PREPARATION AND CHARACTERIZATION OF HALLOYSITE NANOTUBES FILLED PALM KERNEL OIL BASED POLYURETHANE FOAM

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DEDICATION

To my beloved mama,

For her patience, endless prayer and support,

And to my big family,

For their great helps and encouragements.

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ABSTRACT

A demand for renewable polymer foams has led to the study of rigid palm oil based polyurethane (PU) filled with halloysite nanotubes (HNTs). Studies on the effects of hydroxyl:isocyanate (OH:NCO) ratio, amount of distilled water and surfactant were conducted to obtain the optimum foam formulations. The bio-based rigid polyurethane (PU) nanocomposite foam was prepared by reacting palm kernel oil polyol (POP) with 4, 4-polydiphenylmethane diisocyanate (p-MDI) at 1:1 OH:NCO ratio via direct mixing method. HNTs were incorporated into the designated formulations at 1 to 5 wt% contents. The amount of silicone surfactant and distilled water as blowing agent were fixed at 4 parts per hundred polyol (pphp) and 2 pphp according to the formulations, respectively. The effect of HNTs on the density, surface morphology, mechanical strength and thermal properties of foams were investigated. Fourier transform infrared spectroscopy spectra confirmed the formation of urethane linkage with the existence of 1714 cm^{-1}, 1518 cm^{-1} and 1209 cm^{-1} peaks. All PU/HNTs nanocomposite foams exhibited an average 200 cell sizes of 139 mm, which was larger than the average 200 cell sizes of PU foam (i.e. 126 mm) without HNT. This finding also indicated that there was no extra nucleation process occurring during the cell growth as the average number of cell per 0.7 mm^2 (i.e. 312) was lower than that of PU foam without HNT (i.e. 326). The microimages captured by scanning electron microscopy supported the result. The addition of HNT in PU foam produced a 14 % decrease in density and 27 % increase in the compressive strength at 4 % HNT loading. Meanwhile, the thermal degradation temperature of PU/HNTs foams increased with the increasing of HNT loading as shown by thermogravimetric analysis plots. At 80 wt% weight loss, T_{80} of foam containing 5 wt% HNT (551 ^{o}C) exhibited 18 % increase compared to PU foam without HNT (466 ^{o}C). The presence of HNTs in PU cellular matrix did not significantly affect the flammability of the foams, as measured by limiting oxygen index (LOI) analysis. At the highest HNT loading i.e. 5 wt% the LOI increased about 5.5 % with respect to the PU foam without HNT. This finding suggests that the cellular matrix or foaming texture influences the formation of the continuous protective layer on the burning surface of the foam. From the obtained results, palm oil based rigid PU nanocomposite foam shows strong potential to be used as thermal insulation materials.

