

CHARACTERISATION AND OPTIMISATION OF FLAME-RETARDING
PALM OIL-BASED POLYURETHANE/MONTMORILLONITE-
AMMONIUM POLYPHOSPHATE FOAM

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DEDICATION

To those who chose to rise up and fight further

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ABSTRACT

The organic chemical composition in polyurethane (PU) foam has adversely affected the flammability of the foam that causes high susceptibility to fire. Many researchers and industrialists have invested vast efforts to counter this issue, including incorporation of synthetically-produced flame retardants and fillers, and chemical modification on the constituting materials of PU foam. All these methods are not environmentally-friendly. Montmorillonite (MMT) has been known to have flame-retarding properties in numerous polymer composite systems, however, its effects in PU foam application has not been investigated. The aim of this project was to develop and optimise palm oil-based PU foam reinforced with ammonium polyphosphate (APP) and MMT in the form of blended (PU/MMT/APP) and hybrid (PU/APP-MMT) systems. Palm oil-based PU foam was chosen as a matrix due to its renewable resources and sustainability. Two types of multi filler systems were prepared: PU/MMT/APP blend and PU/APP-MMT hybrid. The APP-MMT hybrid filler was prepared through an ion-exchanged surface-treatment method. PU foams were then fabricated at different MMT/APP and APP-MMT loadings, and were characterized for their compressive properties, fire retardancies, thermal stabilities, and morphologies. Hybrid PU/APP-MMT system had improved the fire retardancy where the limiting oxygen index (LOI) had reached 24.19 at 10 wt. % filler loading as opposed to 23.85 showed by blended PU/MMT/APP filler system. This probably indicates the synergistic effect between APP and MMT in fire-retarding mechanism where a more stable alumino-phosphate species was formed during the combustion, which enhanced the thermal-insulating and fire protection properties. However, the compressive modulus of hybrid APP-MMT showed the highest value (2.857 MPa) at 6 wt. %, where further filler inclusion beyond this point had deteriorated the strengths of the foams. Hindered intermolecular hydrogen-bonding was thought as the main contributor for the reduction. Response Surface Methodology was then used to find the optimised filler formulation for both multi-filler systems with compressive modulus and LOI as the responses. The optimisation yielded filler combination of 0.9 wt. % Na-MMT and 4.9 wt. % APP was the best for blended system, whereby the optimised hybrid APP-MMT value was computed as 9.2 wt. %. The characterization of both optimised filler formulations portrayed some improvements, when compared to its pristine counterpart. The LOI values were improved up to 44 %, with compromising only 5 % of compressive modulus. From the results obtained, bio-based PU foam has a great potential to be used in structural panel-related applications that requires moderate load-bearing and flame-retardancy capabilities.

