SYNTHESIS AND CHARACTERIZATION OF RIGID POLYURETHANE-PALM OIL BASED POLYOL/DIAMINOPROPANE-MONTMORILLONITE NANOCOMPOSITE FOAM

NIK NURFATMAH PZ BINTI NIK PAUZI

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To arwah abah, ma, abe am, kak shah, zue, mie, die, adik

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ABSTRACT

Issues on environmental impact and sustainability have driven the development of rigid polyurethane (PU)-palm oil based polyol (POP) /diaminopropane (DAP)-montmorillonite (MMT) nanocomposite foam. PU rigid foam derived from POP and polymeric 4,4-diphenylmethane diisocyanate (*p*-MDI), was successfully prepared via two steps-direct mixing method. Firstly, POP and DAP-MMT were mixed in a flask and stirred at 1500 rpm for 2 minutes to form a homogenous solution. Then, silicone surfactant and distilled water were added and further stirred for 2 minutes to form a pre-mixture. Later, *p*-MDI was added into the pre-mixture under high speed stirring at 1500 rpm for 45 seconds before charged into a mould. Fourier transform infrared energy peaks at 1533 cm^{-1}, 1218 cm^{-1} and 1731 cm^{-1} of N-H, C-N and C=O groups confirmed the formation of urethane linkages. PU foam was prepared at 1:1 diisocyanate: polyol (NCO:OH) ratio exhibited a comparable compressive strength (4969 kPa) with the control PU (4999 kPa). Meanwhile the amount of silicone surfactant as a foam stabilizer at 2 part per hundred polyol (pphp) showed the highest compressive strength (8452 kPa) with uniform and finer cell size. The X-ray diffraction (XRD) test showed that samples with DAP-MMT contents at 2 wt % and 4 wt. % exhibited exfoliated structure while the scanning electron microscopy (SEM) micrographs showed the reduction of cell size of each sample. This morphology effect was clearly manifested on the sample with 4 wt. % MMT loading that had the highest compression strength and density which were 19648 kPa and 0.13 gcm^{-3}. Results from water absorption test revealed that samples with 6 wt. % MMT loadings had about 31% reduction of water uptake against that of pure PU foam.

ABSTRAK

Isu berkaitan dengan perlestarian alam sekitar telah membawa kepada pembangunan busa tegar poliuretena-poliol berasaskan minyak sawit/diaminopropana-montmorillonit nanokomposit. Busa tegar PU dihasilkan melalui tindakbalas poliol berasaskan minyak sawit (POP) dan polimerik-4,4-difenilmetana diisosianida (*p*-MDI) melalui kaedah campuran dua langkah. Pertama, POP dan diaminopropana-montmorillonit (DAP-MMT) dicampurkan ke dalam sebuah balang dan dikacau pada kelajuan 1500 rpm selama 2 minit untuk menghasilkan satu larutan yang sekata. Kemudian, surfaktan silikon dan air suling ditambah dan proses kacauan dilanjutkan selama 2 minit untuk menghasilkan pra-campuran. Selepas itu, *p*-MDI ditambah ke dalam pra-campuran dengan kelajuan yang sama selama 45 minit sebelum dituang ke dalam acuan. Ujian Fourier inframerah telah mengesan kehadiran tenaga puncak pada 1533 cm^{-1}, 1218 cm^{-1} dan 1731 cm^{-1} yang terhasil dari rangkaian kumpulan N-H, C-N dan C=O mengesahkan pembentukan rantai uretana di dalam sampel. Sementara itu, busa PU disediakan pada nisbah 1:1 diisosianida:poliol (NCO:OH) telah menghasilkan kekuatan mampatan (4969 kPa) yang setara dengan sampel kawalan PU (4999 kPa). Kandungan surfaktan silikon sebagai penstabil busa pada 2 bahagian perseratus poliol (pphp) telah menghasilkan kekuatan mampatan tertinggi (8452 kPa) dengan taburan sel yang sekata dan bersaiz lebih kecil. Ujian XRD menunjukkan sampel dengan DAP-MMT kandungan 2 wt.% dan 4 wt.% menghasilkan struktur terkelupas sementara keputusan SEM menunjukkan sampel mempunyai saiz sel yang lebih kecil. Kesan dari morfologi ini dapat dilihat pada sampel 4 wt.% kandungan MMT yang mempunyai kekuatan mampatan tertinggi dan ketumpatan pada 19648 kPa dan 0.13 gcm^{-3}. Keputusan ujian penyerapan air menunjukkan sampel pada 6 wt% kandungan MMT, telah dapat mengurangkan kadar serapan air sebanyak 31% berbanding dengan busa PU tulen.

