

## The Manufacture of Palm Oil-Based Polyurethane Nanocomposite with Organic Montmorillonite Nanoparticle as Paint Coatings

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**Abstract:** This research reports the manufacture of palm oil-based polyurethane nanocomposite with organic montmorillonite nanoparticle as paint coating. This research consists of five stages namely the manufacture of polyol, organic montmorillonite nanoparticle, properties and application of polyurethane nanocomposite as paint coating. Polyols are formed by reacting epoxides with palm oil-based oleic acid hydroxyl. Organic montmorillonite nanoparticle was made through intercalation process of montmorillonite with cetyl trimethyl ammonium bromide (CTAB). Polyurethane nanocomposite (POB-PU/MMT) was made by adding 5% (b/b) of organic montmorillonite nanoparticle into polyol before being combined with isocyanate. Polyurethane nanocomposite functional groups are characterized by spectroscopy FT-IR technique and its thermal characterized by using *Thermogravimetric Analysis* (TGA). The effectiveness of polyurethane nanocomposite as coating additive was determined from its adhesivability and gloss index. FT-IR spectrum of polyurethane nanocomposite shows particular absorption of urethane. Thermogram analysis results indicate that palm oil-based polyurethane nanocomposite with organic montmorillonite nanoparticle has higher temperature of decomposition compared with the one without organic montmorillonite (Commercial PU) and commercial polyurethane. The effectiveness of polyurethane nanocomposite as paint coatings has been analyzed. Commercial PU and POB-PU adhesive forces increase from classification 2 (two) to classification 1 (one) after being added with organic montmorillonite (POB-PU/MMT). As well as adhesivability, the gloss index also increases until 4%.

**Key words:** palm oil, polyol, polyurethane, montmorillonite, adhesive.

### 1. Introduction

Polyurethane is a polymer composed with urethane groups (-NHCOO-) in its main chain, urethane groups are formed by reacting Isocyanate with hydroxyl groups<sup>1</sup>. Polyurethane is a polymer material which is varied, easy to be formed for several applications and can be produced as foam, elastomer, plastic, adhesive and coating.

Indonesia is the largest palm oil producer in the world<sup>2</sup>, and palm oil contains of 45 – 60% unsaturated double bonds. Therefore, epoxidation reaction involving catalyst occurs at certain level of temperature and pressure which forms palm oil-based epoxide that can be used as polyol, the raw material of Polyurethane through epoxidation and hydroxylation reaction<sup>3</sup>. Vegetable oil is one of raw material alternatives that also can be used to produce polyol compound, vegetable oil that can be used as polyol compound are soybean oil<sup>4</sup>,

castor oil, nahar oil<sup>5</sup> and palm oil<sup>6</sup>. Polyol is one of polymer products used in coatings and polyurethane paint industries. Compared with crude oil-based polyol, vegetable oil-based polyol has some advantages because the source is renewable, easily obtained and eco-friendly. In addition, its processing cost is low<sup>7</sup>.

Bentonite is a cheap mineral and is important in polymer industries where its utility as filler is very economical in order to increase material performance. The main content of bentonite is montmorillonite mineral (85%) with chemical formula  $M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4.nH_2O$ . Montmorillonite is often used in a variety of industry applications because of its high ratio, plate morphology, availability and low manufacturing cost. Montmorillonite silicate layers which can be intercalated and exfoliated cause people to use it as nanocomposite fillers in order to increase its physical properties<sup>8</sup>.

The main component in paint coating manufacture is binder or resin derived from synthetic or natural resin, such as vegetable oil, protein or fat. Binder is responsible in film formation and acts as adhesive in paint surface. Among all types of binder, polyurethane resin is more dominant in market because it has very good performance characteristics, such as resistance to corrosion, abrasion and chemical substances. In addition, it is also very flexible so it is often used as coatings for metal and other kinds of industries<sup>9</sup>.

