UNIVERSITI TEKNIKAL MALAYSIA MELAKA

Faculty of Mechanical Engineering

MECHANICAL CHARACTERISATION OF HYBRID GNPS AND FUNCTIONALISED BN AS A THERMAL INTERFACE MATERIAL

Siti Syahirah binti Che Othaman

Master in Mechanical Engineering (Energy Engineering)

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A thesis submitted
in fulfillment of the requirements for the degree of Master
in Mechanical Engineering (Energy Engineering)

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DECLARATION

I declare that this thesis entitled "Mechanical Characterisation of Hybrid GNPs and Functionalized BN as a Thermal Interface Material" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name : SITI SYAHIRAH BINTI CHE OTHAMAN

Date : 15/09/2021

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master in Mechanical Engineering (Energy Engineering).

Signature : ....

Supervisor Name : PROF. DR. GHAZALI BIN OMAR

Date : 15/09/2021

DEDICATION

To my beloved mother, father, siblings and my best friend

ABSTRACT

Electronic industries are continually striving to miniaturise electronic devices that have high power density in many current technologies. This development has caused significant challenges in the removal of heat generated from the small devices, which gradually caused overheat, especially for the electronic components that have a high working temperature like aircraft, Electric Vehicle (EVs), oil and gas and many more. The heat produce will cause damage which affected its life span. Thermal Interface Material (TIM) with high thermal conductivity is one of the methods to reduce the heat generated. From the past decade, the rapid development of new TIM by using high intrinsic thermal conductivity fillers like Boron Nitride (BN) and Graphene nanoplatelets (GNPs) in polymer composite has surged as a novel Thermally Conductive Adhesive (TCA). The focus on improving the thermal conductivity of TIM of polymer composite has heightened the need to hybridise both BN and GNPs filler at different filler sizes. Besides, modification of filler, especially BN filler, can also improve the properties of composites. However, to the best of author knowledge, very few studies have reported on the mechanical properties of the hybrid GNPs/f-BN polymer composite, especially at high temperature, to which these findings have wider relevance remains unclear. This thesis focuses on determining the thermal conductivity of GNPs/f-BN polymer composites at different filler sizes (GNPs-5 µm and BN-10 µm) and silane coupling agents (KH550 and KH560); to study the mechanical properties of hybrid GNPs/f-BN polymer composites at elevated temperatures. Prior to commencing this study, the thermal conductivity of the polymer composite was done using KD2 Pro Thermal Properties Analyzer before undergoing lap shear test for mechanical analysis by using Instron 8872 Universal Testing Machine (UTM). RT, 150ºC, 200ºC and 250ºC was selected as heating temperatures for mechanical analysis. Field Emission Scanning Electron Microscope (FESEM) was used to examine fillers dispersion because it often affects the thermal and mechanical properties of the polymer composite. The result of thermal conductivity for modified BN fillers shows significant improvement for both single and hybrid polymer composite with the value enhancement up to 37% and 86.4%, respectively. Hybridising GNPs with KH560 modified BN (f_BN_KH560) shows the highest thermal conductivity obtained at 0.37 ± 0.060 W/mK, especially at the ratio of 75-GNPs and 25-BN (75/25). The mechanical strength (shear strength and Young's modulus) of f-BN has further shown a good improvement than pristine BN, especially for f_BN_KH560 composite, whose shear strength is 0.80 ± 0.02 MPa, while hybrid GNPs/f_ BN_KH560 is 1.20 ± 0.10 MPa. The silane treated on BN was observed to successfully forms a chemical bond between the inorganic particles and the resin, allowing for more efficient stress transfer from the matrix to the fillers. GNPs/f-BN_KH560 that has good filler dispersion reported the highest shear strength and reveals a cohesive failure. However, when the hybrid composites were exposed to a high temperature, the mechanical strength of the modified hybrid composite starts to degrade due to softening effect and shows partial cohesive adhesion. The knowledge gained was believed would be beneficial to extend the use of functionalised BN with GNPs/BN as TIM.