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LIST OF ABBREVIATIONS

ASTM	-	American society for testing and materials
BD	-	1,4-butanediol
BO	-	Butylene oxide
CEC	-	Cationic exchange capacity
CFCs	-	Chlorofluorocarbons
CO_2	-	Carbon dioxide
$COCl_2$	-	Phosgene
CTAB	-	Cetyl trimethyl ammonium bromide
DAP	-	Diamino propane
DBTDL	-	Dibutyltin dilaurate
DEA	-	Diethanolamine
DEG	-	Diethylene glycol
DMA	-	Dynamic mechanical analysis
DSC	-	Differential scanning calorimetry
DTG	-	Derivative thermogravimetry
EG	-	Ethylene glycol
EMS	-	Electromagnetic shielding
FTIR	-	Fourier transform infrared spectroscopy
GWP	-	Global warming potential
HCFC	-	Halogenated chlorinated fluorocarbons
HFCs	-	Hydrofluorocarbons
HDI	-	Hexamethylene diisocyanate
IPDI	-	Isophorone diisocyanate
MDI	-	Diphenylmethane diisocyanate
MEO	-	Methylsilane- ethylene oxide

MMT	-	Montmorillonite
Mono-G	-	Monoglyceride
MPOB	-	Malaysian Palm Oil Board
NCO	-	Isocyanate
NOPs	-	Natural oil polyols
OH	-	Hydroxyl
OHV	-	Hydroxyl value
PG	-	Propylene glycol
PEG	-	Polyethylene glycol
p-MDI	-	Polymeric diphenylmethane 4,4’- diisocyanate
PO	-	Propylene oxide
POP	-	Palm oil based polyol
PPG	-	Polypropylene glycol
PPO	-	Polypropylene oxide
PPy	-	Polypyrrole
PTMEG	-	Poly(tetramethylene ether) glycols
PU	-	Polyurethane
PUs	-	Polyurethanes
SEM	-	Scanning electron microscopy
SDS	-	Sodium dodecyl sulfate
TEM	-	Transmission electron microscopy
TDI	-	Toluene diisocyanate
TEA	-	Triethanolamine
TEGOSTAB	-	Polyether-modified polysiloxane B-8404
TGA	-	Thermogravimetric analysis
TriGs	-	Triglycerides
XRD	-	X-ray diffraction
WD	-	Wood flour

LIST OF SYMBOLS

λ - Wave length

d - The spacing between diffractional lattice planes

θ - The angle of diffraction

Na^+ - Sodium ion

K^+ - Potassium ion

Ca^{2+} - Calcium ion

NH_2 - Amine

H - Hydrogen

ρ - Density

m - Mass

v - Volume

W*a* - Weight after

W*i* - Weight initial

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polyurethane (PU) foam is not a new material. The foam accounts for the largest global market about 53% from other polymeric foams and have a remarkably broad range of applications from furniture, bedding, footwear, insulation panel, energy absorption (packaging) and aircrafts to automotive parts (Chuayjuljit *et al.*, 2010). PU foam can be modified from flexible, semi-rigid and rigid based on its mechanical strength and density to suit the end applications (Chian and Gan, 1998). The end properties of PU foam can be tailored by altering the amounts and the types of blowing agents, surfactant, polyol, polyisocyanates, catalyst and fillers. Rigid PU foam can be produced at higher isocyanate (NCO) content. The NCO increases the hard segment composition in polymer by restricting the chain motion in polymer that leads to flexible foam. Rigid PU foam consists of closed cell structure with low thermal conductivity, high compression strength, low density, high strength-to-weight ratio, and low moisture permeability (Singh *et al.*, 2007).

Like other polymers, rigid PU foams rely on petroleum feed stocks. However, issues on environmental impact and sustainability, as well as petroleum’s world depletion crisis have driven the development of PU foam from bio-renewable raw materials (Prociak *et al.*, 2012). Researches had proven that vegetables oils such as soybean oil, canola oil, linseed oil, safflower oil, rapeseed oil and palm oil can be transformed into polyols through few routes such as transesterification and glycerolysis (Das *et al.,* 2008; Guo *et al.,* 2000; Narine *et al.,* 2007; Shogren *et al.,* 2004). These polyols have great potentials to replace the conventional petroleum-based polyols that being used as one of the main components to make PU. Among these oils, palm oil is the main interest due to its abundance and availability in Malaysia. Furthermore, its price is cheaper than other vegetable oils (Carter *et al.,* 2007). Previously, quite number of research studies have been reported by using palm oil based polyol for PU foam productions (Abraham *et al.,* 2007; Chuayjuljit *et al.,* 2010; Shaari *et al.,* 2006; Tanaka *et al.,* 2008; Triwulandari *et al.,* 2007). Wong and Badri (2012) has successfully synthesized palm kernel oil based polyol to produce PU.

