# Preparation and Characterization of Palm Oil based Polyurethane Foam with Multi Walled Carbon Nanotubes and Magnesium Fillers

by

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| ASTM | American Society Testing Method |
| CNTs | Carbon Nanotubes |
| DMA | Dynamic Mechanical Analyzer |
| FEA | Finite Element Analysis |
| FTIR | Fourier Transform Infrared Spectroscopy |
| Hours | Hrs |
| MDI | Methylene Diphenyl Diisocyanate |
| Mg | Magnesium |
| MMCs | Metal Matrix Composites |
| MWCNTs | Multi Walled Carbon Nanotubes |
| MSDS | Material Safety Data Sheet |
| $N_2$ | Nitrogen |
| PMCs | Polymer Matric Composites |
| POP | Palm Oil based Polyol |
| PU | Polyurethane |
| rpm | Rotations per Minute |
| SEM | Scanning Electron Microscope |
| SWCNTs | Single Walled Carbon Nanotubes |
| TDI | Toluene Diisocyanate |
| TEM | Transmission Electron Microscope |
| Tg | Glass Transition temperature |
| TGA | Thermogravimetric Analysis |

# LIST OF SYMBOLS

| | |
|---|---|
| % | Percentage |
| °C | Degree Celcius |
| ρ | Rho |
| > | More than |
| < | Less than |
| ~ | Tilde |
| cps | Centipoise |
| $g/cm^3$ | Gram per Cubic Centimeter |
| GPa | Giga Pascal |
| KPa | Kilo Pascal |
| MPa | Mega Pascal |
| mm/s | Milimeter per Second |
| nm | Nanometer |
| s | Seconds |

**Penyediaan dan Pencirian Busa Poliuretana berasaskan Minyak Sawit dengan Pengisi Nanotiub Karbon Berbilang Dinding dan Magnesium**

## ABSTRAK

Poliol berasaskan minyak sawit (POP) semakin popular untuk menggantikan petroleum berasaskan poliol untuk pembuatan busa poliuretana (PU) kerana struktur minyak yang unik, amat banyak, murah dan mesra alam. Busa PU adalah struktur selular yang mempunyai beberapa kelebihan, termasuk beratnya yang ringan, kapasiti penyerapan tenaga yang tinggi dan ketahanan terhadap bahan kimia dan pelarut. Walau bagaimanapun, busa PU mempunyai beberapa kelemahan, termasuk keliangan tinggi dan kebolehhancuran tinggi berliang yang menjejaskan sifat mekanikalnya. Penambahan pengisi telah menjadi kaedah untuk meningkatkan prestasi busa PU. Oleh itu, tujuan penyelidikan ini adalah untuk menyediakan dan mencirikan busa PU berasaskan minyak sawit dengan pengisi tiub nano karbon berdinding pelbagai (MWCNTs) dan magnesium (Mg). Pengisi dicirikan dengan menggunakan piknometer, pengimbas elektron mikroskop (SEM), transmisi elektron mikroskop (TEM), spektroskopi inframerah fourier transformasi (FTIR) dan penganalisis termogravimetrik (TGA). Busa komposit PU (PU/MWCNTs, PU/Mg dan PU/MWCNTs/Mg) dihasilkan melalui tindak balas POP dengan metilena difenil diisosianat (MDI) pada nisbah 1:1.1 dengan menggunakan pengaduk mekanikal berkelajuan tinggi dengan 2000 putaran per minit (rpm). Busa komposit PU telah dituangkan ke dalam acuan tertutup, di matangkan selama 24 jam dan di sambung semula pasca matang di dalam ketuhar pada suhu 80 °C selama 2 jam bagi memastikan tindak balas telah selesai. Kesan kandungan pengisi yang berbeza-beza (0.5, 1.0, 1.5, 2.0, 2.5 dan 3.0 %) ke atas komposit busa PU/MWCNTs, PU/Mg, dan PU/MWCNTs/Mg ditentukan menggunakan ketumpatan, FTIR, analisis haba, morfologi, ujian mampatan, penyerapan tenaga dan analisis morfologi. Kekuatan mampatan optimum daripada komposit busa PU/MWCNTs, PU/Mg dan PU/MWCNTs/Mg yang telah dipilih dan diteruskan penyiasatan kelakuan anjakan dengan keputusan analisis unsur terhingga (FEA) dengan menggunakan multi fizik ANSYS. Morfologi struktur busa diperhatikan menggunakan SEM dan mendedahkan kehadiran struktur sel tertutup dengan dinding sel yang lebih nipis. Penambahan pengisi telah merosakkan sel kepada sel pecah. Saiz nano MWCNTs telah dibuktikan menggunakan TEM dan menunjukkan penambahan pengisi MWCNTs pada 0.5% menunjukkan penyebaran MWCNTs yang baik dalam busa PU daripada 3.0%. Kandungan pengisi yang semakin meningkat telah meningkatkan masing-masing kekuatan mampatan sebanyak 1.547 MPa pada 0.5 PU/MWCNTs, 1.688 MPa untuk 2.0 PU/Mg dan 1.760 MPa untuk 2.5 PU/MWCNTs/Mg. Secara keseluruhannya, 2.5 PU/MWCNTs/Mg menunjukkan kekuatan mampatan yang paling tinggi kerana gabungan yang sangat baik MWCNTs dan Mg. Oleh itu, komposit busa PU ini terus diuji menggunakan perisian ANSYS. Keputusan teori daripada FEA telah menunjukkan perbezaan yang kecil berbanding dengan keputusan eksperimen. Keputusan eksperimen untuk komposit busa 2.5 PU/MWCNTs/Mg ialah 1.76 MPa dan keputusan teori yang diperoleh daripada ANSYS ialah 1.65 MPa. Perbezaan antara keputusan ini adalah 0.11 MPa dan telah diterima kerana perbezaannya sangat kecil.