Synthesis and application of *Jatropha curcas* oil-based polyurethane as coatings on ABS plastic<sup>10</sup> have been carried out and the synthesis has been carried out by extending chains of surface coating by adding butanediol and polycaprolatenediol<sup>11</sup>. Besides its advantages, Polyurethane also has disadvantage which is its nature, such as low resistance to heat compared with other types of polymers<sup>12</sup>. The combination of polyurethane matrix with organoclay<sup>13</sup> as well as its mixture with Polyethylene can increase adhesive property<sup>14</sup>.

From this information, researcher intends to conduct the research in order to increase heat of palm oil-based polyurethane polyol by adding montmorillonite into polyurethane matrix as well as adhesivability and gloss index of polyurethane nanocomposite by adding montmorillonite.

## 2. Experiment

### 2.1 Material

Natural bentonite taken from North Aceh, palm oil oleic acid, Glycerol 85% (Merck), diethyl metana diisocyanate (Merck), Peroxide 35% (Merck), glacial acetic acid (Merck),  $H_2SO_4$  (Merck), dibutyltin dilaurat (Merck), cetyl trimethyl ammonium bromide (Merck).

### 2.2. Epoxidation and hydroxylation of palm oil.

60 ml of glacial acetic acid was put into reactor while 30 ml of 35 percent  $H_2O_2$  added gradually while being stirred. Using funnel dropper, 2 ml of concentrated  $H_2SO_4$  was added and stirred in the temperature of 40-45°C for 1 hour. Then, 100 ml of palm oil oleic acid was added using funnel dropper at the same temperature while being stirred for 2 hours. The reaction result is an epoxy compound of oleic acid which later being separated from water phase. Then, waterbath was connected to the reactor, 50 ml of glycerol added while stirring at room temperature and 2 ml of concentrated  $H_2SO_4$  added. To this mixture, 50 ml of ethanol p.a was added gradually and epoxy compound of oleic acid was put using funnel dropper. The mixture was being refluxed for 5 hours, and the reaction result was being evaporated. Filter result was being evaporated to obtain polyol and being tested using FTIR Shimadzu to prove hydroxyl group<sup>4,10</sup> and to determine hydroxyl value using Wijs, AOAC 1995 method.

### 2.3. The processing of bentonite to montmorillonite (MMT)

Natural bentonite was taken from Blangdalam village, sub-district of Nisam, North Aceh. It was being crushed, sieved and dried at temperature of 105°C and stored in desiccators. Then sample fractionation was carried out in order to obtain pure MMT using sedimentation method. Bentonite suspension was weighed as much as 40 gram and it was put into 2L of aquadest. Ultrasonic waves were given for 15 minutes with 750 Watt power at room temperature. Then, the sediment was taken by pouring floated suspension into other container and its filtrate was being resettled. These fractions were being dried in oven at 105°C for 3 hours and were crushed until reached a size of 250 mesh. These fractions were stored in desiccator and were later identified by FT-IR, X-ray diffraction, and PSA analysis<sup>15</sup>.

## 2.4. The modification of montmorillonite-CTAB

0.05 mol of cetyl trimethyl ammonium bromide (CTAB) was weighed and dissolved with 250 ml of aquadest in 500 ml beaker glass. Then, it was heated at 80 °C for 1 hour. In a separate place, 20 gram of MMT was dissolved with 250 ml of aquadest in 1000 ml beaker glass. Then, MMT solution dispersion was put into CTAB solution stirred for 1 hour and was filtered. Montmorillonit was washed with aquadest until it was free from chloride and bromide. MMT was being stored in oven at 60 °C for 24 hours and was analyzed using FT-IR and XRD<sup>8,16</sup>.

## 2.5. The manufacture of polyurethane paint coatings

The manufacture of polyurethane film followed the procedure modification of polyurethane manufacture<sup>16</sup>. Palm oil-based polyol was mixed with arganoclay at room temperature for 10 minutes. Then, isocyanate (MDI) was added and was stirred again for 5 minutes to obtain homogeneous mixture. Then, it was applied to ABS plastic specimen which had been prepared. Result specimen was being settled at room temperature in order to evaporate the solvent. Gloss index and adhesivibility of polyurethane film layers on specimen were then tested. Table 1 shows the preparation of polyurethane-based paint coating.

