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

NIK NURFATMAH PZ BINTI NIK PAUZI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Master of Engineering (Polymer)

Faculty of Chemical Engineering
Universiti Teknologi Malaysia

MARCH 2014

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

ACKNOWLEDGEMENTS

In the process to prepare this thesis, I have met many people, who have helped and contributed towards my understanding and thoughts. First and foremost, my heartfelt gratitude goes to my supervisor, Dr. Rohah A.Majid. This research work surely would not be a success without all of her encouragement, advices, helps, criticisms and guidance.

I wish to express my deep appreciation to all the technicians of Laboratory of Polymer Engineering: Mr. Nordin, Mr. Izzat, Ms. Zainab and Mr. Azri for their technical supports during the experiments and testing. I am also indebted with Talisman Malaysia Limited (TML) for funding my master study.

My sincere appreciation also extends to all my colleagues who have provided assistance on various occasions. Finally, I would like to express my greatest gratitude to my late father, mother and brothers for making this research a successful one. Thank you.

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.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

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

LIST OF APPENDICES

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.

REFERENCES

Abraham, T. W., Carter, J. A., Malsam, J. and Zlatanic, A. B. (2007). *U.S Patent No US20100261805*. Washington DC: U.S, Patent amd Trademark Office.

Adam, W., Lan, X., Eve, R., Jian, L., Carrie, R. and Christina, H. (2011). Immune Sensitization to Methylene Diphenyl Diisocyanate (Mdi) Resulting from Skin Exposure: Albumin as a Carrier Protein Connecting Skin Exposure to Subsequent Respiratory Responses. *Journal of Occupational Medicine and Toxicology*. 6(1), 1-12.

Ahmad, M. B., Hoidy, W. H., Ibrahim, N. A. B. and AI-Mulla, E. A. J. (2009). Modification of Montmorulonite by New Surfactants. *Journal of Engineering and Applied Sciences*. 4(3), 184-188.

Alexandre, M. and Dubois, P. (2000). Polymer-Layered Silicate Nanocomposites: Preparation, Properties and Uses of a New Class of Materials. *Materials Science and Engineering: R: Reports*. 28(1), 1-63.

Aneja, A. (2002). *Structure-Property Relationships of Flexible Polyurethane Foams.* Doctor Philosophy. Virginia Polytechnic Institute and State University.

Azeredo, H. (2009). Nanocomposites for Food Packaging Applications. *Food Research International*. 42(9), 1240-1253.

Badri. (2012). Biobased Polyurethane from Palm Kernel Oil-Based Polyol. Randall, D. and Lee, S. *The Polyurethane Book.* (pp. 447-470). U.S.A.: Technology and Engineering.

Basiron, Y. (2007). Palm Oil Production through Sustainable Plantations. *European Journal of Lipid Science and Technology*. 109(4), 289-295.

Borduz, L., Hirota, Y. and Tsuda, S. (2002). *EP 1224670 A1*. Ferrotac Corporation: European Patent Register.

Burkhart, G. and Weier, A. (1999). Silicone Surfactants in Polyurethane Foam Production: One Additive for a Wide Range of Tasks. Proceedings of the 1999. *Catalysts and surfactants in polyurethane foams. Seminar*.

Cai, Y., Hu, Y., Song, L., Liu, L., Wang, Z. and Chen, Z. (2007). Synthesis and Characterization of Thermoplastic Polyurethane/Montmorillonite Nanocomposites Produced by Reactive Extrusion. *Journal of Materials Science*. 42(14), 5785-5790.

Cai, D. and Song, M. (2010). Recent Advance in Functionalized Graphene/Polymer Nanocomposites. Journal of Materials Chemistry. 20(37), 7906-7915.

Canaday, J. and Skowronski, M. (1985). A Comparison of Aromatic Polyester Polyols for Rigid Urethane and Isocyanurate Foam. *Journal of Cellular Plastics*. 21(5), 338-344.

Cao, X., Lee, L. J., Widya, T. and Macosko, C. (2005). Polyurethane/Clay Nanocomposites Foams: Processing, Structure and Properties. *Polymer* 46, 775–783.

Carter, C., Finley, W., Fry, J., Jackson, D. and Willis, L. (2007). Palm Oil Markets and Future Supply. *European Journal of Lipid Science and Technology*. 109(4), 307-314.