**Preparation and Characterization of Palm Oil based Polyurethane Foam with Multi Walled Carbon Nanotubes and Magnesium Fillers**

## ABSTRACT

Palm oil based polyol (POP) is gaining popularity to replace polyol based petroleum for manufacture of polyurethane (PU) foam due to the unique structure of oils, abundant, inexpensive and environmentally friendly. PU foam is a cellular structure that has several benefits, including low weight, high energy absorption capacity, and resistance to chemicals and solvents. However, PU foam have some drawbacks, including high porosity and high crushability porous that affects their mechanical properties. The addition of fillers has become a method of improving performance of PU foam. Therefore, the purpose of this research is to prepare and characterize a palm oil based PU foam with multi walled carbon nanotubes (MWCNTs) and magnesium (Mg) as fillers. The fillers were characterized by using pycnometer, scanning electron microscope (SEM), transmission electron microscope (TEM), fourier transform infrared spectroscopy (FTIR) and thermogravimetric analyzer (TGA). The PU foam composites (PU/MWCNTs, PU/Mg and PU/MWCNTs/Mg) were produced through the reaction of POP with methylene diphenyl diisocyanate (MDI) at a ratio of 1:1.1 by using high mechanical stirrer with 2000 rotations per minute (rpm). The PU foam composites were poured into a closed mould, cured for 24 hours and continued post cure in an oven at 80 °C for 2 hrs to confirm the reaction was completed. The effect of varying fillers content (0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 %) on the PU/MWCNTs, PU/Mg, and PU/MWCNTs/Mg foam composites were determined using density, FTIR, thermal analysis, morphology, compression test, energy absorption and morphology analysis. The optimum compressive strength from PU/MWCNTs, PU/Mg and PU/MWCNTs/Mg foam composites were chosen and continued to investigate the displacement behaviour with finite element analysis (FEA) results by using ANSYS Multiphysics. The morphology of the foam structure was observed using the SEM and revealed the presence of a closed cell structure with a thinner cell wall. The addition of fillers has deteriorated the cell to broken cell. The nano size of MWCNTs was proven using the TEM and showed the addition of MWCNTs fillers at 0.5 % show the good MWCNTs dispersion in PU foam than 3.0 %. The increasing fillers content has improved the compressive strength by 1.547 MPa at 0.5 PU/MWCNTs, 1.688 MPa for 2.0 PU/Mg and 1.760 MPa for 2.5 PU/MWCNTs/Mg, respectively. Overall, 2.5 PU/MWCNTs/Mg showed the highest compressive strength due to the excellent combination of MWCNTs and Mg. Therefore, these PU foam composites were continued tested using ANSYS software. The theoretical results from FEA have shown small differences compared to the experimental results. The experimental result for 2.5 PU/MWCNTs/Mg foam composites was 1.76 MPa and the theoretical results obtained from ANSYS was 1.65 MPa. The differences between these were 0.11 MPa and have accepted because the gap is very small.