The preparation of polyurethane-based paint coating which would be made on Polyol : MDI ratio followed<sup>4</sup> and MMT usage ratio followed<sup>17</sup> and can be seen from Table 1.

**Tabel 1. Composition of the Sample**

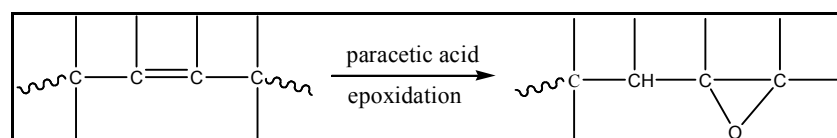
Sample	Composition		
	MDI (gram)	Polyol (gram)	MMT (gram)
Commercial PU	30	70	-
POB-PU	30	70	-
POB-PU/MMT	30	70	5

## 3. Result and Discussion

### 3.1 Polyol compound result of palm oil.

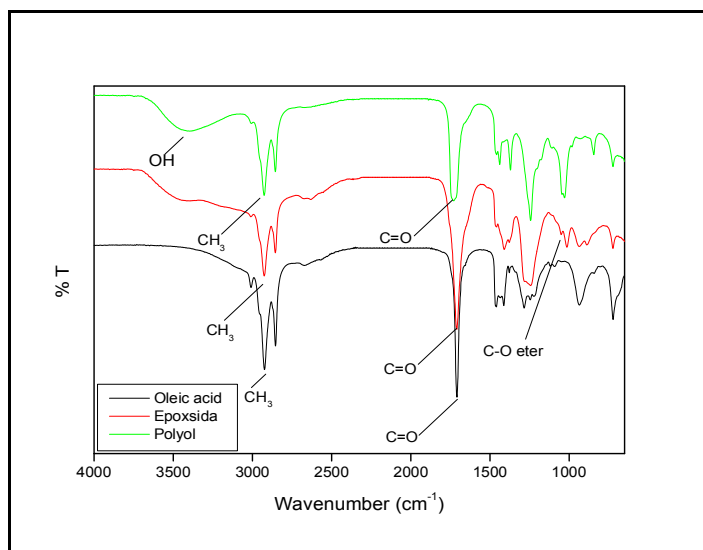
In this research, palm oil-based epoxide resulted from synthesis had brighter color than palm oil oleic acid. The analysis result of iodine value and palm oil oxirane toward palm oil oleic acid epoxide is as follows: iodine value of palm oil oleic acid 56.72 g I<sub>2</sub>/100 g decreased to 14,29 I<sub>2</sub>/100 g while oxirane value increased from 0,64% to 7,12%. The decrease of iodine value indicates double bond oxidation process while oxirane value indicates epoxy ring of double bond oxidation in palm oil oleic acid. In addition, reaction of epoxide compound in vegetable oil has been carried out<sup>3,10</sup>. Epoxides occurred were compounds that can form diol compound in the presence of nucleophile. Synthesis result indicates that specific gravity of palm oil-based polyol is 0.912 gr/ml.

FT-IR spectroscopic analysis result on epoxide compound was carried out in order to detect or to obtain peak shifts which can be related to reaction process. Spectrum in the area of 1050 cm<sup>-1</sup> and 1014 cm<sup>-1</sup> indicates bond of C-O occurs in epoxy ring of palm oil epoxidized compound which occurs during the reaction process.



**Fig.1.** Epoxidation reaction of palm oil oleic acid

First reaction phase of oleic acid-based polyol compound was substance formation of epoxide compounds through reaction between unsaturated hydrocarbon of palm oil and formic acid in reaction equation above. FT-IR analysis result indicates formation of hydroxyl group in palm oil epoxidized compound. The reaction occurs for 5 hours at 60°C which is proved by the increase of wavenumber-stretch at 3396 cm<sup>-1</sup>, hydroxyl group formed in secondary C atom with hydroxyl value of 124, 64 KOH/g and tested using Wijs AOAC, 1995 titration method.



