been widely used in primary automotive with composite materials. One of the most popular fiber reinforcement in PMC is fiberglass¹. To further reduce the weight of the vehicles, hybrid composites have been introduced. Hybrid composites or three-phase composites are already known to industries as these composites possess enhanced mechanical and thermal properties over the monolithic materials. These hybrid composites have been fabricated via various methods using different combination of reinforcing materials. Hybrids composites are usually fabricated by hand lay-up technique², resin transfer molding^{3,4}, pultrusion⁵ and others. Several studies have been performed to incorporate nanofillers, specifically carbon nanotubes (CNT) into the fiber reinforced polymer composites⁶⁻⁹. However, developments of hybrid composites with CNTs are depending on the capability to form homogeneous CNT dispersion in the polymer matrix as well as creating strong interfacial CNT-matrix interaction¹⁰.

CNT buckypapers (CNT BP) or CNT skeleton have been introduced to overcome the agglomeration problems in the dispersion of CNT¹¹. Buckypapers are films with paper-like morphology¹² made of self-supporting network of entangled CNTs. The CNTs in this buckypaper are held together in a random manner by van der Waals interaction at the tube-tube junctions^{13,14}. Nanocomposites made of these CNT BPs are used in filtration devices, capacitors and other electronic devices^{13,15}. However, incorporation of this skeleton into woven laminated composites was limited. Therefore, this research is performed to observe the effect of multi-walled CNT BP (MWCNT BP) and MWCNT BP/epoxy on the properties of fiberglass/epoxy laminated composites.

MWCNT BPs utilized in this study were prepared by vacuum filtration method. In this research, two layers of MWCNT BP or MWCNT BP/epoxy were stacked between three layers of plain woven glass fiber by using hand lay-up and vacuum bagging technique. Composite samples with MWCNT BP are referred as CNTBP whereas samples with MWCNT BP/epoxy are referred as CNTBPE. The density, void contents and flexural properties of the hybrid composites prepared were compared with control samples of fiberglass/epoxy laminated composites (three-ply fiberglass/epoxy (3GF) and four-ply fiberglass/epoxy (4GF) laminated composites).

2. Experimental

2.1. Materials

Multi-walled carbon nanotubes (MWCNT) with average outer diameter of $10 \text{ nm} \pm 1 \text{ nm}$ and $1 - 10 \text{ nm}$ length was purchased from Usains Holding, Universiti Sains Malaysia. The MWCNT with 80 % purity was synthesized by catalytic chemical vapor deposition process. A surfactant, Triton X-100 was purchased from Fluka whereas Whatman, 90 mm diameter sized of nylon membrane filter with pore diameter of $45 \text{ }\mu\text{m}$ was used during filtration process. Epoxy resin DER 332 as well as Polyetheramine D230 (hardener) were purchased from Penchem Industries Sdn. Bhd.

2.2 Method

MWCNT BPs were prepared by vacuum filtration. 150 mg of MWCNT was mixed with 30 ml of Triton X-100 solution (1 %) prior to ultrasonication. Then the mixture was ultrasonicated using ultrasonic probe at 50 % amplitude and 0.5 cycles for 30 minutes. The solution was immediately filtered through membrane filter at vacuum pressure of 30 kPa. The deposited MWCNT BP on the membrane filter then washed with deionized water in order to remove excessive surfactant. After that, the sample together with the membrane filter was left to dry in the oven at $60 \text{ }^\circ\text{C}$ for about 15 to 20 minutes. The dried MWCNT BP was then peeled off and ready to be incorporated in the GF.

In preparation of MWCNT BP/epoxy, the predetermined amount of epoxy and hardener was first mixed. The amount of epoxy resin used to impregnate the MWCNT BP was fixed at 15 vol %. The epoxy resin was then spread evenly on the transparency sheet. After that, the MWCNT BP was laid on top of the evenly spread epoxy resin. The sample was then covered with perforated plastic, breather ply and finally vacuum bag. Then the vacuum bagging procedure was performed for about 45 minutes to impregnate the epoxy resin throughout the MWCNT BP. The prepared sample was left overnight to dry. The curing process was carried out at 80 °C for 2 hours followed by post-curing for 3 hours at temperature of 125 °C. The MWCNT BP/epoxy was ready to be incorporated in the GF.