# CHAPTER 1 : INTRODUCTION

## 1.1 Research Background

Today, polyurethane (PU) foam is widely used in a variety of applications, including cushioning, packaging, toys, mattresses, refrigerators and insulation, as well as automotive and construction materials, due to its attractive properties such as light weight, insulation, simplicity of processing, and commercial potential. It is produced by using a combination of liquid isocyanate and polyol through a blowing agent to form a foam. PU foam can be divided into flexible, semi rigid and rigid PU foam, depending on their chemical composition, cell morphology, degree of crosslinking and physical properties (Gama et al., 2018; Jathin et al., 2016; Madaleno et al., 2013; Dolomanova et al., 2011; Zeng et al., 2010). Furthermore, by controlling PU formulation, it is possible to achieve a wide range of morphology, density and rigidity, making rigid PU foam suitable for various applications due to its combination of strength, lightweight and good heat resistance (Madaleno et al., 2013). Rigid PU foam is a copolymer prepared by the polyaddition reaction of polyol with isocyanate (Badri et al., 2013) in the presence of water, N,N-dimethyl-cyclohexylamine and polydimethylsiloxane as the blowing agent, catalyst and surfactant, respectively (Lorusso et al., 2015; Chuayjuljit et al., 2007). Catalyst can be used to accelerate reaction time, increase production efficiency, promote positive reactions and suppress side reactions. Catalyst are a frequently used ingredient in the manufacture of many PU products and their amount is small but has a great effect (Ruiduan et al., 2018).

Polyol plays an integral part in urethane industries, which is conventionally derived from petrochemical crude oils. Nevertheless, the increasing global consumption of PU and the growing public need for environmentally friendly products have inspired researchers to replace petrochemical polyol with a more versatile, renewable and low cost alternative using vegetable oils (Noor et al., 2013; Lee et al, 2007). To date, vegetable oil based bio-polyols such as canola oil, soybean oil, corn oil, rapeseed oil, sunflower oil, linseed oil and palm oil have been extensively studied. Vegetable oils have a variety of chemical structures and reactive sites that can be easily chemically changed to create a wide variety of tailor-made monomers with a variety of functions. Additionally, the latter are readily available and annually renewable, as photosynthesis regenerates them year after year. Vegetable oils intrinsic biodegradability is also an attractive characteristic in light of growing environmental concerns (Silva et al., 2021; Pawlik & Prociak 2012). Vegetable oils are compatible with hydrocarbon blowing agents, higher hydrofobicity and improved hydrolytic properties of PU foam with a good oxidative stability. Among several types of vegetable oils for bio-polyol production, palm oil is the most capable option to replace polyol from petroleum due to inexpensive and renewable feedstock. Palm oil guarantee secure feedstock supplies without interrupting the food chain supply. The high homogeneity of palm oil based polyol (POP) also provides a controllable foaming process, in which fillers will added in PU foam to enhance the foam properties. POP also changed several mechanical and physical properties such as density, compressive strength, bending strength, brittleness and thermal conductivity in the production of PU foam (Aleksander et al., 2019; Maisonneuve et al., 2016; Pauzi et al., 2014). In the previous studies, up to 70 wt.% of a petrochemical polyol was replaced by POP in the PU system. It was found that due to high viscosity and a low hydroxyl value of the bio-polyols, the formulations containing 30 wt.% of the POP in the polyol premix were the optimal to obtain open-cell foams (Polaczek et al., 2021).

Numerous advancements in the research of PU foam composites have been made to improve their structure and mechanical properties. The mechanical properties of rigid PU composites are dependent on many factors but rely mostly on the PU matrix, properties of the fillers and the interfacial bonding of PU matrix/fillers. For several years, the study of this topic has been extended to the trends of PU foam composites with improvement, development and reinforcement of PU foam by the addition of fillers (Fu et al., 2008). Common fillers include organic and inorganic powders or minerals, whiskers, hollow, solid microspheres, glass, metallic particles and nanoparticles. Their purpose is to reduce the cost of PU foam, decrease the density and improve the mechanical properties of PU foam composites. Moreover, some fillers have been found to enhance the mechanical properties, even when only a small amount is added. However, there are cases where the combination of PU foam and fillers did not improved the mechanical properties but rather deteriorated the properties (Zhang et al., 2020; Czlonka et al., 2020; Marhoon, 2016). The addition nano/micro fillers to PU foam has a range of impacts depending on the loading percentage and particle size. In comparison to the nanoscale, the insertion of fillers into PU foam has a negligible effect on the density and tensile strength at the micrometric scale. For PU foams reinforced with nanoclay, their compressive strength changed little from 1 to 5%, but decreased at 7% due to a lower density and weaker matrix structure (Izarra et al., 2021; Fan et al., 2012).