**Fig. 2.** FT-IR spectra of oleic acid palm oil, palm oil epoxide and palm oil polyols

### 3.2. Results of the Characterization of Bentonit in Becoming Montmorillonite

The samples of natural bentonite were taken from Desa Blangdalam, Sub-district of Nisam, North Aceh, with physical characteristic that is grey as shown in Fig 2a and Fig 2b is the MMT isolation results. Based on the results of chemical analysis, natural bentonite from Desa Blangdalam, Sub-district of Nisam, North Aceh, contains 46% of montmorillonite.

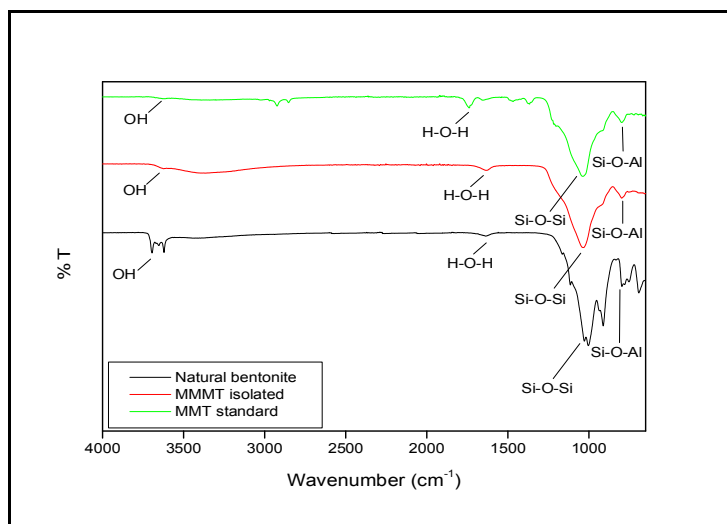


**Fig.3.** Sample a) Natural bentonite from North Aceh and b) MMT isolation results

#### 3.2.1. Characterization using FT-IR

Analysis of FT-IR spectrum in Fig4 illustrates that it is the characteristic of natural to possess the uptake at spectrum domain of  $3651\text{ cm}^{-1}$  and  $16.20\text{ cm}^{-1}$  in which lies the range of  $\text{H}_2\text{O}$  and octahedral OH groups, the uptake at wave number of  $1637\text{ cm}^{-1}$  H-O-H buckling vibration, spectrum of  $1114\text{ cm}^{-1}$ ,  $1003\text{ cm}^{-1}$  are C-H domain, the uptake  $1038\text{ cm}^{-1}$  and  $1027\text{ cm}^{-1}$  are asymmetric to Si-O-Si, the uptake of Si-O-Al at  $796\text{ cm}^{-1}$ ,  $752\text{ cm}^{-1}$ ,  $692\text{ cm}^{-1}$ . This isolation result of spectrum montmorillonite FT-IR can be seen on Fig 4, appeared spectrum is at wave length of  $3367\text{ cm}^{-1}$  that indicates the presence of OH groups (hydrogen bonds) and the octahedral OH groups.

At the wave number  $1631\text{ cm}^{-1}$  is present the buckling vibration of H-O-H, at spectrum  $1032\text{ cm}^{-1}$  lies asymmetric stretch Si-O-Si, and at spectrum  $797\text{ cm}^{-1}$  lies buckling vibration of Al-O-Al. Fig 4 shows the isolation results of MMT that is nearly similar to FT-IR spectrum of standard MMT. The Figure of spectrum  $2923\text{ cm}^{-1}$  standard MMT shows the presence of OH groups (hydrogen bonds) that belongs to octahedral OH groups, spectrum  $1738\text{ cm}^{-1}$  buckling vibration H-O-H, at spectrum  $1467\text{ cm}^{-1}$  and  $1366\text{ cm}^{-1}$  is the stretch of OH. At spectrum  $1038\text{ cm}^{-1}$  lies the asymmetric stretch of Si-O-Si and at spectrum  $798\text{ cm}^{-1}$  lies the buckling vibration of Al-O-Al