PENCIRIAN MEKANIKAL BAGI HIBRID GNPs DAN BN UBAHSUAI SEBAGAI BAHAN ANTARA TERMA

ABSTRAK

Industri elektronik terus berusaha untuk mengecilkan peranti elektronik ynag mempunyai ketumpatan kuasa tinggi dalam banyak teknologi masa kini. Perkembangan ini telah menimbulkan cabaran besar dalammengelurkan haba yang dihasilkan dari alat kecil, yang secara beransur-ansur menyebabkan kepanasan, terutama untuk komponen elektronik yang mempunyai suhu kerja yang tinggi seperti pesawat terbang, Kenderaan Elektrik (EV), industri minyak dan gas dan banyak lagi. Haba yang terhasil akan menyebabkan kerosakan yang mempengaruhi jangka hayatnya. Bahan antara termal (TIM) dengan kekonduksian termal yang tinggi adalah salah satu kaedah untuk mengurangkan haba yang dihasilkan. Dari dekad yang lalu, perkembangan pesat TIM yang baru dengan menggunakan pengisi kekonduksian termal intrinsik yang tinggi seperti Boron Nitrida (BN) dan Nanoplatelet Graphene (GNPs) dalam komposit polimer yang juga dikenali sebagai termal pelekat yang berkonduksi (TCA). Tumpuan untuk meningkatkan kekonduksian termal TIM telah meningkatkan keperluan untuk menghibridisasikan BN dan GNPs pada saiz yang berbeza. Selain itu, pengubahsuaian pengisi, terutama pengisi BN, juga dapat meningkatkan sifat komposit. Walau bagaimanapun, sepanjang pengetahuan penulis, sangat sedikit kajian yang melaporkan sifat mekanik komposit polimer GNPs / f-BN hibrid, terutama pada suhu tinggi, yang mana penemuan ini masih banyak yang belum jelas. Tesis ini memfokuskan untuk menentukan kekonduksian terma komposit polimer GNPs / f-BN pada saiz pengisi yang berbeza (GNPs-5 µm dan BN-10 µm) dan agen gandingan silan yang berbeza (KH550 dan KH560); untuk mengkaji sifat mekanik komposit polimer GNPs/f-BN hibrid pada suhu tinggi. Bagi nemjalankan kajian ini, kekonduksian termal komposit polimer dilakukan dengan menggunakan KD2 Pro Thermal Properties Analyzer sebelum menjalani ujian ricih pusingan untuk mekanikal analisis dengan menggunakan Instron 8872 Universal Testing Machine (UTM). RT, 150ºC, 200ºC dan 250ºC dipilih sebagai suhu pemanasan untuk mekanikal analisis. Mikroskop Elektron Pengimbasan Pelepasan Medan (FESEM) digunakan untuk memeriksa penyebaran pengisi kerana ianya akan mempengaruhi sifat termal dan mekanikal komposit polimer. Hasil kekonduksian terma untuk pengisi BN yang diubah menunjukkan peningkatan yang ketara untuk komposit polimer tunggal dan hibrid dengan peningkatan nilai masing-masing hingga 37% dan 86.4%. Hibridisasi GNP dengan BN yang diubahsuai KH560 (f_BN_KH560) menunjukkan kekonduksian termal tertinggi yang diperoleh pada 0.37 ± 0.060 W / mK, terutamanya pada nisbah 75-GNP dan 25-BN (75/25). Kekuatan mekanikal (kekuatan ricih dan modulus Young) f-BN telah menunjukkan peningkatan yang baik daripada BN yang asal, terutama untuk komposit f_BN_KH560, dan kekuatan ricihnya adalah 0.80 ± 0.02 MPa, sementara untuk GNP hibrid f_ BN_KH560 adalah 1.2 ± 0.10 MPa. Silan yang dirawat pada BN diperhatikan berjaya membentuk ikatan kimia antara zarah-zarah anorganik dan resin, yang memungkinkan pemindahan tekanan yang lebih cekap dari matriks ke pengisi. GNP / f-BN_KH560 yang mempunyai penyebaran pengisi yang baik melaporkan kekuatan ricih tertinggi dan mendedahkan kegagalan padu. Walau bagaimanapun, apabila komposit hibrid terdedah pada suhu tinggi, kekuatan mekanik komposit hibrid yang diubah mula merosot kerana kesan pelembutan dan menunjukkan lekatan separa padu. Pengetahuan yang diperoleh diyakini akan bermanfaat untuk memperluas penggunaan BN yang diubahsuai dengan GNPs / BN sebagai TIM.