Chalermpan Keawkumay (2009). *Effect of Clay Surface Modification on Physical Properties of Natural Rubber Nanocomposites.* Degree of Master of Engineering in Polymer Engineering. Suranee University of Technology.

Chen, T. K., Tien, Y. I. and Wei, K. H. (2000). Synthesis and Characterization of Novel Segmented Polyurethane/Clay Nanocomposites. *Polymer*. 41(4), 1345-1353.

Cheong, I. W., Kong, H. C., An, J. H. and Kim, J. H. (2004). Synthesis and Characterization of Polyurethane–Urea Nanoparticles Containing Methylenedi-P-Phenyl Diisocyanate and Isophorone Diisocyanate. *Journal of Polymer Science Part A: Polymer Chemistry*. 42(17), 4353-4369.

Chian, K. and Gan, L. (1998). Development of a Rigid Polyurethane Foam from Palm Oil. *Journal of Applied Polymer Science*. 68(3), 509-515.

Chuayjuljit, S., Maungchareon, A. and Saravari, O. (2010). Preparation and Properties of Palm Oil-Based Rigid Polyurethane Nanocomposite Foams. *Journal of Reinforced Plastics and Composites*. 29(2), 218-225.

Chuayjuljit, S., Sangpakdee, T. and Saravari, O. (2007). Processing and Properties of Palm Oil-Based Rigid Polyurethane Foam. *Journal of Metals, Materials and Minerals*. 17(1), 17-23.

Chun, B. C., Cho, T. K., Chong, M. H., Chung, Y. C., Chen, J., Martin, D. (2007). Mechanical Properties of Polyurethane/Montmorillonite Nanocomposite Prepared by Melt Mixing. *Journal of Applied Polymer Science*. 106(1), 712-721.

Cyras, V. P., Manfredi, L. B., Ton-That, M.-T. and Vázquez, A. (2008). Physical and Mechanical Properties of Thermoplastic Starch/Montmorillonite Nanocomposite Films. *Carbohydrate Polymers*. 73(1), 55-63.

Das, S., Dave, M. and Wilkes, G. (2008). Characterization of Flexible Polyurethane Foams Based on Soybean-Based Polyols. *Journal of Applied Polymer Science*. 112(1), 299-308.

Decaire, B. R.; Pham, H. T.; Richard, R. G.; Shankland, I. R (1992). BlowingAgents: The Next Generation. Proceedings of the SPI-34th Annual Technical /Marketing Conference. Technomic, Lancaster: 2-11.

Desroches, M., Escouvois, M., Auvergne, R., Caillol, S. and Boutevin, B. (2012). From Vegetable Oils to Polyurethanes: Synthetic Routes to Polyols and Main Industrial Products. Polymer Reviews. 52(1), 38-79.

Ding, Q., Liu, B., Zhang, Q., He, Q., Hu, B. and Shen, J. (2006). Synthesis and Characterization of Polyurethane/Montmorillonite Nanocomposites by in Situ Polymerization. *Polymer International*. 55(5), 500-504.

Dong, H. and Stucki, J. W. (2011). Advances in Clay Science in China. *Clays and Clay Minerals*. 59(5), 435-437.

Efstathiou, K. (2008). Synthesis and Characterization of a Polyurethane Prepolymer for the Development of a Novel Acrylate-Based Polymer Foam.

Erdodi, G., Kang, J., Kennedy, J. P., Yilgor, E. and Yilgor, I. (2009). Polyisobutylene-Based Polyurethanes. III. Polyurethanes Containing Pib/Ptmo Soft Co-Segments. *Journal of Polymer Science Part A: Polymer Chemistry*. 47(20), 5278-5290.

Esmaeilnezhad, E., Rezaei, M. and Karim Razavi, M. (2009). The Effect of Alternative Blowing Agents on Microstructure and Mechanical Characteristics of Rigid Polyurethane Foam. *Iranian Polymer Journal*. 18, 569-579.

Fan, H., Tekeei, A., Suppes, G. J. and Hsieh, F. H. (2012). Properties of Biobased Rigid Polyurethane Foams Reinforced with Fillers: Microspheres and Nanoclay. *International Journal of Polymer Science.* 2012.

Fischer, W. and Magdeburg, D. (1998). Production of High Concentrated Monoglyceride. Proceedings of the 1998 *DGF-Symposium in Magdeburg. Germany: UIC, GmbH*, 2-14.