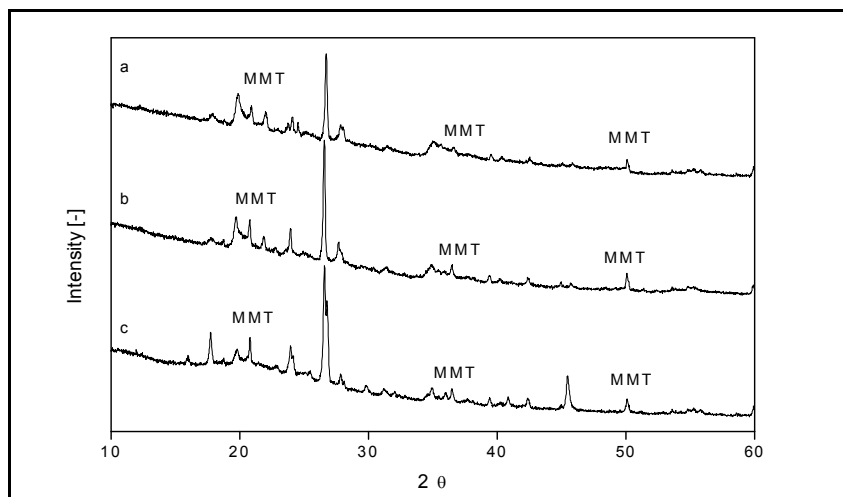


**Fig.4. FT-IR Spectra natural bentonite, MMT isolation and MMT standard**

### 3.2.2. Characterization using X-Ray Diffraction

The characterization results of X-Ray diffraction (XRD) of natural bentonite from Desa Blangdalam, sub-district of Nisam, North Aceh, can be seen in Fig 5c. The identification results show that this natural bentonite contains montmorillonite, the peaks showing the presence of MMT are  $19.98^\circ$ ,  $35.86^\circ$ , and  $62.97^\circ$ <sup>18</sup>.

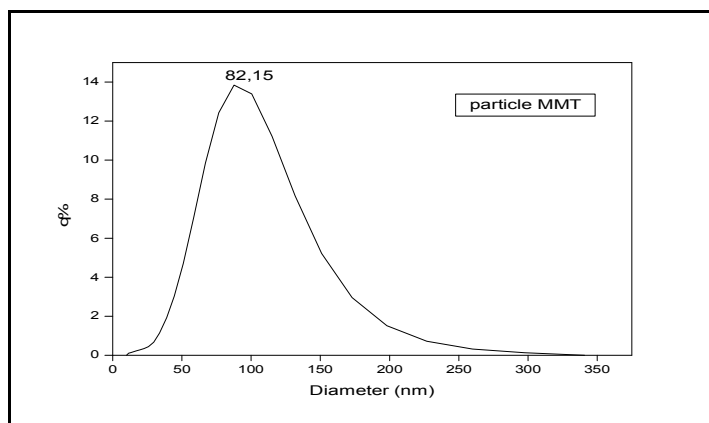
After natural bentonite is processed into XRD spectrum MMT (presented in Fig 5b), the appeared spectrums are the characteristic peaks of MMT at 2 theta, they are  $18.39^\circ$ ,  $19.98^\circ$ ,  $36.46^\circ$ , and  $30.58^\circ$ . This XRD spectrum matches the standard montmorillonite XRD spectrum as shown in Fig 5a.