ABSTRAK

Komposisi kimia organik dalam busa poliuretena (PU) telah memudaratkan kemudahbakaran busa tersebut dengan menyebabkannya mudah terbakar. Ramai penyelidik dan ahli perindustrian telah menggembeng tenaga untuk mengatasi isu ini, termasuk menggunakan bahan cegah kebakaran dan pengisi yang dihasilkan secara sintetik, dan pengubahsuaian kimia bahan-bahan penghasilan busa PU. Kesemua kaedah ini adalah tidak mesra alam. Montmorillonit (MMT) telah diketahui mempunyai sifat cegah kebakaran dalam berbagai sistem komposit polimer, namun kesannya terhadap sistem busa PU belum pernah dikaji. Tujuan kajian ini adalah untuk membangun dan mengoptimumkan busa PU berasaskan kelapa sawit bertetulangankan ammonium polifosfat (APP) dan tanah liat nano MMT, di dalam bentuk campuran (PU/MMT/APP) dan hibrid (PU/APP-MMT). Busa PU berasaskan kelapa sawit telah dipilih sebagai matriks kerana sifat sumber boleh diperbaharui dan kelestariannya. Dua jenis sistem pelbagai pengisi telah disediakan: PU/MMT/APP campuran dan juga PU/APP-MMT hibrid. Pengisi APP-MMT hibrid telah disediakan melalui proses rawatan permukaan pertukaran ion. Busa PU kemudiannya dihasilkan dengan muatan MMT/APP dan APP-MMT yang berbeza, dan dicirikan mengikut sifat mampatan, kecegahbakaran, kestabilan haba, dan morfologi. Sistem hibrid APP-MMT telah meningkatkan kecegahbakaran yang mana nilai Indeks Oksigen Pengehad (LOI) mencapai 24.19 pada 10 wt. % muatan pengisi, berbanding 23.85 menggunakan sistem campuran Na-MMT/APP. Ini mungkin menunjukkan kesan sinergi antara MMT dan APP dalam mekanisme mencegah kebakaran yang mana spesies alumino-fosfat lebih stabil telah terbentuk ketika pembakaran yang meningkatkan sifat penebat haba dan kalis api. Walau bagaimanapun, modulus mampatan PU/APP-MMT mencapai nilai tertinggi (2.857 MPa) pada 6 wt. % yang mana penambahan pengisi melebihi nilai ini menyebabkan kemerosotan pada kekuatan busa. Penyumbang utama kepada kemerosotan ini adalah dikaitkan dengan ikatan hidrogen antara-molekul yang terhalang. Kaedah Gerak Balas Permukaan kemudiannya digunakan untuk mencari formulasi pengisi optimum bagi kedua-dua sistem busa PU pelbagai pengisi dengan nilai LOI dan modulus mampatan sebagai tindak balas. Pengoptimuman telah menghasilkan nilai gabungan pengisi 0.9 wt. % Na-MMT dan 4.9 wt. % APP sebagai terbaik untuk sistem campuran MMT/APP, manakala nilai teroptimum hibrid APP-MMT adalah 9.2 wt. %. Pencirian kedua-dua formulasi teroptimum telah menunjukkan beberapa peningkatan berbanding busa tanpa pengisi. Nilai LOI meningkat sehingga 44 % dengan hanya pengurangan nilai modulus mampatan sebanyak 5 %. Melalui hasil dapatan kajian, busa PU berasaskan bio mempunyai potensi yang besar untuk digunapakai dalam aplikasi berkaitan panel struktur yang memerlukan beban galas dan keupayaan pencegahan kemudahbakaran yang sederhana.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
AP	-	Adequate precision
APP	-	Ammonium polyphosphate
ASTM	-	American Society of Testing and Materials
ATH	-	Aluminium trihydroxide
ATR	-	Attenuated Total Reflectance
CCD	-	Central composite design
CDA	-	Chlorhexidine diacetate
CDWs	-	Construction and Demolition Wastes
CEC	-	Cation exchange capacity
CNTs	-	Carbon nanotubes
CTAB	-	Cetyl trimethylammonium bromide
CV	-	Coefficient of variance
DAMP	-	Diamino methylpentane
DAO	-	Diamino octane
DAP	-	Diamino propane
DOE	-	Design of experiment
DOPO	-	Dihydro oxaphosphaphenanthrene oxide
DTG	-	Derivative thermogravimetry
EGs	-	Expandable graphites
FESEM	-	Field Emission Scanning Electron Microscopy
FRs	-	Fire-retardants
FTIR	-	Fourier-Transform Infrared
HCl	-	Hydrochloric acid
HNTs	-	Halloysite nanotubes
HPEPO	-	Epoxidized palm oil hydrogel
HRR	-	Heat release rate
IFRs	-	Intumescent fire retardants
LOI	-	Limiting oxygen index
MDH	-	Magnesium hydroxide

MFAPP	-	Melamine-formaldehyde ammonium polyphosphate
MMT	-	Montmorillonite nanoclay
MWCNT	-	Multi-walled carbon nanotubes
Na-MMT	-	Sodium montmorillonite nanoclay
NIPU	-	Non-isocyanate polyurethane
OMMT	-	Organically-modified montmorillonite nanoclay
PA6	-	Polyamide 6
PEG	-	Poly(ethylene glycol)
PET	-	Polyethylene terephthalate
PF	-	Phenol formaldehyde
p-HRR	-	Peak heat release rate
PHU	-	Polyhydroxyurethane
PIR	-	polyisocyanurate
PMC	-	Polymer matrix composite
POP	-	Palm oil polyol
PP	-	Polypropylene
PPG	-	Poly(propylene glycol)
pphp	-	Parts per hundred parts of polyol
PS	-	Polystyrene
PU, PUR	-	Polyurethane
PVC	-	Poly(vinyl chloride)
RBD	-	Refined, bleached, and deodorised
RSM	-	Response Surface Methodology
SEM	-	Scanning Electron Microscopy
TGA	-	Thermogravimetry analysis
THE	-	Total heat evolved
THR	-	Total heat release
TML	-	Total mass loss
TPP	-	Triphenyl phosphate
VMFAPP	-	Vinyl-melamine-formaldehyde ammonium polyphosphate
XRD	-	X-ray diffraction