Grimminger, J. and Muha, K. (1995). Silicone Surfactants for Pentane Blown Rigid Foam. *Journal of Cellular Plastics*. 31(1), 48-72.

Guo, A., Javni, I. and Petrovic, Z. (2000). Rigid Polyurethane Foams Based on Soybean Oil. *Journal of Applied Polymer Science*. 77(2), 467-473.

Han, M. S., Choi, S. J., Kim, J. M., Kim, Y. H., Kim, W. N., Lee, H. S. (2009). Effects of Silicone Surfactant on the Cell Size and Thermal Conductivity of Rigid Polyurethane Foams by Environmentally Friendly Blowing Agents. *Macromolecular Research*. 17(1), 44-50.

He, H., Zhou, Q., Martens, W. N., Kloprogge, T. J., Yuan, P., Xi, Y., et al. (2006). Microstructure of Hdtma+-Modified Montmorillonite and Its Influence on Sorption Characteristics. *Clays and Clay Minerals*. 54(6), 689-696.

Herrington, R. and Hock, K. (1998). Flexible Polyurethane Foams Dow Chemical Co. *Midland, MI*.

Hirose, S., Kobashigawa, K. and Hatakeyama, H. (1994). Preparation and Physical Properties of Polyurethanes Derived from Molasses. *Sen'i Gakkaishi*. 50(11), 538-542.

Hussain, F., Hojjati, M., Okamoto, M. and Gorga, R. E. (2006). Review Article: Polymer-Matrix Nanocomposites, Processing, Manufacturing, and Application: An Overview. *Journal of Composite Materials*. 40(17), 1511-1575.

Jang, E. S., Khan, S. B., Seo, J., Nam, Y. H., Choi, W. J., Akhtar, K. (2011). Synthesis and Characterization of Novel Uv-Curable Polyurethane–Clay Nanohybrid: Influence of Organically Modified Layered Silicates on the Properties of Polyurethane. *Progress in Organic Coatings*. 71(1), 36-42.

Jang, L. W., Kim, E. S., Kim, H. S. and Yoon, J. S. (2005). Preparation and Characterization of Polypropylene/Clay Nanocomposites with Polypropylene-Graft-Maleic Anhydride. *Journal of Applied Polymer Science*. 98(3), 1229-1234.

Javni, I., Petrović, Z. S., Guo, A. and Fuller, R. (2000). Thermal Stability of Polyurethanes Based on Vegetable Oils. *Journal of Applied Polymer Science*. 77(8), 1723-1734.

Javni, I., Zhang, W. and Petrović, Z. S. (2003). Effect of Different Isocyanates on the Properties of Soy-Based Polyurethanes. *Journal of Applied Polymer Science*. 88(13), 2912-2916.

Jiang, H., Qian, J., Bai, Y., Fang, M. and Qian, X. (2006). Preparation and Properties of Polyurethane/Montmorillonite Nanocomposites Cured under Room Temperature. *Polymer Composites*. 27(5), 470-474.

Kadkin, O., Osajda, K., Kaszynski, P. and Barber, T. A. (2003). Polyester Polyols: Synthesis and Characterization of Diethylene Glycol Terephthalate Oligomers. *Journal of Polymer Science Part A: Polymer Chemistry*. 41(8), 1114-1123.

Kato, R., Liauw, C. M., Allen, N. S., Irure, A., Wilkinson, A. N., Stanford, J. L. (2008). Interfacial Interactions in Polymer-Layered Silicate Nanocomposites. *Langmuir*. 24(5), 1943-1951.

Kaushiva, B. D. (1999). *Structure-Property Relationships of Flexible Polyurethane Foams.* Virginia Polytechnic Institute and State University.

Kim, D. W., Lim, C. H., Choi, J. K. and Noh, S. T. (2004). Thermal Properties of Polydisperse Oligo (Propylene Oxide-Block-Ethylene Oxide) Allyl (Methyl) Ether Surfactants Containing Polysiloxane Backbone. *Journal Of Industrial And Engineering Chemistry-Seoul*. 10(4), 569-576.

Krupers, M. J., Bartelink, C. F., Grünhauer, H. J. and Moller, M. (1998). Formation of Rigid Polyurethane Foams with Semi-Fluorinated Diblock Copolymeric Surfactants. *Polymer*. 39(10), 2049-2053.

