

RIGID POLYURETHANE-PALM OIL BASED POLYOL/KENAF FIBRE
BIOCOMPOSITE FOAM

FARHANA SHAKIRA BINTI MD. AKHIR

UNIVERSITI TEKNOLOGI MALAYSIA

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FARHANA SHAKIRA BINTI MD. AKHIR

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“Special dedicated to my beloved family. Thanks for all your support,
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ABSTRACT

Economic and environmental issues have driven the use of palm oil based polyol (PO-p) to replace petrochemical-based polyol as one of the components in polyurethane (PU) foam's production. PO-p was reacted with polymeric 4, 4 – diphenylmethane diisocyanate (p-MDI) in the presence of silicone surfactant as a foam stabiliser and distilled water as a blowing agent to produce rigid PU foam. The PU/PO-p-based foam has good compression strength but moderate thermal stability. The benefits offered by the polymer-natural fiber blend had triggered the idea to incorporate kenaf fiber as filler in PU foam. Few reaction parameter were varied such as the amounts of surfactant (1.5, 1.75, 2.0, 2.25 and 2.5 pphp), fiber sizes (150-300 μm and 300-500 μm) and fiber contents (2.5, 5.0, 7.5, 10.0 and 12.5 wt. %). Their effects towards the foam properties and morphology were studied. The wavebands detected at 3300 cm^{-1} , 1710 cm^{-1} and 1500 cm^{-1} by Fourier transform infrared confirmed the formation of urethane linkages in all samples. The addition of silicone surfactant as foam stabiliser at 2.0 pphp, imparted good thermal stability, regular cell shape and size with fewer voids, higher compressive strength, and moderate biodegradability when compared to the control sample. Meanwhile, by varying the fiber size, it was found that sample with bigger fiber size (300 – 500 μm) showed two apparent peaks i.e. hydrogen bonded $-\text{OH}/-\text{NH}_2$ at 3300 cm^{-1} and free $-\text{OH}/-\text{NH}$ at 3600 cm^{-1} . The presence of many hydrogen bonded molecules contributed to the increase of thermal stability, smaller cell size, higher compression strength, and density, as well as the slowest fungi growth rate. Apart from that, the effects of various fiber loadings on the samples had revealed that 7.5 pphp was the best amount that gave the highest compression strength (0.89 MPa) and density (0.117 g/cm^3) with the smallest cell size. The sample also exhibited the fastest fungi growth rate, as well as higher percentage of biodegradability.

