PREPARATION AND CHARACTERIZATION OF PU/GNPs NANOCOMPOSITES FOAM

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Engineering Materials) (Hons.)

by

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Date : 1 July 2017

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Engineering Materials) (Hons). The member of the supervisory committee are as follow:

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(Dr. Jeefferie bin Abd Razak)

ABSTRAK

Poliuretana adalah bahan yang versatil yang boleh dijadikan termoset dan termoplastik berdasakan struktur kimia. Poliuretana termoset (PU) gabus telah digunakan secara meluas untuk aplikasi ringan. Oleh itu, tujuan kajian ini dijalankan untuk membangunkan gabus berasaskan PU yang diperkukuhkan dengan nanoplatelets graphene (GNPs). Tujuan menambahkan GNPs sebagai 'nanofillers' kedalam PU adalah untuk meningkatkan sifat-sifat mekanikal dan haba PU. PU/GNPs gabus dihasilkan dengan menggunakan dua kaedah iaitu ultrasonication dan penyelesaian kaedah pengkompaunan. Pemilihan komposisi optimum daripada PU matriks adalah berdasarkan peratus berat GNPs. Oleh itu, peratus berat GNPs yang digunakan dalam kajian (0.00% berat, 0.25% berat, 0.50% berat, 1.00% berat, 3.00% berat, dan 5.00% berat) untuk mengkaji sifat-sifat mekanikal dan sifat haba daripada nanocomposites dihasilkan buih. Kemudian, spesimen yang telah diuji oleh mekanikal dipilih untuk mengkaji permukaan patah menggunakan alat pemerhatian SEM dan OM. Pada akhir kajian ini, kekuatan yang lebih tinggi dan prestasi PU/GNPs gabus telah dibaikpulih. Penambahan 0.25% GNPs telah berjaya mempertingkatkan ciri-ciri mekanikal nanocomposites gabus dari segi kelakuan lenturan dan mampatan. Bagi ciri – ciri haba, PU/GNPs gabus juga menunjukkan peningkatan. PU/GNPs gabus dengan 0.25% GNPS kemasukan menghasilkan peningkatan yang luar biasa mengenai 52,28% dalam sifat-sifat lenturan, dan 3% daripada kekuatan mampatan. Selain daripada itu, penambahan GNPs telah bertambah baik dengan ketara kestabilan haba dengan menghasilkan sisa kira-kira 38% pada kemasukan 5.00% GNPs. Kajian ini adalah penting untuk menyediakan satu lagi bahan seli maju menggunakan kelebihan teknologi nano sebagai bahan komposit aplikasi seperti dalam automotif, aeroangkasa, bidang maritim.

ABSTRACT

Polyurethane is a versatile material which can be thermoset and thermoplastic based on their chemical structure. Thermoset polyurethane foams (PU) have been widely used for light weight applications. Thus, this research was carried out to develop PU foams reinforced with graphene nanoplatelets (GNPs). The purpose of reinforce the PU with GNPs nanofiller is to enhance the mechanical and thermal properties of PU based foams. The PU/GNPs nanocomposites foams were produced by using ultrasonication and solution compounding methods. The selection of optimum composition for PU foam matrix is based on the GNPs loadings. Therefore, in this study, different loading of GNPs (0.00 wt%, 0.25 wt%, 0.50 wt%, 1.00 wt%, 3.00 wt%, and 5.00 wt%) were used to investigate the mechanical and thermal properties of produced PU/GNPs nanocomposites foams. Later, the fracture surface morphology of the selected mechanical tested specimen were analyzed by using an SEM and OM observation tools. At the end of this study, the higher mechanical strength and thermal performance of PU/GNPs nanocomposites foams were developed and proposed. It was found that at 0.25 wt% of GNPs addition, the produced PU/GNPs nanocomposites foams were successfully enhanced the mechanical characteristics of nanocomposites foams in terms of their flexural and compression behaviour. This scenario was applicable to the thermal improvement. PU/GNPs nanocomposites foams with 0.25 wt% of GNPS inclusion had yielded an extraordinary improvement about 52.28 % in the flexural properties, and 3.00 % of compression strength. Other than that, GNPs addition was significantly improved the thermal stability by yielded about 38 % of residue with 5.00 wt% of GNPs addition. This research is significantly important as it could to provide another alternative for advanced materials which utilizing the advantages of nanotechnology for many possible high performance applications like in automotive, aerospace, and maritime fields.