ABSTRAK

Permintaan terhadap busa polimer yang diperbaharui telah membawa kepada kajian busa poliuretana (PU) tegar berasaskan minyak sawit yang diisi dengan tiubnano haloisit (HNT). Kajian mengenai kesan nisbah hidroksil:isosianat (OH:NCO), kandungan air suling dan kandungan surfaktan telah dijalankan untuk memperoleh formulasi optimum busa. Busa poliuretana komposit tegar berasaskan bio disediakan dengan menindak balas poliol berasaskan minyak isirung sawit (POP) dan 4, 4-polidifenilmetana diisosianat (p-MDI) pada nisbah 1:1 OH:NCO melalui kaedah pencampuran langsung. HNT ditambah kepada formulasi yang ditetapkan pada kandungan 1 hingga 5 wt%. Jumlah surfaktan silikon dan air suling sebagai agen peniupan telah ditetapkan masing-masing pada 4 bahagian setiap seratus poliol (pphp) dan 2 pphp mengikut formulasi masing-masing. Kesan HNT terhadap ketumpatan, morfologi permukaan, kekuatan mekanikal dan sifat terma busa telah dikaji. Spektra spektroskopi jelmaan infra merah Fourier mengesahkan pembentukan jaringan poliuretana dengan kehadiran puncak pada 1714 cm^{-1}, 1518 cm^{-1} dan 1209 cm^{-1}. Saiz purata 200 sel 139 mm, bagi kesemua busa nanokomposit PU/HNTs adalah lebih besar berbanding saiz purata 200 sel bagi busa tanpa HNT (i.e. 126 mm). Penemuan ini juga menunjukkan bahawa tiada proses nukleasi tambahan berlaku semasa pertumbuhan sel apabila purata bilangan sel setiap 0.7 mm^2 (i.e. 312) adalah lebih rendah berbanding busa PU tanpa HNT (i.e. 326). Keputusan ini disokong oleh imej mikro yang diambil oleh mikroskop elektron imbasan. Penambahan HNT ke dalam busa PU telah mengurangkan ketumpatan sebanyak 14 % serta meningkatkan kekuatan mampatan sebanyak 27 % pada 4 % muatan HNT. Manakala, suhu perosotan terma bagi busa PU/HNTs meningkat dengan peningkatan pemuatan HNT sebagaimana ditunjukkan oleh plot analisis termo gravimetri. Pada kehilangan berat 80 wt%, T_{80} bagi busa yang mengandungi 5 wt% HNT (551 ^{o}C) menunjukkan 18 % kenaikan berbanding busa PU tanpa HNT (466 ^{o}C). Kehadiran HNT dalam matriks bersel PU tidak memberi kesan yang ketara terhadap kebolehbakaran busa sebagaimana diukur oleh analisis indeks pengehad oksigen (LOI). Pada pemuatan HNT tertinggi iaitu 5 wt%, LOI meningkat kira-kira 5.5 % berbanding busa PU tanpa HNT. Hasil kajian menunjukkan bahawa matriks bersel atau tekstur pembusa mempengaruhi pembentukan lapisan pelindungan yang berterusan pada permukaan pembakaran busa. Daripada keputusan yang diperoleh, busa nanokomposit PU tegar berasaskan minyak sawit berkeupayaan untuk digunakan sebagai bahan penebat haba.

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LIST OF ABBREVIATIONS

ATR- FTIR	-	Attenuated total reflection-fourier transform infrared
BPEI	-	Branched polyethylenimine
CFC	-	Chlorofluorocarbons
CNF	-	Carbon nanofiber
CNT	-	Carbon nanotube
CPO	-	Crude palm oil
cps	-	Centipoise
DPPM	-	Diethyl propanediol phosphoryl melamine
DPTP	-	Diphenyl phosphorus triethoxysilicon propylamine
EFB	-	Empty fruit bunches
EO	-	Ethylene oxide
EPDM	-	Ethylene propylene diene monomers
FFB	-	Fresh fruit bunches
FTIR	-	Fourier transform infrared
GAIN	-	Global agriculture information network
HCFC	-	Hydrochlorofluorocarbons
HDI	-	Hexamethylene diisocyanate
HFC	-	Hydrofluorocarbons
HNT	-	Halloysite nanotube
HRR	-	Heat release rate
IFR	-	Intumescent flame retardants
IPDI	-	Isophorone diisocyanate
LOI	-	Limiting oxygen index
MDI	-	Methylene diphenyl diisocyanate
MLR	-	Mass loss rate
MMT	-	Montmorillonite
MPOB	-	Malaysian Palm Oil Board
MWCNT	-	Multiwalled carbon nanotube
NCO	-	Isocyanates
OH	-	Hydroxyl

pbw	-	Part by weight
PAA	-	Polyacrylic acid
PA 6	-	Polyamide 6
PDMS	-	Polydimethylsiloxane
PE	-	Polyethylene
PEO	-	Polyoxyethylene
PKO	-	Palm kernel oil
PLA	-	Polylactid acid
P-MDI	-	Polymeric methylene diphenyl diisocyanate
POP	-	Palm oil polyol
PO	-	Propylene oxide
PP	-	Polypropylene
pphp	-	Part per hundred polyol
PPO	-	Polyoxypropylene
PS	-	Polystyrene
PU	-	Polyurethane
rpm	-	Revolution per minute
SEA	-	Specific extinction area
SEM	-	Scanning electron microscopy
TDI	-	Toluene diisocyanate
TEM	-	Transmission electron microscopy
TGA	-	Thermogravimetry analysis
UL	-	Underwriters laboratories
XRD	-	X-ray diffraction
wt %	-	Weight percent

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In foam industries, polyurethane (PU) contributes the largest market among other polymeric foams such as polystyrene (PS), polypropylene (PP) and polyethylene (PE) due to its versatility where wide range of physical, mechanical and chemical properties can be obtained just by changing type and ratio of precursor materials i.e. polyol and isoscyanates (Nikje and Farazfar, 2012; Njuguna *et al.*, 2011). Foams with different rigidities such as rigid, semi rigid and flexible can be produced. Rigid foams which have combination of strength, lightweight and good thermal resistance are usually used in sandwich structures, footwear, construction and insulation, while semi-rigid and flexible foams which have excellent plastic deformation and recovery characteristics can be found in packaging materials, furniture and automotive seating (Kumar and Kaur, 2013; Piszczyk *et al.*, 2012; Saifuddin *et al.*, 2010).