LIST OF SYMBOLS

A	-	Area in microscopy image
Al(OH)_3	-	Aluminium hydroxide
Al_2O_3	-	Aluminium oxide
A_o	-	Initial cross section area of specimen
APP-1	-	Pristine ammonium polyphosphate
APP-2	-	Silane-treated ammonium polyphosphate
Ca^{2+}	-	Calcium ion
CaO	-	Calcium oxide
C_F	-	Final value of measured oxygen concentration
CO	-	Carbon monoxide gas
CO_2	-	Carbon dioxide gas
C_V	-	Closed cell content of foam
d , d -spacing	-	Spacing between diffractional lattice planes
d_{001}	-	Spacing between lattice planes in [001] orientation
d_{LOI}	-	Interval between oxygen concentrations
E	-	Compressive modulus of foam
h	-	Initial height of foam
H_2	-	Helium gas
k	-	Combustion pattern-dependent factor in LOI determination
K^+	-	Potassium ion
M	-	Microscopy image magnification
m	-	Mass of specimen
Mg(OH)_3	-	Magnesium hydroxide
MgO	-	Magnesium oxide
MnO_2	-	Manganese dioxide
N	-	Cellular density
n	-	Number of cells in microscopy image
N_2	-	Nitrogen gas
Na^+	-	Sodium ion
NCO	-	Isocyanate group

NH_2	-	Amine group
NH_3	-	Ammonia group
NH_4^+	-	Ammonium ions
O_2	-	Oxygen gas
OH	-	Hydroxyl group
O_V	-	Open cell content of foam
$P_{10\%}$	-	Load at 10 % deformation
$p\text{-MDI}$	-	Diphenylmethane diisocyanate
R^2	-	Coefficient of multiple determination
$R_{H\text{-bond}}$	-	Carbonyl hydrogen index
sg	-	Specific gravity of material in solid form
SiCl_4	-	Silicon tetrachloride
SiO_2	-	Silicon dioxide
SiO_4	-	Siloxane group
SiOH	-	Silanol group
T_5	-	Onset degradation temperature at 5 % mass loss
T_{50}	-	Onset degradation temperature at 50 % mass loss
T_{bonded}	-	Intensity of transmittance at bonded urethane peak
T_{free}	-	Intensity of transmittance at free urethane peak
TiO_2	-	Titanium dioxide
V	-	Volume of foam determined by measurement
V-0, V-1, V-2	-	Ratings in UL-94 Vertical Burning Test
V_{SPEC}	-	Volume of foam determined by pycnometer
δ	-	Deformation of foam
θ	-	diffraction angle
λ	-	X-ray radiation wavelength
ρ_{foam}	-	Density of foam
ρ_{solid}	-	Density of solid polymer
σ	-	Compressive strength of foam

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

It is not an overstatement to claim that today, polyurethane (PU) has found its niche among the most widely utilised polymer products in the world. Ever since its discovery by Professor Otto Bayer and colleagues in 1938 [1], PU can be found across numerous applications, ranging from consumer level products such as shoe insoles, cushions, mattresses, piping insulations, and food packaging; to high-end applications such as in maritime and aeronautics [2–6]. This is perhaps owed to PU's versatility and ease of tailoring to suit the end product, as PU can be synthesised across numerous forms such as elastomers, flexible foams, rigid foams, shape memory foams, coatings, films, and sealants [4,7–9]. Because of its versatility, rigid PU foams emerge as the plastic with the second highest global consumption, accounting for 25 % within the PU family [10]. Although commonly found as thermal insulators and barriers, due to its improved thermal insulating properties, it is not uncommon to discover rigid PU foams in structural applications – especially as a core material in sandwich composites – due to its superior strength-to-weight ratio, high chemical and moisture resistance, high weatherability, and high durability [6,11,12].