Lakard, B., Herlem, G., Lakard, S., Guyetant, R. and Fahys, B. (2005). Potentiometric Ph Sensors Based on Electrodeposited Polymers. *Polymer*. 46(26), 12233-12239.

Lay, D., G. and Cranley, P. (2003). *Handbook of Adhesive Technology*. 2nd. ed. Texas, U.S.A.: Taylor and Francais Group.

Learning Center Surfactant (2006). *Polyurethanes* [Brochure]. Werner Blank.

Lee, L. J., Zeng, C., Cao, X., Han, X., Shen, J. and Xu, G. (2005). Polymer Nanocomposite Foams. *Composites Science and Technology*. 65(15), 2344-2363.

Leszczyńska, A., Njuguna, J., Pielichowski, K. and Banerjee, J. (2007). Polymer/Montmorillonite Nanocomposites with Improved Thermal Properties: Part I. Factors Influencing Thermal Stability and Mechanisms of Thermal Stability Improvement. *Thermochimica Acta*. 453(2), 75-96.

Liang, Z. M., Yin, J. and Xu, H. J. (2003). Polyimide/Montmorillonite Nanocomposites Based on Thermally Stable, Rigid-Rod Aromatic Amine Modifiers. *Polymer*. 44(5), 1391-1399.

Lim, H., Kim, S. and Kim, B. (2008). Effects of Silicon Surfactant in Rigid Polyurethane Foams. *Express Polymer Letters*. 2(3), 194-200.

Mahesh, K. R. V., Murthy, H. N. N., Kumaraswamy, B. E., Raghavendra, N., Sridhar, R., Krishna, M. (2011). Synthesis and Characterization of Organomodified Na-Mmt Using Cation and Anion Surfactants. *Frontiers of Chemistry in China*. 6(2), 153-158.

Marten, M., Godau, C. and Schmelzer, H. (1991). Use of Polyamidoamines as Curing Agents for Epoxy Resins and Curable Mixtures Containing These Substances Wherein the Acid Component Has Oxyalkylene (Repeating) Units: Google Patents.

Miri, V., Elkoun, S., Peurton, F., Vanmansart, C., Lefebvre, J.-M., Krawczak, P. (2008). Crystallization Kinetics and Crystal Structure of Nylon6-Clay Nanocomposites: Combined Effects of Thermomechanical History, Clay Content, and Cooling Conditions. *Macromolecules*. 41(23), 9234-9244.

Mishra, A. and Maiti, P. (2011). Morphology of Polyurethanes at Various Length Scale: The Influence of Chain Structure. *Journal of Applied Polymer Science*. 120(6), 3546-3555.

Modesti, M., Lorenzetti, A., Besco, S., Hrelja, D., Semenzato, S., Bertani, R. (2008). Synergism between Flame Retardant and Modified Layered Silicate on Thermal Stability and Fire Behaviour of Polyurethane Nanocomposite Foams. *Polymer Degradation and Stability*. 93(12), 2166-2171.

Mondal, P. and Khakhar, D. (2004). Hydraulic Resistance of Rigid Polyurethane Foams. I. Effect of Different Surfactants on Foam Structure and Properties. *Journal of Applied Polymer Science*. 93(6), 2821-2829.

Mosiewicki, M., Dell'Arciprete, G., Aranguren, M. and Marcovich, N. (2009). Polyurethane Foams Obtained from Castor Oil-Based Polyol and Filled with Wood Flour. *Journal of Composite Materials*. 43(25), 3057-3072.

Mravcakova, M., Omastova, M., Pötschke, P., Pozsgay, A., Pukanszky, B. and Pionteck, J. (2006). Poly (Propylene)/Montmorillonite/Polypyrrole Composites: Structure and Conductivity. *Polymers for Advanced Technologies*. 17(9-10), 715-726.

Narine, S. S., Kong, X., Bouzidi, L. and Sporns, P. (2007). Physical Properties of Polyurethanes Produced from Polyols from Seed Oils: II. Foams. *Journal of the American Oil Chemists' Society*. 84(1), 65-72.

Ni, P., Li, J., Suo, J. and Li, S. (2004). Novel Polyether Polyurethane/Clay Nanocomposites Synthesized with Organic-Modified Montmorillonite as Chain Extenders. *Journal of Applied Polymer Science*. 94(2), 534-541.