DEDICATIONS

Dedicated to
My beloved father, Mohd Nor
My beloved mother, Fatimah Wati bt Alias
My appreciated siblings, Ahmad Najmi and Aishah Munirah
And friends for giving me moral support, cooperation, encouragement and also understanding

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TABLE OF CONTENT

LIST OF TABLE

LIST OF FIGURE

LIST OF ABBREVIATIONS

PU	-	Polyurethane
GNPs	-	Graphene Nanoplatelets
SEM	-	Scanning Electron Microscopy
DMA	-	Differential mechanical analysis
TGA	-	Thermogravimetric analysis
DSC	-	Differential scanning calorimeter
OM	-	Optical microscope
TDI	-	Toluene diisocyante
MDI	-	Methyl diphenyl diisocyanate
CVD	-	Chemical vapour deposition
PNC	-	Polymer nanocomposites
ASTM	-	American society for testing and materials

LIST OF SYMBOLS

mm	-	Millimetre
m	-	Metre
g/cm^3	-	Grams per centimetre cube
Wt%	-	Weight percent
MPa	-	Mega pascal
GPa	-	Giga pascal
℃	-	Degree celcius
W/mK	-	Watt per metre per Kelvin

CHAPTER 1

INTRODUCTION

This chapter briefly explained about the background of study, problems statement, objectives, scope of study, significant of study, and an overall summarization for this chapter.

1.1 Background

Over the years, polymeric foams have been widely used due to their outstanding strength-to-weight ratio. Lee et al. (2005) was defined foam as materials which contain gaseous voids surrounded by a denser matrix. Basically, cell morphology and physical properties of polymer foams can be categorized as rigid foam or flexible foam which are based on their materials composition. Both of these foams can be used for thermal insulation applications (Loebel, 2012), aerospace application (Saha, Kabir, & Jeelani, 2008), and automotive applications (Mike and Brady 2008). Polymer polyurethane (PU), polypropylene (PP), polycarbonate (PC), and polyvinyl chloride (PVC) are the examples of polymer engineering materials which have been generally utilized for foam applications.

In US, polyurethane foams remarks for the largest market among other polymeric foams which is estimated about two billion kilograms (Cao, James Lee, Widya, & Macosko, 2005). Theoretically, PU foams are the combination and reaction of polyisocyanate and polyol matrix. The reaction of these two phase produces urethane bonds (R. Verdejo et al., 2009). The cell density of neat PU is 5.8 x 10^5 cells/cm^3 (Saha et al., 2008) compared than cell density of neat PP which is 1.5 x 10^7 cells/cm^3 (Wang et al., 2016). Thus, PU foam is higher strength compared to PP foam as the tensile strength of foams is inversely proportional to the density of foam (L. J. Lee et al., 2005). The most application of PU foams is as a core sandwich in conjunction with two face sheet materials around it. This sandwich structure is usually to be used in aerospace and marine applications (Saha et al., 2008). However, they said that this sandwich structures are tend to failure due to weak core. The examples of failure during these applications are core – shear and core – skin debonding.

In order to reduce the occurrence of failure, it is important to improve the mechanical properties of the core sandwich. The improvement of polymeric foam can be achieved by adding fillers materials which have a larger aspect ratio (Tjong, 2006). Therefore, nanocomposite is seen as one of the promising approaches in the field of materials science towards the development of advanced materials. Basically, nanocomposites means the inclusion of nanoparticles which possess very high mechanical and thermal properties that can encounter the weakness of polymeric foam (Oliveira & Machado, 2013). Nanocomposites contain one phase of materials which has dimension in the nanometer siza range of 1 – 100 nm (Saha et al., 2008).