ABSTRAK

Isu-isu ekonomi dan alam sekitar telah mendorong penggunaan polioliol berasaskan minyak sawit (PO-p) untuk menggantikan polioliol berasaskan petrokimia sebagai salah satu komponen dalam penghasilan busa poliuretana (PU). PO-p telah bertindak balas dengan polimer 4,4-difenilmetana diisocyanida (p-MDI) dengan kehadiran surfaktan silikon sebagai penstabil busa dan air suling sebagai ejen pembuih untuk menghasilkan busa PU tegar. Busa berasaskan PU/PO-p mempunyai kekuatan mampatan yang bagus tetapi kestabilan terma yang sederhana. Kelebihan yang ditawarkan oleh adunan polimer-serat semula jadi telah mencetuskan idea untuk menggabungkan serat kenaf sebagai pengisi ke dalam busa PU. Beberapa parameter tindakbalas telah dipelbagaikan seperti kuantiti surfaktan (1.5, 1.75, 2.0, 2.25 and 2.5 pphp), saiz serat (150-300 μm and 300-500 μm) dan kandungan serat (2.5, 5.0, 7.5, 10.0 and 12.5 wt.%). Kesan mereka ke atas sifat-sifat busa dan morfologi telah dikaji. Getaran dikesan pada 3300 cm^{-1} , 1710 cm^{-1} , dan 1500 cm^{-1} oleh inframerah transformasi Fourier telah mengesahkan pembentukan rangkaian uretana dalam semua sampel. Penambahan surfaktan silikon sebagai penstabil busa pada 2.0 pphp telah menunjukkan kestabilan haba yang baik, bentuk sel busa yang seragam dan pengurangan ruang udara, kekuatan mampatan yang lebih tinggi dan kebolehuraian yang sederhana jika dibandingkan dengan sampel kawalan. Sementara itu, dengan mengubah saiz serat, didapati bahawa sampel dengan saiz serat yang besar (300-500 μm) menunjukkan dua puncak jelas hidrogen terikat $-\text{OH}/-\text{NH}_2$ pada 3300 cm^{-1} dan hidrogen bebas pada 3600 cm^{-1} . Kehadiran banyak molekul hidrogen terikat menyumbang kepada peningkatan kestabilan haba, saiz sel yang lebih kecil, kekuatan mampatan dan ketumpatan yang lebih tinggi, serta kadar pertumbuhan kulat yang paling perlahan. Kesan pelbagai kandungan serat pada sampel menunjukkan bahawa 7.5 pphp adalah jumlah terbaik yang memberikan kekuatan mampatan tertinggi (0.89 MPa) dan ketumpatan (0.117 g/cm^3) dengan saiz sel yang paling kecil. Sampel itu juga menunjukkan kadar pertumbuhan kulat yang paling cepat serta kebolehan penguraian yang lebih tinggi.

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LIST OF ABBREVIATIONS

ASTM	-	America Society for Testing and Materials
CFCs	-	Chlorofluorocarbons
DEG	-	Diethyleneglycol
EFB	-	Empty fruit bunch
EO	-	Ethylene oxide
HCFCs	-	Hydro chlorofluorocarbons
IUPAC	-	International Union of Pure and Applied Chemistry
MDI	-	Methylene diphenyl diisocyanate
MPOB	-	Malaysian Palm Oil Board
NaCl	-	Sodium chloride
NaOH	-	Sodium hydroxide
NCO	-	Isocyanate
NFs	-	Natural fibres
NO-p	-	Natural oil-based polyols
OH	-	Hydroxyl
PBDE	-	Polybrominated diphenylether
PDMS	-	Polydimethylsiloxane
PEG	-	Polyethylene glycol
p-MDI	-	Polymeric methylene diphenyl diisocyanate
PO	-	Propylene oxide
PO-p	-	Palm oil-based polyol
PPG	-	Polypropylene glycol
PPO	-	Propylene oxide
PU	-	Polyurethane
RBD	-	Refined-bleached-deodorized
TDI	-	Toluene diisocyanate

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Polyurethane (PU) foam accounts for the largest global market at about 53% compared to other polymeric foams. It has a remarkably broad range of applications from furniture, bedding, footwear, insulation panel, energy absorption (packaging) and aircrafts to automotive parts (Chuayjuljit *et al.*, 2010; Chan *et al.*, 2012). PU foam can be modified into flexible, semi-rigid and rigid based on its mechanical strength and density by altering the amounts and the types of blowing agents, surfactant, polyol, polyisocyanates, catalyst and fillers (Chian and Gan, 1998). Rigid PU foam can be produced at higher isocyanate (NCO) content, where NCO increases the hard segment composition in the system. 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 from bio-renewable raw materials (Prociak *et al.*, 2012; Sari *et al.*, 2015; Lumcharoen *et al.*, 2014). Vegetable oils such as soybean oil, canola oil and linseed 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 has been the main interest due to its abundance and availability in Malaysia. Furthermore, its price is cheaper than other vegetable oils (Carter *et al.*, 2007; Lumcharoen *et al.*, 2014). Badri (2012) have successfully synthesized palm kernel oil based polyol to produce PU. Previously, quite number of research studies had been reported using palm oil based polyol (PO-p) for PU foam productions (Abraham *et al.*, 2007; Chuayjuljit *et al.*, 2010; Shaari *et al.*, 2006; Tanaka *et al.*, 2008; Thirumal *et al.*, 2007).