(MWCNTBP/epoxy)/GF/epoxy (referred as CNTBPE) was prepared by the same technique as mentioned above. Another 25 vol % of epoxy was used to fabricate a laminated composite. Adequate amount of epoxy was spread evenly on top of the transparency sheet. Then GF was laid on top of the resin. Roller was used to roll-over the GF so that the GF was laid flat and the resin could wet the GF uniformly. Same processes were repeated for each layer. The GF and MWCNT BP/epoxy were alternately laid on top of the resin. The final layer of GF was then spread with epoxy resin and then the sample was then consolidated via vacuum bagging. The curing and post-curing were performed at similar time and duration as mention in previous. The same procedure was repeated in preparation of MWCNT BP/GF/epoxy using a total 40 vol % of epoxy resin. This sample is referred as CNTBP. The samples prepared were cut accordingly and characterized for density, void content and flexural test. Control samples of 3GF and 4GF were also fabricated using similar method with epoxy resin fixed at 40 vol %. Fig. 1. shows the schematic diagram of the fabrication procedure for CNTBPE and CNTBP samples.

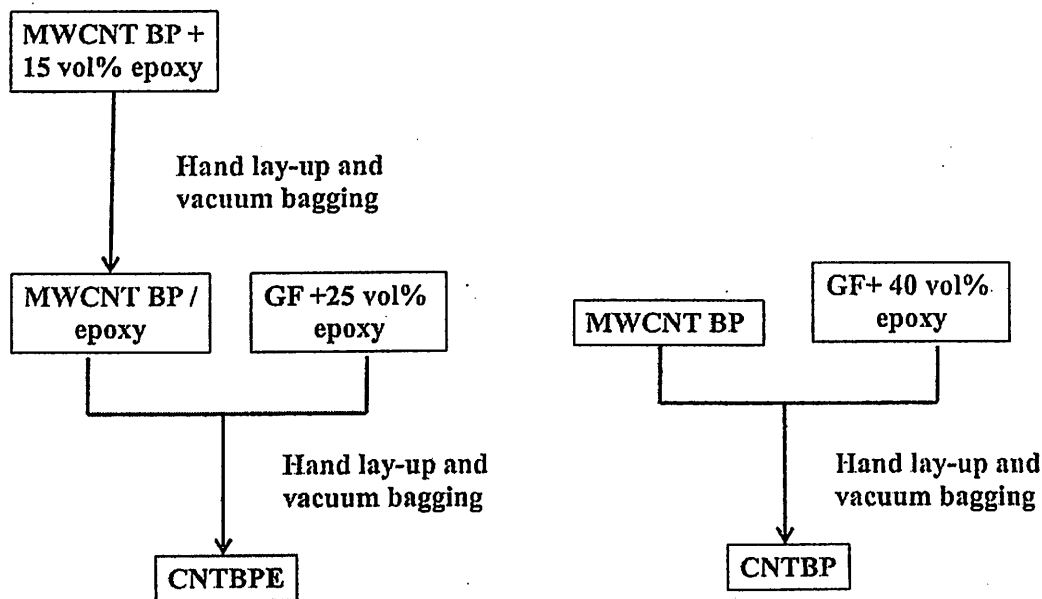


Fig. 1. Schematic diagram of the fabrication procedure for CNTBPE and CNTBP samples.

2.3 Characterization

The density of the sample was measured according ASTM D792. In this method, the densities of five specimens were obtained by applying Archimedes's Principle. The average density of the sample was then calculated. On the other hand, the void content of the sample was determined according to ASTM D 2734-97. The theoretical density of the samples was obtained via matrix burning off method in accordance with ASTM D2584. The difference between the theoretical densities compared to actual densities (ASTM D792) was calculated. The ratio of the difference between the actual density and the theoretical density, to the theoretical density is referred as void content. The flexural properties of the samples were determined according to ASTM D3039. Ten specimens with

dimension of 60 mm x 13 mm x t mm were tested by using INSTRON 5982 aided with Bluehill 2 software. The span of each specimen is fixed at 34 mm so that the ratio of span-to-depth ratio was more than 16:1. The flexural test was performed with cross head speed of set at 2 mm/min. The fractured surfaces of the composite samples were observed using scanning electron microscopy (SEM).