Like other polymeric materials, PU foams depend on petrochemical feedstock. Issues on sustainability, environmental impact, and the global crisis of petroleum supply depletion however, has caused PU industrialists to find alternatives for polymeric foam production from bio-renewable resources [13]. Vegetable oils such as rapeseed oil, soybean oil, canola oil, castor oil, and palm oil have been proven, through various research projects, to be suitable replacements for petroleum-based polyols. The vegetable oils however, need to undergo modifications like transesterification and glycerolysis to introduce hydroxyl groups, which is essential to react with isocyanates to form urethane linkages [11,13–15]. Though, this process is not necessary for castor

oil as it already possess built-in hydroxyl groups [11,13]. Numerous studies have been conducted to replace petroleum-based polyol, such as polyethylene glycol (PEG), with bio-renewable polyols in the production of PU foams [12,13,16–18]. Apart from acting as an alternative for petrochemical-based polyols, bio-renewable polyols also improve the properties of the foam. It has been found that PU foams produced from vegetable oils possess a higher thermal stability than those prepared with polypropylene oxide polyols [19]. Among these bio-based polyols, palm oil polyols have garnered more attention due to their low cost in production and their abundance in countries across regions like Malaysia, Indonesia, and Thailand.

Despite, however, possessing superior mechanical properties, one major drawback of polymeric materials is its high flammability due to it being organic. And since they are widely applied in industrial settings, efforts are being undertaken to ensure that the polymers are produced with the least flammability possible. Flame retardants are therefore commonly introduced to the polymers in order to reduce their susceptibility to fires. Common strategies to incorporate these flame retardants include the addition of non-flammable fillers, inclusion of substances that promote char formation, use of endothermic-decomposing materials, and use of materials that release gas or vapours in fire scenarios [20,21]. For this last approach mentioned, halogenated compounds are usually utilised, from which fire will liberate hydrogen halides. While this method offers a low-cost solution without compromising the polymers' mechanical properties, halogen combustions release hazardous toxic gases. This toxicity is a worldwide concern and has led to the restrict the use of halogen-based flame retardants, and to find safer, more environmental-friendly counterparts [22].

One of the solutions achieved in dealing with the toxic combustion gas issue is by employing non-halogen flame retarding additives such as ammonium polyphosphate (APP), triphenyl phosphate (TPP), and melamine polyphosphate. It has been affirmed in past research literature of the flame retarding properties of these materials across different polymeric systems [23–26]. These additives respond to combustion by forming carbonaceous char which acts as a thermal barrier and hinders the transfer of heat between the polymer and burning surface; resulting in insufficient

heat to sustain the combustion and hence breaking the ‘combustion cycle’. These phosphate-based additives also combat flame growth and spread by imparting ‘*fuel cooling*’ effect [27,28], which absorbs part of the heat and again interferes with the ‘combustion cycle.’ However, even though these flame retardants have been successful in countering the fire vulnerability of polymeric materials, they are synthetically produced. One of the greener alternatives has been to incorporate nanoclays, such as montmorillonite (MMT) into the polymeric system. It has been extensively shown in past publications that these nanoclays are able to decrease fire susceptibility of polymers via the rapid formation of char layering, while at the same time enhancing the thermal stability of the polymeric system [29–31].

Apart from thermal and fire-response improvement, incorporation of MMT into polymer systems also enables improved mechanical properties for load-bearing capabilities, as reported across previous research [17,32–35]. The polymer system, however, suffers a distinguishable drop in mechanical properties with an over-inclusion of MMT. This is understood to be due to a segregation of the nanoclays and forcing the nanoclays to be intercalated within the polymer gallery rather than exfoliated [17,32,36]. Surface treatment of the MMT, via an ion exchange method, can modify MMT to be hydrophobic and facilitates its assimilation within the polymer system; allowing the clays to be exfoliated within the polymer gallery. Previous studies have shown enhanced mechanical properties and thermal stability with the inclusion of organically-modified MMT nanoclays up to a certain limit [32,37,38]. Apart from this limitation, MMT modification can be conducted with a wide array of different suitable surfactants which opens up possibilities of ‘attaching’ various material-enhancing properties onto the clay, and subsequently onto the polymeric foam being embedded by the clay – such as anti-bacterial and fire-proofing properties [39–41].