Apart of using renewable resources such as palm oil polyol to make green PU foam, the development of bio composite materials using natural fibres is another alternative to sustain environmental issue. Nearly all natural fibres are cellulosic sources and biodegradable, but only few of them, especially kenaf exhibits good mechanical behaviour, due to higher cellulosic content of the outer bast fibre i.e. 25-40% (Saad and Kamal, 2013). Despite of few advantages offered by natural fibres, their major disadvantages that they are hydrophilic and incompatible with the hydrophobic polymers. The incompatibility can be reduced or eliminated through a chemical modification with an alkali such as sodium hydroxide (NaOH). This reduces the hydrophilic property of the fibre, thus significantly improving the wettability of fibre with polymer matrix (Khalid *et al.*, 2008). Shan *et al.* (2012) found that at 5% NaOH concentration helped to remove the dirt or the impurity layer on the fibre surface.

Meanwhile, for many biocomposite systems, fibre size has large influences on the physical structure, mechanical behaviour and density, as these properties depend on the types and the aspect ratios of length/diameter of fibres (L/D). Although small size of fibre mixes well with polymer during compounding, low L/D ratios causes stress concentration that reduces the mechanical strength of the composite system when compared to that of pure PU foam (Gamstedt *et al.*, 2007). Small or fine fibre size gives unnoticeable effect on the mechanical behavior of the system (Le *et al.*, 2006; Yam *et al.*, 1990; Abdelmouleh *et al.*, 2007; Rezaei *et al.*, 2009), while bigger fibre size imparts high stiffness and volumetric swelling (Migneault *et al.*, 2009). Generally, many researchers used the fibre that sized in the range of 0.1 mm to 0.5 mm (Migneault *et al.*, 2009; Patterson, *et al.*, 2001).

PU foam has high potential to collapse during synthesis due to different polarity between diisocyanates and distilled water. Many foam systems use silicone surfactant to stabilize the system. Silicone surfactant consists of polydimethylsiloxane backbone grafted with polyethylene oxide-co-propylene pendant group copolymers. The siloxane backbone exhibits a hydrophobic section while the pendant group is a polar hydrophilic polyether (Zhang *et al.*, 1999). The addition of surfactant can retard the cell window drainage by creating a surface tension gradient along the surface, thus reducing the surface tension between the cells (Mondal and Khakhar, 2004). In return, it prevents the coalescence of the cell during the nucleation process and forms stable foam (Han *et al.*, 2009). A study conducted by Grimminger and Muha (1995) had found that the closed cell content for rigid PU foam was increased at about 93.3-96.7 % by using different silicone surfactants. However, insufficient amount of surfactant produces foam with smaller irregular cell shape that collapses in a short period of time, whereas an excess amount of surfactant produces distorted cell shape due to over-stabilizing of cell foam (Guo *et al.*, 2000).

1.2 Problem Statement

PU foam is made by reacting diisocyanates with polyol. Unlike others PU petroleum-based polyols, PU palm oil-based polyol has moderate mechanical strength and thermal stability due to the nature of the process to produce palm oil polyol. A process such as transesterification of palm oil introduces hydroxyl group, OH on the fatty acid chains of palm oil, but inevitably this reaction leads to decrease in the molecular weight and viscosity (Petrovic *et al.*, 2004). Common practice to enhance these properties is by adding filler into polymer matrix.