3. Results

3.1. Density and void content

Table 1 shows the density and void content of the composite samples. The density of 3GF and 4GF are expected to be similar as both composite systems consist of 60 vol % of fiber and 40 vol % of epoxy resin. However due to higher void contents presence in 3GF compared to 4GF composites caused the 3GF composite to have lower density in comparison to 4 GF. Hybrid composite samples of CNTBP and CNTBPE showed a lower density value compared to 3GF and 4GF. Even though the epoxy content in the hybrid composites are similar to the 3GF and 4GF, the fiber content in the hybrid system was reduced by 2.8 vol % due to addition of buckypaper (2.8 vol % MWCNT content). As the density of the MWCNT in the buckypaper is lower than the density of glass fiber, addition of 2.8 vol % of MWCNT in form of buckypaper caused reduction in the density of the composite. Amount of MWCNT in both hybrid composites of CNTBP and CNTBPE samples were 2.8 vol %. Similar amount of filler loading, fiber reinforcement as well as epoxy matrix results in similar density. Therefore, CNTBP and CNTBPE possessed similar density. CNTBP was found to have the highest void content compared to other composite samples. The voids formation in the composite might be due to failure of the epoxy to impregnate through the MWCNTBP during composite fabrication process. The presence of voids which is normally existing in between laminates may affect the composite performance.

Table 1. Density and void content of the composites.

Composite Samples	Density (g/cm^3)	Void Content (%)
3GF	1.97	2.91
4 GF	1.99	1.65
CNTBP	1.74	5.64
CNTBPE	1.75	5.33

3.2. Flexural test

Fig. 2. shows the flexural properties of the 3-ply hybrid composites, 3GF and 4GF composites. It is observed that flexural modulus of the CNTBP and CNTBPE samples were increased up to 13 % when compared to 3GF but were 8 % lower when compared to 4GF. On the other hand, CNTBP and CNTBPE possessed flexural strength 20 and 50 %, respectively higher than flexural strength of 3GF. For CNTBPE, the flexural strength was 30 % higher than 4GF. Such increment occurred due to the presence of MWCNT. MWCNT provides a better load transfer from epoxy towards GF reinforcement thus promoting an even distribution of forces throughout the whole composite system^{8,9} Comparing the samples between CNTBP and CNTBPE, it was found that CNTBP possessed lower flexural strength. This observation might be due to inefficient epoxy impregnation through the MWCNT BP during vacuum bagging procedure and thus creating voids. The voids hinder uniform stress distribution from the brittle matrix to the strong fiber reinforcement. The presence of voids in the composite creates weak bonding between the fibers or fillers and thus reduced the strength and stiffness of the composite¹⁶. Besides that, inefficient epoxy impregnation creates regions that have weak buckypaper-matrix interface. As CNTBP samples were made of free-standing MWCNT BP, the weakly bonded MWCNTs inside the buckypaper create weak regions in the composite. Therefore, CNTBP sample possessed lower flexural strength as compared to CNTBPE.

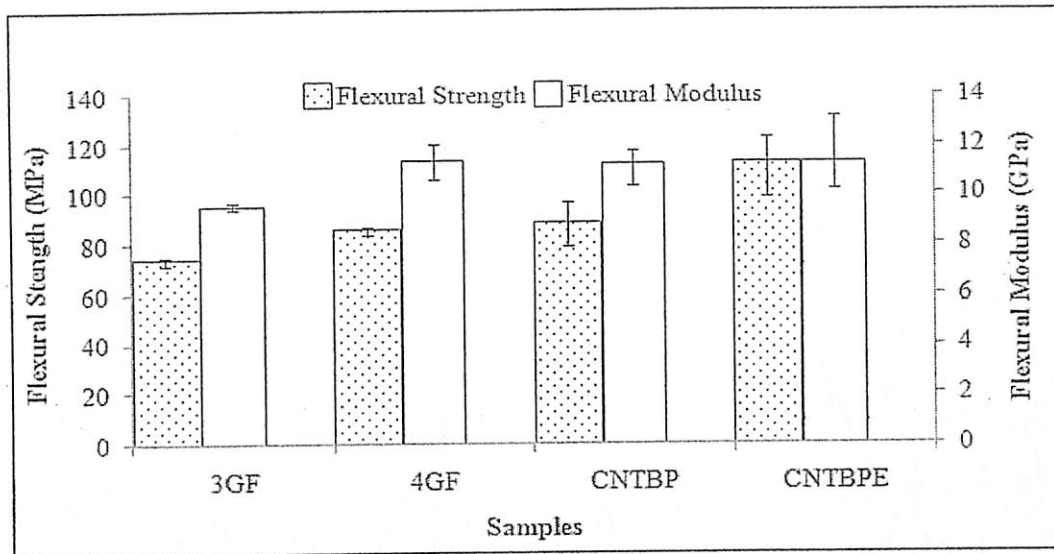


Fig. 2. Flexural strength and flexural modulus of composite samples of CNTBP and CNTBPE in compared to control samples, 3GF and 4GF.