However, problems arise when using PU foam alone as it has low mechanical strength and thermal stability. Hence, the addition of filler is needed to increase these properties. Since the successful work on montomorillonite (MMT)/nylon-6 nanocomposite, research on polymer/clay nanocomposites have been extended to many other polymeric systems (Alexandre and Dubois, 2000). The incorporation of MMT into PU is one of example of such system (Cao *et al.,* 2005; Xu *et al.,* 2007). The clays can improve the physical and chemical properties of PU due to their large aspect ratio and surface area, when compared to conventional particulate filled microcomposites (Cao *et al.,* 2005; Ding *et al.,* 2006). MMT nanoparticles can be dispersed in PU matrices either in intercalated or exfoliated form, resulting in improving mechanical properties, increased storage and loss moduli, improved stiffness, reduced gas permeability, increase thermal stability (Semenzato *et al.,* 2009) and flame retardance (Modesti *et al.,* 2008; Semenzato *et al.,* 2009; Song *et al.,* 2005). However, the modification of MMT's character from hydrophilic to hydrophobic is needed to enhance the compatibility and dispersibility of MMT particle in the organic polymer matrix. This can be achieved via an ion exchange process by using surfactants that can lower the surface energy of the inorganic host and improve its wetting characteristics with the polymer. The modification of MMT can be done either with cationic, anionic and nonionic surfactants (Zhang *et al.,* 2010). Mahesh *et al.* (2011) had successfully synthesized the organomodification of Na-MMT using cation and anion surfactants such as cetyl trimethyl ammonium bromide (CTAB) and sodium dodecyl sulfate (SDS). However, Na-MMT is anionic in nature and it is difficult for anionic surfactants to intercalate within the MMT galleries (Zhang *et al.*, 2010). Hence the easier way to modified Na-MMT is via cation exchange method. Furthermore, the modification causes the expansion of MMT's interlayers thus allowing large polymer molecules to intercalate or exfoliate between these layers. This improves the miscibility of MMT with the polymer, thereby achieving a good dispersion in the polymer matrix (Semenzato *et al.*, 2009).

The right candidate for cationic modification is by using diamine based modifier such as 1,3-diamino-propane (DAP). DAP has been used as a crosslinking agent for epoxy resin systems (Marten *et al.*, 1991), a monomer in production of potentiometric pH sensors (Lakard *et al.*, 2005) and as coupling agent between graphene oxide and N-hydroxysuccinimide (Cai and Song, 2010). Base on their findings, this project has adopted the working concept of DAP to be used for modifying MMT. Positive charge of NH_2^+ from DAP is capable of cationic exchanging with Na^+ of MMT. DAP contains two terminal $-NH_2$ groups which one of them is capable of reacting with MMT clay, while the other part is free. This free group is thought can react with isocyanate group of PU to form urea linkages. Thus, this is thought led to increase in the rigidity of the PU foam.

Silicone surfactant has been used widely in many PU foam productions that stabilize the foam by preventing the coalescence of the cell during the nucleation process (Han *et al.*, 2000). Polyether-modified polysiloxane (TEGOSTAB B-8404) used in this study is one type of a silicone surfactant used as stabilizer for PU foam. It consists of grafted random or block copolymers of ethylene oxide (EO) and PO. By increasing the polyether chain, EO and siloxanes backbone increases the stability. Addition of surfactant can slow down the cell window drainage by creating a surface tension gradient along the surface and by reducing the surface tension. (Mondal and Khakhar, 2004). A study conducted by Grimminger and Muha (1995) have found that the closed cell content for rigid PU foam could be increased about 93.3-96.7 % by using different silicone surfactants. Therefore, in this study, silicone content has been varied in order to study the effect upon the morphology and compression strength of the foam.

1.2 Problem Statement

The aim of this research is to prepare rigid polyurethane-palm oil based polyol/DAP-MMT nanocomposite foam that has potential to be used in non-load bearing applications such as interior wall panel or insulation panel for construction building. The foaming process can be done by using direct mixing method by adopting two shot method. Since now, there no research on modification of MMT with DAP modifier is being studied.

Few questions need to be answered as follows:

i. Could MMT be successfully modified with DAP modifier?
ii. Does NCO:OH ratio affect the properties of rigid PU foam?
iii. Does surfactant content affect the properties and morphology of PU-POP/MMT nanocomposite foam?
iv. Does MMT loading affect the properties and morphology of PU-POP/MMT nanocomposite foam?

1.3 Objective of the Study

The objectives of this research are:

i. To modify MMT with DAP modifier via cation exchange method.
ii. To select the best NCO:OH ratio composition for rigid PU foam based on mechanical strength.
iii. To study the effects of silicone surfactant content on the properties and morphology of rigid PU-POP/MMT nanocomposite foam.
iv. To study the effects of MMT loading on the properties and
v. morphology of rigid PU-POP/MMT nanocomposite foam.

1.4 Scope of the Study

The scopes of study:

i. Modification of MMT with DAP modifier via cation exchange method.
ii. Synthesis of PU-POP/DAP-MMT foam via direct mixing method.
iii. Select the best NCO:OH ratio composition based on mechanical strength for rigid PU foam along the studied ratio of 1.5:1, 1:1 and 1:1.5.
iv. Variation contents of surfactant from 0.5, 1.0, 1.5, 2.0 and 2.5 pphp were used to produce rigid PU-POP/MMT nanocomposite foams.
v. Variation loadings of MMT from 2, 4, 6, 8 and 10 wt. % were used to produce rigid PU-POP/MMT nanocomposite foams.
vi. Testing fourier transform infrared spectroscopy (ftir), x-ray diffraction (xrd), thermogravimetry analysis (tga), scanning electron microscopy (sem), compression, density and water absorption tests were performed to determine the thermal, mechanical and morphologies study of this foam.

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