Njuguna, J., Michałowski, S., Pielichowski, K., Kayvantash, K. and Walton, A. C. (2011). Fabrication, Characterization and Low-Velocity Impact Testing of Hybrid Sandwich Composites with Polyurethane/Layered Silicate Foam Cores. *Polymer Composites*. 32(1), 6-13.

Noureddini, H. and Medikonduru, V. (1997). Glycerolysis of Fats and Methyl Esters. *Journal of the American Oil Chemists' Society*. 74(4), 419-425.

Oertel, G. and Abele, L. (1985). *Polyurethane Handbook: Chemistry, Raw Materials, Processing, Application, Properties*: Hanser Publishers. Distributed in USA by Scientific and Technical Books, Macmillan.

Okamoto, M. (2006). Recent Advances in Polymer/Layered Silicate Nanocomposites: An Overview from Science to Technology. *Materials Science and Technology*. 22(7), 756-779.

Ooi, T., Ahmad, S., Hassan, H. and Chong, Y. (2006). An Overview of R&D in Palm Oil-Based Polyols and Polyurethanes in Mpob. *Palm Oil Developments*. 44, 1-7.

Pan, X. and Saddler, J. N. (2013). Effect of Replacing Polyol by Organosolv and Kraft Lignin on the Property and Structure of Rigid Polyurethane Foam. *Biotechnology for Biofuels*. 6(1), 12.

Park, S. J., Li, K. and Hong, S. K. (2005). Preparation and Characterization of Layered Silicate-Modified Ultrahigh-Molecular-Weight Polyethylene Nanocomposites. *Journal Industrial Engineering Chemical*. 4(11), 561-566.

Pashaei, S., Siddaramaiah and Syed, A. A. (2011). Thermal Characteristics of Nanostructured Filler-Incorporated Polyvinylester Nanocomposites. *Polymer-Plastics Technology and Engineering*. 50(10), 973-982.

Pauluhn, J., Brown, W. E., Hext, P., Leibold, E. and Leng, G. (2006). Analysis of Biomarkers in Rats and Dogs Exposed to Polymeric Methylenediphenyl Diisocyanate (Pmdi) and Its Glutathione Adduct. *Toxicology*. 222(3), 202-212.

Petrović, Z. S. (2008). Polyurethanes from Vegetable Oils. *Polymer Reviews*. 48(1), 109-155.

Pfister, D. P., Xia, Y. and Larock, R. C. (2011). Recent Advances in Vegetable Oil-Based Polyurethanes. *ChemSusChem*. 4(6), 703-717.

Pradhan, K. C. and Nayak, P. (2012). Synthesis and Characterization of Polyurethane Nanocomposite from Castor Oil-Hexamethylene Diisocyanate (HMDI). *Advances in Applied Science Research.*

Press, I. (2010). Nano Modified Food Starch and the Therapeutic Use of Essential Oils and Oil Blends.

Prociak, A., Rojek, P. and Pawlik, H. (2012). Flexible Polyurethane Foams Modified with Natural Oil Based Polyols. *Journal of Cellular Plastics*. 3(5), 3045-3052.

Richter, R. and Ulrich, H. (2010). Syntheses and Preparative Applications of Isocyanates. *Cyanates and Their Thio Derivatives.* 2 (1977), 619-818.

Rihayat, T., Saari, M., Suraya, A., Mahmood, M. H., Dahlan, K. Z. H. M., Yunus, W. M. Z. W. (2006). Synthesis and Thermal Characterization of Polyurethane/Clay Nanocomposites Based on Palm Oil Polyol. *Polymer-Plastics Technology and Engineering*. 45(12), 1323-1326.

Saha, M., Kabir, M. E. and Jeelani, S. (2008). Enhancement in Thermal and Mechanical Properties of Polyurethane Foam Infused with Nanoparticles. *Materials Science and Engineering: A*. 479(1), 213-222.

Saint-Michel, F., Chazeau, L. and Cavaillé, J. Y. (2006). Mechanical Properties of High Density Polyurethane Foams: II Effect of the Filler Size. *Composites Science and Technology*. 66(15), 2709-2718.

Semenzato, S., Lorenzetti, A., Modesti, M., Ugel, E., Hrelja, D., Besco, S., (2009). A Novel Phosphorus Polyurethane Foam/Montmorillonite Nanocomposite: Preparation, Characterization and Thermal Behaviour. *Applied Clay Science*. 44(1–2), 35-42.