Fig. 3 shows the fracture surface of CNTBP sample. Referring to Figure 3 (a) and (b), it seems that the load applied to the composite caused fiber breakage. The crack in the glass fiber was observed propagated along the fiber-matrix interface region as shown in Figure 3 (d). The cracks that propagated further along the epoxy-MWCNT BP interface results in failure of the composite system. The MWCNTs were weakly bonded together to form the MWCNT network in the buckypaper. The stress distributed in buckypaper caused buckypaper to break as showed in Figure 3(c).

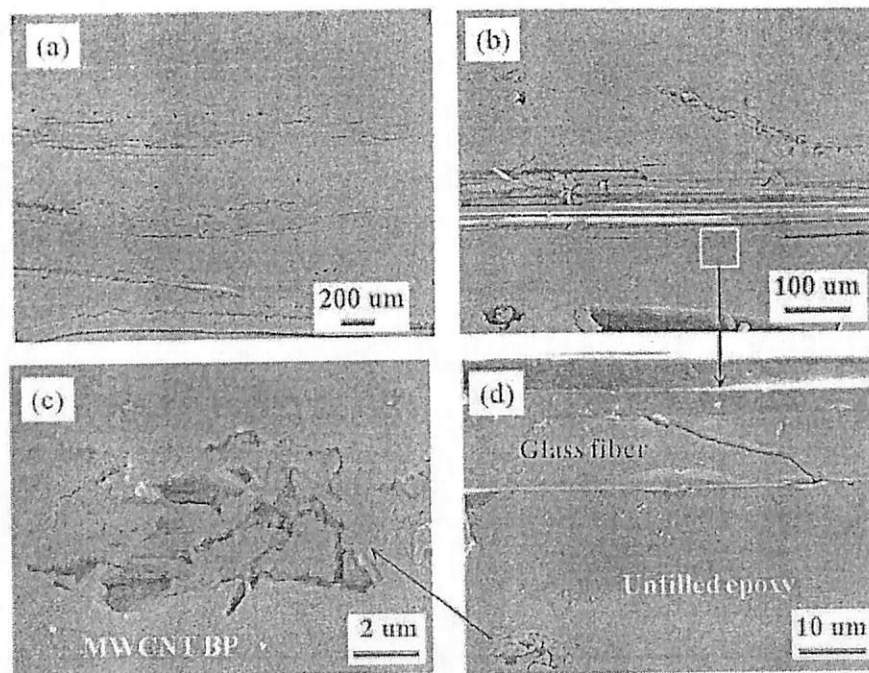


Fig.3. Fracture surface of CNTBP sample; (a) overall fracture surface at 25 x magnification; (b) fiber broken in the composites at 100 x magnification; (c) failure in the matrix-MWCNTBP interface at 5K x magnification; (d) cracks in the fiber propagated along the fiber-matrix interface at 1K x magnification.

Fig. 4. shows the fracture surface of CNTBPE composite. As expected, the failure in the composite such as broken fiber and cracks propagation (as shown in Figure (a), (b), and (d)) occurred in a similar way as experienced by the CNTBP samples. However, a rough crack between the unfilled epoxy matrix and MWCNT BP/epoxy was found in the composite as shown in Figure 4 (c). This indicates a strong adhesion between the unfilled epoxy matrix and MWCNT BP. The strong adhesion might be promoted by the rough surface of MWCNT BP/epoxy and explains the increment of flexural strength in CNTBPE as compared to CNTBP samples. This showed that the strength of materials is affected by the particles-matrix interface adhesion and incorporation of MWCNT in form of buckypaper has the ability to strengthen the composites.