Due to the nano dimension range of filler, its offered very high surface energy which allowed the maximum contact between matrix and filler. By having maximum contact surface between filler and matrix, the stress can be transferred clearly which mean significant increase in their resulted mechanical properties. Other than that, inclusion of nanofiller will introduce thermal barrier effect in polymeric foams (Ponnamma, Rouxel, & Thomas, 2016). However, high quality dispersion is required during preparation of polymer nanocomposites foams. Besides, the quantity of nanofiller should be controlled to avoid agglomeration and worst filler dispersion. Over the years, carbon based nanomaterials are well known as a nanofiller materials which extremely increase the mechanical and thermal properties. Carbon based materials offered superior mechanical properties and lightweight characteristic due to honeycomb atomic structure (Amir et al., 2016).

Among other high performance filler that are commercially available in the market is carbon based nanomaterials. These nanomaterials were utterly researched due to their promising performance as functional and filler reinforcement for composites reinforcement. For examples, carbon nanofibers, carbon nanofillers, and graphene nanoplatelets are most popular. Nowadays, research on graphene nanoplatelets (GNPs) are getting spotlight with high interest from the scientific community, as this miracle materials are claimed to possessed an extraordinary thermal stability, thermal conductivity and higher resistance towards heat degradation. Nanocomposites reinforced by the nanomaterials likes GNPs could demonstrate energy dissipation capability. The energy dissipation had caused by interfacial slippage between the polymer and GNPs, which is known as direct consequences of unique matrix – filler interfacial characteristic in polymer based nanocomposites filled GNPs. Then, GNPs will form the percolated network within matrix which can be utilized to dissipate heat effectively that later will make the filled composites with GNPs are more resistance into heat or thermally stable.

Thus, it is expected that polyurethane foam embedded with carbon based nanomaterials, could resulted the thermal properties and mechanical properties of this polymer nanocomposites foams will be further enhanced, as compared than other polymer nanocomposites foams which commonly available in the commercial market nowadays.

1.2 Problems statement

Polyurethane is one of the most versatile engineering materials among other polymers. It is because of their uniqueness which can be readily customized by the type and composition of their components. Polyurethane possessed flexibility whereas it can be hard like fiberglass, soft like foam, defensive like varnish, and sticky like glue. Polyurethane has been widely used in various types of applications such as transportation, electronic devices, construction and many more. Yet, there are some limitations to consider when deciding on the usage of polyurethane for specific applications.

For transportation or vehicles application, lightweight attributes of materials are very important attribute to be considered as to enhance the performance of manufactured vehicles. Moreover, heavy transport will consume more fuel compared than light weight vehicles. Thus, the weight of transportation itself can help on reduction of oil consumption. By 2050, more than 3.5 billion vehicles will be on the road worldwide. This will exceed the demand of oil which escalated to 1 trillion barrels in the ground. Besides, there are some challenges in term of consuming oil which are environmental pollution, growing demand for oil, and global climate changes (Mike and Brady 2008). Instead of controlling the consumption of oil, industrial bodies can design the lightweight car by manipulating the source of engineering materials through correct design and carefull selection of materials. Polymer materials like polyurethane could offer some of the promising characteristics of lightweight attributes when it accurately designed and fabricated as foam structure.

Besides, due to interesting properties of polyurethane; this PU also had lower in their cost and possessed appreciable shape recovery characteristic at a broad range of shape recovery temperature. Hence, these factors could attract the interest from many researchers to work with polyurethane. However, polyurethane itself are not able to withstand higher temperature and will rapidly burn in case of fire and producing amount of hazardous smoke and gases during combustion. This is due to heat entrapment within the microstructural chain, which later develops passive heat absorption capacity (Gama, et. al 2016). The heat entrapment in microstructure of PU will tremendously change their molecular structure. Thus, there will be a significant reduction to PU based materials and their product performances. At this point, PU polymers are generally suffers with lower thermal or heat stability performance and this must be improvised by incorporating it with higher heat resistance filler materials as to compensate with the drawbacks of PU and to ensure their sustainability at real service environment.

Graphene nanoplatelets is one of the example carbon based nanomaterials which have a range of thickness 0.3 – 100 nm and density of GNPs is about 2 gcm^{-3} (Abd Razak, Haji Ahmad, Ratnam, Mahamood, & Mohamad, 2015). The high aspect ratio and strength – to – weight ratio qualifies them as an ideal reinforcing filler for polymer nanocomposites foams. Moreover, homogenous dispersion of GNPs into the polymer matrix could generate an interesting phenomenon due to their tremendous potential of nano – filler. The integration of GNPs into PU could promote the benefits of lightweight performance for PU/GNPs nanocomposites. The higher aspect ratio of 2D planar structure combines with extreme properties of GNPs had qualifies them as an ideal filler reinforcement material for polymer nanocomposites applications. Because of their large surface area of GNPs, it allows a maximum surface contact area with polyurethane which contributes to the improvement of thermal stability for polymer based nanocomposites produced.