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LIST OF ABBREVIATIONS

0D	-	Zero-dimensional
1D	-	One-dimensional
2D	-	Two-dimensional
Ag	-	Silver
BN	-	Boron nitride
C_2H_5OH	-	Ethanol
CNH	-	Single-walled carbon nanohorns
CNT	-	Carbon nanotube
CTE	-	Coefficient of thermal expansion
EE	-	Energy-efficient
EVs	-	Electric vehicles
FESEM	-	Field emission scanning electron microscope
GNPs	-	Graphene
HEVs	-	Hybrid electrical vehicles
HSP	-	Hansen solubility parameter
IHS	-	Integrated heat spreader
KH550	-	3-Aminopropyltriethoxysilane
KH560	-	3-Glycidoxypropyl-trimethoxysilane
LED	-	Light-emitting diode
f-BN	-	modified BN
NaOH	-	Sodium hydroxide
–OH	-	Hydroxide functional groups

O-LED	-	Omitted- light emitting diode
Pb	-	Lead
PCMs	-	Phase change materials
RoHS	-	Restriction of hazardous substances directive
SEM	-	Scanning electron microscopy
SET	-	Single-electron transistor
SLJ	-	Single lap joint
Sn	-	Tin
SSA	-	Specific surface area
TBR	-	Thermal boundary resistance
TCAs	-	Thermally conductive adhesives
TCEF	-	Thermal conductivity enhancement factor
TIMs	-	Thermal interface materials
UTM	-	Universal tensile machine

LIST OF SYMBOLS

A	- Cross-sectional transfer area
BLT	- Bond line thickness
D	- Diameter or thickness
dx	- Conduction path length
F	- Frequency
F_{max}	- Maximum tensile force
k	- Thermal conductivity
k_c	- Thermal conductivity of composite
k_m	- Volume percentage of filler
q	- Rate of heat transfer
R_a	- Difference of HSP between two materials
R_{C1}	- Contact resistances at surface 1
R_{C2}	- Contact resistances at surface 2
R_{eff}	- Effective total thermal resistance
T_g	- Glass transition temperature
v_f	- Thermal conductivity of polymer matrix
V_m	- Molar volume
W	- Width
δ_h	- Hydrogen-bonding force
δ_d	- Dispersion force

δ_p - Polar force

δ_t - Solubility parameter

τ_{lap} - Maximum lap shear strength

ΔT - Temperature difference

LIST OF PUBLICATIONS

The research papers produced and published and awards during the course of this research are as follows:

Journals papers:

1. Jasmee, S., Omar, G., Othaman, S.S.C., Masripan, N.A. and A. Hamid, H., 2021. Interface thermal resistance and thermal conductivity of polymer composites at different types, shapes, and sizes of fillers: A review. *Polymer Composites*, 42(6), pp.2629-2652. (Published)

2. Jasmee, S., Omar, G., Othaman, S.S.C., Masripan, N.A., A. Hamid, H. and Kamarolzaman, A.A., 2021. Preparation of GNPs thermally conductive adhesive at different epoxy resin/curing agent ratio and mixing method. *International Journal of Nanoelectronics and Materials*, 14, pp.159-176. (Published)

CHAPTER 1

INTRODUCTION

1.1 Research background

The pervasive concern to conserve the global environment from the greenhouse effect, climate change, and global warming has led to research to find alternative renewable energy sources to save the earth. For instance, instead of using biomass for electricity, the solar system was introduced as renewable and sustainable energy (Chen et al., 2016). Besides, electric vehicles (EVs) and hybrid electrical vehicles (HEVs) were also introduced to replace fossil fuel combustion vehicles (Chen et al., 2016). However, due to limited sources, providing an energy-efficient (EE) solution becoming increasingly important to save energy.

Basically, energy production and management are highly reliant on energy conversion and storage technology. As a result, it is reasonable to expect power electronics conversion technologies to continue to evolve and use in a growing number of energy production and management applications. For example, compared to conventional lighting, light-emitting diode (LED) and Omitted-light emitting diode (O-LED) were used and will save about 70% of electric energy (Jägerbrand, 2016). Over the years, the evolution in technology especially related to electronic industries like O-LED, solar panels, automotive electronic control unit and batteries of EVs and HEVs, shows a positive growth towards a EE solution.

However, the increase in the heat generation of the technology due to the miniaturisation of electronic components but high power density in current technology has caused great challenges, especially in removing heat generated from the high flux devices. According to Liao et al. (2016), as the actual size of the device is reduced, electronic devices are becoming more likely to overheat. Usually, a power chip generates more than 100 W/m^2 of heat flux, and the value is still in constant growth (Christensen and Graham, 2009; Sivasamy, Selladurai and Rajesh Kanna, 2010).

Normally, any electronic system operates at a temperature around 85 – 100°C; over this level, the efficiency of the device would deteriorate dramatically (Mauro et al., 2010). Consequently, if the high heat flux cannot be dissipated in time, it will disturb the stability of heat management of the device and would be a significant risk to chip efficiency and lifespan (Almubarak, 2017). Thus, electronic industries are continually striving to find the best solution of miniaturization of power electronic packaging and high power devices, which are evolving tremendously to satisfy industrial requirements.