Recently, polymer nanocomposites have displayed steady development over the past several years due to improved mechanical strength, stiffness, toughness, electrical conductivity and thermal conductivity. The addition of nanoparticles in polymer foam showed excellent reinforcement of foam materials. The addition of nanoparticles fillers such as nanoclays, layered silicates, carbon nanofibers and carbon nanotubes (CNTs) into

PU foam has shown significant improvement in thermal and mechanical properties (Oliveira & Beatrice, 2019; Lorusso et al., 2015; Li et al., 2010; Zeng et al., 2010). It is possible to enhance their properties by adding a low contents of nanoparticles to the polymer matrix. Usually, nanoparticles like multi walled carbon nanotubes (MWCNTs) must be subjected to surface treatment and dedicated processing techniques to avoid the agglomeration of nanoparticles due to strong van der Waals interaction (Madaleno et al., 2013; Jang & Sakka, 2010). To date, there is less research has been conducted on the usage of metal fillers such as alumina and magnesium (Mg) powder in PU foam. Mg has gained widespread attention in the scientific research due to its great specific strength, low density and light weight metal compared to other metals. As Mg is the lightest structural metal, it has extensive applications in the aerospace and automotive industries for reducing in fuel consumption and greenhouse emissions. Therefore, the addition of Mg in this research is expected to increase the thermal and mechanical properties of PU foam. Mg is usually used in metal matrix composites (MMCs) as a matrix and the reinforcement materials are usually CNTs. The inclusion of CNTs does not only improve the mechanical properties of Mg matrix, but also maintain the low density of MMCs (Rashad et al., 2015; Dey & Pandey, 2015).



Hybridization is a method of combining two fillers in one polymer matrix to gain high mechanical strength, thermal stability, stiffness and low water absorption properties, that cannot be achieved by conventional polymer composites (Sarifuddin & Ismail 2018). However, the characteristics of hybrid composites are determined by the more complex nature of the fillers' resulting interfacial properties and the fabrication method used. The significant benefits of successful filler hybridization include the economic benefits associated with the incorporation of an expensive filler in a low-cost polymer matrix and the achievement of a broader range of properties, which may include physical, mechanical, thermal, or dielectric parameters, or a proper balance of all desirable characteristics. Due to the inability of engineering materials to possess all desirable properties, hybrid composites are used to compensate for the polymer's shortcomings and to maintain a proper balance of different parameters (Kuruvilla, S. P., 2020). However, currently no study has developed rigid PU foam filled with hybrid fillers using Mg and MWCNTs. Several studies showed that the addition of hybrid fillers improved the mechanical properties and could overcome the dispersion issues of MWCNTs in the polymer matrix. PU foam composites is used to create a new class of foam insulation, electronic packaging and structural foam (Saba et al., 2016). In this research, the combination of Mg and MWCNTs in PU foam based POP was chosen to improve the mechanical and thermal properties.



Simulation is an alternative method often used in studying the mechanical behaviour of materials or products rather than through experiments. In order to describe the behaviour of materials, finite element analysis (FEA), constitutive modelling and molecular dynamics simulation have been utilized by researchers to find and solve the potential structural or performance issues. According to previous researchers, mechanical behaviours such as stress strain behaviours, could be described by the constitutive equation from the Maxwell model. The FEA program is suitable for static, dynamics and multiphysics analysis. However, the accuracy of the simulation depends on the availability of accurate mechanical properties of the sample such as polymers. The methods for determining strength, displacement or other properties by comparing experimental and simulation results have been widely utilized. (Petru & Novak, 2017; Srivastava & Srivastava, 2014; Reisgen et al., 2011). The FEA simulation was chosen to to evaluate the effects of mechanical properties subject to compression test by using ANSYS Multiphysics.

## 1.2 Problem Statement

The basic raw materials to produce PU foam are polyols and isocyanates commonly derived from petrochemicals. Polyol from petrochemical is a depleting resource, toxic, carcinogen, corrosive and non-biodegradable. It causes the increasing of the interest in bio renewable feedstock for both economic and environmental reasons. Hence, in this research, the use of polyols from vegetable oils in PU foam production should be able to reduce the dependency on the diminishing petroleum product, reduction usage of fossil resources and produce low greenhouse gas emission. POP is gaining popularity due to some properties related to the specific structure of oils, abundant, inexpensive and environmentally friendly. Although PU foam has a number of advantages, including its light weight, high energy absorption capacity and resistance to chemicals and solvents, it does have some drawbacks, including high porosity and high crushability porous PU foam, which affects mechanical properties. PU materials are highly dependent on their polymer matrix and cellular structure. After prolonged use, PU foam degrades slowly and deteriorate more faster than other types of PU due to their high porosity, which allows the polymer to be exposed to ambient oxygen, light, and moisture (Derieux et al., 2011). Another problem that can be observed is PU from bio-material based polyols will exhibit poor dimensional stabilities (Saba et al., 2016). Several approaches are available for raw materials modification of PU foam to overcome these problems. The addition of nano fillers such as MWCNTs is expected to improve the physical and mechanical properties of PU foam. Carbon nano fillers were recently incorporated into PU foams,demonstrating that they improved not only the physical