Regrettably, the dispersion of nanomaterials is extremely a critical issue in determining the final properties of polymer based nanocomposites. When GNPs are not well dispersed in polymer it will tend to form an agglomeration inside the polymer matrix. It may occur because of their large surface area which increases the *van der Waals* force that creating strong $n - n$ interaction between them. Agglomeration of GNPs in polymer has a significant negative impact to their thermal conductivity of produced polymer nanocomposites. It is due to weak contact between interface GNPs and polyurethane that will produce an obstacle for heat to flow and dissipates.

In addition, there will be more critical issues to produces homogenous dispersion of GNPs in porous structure of polyurethane. Inclusion of nanofiller likes GNPs in polymer foam nanocomposites may have a tendency for the bubbles to start nucleate concurrently. This is caused by amount of gas available for bubble to growth. Thus this phenomenon will lead to a decreasing the size of pores cell. Addition of GNPs into polymer foams may produce finer cellular structure and higher cell densities (Abbasi, Antunes, & Velasco, 2015). However, the properties of PU will definitely change because of changing in their composites microstructures.

In short, by considering all the related matters, this research is reasonable to be corned out as to explore the potential of improving the thermal properties of PU based nanocomposites foam. This is due to no available previous similar research have been found in the existing literature, specifically focusing on polyurethane based foam nanocomposites; that utilizing the graphene nanoplatelets as their reinforcement or functional filler for the development of thermally stable polymeric foam types materials.

1.3 Objectives

1. To prepare PU reinforced GNPs nanocomposites foam with various GNPs nanofiller loadings
2. To characterize the thermal and mechanical properties of PU filled GNPs nanocomposites foams
3. To analyse the fractured surface morphologies of PU filled GNPs nanocomposites via SEM observation

1.4 Scope of Study

This research scopes are as follow:

a) Develop the PU embedded with GNPs polymer nanocomposites foams by using solution compounding method.

b) Characterize the mechanical properties, physical properties, and thermal properties of polymer nanocomposite foams. The properties that will be evaluated are flexural, compression, thermogravimetric analysis (TGA), and density and void content analysis.

c) Analyse the failure mechanism of polyurethane embedded with GNPs nanocomposites foam by using SEM and OM observation.

1.5 Significant of Study

The rationales of study are detailed as follows:

a) Higher strength of nanocomposite foams product would be delevoped from this research. This is due to inclusion of GNPs into polyurethane foam; the strength of nanocomposite foams might be significantly improved. The research is to study on how the GNPs enhance the nanocomposite foams strength when it is incorporated with the polyurethane foams.

b) Develop more information and also keep understanding about the role of GNPs when it incorporate to the polyurethane foams as to enhance the properties of PU composite based foams.

c) To gain new knowledge for PU/GNPs nanocomposites foams by carrying out some related properties testing and characterization.

d) To develop an alternative composite material that possesses a lower cost and high performance attributes. The inclusion of small amount of GNPs might be tremendously enhanced the properties of polyurethane foams.

1.6 Structure of Report

This report is mainly consisting of five major chapters which are introduction, literature review, methodology, result and discussion, and lastly the conclusion and recommendation. Firstly, Chapter 1 gives an overview and details on the background study of PU/GNPs nanocomposites foam, problem statement of the study, objectives, research scope, the significant of study, and summary of overall findings in Chapter 1. Next, Chapter 2 will cover the literature review and related theory of PU, nanomaterial used which is GNPs, properties of each material, polymer nanocomposites systems, and its processing methods. In Chapter 3, there will be an explanation on the preparation of the samples, testing method, and morphological studies of each samples. Then, the result and discussion for every test including the physical testing, mechanical and thermal testing, and morphological characteristic were discussed in the Chapter 4. Finally, Chapter 5 gives