**Fig.5. XRD spectrum of the a)Standard MMT; b)Isolated MMT, c)Natural Bentonite.**

### 3.2.3. Test using Particle Size Analyzer (PSA)

Montmorillonite which is the isolation result of natural bentonite in size of 50-100  $\mu\text{m}$  was then processed into nanoparticle by sedimentation method, ultrasonic stirring and heating<sup>18</sup>. In order to prove that nanoparticle has been formed, analysis was performed using Particle Size Analyzer (PSA). The test results of isolation result MMT are presented in Fig 7. The graph shows that the average of diameter isolation result MMT after given the treatment became nanoparticle with average rate of 82.15 nm.



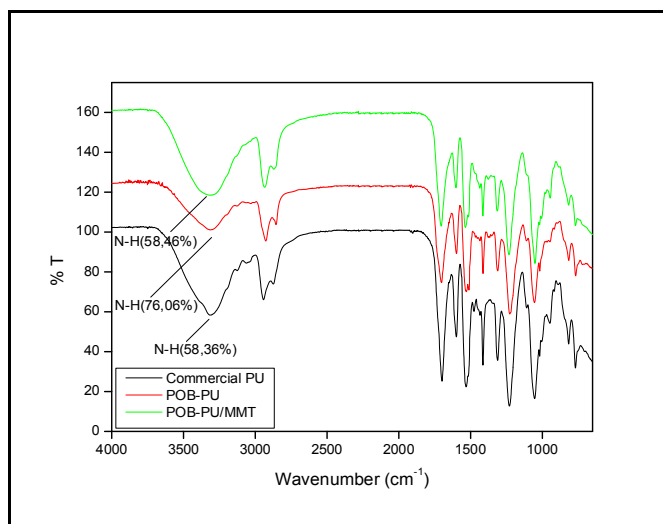
**Fig.6. Diameter of isolated montmorillonite,**

### 3.3. The results of Characterizing Polyurethane as Paint Coating

#### 3.3.1. Characterization of the Reaction of PU Forming by FT-IR

Palm oil polyol reaction with MDI produces polyurethane, and commercial polyol reaction with MDI produces commercial polyurethane. The results of the characterization of the three types of polyurethanes synthesized by spectroscopy is nearly similar, for N-H group are  $3311\text{ cm}^{-1}$ ,  $3315\text{ cm}^{-1}$ ,  $3316\text{ cm}^{-1}$  and for C=O of amide compound are  $1698\text{ cm}^{-1}$ ,  $1701\text{ cm}^{-1}$  and  $1704\text{ cm}^{-1}$ . Additionally, for PU commercial is  $2942\text{ cm}^{-1}$ , for POB- PU are  $2926\text{ cm}^{-1}$ ,  $2855\text{ cm}^{-1}$  and  $2934\text{ cm}^{-1}$ ,  $2870\text{ cm}^{-1}$  for POB-PU/MMT Brazilians alkane CH as well as  $816\text{ cm}^{-1}$ ,  $816\text{ cm}^{-1}$  and  $816\text{ cm}^{-1}$  aromatic CH group of MDI compounds.

The absorption at  $1310\text{ cm}^{-1}$ ,  $1311\text{ cm}^{-1}$  and  $1313\text{ cm}^{-1}$  is a C = N group absorption of isocyanate compounds. Comparison of the spectrum of commercial polyurethanes and palm oil polyurethane showed nearly similar absorption area. Figure 8 shows spacious area on the absorption of NH results of FT-IR spectra of commercial polyurethane as much as 58.36%, 76.06% of palm oil polyurethane and 58.46% of palm oil polyurethane added with MMT.