Shaari, N. Z. K., Lye, O. and Ahmad, S. (2006). Production of Moulded Palm-Based Flexible Polyurethane Foams. *Journal of Oil Palm Research*. 18, 198.

Sharma, V. and Kundu, P. (2008). Condensation Polymers from Natural Oils. *Progress in Polymer Science*. 33(12), 1199-1215.

Shogren, R., Petrovic, Z., Liu, Z. and Erhan, S. (2004). Biodegradation Behavior of Some Vegetable Oil-Based Polymers. *Journal of Polymers and the Environment*. 12(3), 173-178.

Singh, H., Sharma, T. and Jain, A. (2007). Reactivity of the Raw Materials and Their Effects on the Structure and Properties of Rigid Polyurethane Foams. *Journal of Applied Polymer Science*. 106(2), 1014-1023.

Singla, P., Mehta, R. and Upadhyay, S. N. (2012). Clay Modification by the Use of Organic Cations. *Green and Sustainable Chemistry*. 2(1), 21-25.

Siwayanan, P., Shaari, N. Z. K., Ahmad, S., Wiese, D. and Chua, M. (1999). Polyurethanes from Palm-Based Polyols. *Palm Oil Technical Bulletin*. 5.

Song, L., Hu, Y., Tang, Y., Zhang, R., Chen, Z. and Fan, W. (2005). Study on the Properties of Flame Retardant Polyurethane/Organoclay Nanocomposite. *Polymer Degradation and Stability*. 87(1), 111-116.

Soulestin, J., Rashmi, B. J., Bourbigot, S., Lacrampe, M. F. and Krawczak, P. (2012). Mechanical and Optical Properties of Polyamide 6/Clay Nanocomposite Cast Films: Influence of the Degree of Exfoliation. *Macromolecular Materials and Engineering*. 297(5), 444-454.

Stirna, U., Cabulis, U. and Beverte, I. (2008). Water-Blown Polyisocyanurate Foams from Vegetable Oil Polyols. *Journal of Cellular Plastics*. 44(2), 139-160.

Tan, S., Abraham, T., Ference, D. and Macosko, C. W. (2011). Rigid Polyurethane Foams from a Soybean Oil-Based Polyol. *Polymer*. 52(13), 2840-2846.

Tanaka, R., Hirose, S. and Hatakeyama, H. (2008). Preparation and Characterization of Polyurethane Foams Using a Palm Oil-Based Polyol. *Bioresource Technology*. 99(9), 3810-3816.

Tang, Z., Maroto-Valer, M. M., Andrésen, J. M., Miller, J. W., Listemann, M. L., McDaniel, P. L. (2002). Thermal Degradation Behavior of Rigid Polyurethane Foams Prepared with Different Fire Retardant Concentrations and Blowing Agents. *Polymer*. 43(24), 6471-6479.

Taverna, M. and Corradi, P. (1996). Liquid-Carbon-Dioxide-Blown Moulded Foams: Latest Developments for an Industrial Application. UTECH96. London, Paper 10.

Thirumal, M., Khastgir, D., Singha, N. K., Manjunath, B. and Naik, Y. (2008). Effect of Foam Density on the Properties of Water Blown Rigid Polyurethane Foam. *Journal of Applied Polymer Science*. 108(3), 1810-1817.

Tiwari, R. R., Khilar, K. C. and Natarajan, U. (2008). Synthesis and Characterization of Novel Organo-Montmorillonites. *Applied Clay Science*. 38(3), 203-208.

Tjong, S. (2006). Structural and Mechanical Properties of Polymer Nanocomposites. *Materials Science and Engineering: R: Reports*. 53(3), 73-197.

Triwulandari, E., Prihastuti, H., Haryono, A. and Susilo, E. (2007). Synthesis and Structure Properties of Rigid Polyurethane Foam from Palm Oil Based Polyol. *Indonesian Journal of Materials Science.* 31-36.

Tu, Y. C., Kiatsimkul, P., Suppes, G. and Hsieh, F. H. (2007). Physical Properties of Water-Blown Rigid Polyurethane Foams from Vegetable Oil-Based Polyols. *Journal of Applied Polymer Science*. 105(2), 453-459.