In line with global efforts towards ‘*Green Chemistry*’ [42], it is hoped that this research will not only be able synthesise PU foam from renewable resources that possess superior mechanical and flame-retarding properties, but the products will also be on par with its synthetically-manufactured counterparts.

1.2 Problem Statement

PU foams are one of the largest polymeric materials used in many cellular applications which need on-going studies to improve their properties to meet the demands. As faced by other non-renewable petroleum-based polymers and non-biodegradability characteristics, PU foams also contribute to the environmental impact and sustainability. Renewable palm oil-based polyol is a good alternative to overcome the issue, owing to its abundance and eco-friendly. However, the process of converting palm oil into polyol (one of the raw materials to make PU) has shorten the molecular chain of palm oil which negatively influences the mechanical and thermal properties of the fabricated PU foam. Furthermore, the presence of various organic chemical compounds in palm oil such as fatty acids contribute to the flammability of the foam. Issue on poor mechanical strength and thermal stability can be countered back by incorporating filler such as montmorillonite (MMT) nanoclay into the foam. A drawback, a hydrophilic nature of MMT nanoclay tends to segregate upon the incorporation into the hydrophobic PU matrix. As such, surface modification via ion-exchange method can be carried out to increase the dispersion of MMT into the matrix. On the other hand, issue on the high flammability of PU foam can be diminished by adding fire retardants (FRs) such as ammonium polyphosphate (APP) into the formulation. However, PUs with a single-FR system struggled to achieve the desired level of commercially flame-retardant systems; and as such, multiple FRs system is often applied. Apart from this, another common issue is inefficient dispersion of FRs in the PU matrix, especially at higher loadings. This problem is more prominent in multiple-filler PU system. Studies show that surface modification of MMT with an ionic-bearing compound such as amine via ionic exchange process is able to increase the interfacial adhesion between the MMT and the matrix. Hence, this study had adopted the technique by manipulating the cationic-bearing ammonium groups, $-\text{NH}_4^+$ in APP to undergo the cation exchange process with the MMT to produce APP-MMT hybrid filler. APP-MMT is thought able to impart the synergistic effect in flame retarding and smoke suppression, and also can be regarded as a 'green filler' since it is non-halogenated and releases no toxic gases. Furthermore, the ammonium tail of APP-MMT could form the hydrogen bonding with the hydroxyl groups (OH) of PU chain, thus improving the strength of the foam. The later caters the issue on the shorten

molecular chain of palm oil polyol. To overcome the issue of imbalanced enhancement and deterioration of properties, the amounts of APP-MMT loadings were optimised, using response surface methodology (RSM) as the optimization tool. Optimisation using RSM is an important process to evaluate and determine the governing effects in a multiple-fillers system. To obtain an optimised PU foam formulation, the parameters involved are the Limiting Oxygen Index (LOI) and the compressive modulus, E_c .

1.3 Research Objectives

The main aim of this study is to develop a nature-based rigid polyurethane (PU) foam which possesses high modulus and flame-retarding capabilities for use in structural applications, such as wall panels and doors. Specific objectives include:

1. To investigate the effect of polyol substitution from petrochemical-based to palm oil-based on the flame retardancy, thermal stability, material, and mechanical properties of PU foam.
2. To investigate the influence of different types and loadings of fillers on the flame retardancy, thermal stability, material, and mechanical properties of palm oil-based PU foam.
3. To determine the effect of adding MMT modified with APP on the flame retardancy, thermal stability, material, and mechanical properties of palm oil-based PU foam.
4. To obtain optimised filler loading of palm oil-based PU foam with respect to its Limiting Oxygen Index (LOI) and compressive modulus.