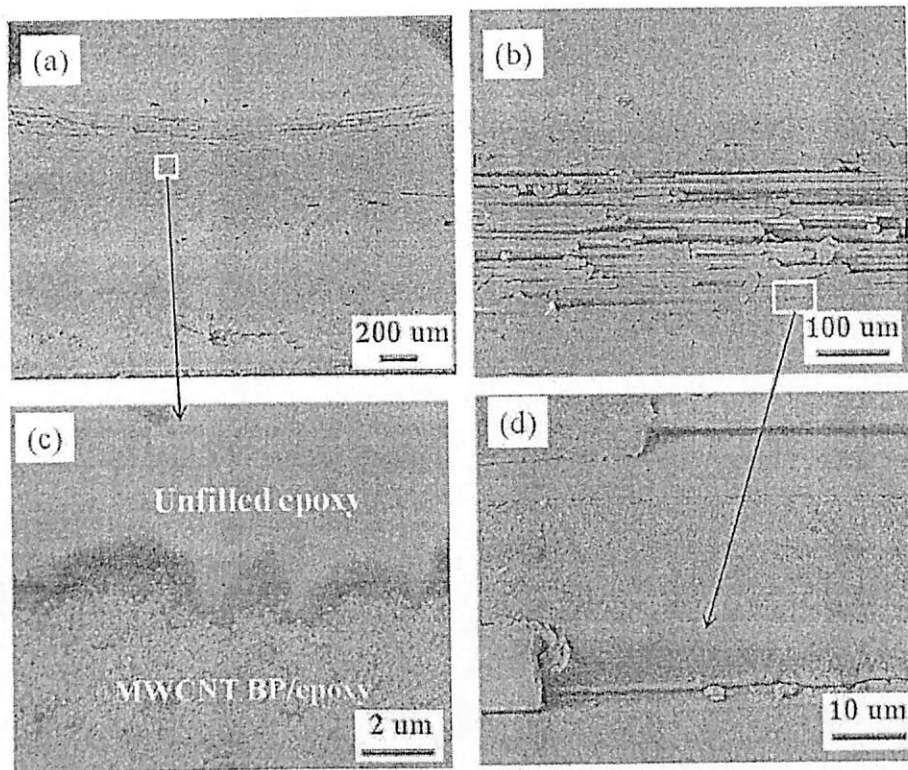


Fig. 4. Fracture surface of CNTBPE sample; (a) overall fracture surface at 25 x magnification; (b) fiber broken in the composites at 100 x magnification; (c) failure in the matrix-MWCNTBP interface at 5K x magnification; (d) cracks in the fiber propagated along the fiber-matrix interface at 1K x magnification.

Fig. 5. demonstrates the stress-strain curves of the control samples and hybrid composites of CNTBP and CNTBPE. 4GF seems to be stiffer compared to 3GF samples. Even though the vol % of fiber for both samples were fixed at 60 %, sample with 3-ply glass fiber are more flexible compared to 4GF due to the reduction in the thickness of the sample. The flexibility of the laminated samples is indirectly proportional to the thickness of the sample. Both CNTBP and CNTBPE possessed similar trends as 3GF sample. CNTBPE seems to be more flexible compared to the other composite samples and possessed the highest strength due to incorporation of buckypaper. This shows that the MWCNT helps to transfer load evenly throughout the matrix and the whole composite. Table 2 shows the specific strength and specific modulus of the control samples as well as CNTBP and CNTBPE composites. Based on Table 2, CNTBP sample possessed the highest specific strength and specific modulus compared to other samples. CNTBPE possessed the highest specific strength due to its lower densities and high flexural strength compared to 3GF and 4GF composites¹⁷.

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PROPERTIES OF CARBON NANOTUBES/ CARBON FIBER/ EPOXY LAMINATED COMPOSITES

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Abstract: *Carbon fiber reinforced epoxy composites promote achievement of light weight products with superior flexural and burning properties. Studies on carbon nanotubes revealed that well dispersed CNTs offer the nanocomposites with excellent flexural properties. In this study, three phase composites of carbon fiber, multi-walled carbon nanotubes (MWCNTs) and epoxy are fabricated by using the hand lay-up and vacuum bagging method. The MWCNTs utilized are dispersed by two different methods namely solution mixing and solvent spraying.*

Keywords: Epoxy resin; Carbon fiber; Multi-walled carbon nanotubes; Flexural test; Burning rate