Utracki, L., Sepehr, M. and Boccaleri, E. (2007). Synthetic, Layered Nano-Particles for Polymeric Nanocomposites (Pnc's). *Polymers for Advanced Technologies*. 18(1), 1-37.

Vaidya, U. and Nadkarni, V. (2003). Polyester Polyols for Polyurethanes from Pet Waste: Kinetics of Polycondensation. *Journal of Applied Polymer Science*. 35(3), 775-785.

Veronese, V. B., Menger, R. K., Forte, M. M. d. C. and Petzhold, C. L. (2011). Rigid Polyurethane Foam Based on Modified Vegetable Oil. *Journal of Applied Polymer Science*. 120(1), 530-537.

Wang, C. C., Juang, L. C., Lee, C.-K., Hsu, T. C., Lee, J. F. and Chao, H. P. (2004). Effects of Exchanged Surfactant Cations on the Pore Structure and Adsorption Characteristics of Montmorillonite. *Journal of Colloid and Interface Science*. 280(1), 27-35.

Widya, T. and Macosko, C. W. (2005). Nanoclay-Modified Rigid Polyurethane Foam. *Journal of Macromolecular Science, Part B: Physics*. 44(6), 897-908.

Williams, S. R., Wang, W., Winey, K. I. and Long, T. E. (2008). Synthesis and Morphology of Segmented Poly (Tetramethylene Oxide)-Based Polyurethanes Containing Phosphonium Salts. *Macromolecules*. 41(23), 9072-9079.

Wong, C. S. and Badri, K. H. (2012). Chemical Analyses of Palm Kernel Oil-Based Polyurethane Prepolymer. *Materials Sciences and Applications*. 3(2), 78-86.

Woods, G. (1982). *Flexible Polyurethane Foams: Chemistry and Technology*: Applied Science Publishers London.

Wu, J.-W., Sung, W.-F. and Chu, H.-S. (1999). Thermal Conductivity of Polyurethane Foams. International journal of heat and mass transfer. 42(12), 2211-2217.

Xi, Y., Frost, R. L. and He, H. (2007). Modification of the Surfaces of Wyoming Montmorillonite by the Cationic Surfactants Alkyl Trimethyl, Dialkyl Dimethyl, and Trialkyl Methyl Ammonium Bromides. *Journal of Colloid and Interface Science*. 305(1), 150-158.

Xu, Z., Tang, X., Gu, A. and Fang, Z. (2007). Novel Preparation and Mechanical Properties of Rigid Polyurethane Foam/Organoclay Nanocomposites. *Journal of Applied Polymer Science*. 106(1), 439-447.

Yoon, K. B., Sung, H. D., Hwang, Y. Y., Kyun Noh, S. and Lee, D. H. (2007). Modification of Montmorillonite with Oligomeric Amine Derivatives for Polymer Nanocomposite Preparation. *Applied Clay Science*. 38(1), 1-8.

Yunus, R., Fakhru'l-Razi, A., Ooi, T. L., Iyuke, S. E. and Perez, J. M. (2004). Lubrication Properties of Trimethylolpropane Esters Based on Palm Oil and Palm Kernel Oils. *European Journal of Lipid Science and Technology*. 106(1), 52-60.

Zeng, Q., Yu, A., Lu, G. and Paul, D. (2005). Clay-Based Polymer Nanocomposites: Research and Commercial Development. *Journal Of Nanoscience and Nanotechnology*. 5(10), 1574-1592.

Zhang, X., Macosko, C., Davis, H., Nikolov, A. and Wasan, D. (1999). Role of Silicone Surfactant in Flexible Polyurethane Foam. *Journal of Colloid and Interface Science*. 215(2), 270-279.

Zhang, X., Xu, R., Wu, Z. and Zhou, C. (2003). The Synthesis and Characterization of Polyurethane/Clay Nanocomposites. Polymer International. 52(5), 790-794.

Zhang, Z., Liao, L. and Xia, Z. (2010). Ultrasound-Assisted Preparation and Characterization of Anionic Surfactant Modified Montmorillonites. *Applied Clay Science*. 50(4), 576-581.

Zlatanić, A., Lava, C., Zhang, W. and Petrović, Z. S. (2004). Effect of Structure on Properties of Polyols and Polyurethanes Based on Different Vegetable Oils. *Journal of Polymer Science Part B: Polymer Physics*. 42(5), 809-819.