1.4 Scope of Study

The scope for this study includes the following:

1. Fabrication of PU foam utilizing either poly(ethylene glycol) (PEG) or palm oil as its polyol source, prior to conducting characterisation tests on both types of foam.
2. Production of several single-filler palm oil-based PU foam formulation systems; incorporating either montmorillonite (MMT) nanoclay, pristine and silane-treated ammonium polyphosphates (APPs), fumed nanosilica particles, or basalt-based rockwool fibres at varied amounts. This is followed by characterisation process on the filled-foam systems.
3. Development of multi-filler palm oil-based PU foam systems, comprising of MMT nanoclay and silane-treated APP. One system utilises both fillers separately; while the other system incorporates APP-treated MMT organoclay as filler. The filler in latter PU system is obtained by first carrying out ion exchange surface modification process on the MMT nanoclay with silane-treated APP as its surfactant.
4. Foam formulation optimisation via surface response methodology (RSM); with compressive modulus and Limiting Oxygen Index (LOI) as its output responses. Filler loading is set as the input, with two different input groups are used for optimisation process, namely combined fillers (comprising of MMT and APP) and also single filler (comprising of APP-treated MMT organoclay).

The characterisation tests involved are as follows:

- (a) Optical Microscopy
- (b) Field Emission Scanning Electron Microscopy (FESEM)
- (c) X-ray Diffraction (XRD)
- (d) Fourier Transform Infrared (FTIR) spectroscopy

- (e) Thermogravimetric Analysis (TGA)
- (f) Helium gas pycnometry – ASTM D6226
- (g) Apparent Density – ASTM D1622
- (h) Limiting Oxygen Index (LOI) – ASTM D2863
- (i) Vertical Burning Test UL-94 – ASTM D3801
- (j) Compressive properties – ASTM D1621

1.5 Significance of Study

Production of conventional polyurethane (PU) foam relies on petrochemical feedstock. With global consensus towards environment sustainability, it is becoming vital for the utilisation of bio-based resources in the production of polymers such as PU. This study seeks to develop a nature-based PU foam composite that possesses both high modulus and flame-retarding properties, on par with its conventional counterparts. This polymeric foam is synthesised using palm oil-based polyol and distilled water as the blowing agent, and uses nature-based resources in its production. The fillers also comprise of bio-based resources such as montmorillonite (MMT) nanoclay and basalt-based rockwool, which possess latent potential to enhance flame-retardancy, thermal stability, mechanical and material properties. To date, little emphasis has been given to the study of flame-retardancy and other property enhancements using nature-based materials such as MMT in polymeric foams – let alone investigating the flame, thermal, material, and mechanical response of ammonium polyphosphate (APP) -modified nanoclays in palm oil-based PU foam – a novel aspect of this study.

1.6 Summary of Thesis

CHAPTER 1 is the introduction chapter. This chapter introduces the study by explaining its background, the problem statement, the research objectives and scopes, and also the significance of the study.

CHAPTER 2 is the study's literature review which is divided into three main parts. The first part elaborates polyurethane (PU) foam attributes. Topics covered include the background of polyurethane and different types of bio-based polyurethane foam is reviewed in detail in this sub-chapter. The second part considers the flame retardancy component of the research, which covers topics such as mechanics and modes of flame retardancy, as well as its methods of employment in polymers. The third and last part of this chapter discusses this study's optimisation, specifically on the response surface methodology (RSM). Topics that are investigated in this sub-chapter include the theory behind RSM and the application of RSM as an optimisation tool.

CHAPTER 3 explains the research methodology used in the research. The research methodology includes details on the materials used, the fabrication process of foams, clay modification process, and also the characterisation testing methods.

CHAPTER 4 explains the outcome of this research. Detailed explanations and discussions are provided based on the data obtained from the characterisation tests. Results from this study are also compared to other studies, where applicable.

CHAPTER 5 concludes the study. A brief and concise concluding remark is provided in this chapter, which highlights the overall outcome of this research. The end of this chapter includes a number of recommendations for future research enquiries.

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LIST OF PUBLICATIONS

Indexed Journal

1. **Dzulkifli, M. H.**, Yahya, M. Y. and Majid, R. A. Rigid palm oil-based polyurethane foam reinforced with diamine-modified montmorillonite nanoclay. *IOP Conference Series: Materials Science and Engineering*, 2017. 204: 012024. <https://doi.org/10.1088/1757-899X/204/1012024>. (**Indexed by SCOPUS**)

Non-Indexed Conference Proceedings

1. **Dzulkifli, M. H.**, Yahya, M. Y. and Majid, R. A. Bio-based rigid polyurethane foam reinforced with diamine-modified montmorillonite. In *2017 International Conference on Bio and Nanotechnology (ICBN 2017)*.