PUs industries are heavily rely on petroleum feedstock but with future sustainability of petroleum sources and growing concern about environmental problem; a few significant studies had been conducted to find alternative ways to develop PU from bio-renewable resources (Hongyu, 2011; Hu *et al.*, 2012; Septevani *et al.*, 2015; Yang *et al.*, 2015). Many studies were reported on various vegetable oils used in producing bio-based polyol such as palm oil (Badri, 2012; Septevani *et al.*, 2015) sunflower and rapeseed oil (Kairyte and Vejelis, 2015), soybean (Hongyu, 2011; Hu *et al.*, 2012; Tan *et al.*, 2011; Yang *et al.*, 2012) and castor oil (Ganji *et al.*, 2014). Malaysia is the world's largest exporter of crude palm oil and the second largest palm oil producer after Indonesia (Darshini *et al.*, 2013). With an abundant source of palm oil, this study focuses on palm kernel oil-based polyol (POP) reacting with polymeric diphenylmethane 4,4'- diisocyanate (p-MDI) to produce rigid PU

foam. PMDI was selected due to its less toxicity when compared with a common aromatic isocyanate such as toluene diisocyanate (TDI).

Despite of those great properties, rigid PU foams have some limitations in mechanical strength and thermal stability (Antunes *et al.*, 2011; Nikje and Tehrani, 2010; Piszczyk *et al.*, 2012). Their poor dimensional stabilities create problems in insulation (Wang *et al.*, 2012). Studies showed that the addition of micron-sized fillers such as particles, flakes or fibers into the polymer matrices could enhance certain properties (such as mechanical strength, physical properties and thermal stability) (Jawaid and Abdul Khalil, 2011; Jonoobi *et al.*, 2009; Peng *et al.*, 2010). Thus the insertion of a small amount of filler into the matrix foam was thought could overcome some of these limitations.

However size of filler is crucial where inappropriate size of filler affects foam structure. If the size of filler is similar or bigger than the size of the elements in the foams, the filler damages the foams rather than strengthening their structures (Yakushin *et al.*, 2011). Therefore several studies on the usage of nano-sized fillers such as carbon nanotubes (CNT) (Jogi *et al.,* 2012; Wang *et al.,* 2014), carbon nanofiber (CNF) (Harikrishnan *et al.*, 2010) and nanoclay (Madaleno *et al.*, 2013; Piszczyk *et al.,* 2014*)* have been reported. The reinforcement of these nano fillers in PU foam has resulted superior mechanical strength, thermal stability (Antunes *et al.*, 2011; Nikje and Tehrani, 2010) and good gas permeability (Nikje and Farazfar, 2012; Piszczyk *et al.*, 2012).

New classes of nano silicates have drawing much attention as fillers for polymers, namely, halloysite nanotubes (HNTs). The incorporation of HNTs in polymer matrices such as polyamide, polypropylene, termoplastic PU and polyethylene had improved the mechanical and thermal properties of the polymers as well as fire retardant performance (Alhuthali and Low, 2013; Prashantha *et al.*, 2013; Liu *et al.*, 2011; Marini *et al.*, 2014). Since HNTs exist as hollow tubes, they impart very high surface area, thus providing excellent interaction between the filler and the matrix (Alhuthali and Low, 2013). Interestingly, HNTs unique crystal structures resemble carbon nanotubes (CNTs) in terms of aspect ratio, which have the potential

to provide cheap alternatives to the expensive CNTs (Du *et al.*, 2010). They are also easily available, abundant and biocompatible compared to CNTs (Prashantha *et al.*, 2011).