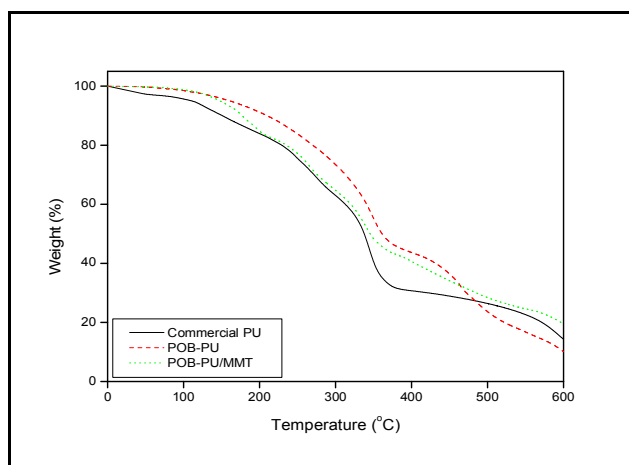


**Fig.7. FT-IR spectra of commercial PU, POB-PU and POB-PU/MMT**

#### 3.3.2. Thermal characterization by TGA

Thermogravimetric analysis (TGA) of Commercial PU, POB-PU and POB-PU/MMT is shown in Fig 8, TGA can be used to characterize any material that shows the material weight change upon heating, and to detect changes due to decomposition. The weight reduction at the beginning of  $50\text{--}150^\circ\text{C}$  water to evaporate for Commercial PU, PU MKS and POB-PU/MMT are  $-1.00\text{ mg}$ ,  $-0.15\text{ mg}$  and  $-0.53\text{ mg}$  or about 5% respectively. The residue of commercial PU decomposition at  $380^\circ\text{C}$  is  $1.40\text{ mg}$  or about 14%.

For the decomposition of POB-PU and POB-PU/MMT weight reduction at the beginning of 150-200 °C are as much as 5% and the decomposition occurred at temperature of 490 °C, this proves that the POB-PU/MMT has increased thermal stability .



**Fig.8. Thermogram of Commercial PU, POB-PU and POB-PU/MMT**

### 3.3.3.Characterization of Adhesivibility classification

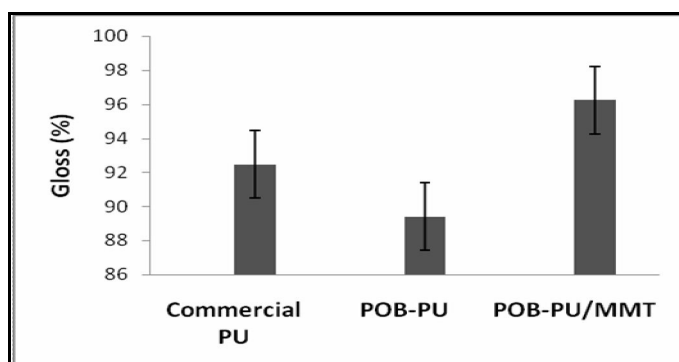
Table 2 shows that commercial PU and POB-PU were classified as 2, it states that the ABS plastic specimen applied with Commercial PU and POB-PU has decay rate of about 15 %. Steel specimen that was applied with POB-PU/MMT was classified as 1, it implies the damage level of POB-PU which was approximately 5% (ISO 2409). Addition of MMT on palm oil-based polyurethane can increase the adhesivibility. Polyimide coating adhesivibility with the addition of 3% clay was increased with polyimide coatings adhesion without clay.

**Table 2. Classification of Adhesivibility**

No	Speciment	Classification
1	Commercial PU	2
2	POB-PU	2
3	POB-PU/MMT	1

### 3.3.4.Characterization of speciment Gloss index

Fig 9 shows that Commercial PU film coating gloss index on the specimen applications of ABS plastic was statistically better than the gloss index of synthetic POB-PU, and the gloss of POB-PU/MMT is better than the gloss index of Commercial PU. Film gloss index depends on the smoothness of the coating film formed. The addition of MMT in the polyol synthesis results produces film layer polyurethane with higher gloss index. It can be defined as the ability of the film coating surface to reflect light



**Fig.9. The effect of polyols on PU film Gloss index**

## Conclusion

Based on the thermal test, it is obtained that the palm oil polyurethane coatings added with MMT isolation results underwent an increased heat in comparison with polyurethane without addition of montmorillonite (PU Commercial). The decomposition of PU Commercial occurred at 380°C, while the POB-PU with the addition of 5% MMT underwent decomposition at higher temperature at 490° C. The addition of MMT can improve adhesion to applications of polyurethane paint coatings and as well as increase the gloss index of paint coating surface.