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		data mining techniques. This simulator stands as a complete package in generating single supply chain partner datasets, simulate overall single and multi-link supply chain datasets, generating cloned and fraud dataset and tracking and tracing the whereabouts of cloned and fraud RFID-tag. A cost-sensitive experiment is also evaluated by using dataset generated from the Monte Carlo Simulation and Weka tool.
19	166T-ICBST2014	<p>Visual and Aural Multi-Modal Interactions in Traditional Foot Reflexology Practice</p> <p>Okere Hector Chimereze, Suzali Sulaiman, Dayang Rohaya Awang Rambli, Gh-Mena Foung</p> <p>Universiti Teknologi PETRONAS</p> <p>Abstract: The application of multimodal interactivity in HCI and VR avails a host of advantages which includes enhancement of realism and the achievement of interactivity that is relatively close or identical to the conventional human to human interactions. Visual and aural interactions have been widely applied in various domains ranging from mobile industry to medical field. In Virtual reality stress therapy application, particularly in the proliferation development towards the visualization of traditional foot reflexology therapy, little is understood on the visual and aural interactive nature of the therapy and to what extent they contribute in relaxation and stress relief. This paper presents a study that examines from both the patients' and practitioners' perspective, the visual and aural interactive nature in foot reflexology domain since the practices promote relaxation and stress relief. The study explored 2 traditional foot reflexology sessions; data were collected through audio recorded semi-structured interview, and was analyzed using content analysis. Results were compared with the existing hapic exploratory procedures. The study findings presented the visual and aural interactive nature involved from the patients' and practitioners' perspective. Implications for future research are also discussed.</p>
20	114T-ICBST2014	<p>Modern Method of Construction: An Experience from UK Construction Industry</p> <p>Mohd Nasrudin Mohd Nawar, Faizatul Akmar Abu Haniffa, Kamarul Anwar Mohamad Kamar, Angela Lee, Mohamed Nor Azhari Azman</p> <p>Universiti Utara Malaysia-06010 Sintok, Kedah, Malaysia</p> <p>Abstract: Industrialised Building Systems (IBS) is commonly used interchangeably with other terms such as offsite construction, prefabrication, offsite manufacturing, modern method of construction (MMC), industrialised building and industrialised construction. However, the term modern method of construction (MMC) is used to collectively describe both offsite-based construction technologies and innovative on-site technologies in the United Kingdom. It is evident that there exist a wide range of contextual issues which stems from the definition of these terminologies. Nonetheless, no previous research has explored the relationship between these terminologies. This paper highlights the contrasting concepts of IBS and MMC, and concludes that ill-defining the MMC-IBS terms leads to misunderstanding, uncertainty and prejudice of the IBS concept and its benefits, which will be detrimental to efforts promoting the use of IBS in the construction industry.</p>
21	154T-ICBST2014	<p>Flexural Properties of Carbon Fiber Multi-walled Carbon Nanotubes Epoxy Laminated Composites</p> <p>W.A.D. Wan Daliah, M. Marudha P., Z. A. Mohd Shukh, and A. R. Mohamed</p> <p>Universiti Sains Malaysia</p> <p>Abstract: Carbon fiber laminated composites incorporated with multi-walled carbon nanotubes (MWCNT) were fabricated using hand lay-up technique and filled with vacuum bagging. The filler loading varies from 0.5 to 1.5 volume percent and they were dispersed through different methods namely solution mixing method and solvent spraying method. The density and flexural properties of the hybrid composites were investigated. Incorporation of 1.0 volume percent of MWCNT by solvent spraying method with ethanol in the 4-ply CF laminated composite resulted in a better flexural properties compared to 5-ply laminated carbon fiber composite. This hybrid composite possessed flexural strength which is 75% higher to that of 5-ply carbon fiber/epoxy laminated composites.</p>
22	151T-ICBST2014	<p>SYNTHESIS AND GAS SENSING PROPERTIES OF SnO₂ NANOSTRUCTURES IN ETHANOL AND CARBON MONOXIDE GASES</p> <p>Malsara Azad Mat Akhir, Khuram Mohamed, Sheikh Abdul Reza, Sabar Derraf Hatagaling, Wan Norhiza Wan Mustapha, Nguyen Van Hien, Chan Kok Yau, A. S. M. J. Abdul Haseeb, Wong Yew Hong</p> <p>Universiti Sains Malaysia</p> <p>Abstract: The study focused on synthesis and investigation on gas sensing properties of tin oxide (SnO₂) nanostructure (NS) toward ethanol and carbon monoxide gases. The nanoSnO₂ sensing materials were prepared by thermal evaporation method grown on silicon substrates by varying three different parameters. These parameters were temperatures (650 °C, 750 °C and 850 °C), nickel catalyst concentrations (0.5 and 1.0 millimoles) and tin powder source to substrate distance (2cm, 4cm and 6cm). Another catalyst used was Aurum (Au) coated silicon substrates. The parameters were found to affect the size and morphology of the synthesized nanostructures. Scanning Electron Microscope (SEM)</p>