One of the crucial elements to dissipate heat in an electronic device is thermal interface materials (TIMs). TIMs are normally placed between the surfaces of the touch pair to minimise the thermal contact resistance (Singhal, Siegmund and Garimella, 2004). Some of the commercially available TIMs are solders, greases, thermal pads, thermal tapes, phase change materials (PCMs), gels, and thermally conductive adhesives (TCAs). Those TIMs are often manufactured by reinforcing high conductive filler like carbon, ceramic, and metal into a lower conductive organic phase. A great deal of work has been made to explore different forms of composite TIM fillers to enhance thermal and mechanical properties of the material but cost-effective for thermal control implementation (Song et al., 2015; Wondu, Lule and Kim, 2019; Chung, 2020).

As a potential option for a filler material into composite TIMs, graphene (GNPs) and boron nitride (BN) has gained significant recognition due to their outstanding thermal and mechanical properties. Since the thermal conductivity and mechanical properties depend greatly on filler dispersion in the polymer matrix, surface modification of BN filler has been implemented to improve the thermal conductivity, wettability and dispersion of fillers. Thus, by hybridising both fillers into the polymer matrix, it is expected that the thermal conductivity and mechanical properties of TIMs will improve significantly. Nonetheless, the study of hybrid composite is still at the developing stage since many aspects should be considered, especially when mixing the polymer matrix with different sizes of fillers, modified BN (f-BN), and its environmental effect when exposed to high temperature. Therefore, this study will focus on determining the thermal conductivity of hybrid GNPs/f-BN composite at different filler sizes and surface modification, as well as the mechanical properties of hybrid GNPs/f-BN composite when exposed to high temperature as TIM material.

Generally, the research methodology for this study involves using a KD2 Pro and a universal tensile machine (UTM) to measure TC and mechanical strength, respectively. The hybrid composite will be mixed using a bath sonication and planetary centrifugal thinking mixer before curing in an oven. Prior to that, the BN particles will be treated with the silane coupling agent, 3-Aminopropyltriethoxysilane (KH550) and 3-Glycidoxypropyl-trimethoxysilane (KH560). The mechanical properties of the hybrid material will be studied at varying temperatures, including room temperature, to investigate the effect of temperature on its mechanical performance. Further characterisation of composite morphology will be done in more detail on fillers dispersion using Field Emission Scanning Electron Microscope (FESEM) as it significantly affects both the thermal conductivity and mechanical performance of the hybrid composite.

1.2 Problem statement

The study on single filler polymer composite as a new material for TIM shows that it can significantly improve the thermal conductivity of a pristine polymer matrix, especially with a large and high aspect ratio of filler. However, the thermal conductivity increases is not as high as needed in the electronics industry. The latest data on the thermal conductivity of the TIM indicates that it is available in the range of 0.5 - 5 W/mK, which falls short of the industrial requirement (Lv et al., 2018; Adhikari, 2019). But still, there are also single-filled polymer composites that show a higher result of thermal conductivity. However, it will require a very high filler loading, around 50 to 70 wt%, which is unfavourable as the composite will become brittle and has poor processability.

Incorporating two or more types and sizes of fillers with high intrinsic thermal conductivity might exhibit superior properties than the single filler used. A filler with a high aspect ratio is expected to reach the percolation threshold at lower filler loading but still provides a high thermal conductivity to the composite. Hybridizing BN and GNPs have drawn current attention due to the fact that both fillers have a high intrinsic thermal conductivity and aspect ratio. Though, in some circumstances, the enhancement of thermal conductivity is still limited because of the resistance at the interface of filler-filler and polymer-filler. However, the use of two fillers at different sizes and surface modification of BN filler was mention as able to enhance the thermal conductivity of composite further since the smaller filler size can fill the gap or void between the larger filler size while surface modification of BN filler able to improve the filler dispersion in the polymer matrix. A well-dispersed filler will reduce the effect of interface resistance. This approach can ensure a continuous heat transfer because of the extended contact area formed.

Interfacial strength between adhesive and adherent material plays a big role in TIM application, especially in the power device that is always exposed to high operating temperatures. However, very few studies have reported the mechanical performance of the hybrid GNPs/f-BN polymer composite at different filler sizes under varying temperatures to the best of found knowledge. Therefore, the extent to which these findings have wider