## References

1. Ionescu. M, Chemistry and Technology of Polyols for Polyurethanes, Rapra Technology, 2005.
2. Cheng HT, Persoalan Keberlanjutan Kunci dalam Sektor Minyak Kelapa Sawit, International Finance Corporation, World Bank Group. 2012, Jakarta.
3. Odetoeye T.E., D. S. Ogunniyi., G.A.Olatunji., Improving Jatropha Curacas Linnaeus Oil Alkyd Drying Properties, Progress in Organic Coating, 2012, 73, 374-381..
4. Ginting, M, Pemanfaatan Hasil Hidrolisis dan Alkoksilasi dengan Gliserol dari Epoksida Minyak Kemiri sebagai Sumber Polioli untuk Pembuatan Poliuretan, Desertasi Doktor, Pascasarjana USU. 2010, Medan.
5. S. Dutta, N.Karak,T.Jana, Evaluation of *Mesua ferrea* L.seed oil modified polyurethane paints. Progress in Organic Coating, 2009, 65, 131-135.
6. Tanaka R, Hirose S, Preparation and Charaterization of Polyurethane Foams Using a Palm Oil-Based Polyol, Biorsource Technology, 2008, 99, 3810-3816.
7. Nerine, S.S, Kong,X.,Bo, Uzidi, L, Sporas, P, Physical Properties of Polyurethane Produced from Polyol From Seed Oil: I.Elastomers, J. Am. Oil.Chem. Soc. 2007, 84, 55-63.
8. Rihayat.T., M. Saari., M. H.Mahmood., W.M.Z. Wan Yunus., A.R. Suraya., K. Z. H.Dahlan and S.M. Sapuan, Mechanical Characterization of Polyurethane/Clay Nanocomposites, Polymers & Polymer Composites, 2007, 647-652.
9. Lambourne. R and T A Strevens, Paint and Surface Coating,Wood head Publishing Ltd, ISBN 1 85573 348 X. 1999.
10. Harjono, Sugita, Mas'ud, Synthesis and Application of Jatropha Oil based Polyurethane as Paint Coating Material, Makara Journal of Science, 2012, 16/2, 134-140.
11. Suman,T., N. Karak, Castor Oil-Based Hyperbranched Polyurethanes as Advaned Surface Coating Materials. Progress in Organic Coating, 2013, 76, 157-164.
12. Rehab. A., Nehal. S; Nanocomposite materials based on polyurethane intercalated into montmorillonite clay. Materials Science and Enginering A, 2005, 368-376.
13. Ahmadi. B, Mahmoud K, KhosrowK, Ehsan R.M, Effect of nano layered silicateson automotive polyurethane refinish clear coat, Progress in Organic Coatings 2007 60 99-104.
14. Song. J., Ashish. B., Jose. M. R Choistoper W. Macosko, Polyethylene /Polyurethane Blends for Improved Paint Adhesion, Progress in Organic Coatings, 2011, 72, 492-497.
15. Julinawati, Karakterisasi dan Pengolahan Bentonit Alam Aceh sebagai Pengisi Nanokomposit Polipropilena-Montmorillonit, Disertasi Pasca USU, 2012, Medan.
16. Kishore K. J., K.V.S.N. Raju.,R. Narayan., Sodium montmorillonit clay loadedorganic-inorganic hybrid composites: Synthesis and characterization, Progress in Organic Coatings , 2012, 75, 33-37.
17. Nayani.M., Gunashekar.S., Nidal; Synthesis and Characterization of Polyurethane-Nanoclay Composites”, International Journal Polymer Science, Research Article, 2013, 1-5.
18. Fisli, A, Isolasi dan Karakterisasi Montmorillonite dari Bentonit Sukabumi (Indonesia), Indonesian Journal of Materials Science, 2008, 10(1) ; 12 – 17.

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