It is well known that PU foams are categorized as flammable material (Bian *et al.*, 2007; Meng *et al.*, 2009; Shi *et al.*, 2006). This could limit their applications especially as insulation material. Several studies had been reported for using flame retardant in order to improve the flammability of PU foam (Bian *et al.*, 2007; Meng *et al.*, 2009; Shi *et al.*, 2006). However the commonly used flame retardants are chemically derived and complex process is involved. HNT has been testified as an excellent flame retardant in many polymers matrix (Du *et al.*, 2006; Lecouvet *et al.*, 2013; Marney *et al.*, 2008; Nakamura *et al.*, 2013; Vahabi *et al.*, 2013). Therefore, HNT filler was used as natural flame retardant in PU foam.

This study was conducted to investigate the influence of HNTs on the physical properties, mechanical properties, thermal properties and fire retardancy of rigid PU foam derived from POP.

1.2 Problem Statement

The production of polymeric materials from non-renewable resources has become a major issue due to environmental concerns and unstable supply of petrochemical raw materials. The use of palm kernel oil based polyester polyol as the substitution of polyether polyol in PU foam production is the answer to this problem. The structure, molecular weights and functional groups of the polyols play vital roles in determining the properties of the final polyurethane foams. For rigid foam, there must be a stiff polymer network and hence, a high degree of cross linking is needed in the system. However, it is well known that palm oil based polyol is relatively weak in terms of its reactivity with isocyanates to form urethane linkage, as compared to the other bio-based polyols such as rapeseed oil (Dzulkifli *et al.*, 2014). Thus the incorporation of filler from micro to nanoscale can improve the properties

of foaming system. Still, nanocomposite reinforcement such as MMT and sepiolite need to deal with agglomeration problems; unless surface modification is done (Nik Pauzi *et al.,* 2014; Wang *et al.,* 2012). To overcome this issue, HNT can be utilized as filler of polymeric foam without any modification as their unique tubular structure and low tube-tube interaction properties give a better dispersion and interfacial interaction within polymeric foams (Liu *et al.*, 2014). It is practical to study the flammability properties, as PU foam is widely used in thermal insulation application. The ability of HNTs to form a thermally stable layer on the surface of designated polymer can introduce them as good flame retardant material (Liu *et al.*, 2014). Therefore it is important to investigate whether HNT can act as natural flame retardant in polyurethane foams. To date, there is no study has been made on PU-HNT nanocomposite foam using palm kernel oil-based polyol.

1.3 Objective of Study

The objective of the research is to produce polyurethane-halloysite nanocomposite foam using palm kernel oil-based polyol. The objective can be sub-divided as follows;

i. To obtain the best OH: NCO ratio based on the trace of unreacted NCO, cell morphology, density value and compressive strength of the foams.

ii. To study the effects of adding HNTs at OH:NCO ratio obtained from i) towards the mechanical and physical properties, and surface morphology of PU foams.

iii. To investigate the effect of HNTs on thermal properties and flammability of the foam

1.4 Scopes of Study

The scopes of study are as follows:

1. Determination of optimum foam formulation

The optimum formulation for production of semi-rigid PU foam was studied. Four main materials were involved in order to find the best formulation of semi-rigid PU foam. The ratio of POP and MDI was varied to find the best rigidity for rigid PU nanocomposite foam. Formulation of surfactant was done to determine the right amount of surfactant that was needed to stabilize the foam. The accurate amount of foaming agent was defined by varying water content in the foam. Optimum mixture speed was also studied to ensure the polymer mixture was well mixed. Few testing was done to verify the result; Fourier transform infrared spectroscopy (FTIR) was done to confirm the formation of urethane linkage, Scanning electron microscopy (SEM) was conducted to study the morphology of the foam, density and compression test were completed to identify the mechanical strength of the foam.

2. Preparation of PU nanocomposite foam

Rigid nanocomposite PU foams were synthesized via direct mixing method. Palm kernel oil polyol, surfactant, distilled water and HNT were homogenously mixed at predefined mixing speed prior to addition of PMDI. Six samples of PU foam with various HNT loadings were prepared. The HNT contents were varied from 1-5 wt %.

3. Testing and characterizations

Several test and characterizations were conducted such as Fourier transform infrared (FTIR) –to identity formation of urethane linkages and trace of unreacted NCO, thermogravimetry analysis (TGA)-to analyze thermal degradation profile of sample, X-ray diffraction (XRD)-to investigate the inclusion of filler in the matrix, flammability testing (LOI)- to measure flame retardancy of sample, compression

test-to measure compression strength, density measurement-to measure density of foam and scanning electron microscopy (SEM)-to analyze surface morphology of foam.

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