In this study, fiber of bast kenaf was used as filler, based on the successful work of Ibraheem *et al.*, (2011) on developing PU/long kenaf fibre insulation hardboard. As stated earlier, kenaf bast fibre that rich with cellulose is able to improve the mechanical and thermal stability (Saad and Kamal, 2013). In this work, two different fibre sizes were utilized i.e. 150-300 μm and 300-500 μm . The fibre size was

selected according to some previous works. Gu *et al.* (2013) used maple wood fibre that sized from 180-850 μm at 0-13.3 php content to fabricate PU composite foams. Rezaei *et al.* (2009) prepared five different carbon fibre sizes ranging from 500 μm to 10 mm at 10 wt. % fibre loading while Subramaniyan *et al.* (2013) used 80 mesh (about 177 μm) of kenaf /tire rubber particles at the percentage range of 2, 4, 6, 8 and 10 wt. % to fabricate PU composite foams.

Apart from the fibre size, study showed that fibre loading also gives some influences on the properties of systems. This is because the cellulosic materials of fibres act as a hydroxyl functionality source, thus able to modify the foam behaviours and strength (Rivera-Armenta *et al.*, 2004). Higher fibre contents cause the chain to entangle, due to the increase of functionality from the fibre. In return, this causes the fibre to agglomerate thus, reducing the rate of heat transfer through system and enhancing the thermal stability (Banik *et al.*, 2008; Chakraborty *et al.*, 2006). However, the agglomeration also causes the formation of weak point and poor wetting interface between fibres-PU matrix (Ray and Rout, 2005). The agglomeration is also interfered the formation of urea and urethane linkages in PU, thus lowering the mechanical strength of the sample (Dehbari *et al.*, 2013). In this study, the amount of fibre loadings were varied at 2.5, 5.0, 7.5, 10.0 and 12.5 wt. %. Effects on the physical, mechanical and morphology of PU biocomposite foam were studied.

As mentioned earlier, the amount of silicone surfactant has large influences on the stability of the foam. However, those systems studied were valid for PU-petroleum based polyol foams and not for PU-palm oil based biocomposite foams. Therefore, in this study the silicone contents were at 5 different values i.e. 1.5 php-2.5 pphp. In order to determine the best surfactant amount upon the morphology and compression strength of the biocomposite foam, fibre loading was fixed at 5.0 pphp with the fibre size at 300-500 μm .

1.3 Objective of the Study

The objectives of this study is to prepare rigid polyurethane-palm oil based polyol/kenaf fibre biocomposite foam that has potential to be used in non-load bearing applications such as interior wall panel or insulation panel for construction building. The objectives can be divided into sub-objectives as follows;

1. To investigate the effects of surfactant on thermal stability, compression strength, density and surface morphology of the foam at fixed fibre size and loading.
2. To determine the effects of different fibre sizes on the thermal stability, compression strength, density, biodegradability and surface morphology of the foam at fixed fibre loading and surfactant content.
3. To measure the effects of kenaf fibre loading on the thermal stability, compression strength, density, biodegradability and surface morphology of the foam at fixed fibre size and surfactant loading.

1.4 Scope of the study

The scopes of study are as follows:

1. Preparation of kenaf
 - i) Kenaf was treated with 5% NaOH solution at specific concentration for 24 hours at room temperature.
 - ii) Kenaf was cleaned with distilled water and dried in an oven at temperature 60 °C for 2 days.
 - iii) Kenaf was ground and sieved to obtain fibre sizes of 150-300 µm and 300-500 µm.

2. Preparation of PU biocomposite foam

Rigid PU-POP-kenaf foam was synthesized via a direct mixing method by varying the reaction parameter as follows;

- i) Surfactant contents were varied from 1.5, 1.75, 2.0, 2.25 and 2.5 pphp
- ii) Fibre size were varied from 150-300 μm and 300-500 μm .
- iii) Kenaf loading were varied from 2.5, 5.0, 7.5, 10.0 and 12.5 wt. %

3. Testing and characterizations

- i) Fourier-transform infrared spectroscopy (FTIR)
- ii) Thermogravimetric analysis (TGA)
- iii) Scanning electron microscopy (SEM)
- iv) Compression strength test
- v) Density measurement
- vi) Biodegradability test

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