Bio-Nanocomposite Polyurethane / Clay / Chitosan Paints that have thermal resistance and antibacterial properties for biomedical applications

T Rihayat1, Suryani1, S Riskina1, J P Siregar2, J Jaafar2, T Cionita3 and Fitria4

1 Department of Chemical Engineering, Politeknik Negeri Lhokseumawe, 24301, Aceh Indonesia
2 Faculty of Mechanical Engineering, Universiti Malaysia Pahang, 26600 Pekan, Malaysia
3 Department of Mechanical Engineering, Faculty of Engineering and Quantity Surveying, INTI International University, 71800 Nilai, Negeri Sembilan, Malaysia
4 Department of Dermato Venereology, Medical Faculty, Syiah Kuala University, 23111, Aceh

*Corresponding author: teukurihayat@yahoo.com

Abstract. The coating material used for the manufacture of polyurethane paints is a coating of hybrid organic-inorganic materials based on palm oil (oleic acid). Polyols are produced from the synthesis of oleic acid by adding organic and inorganic ingredients. Chitosan and bentonite are organic and inorganic elements, which are used to improve thermal capability and antibacterial properties of polyurethane paint produced. Hybrid bentonite-chitosan is then synthesized with polyols and isocyanate is added, namely TDI (Toluene Diisocyanate) to form polyurethane. In the FTIR spectrum of the polyol on O-H bond at Wavelength 3210.25 cm-1, C-H bond at Wavelength 2856.87 cm-1 and C = O bond at Wavelength 1610.86 cm-1, and hybrid bentonite-chitosan of FTIR Analysis Chitosan: -OH group at Wavelength 3250 cm-1, N-H at 3545 cm-1, C = O at wavelength 1681 cm-1, C-H group at Wavelength 2810 cm-1. Bentonite: -OH group at Wavelength 3435 cm-1, Si-O group at Wavelength of 1161 cm-1 and Al-O and Si-O groups at Wavelength 820 cm-1. Aliphatic C-H Cluster at 2815 cm-1 Wavelength and 1125 cm-1 Wavelength indicates the presence of a C-O group. While the results of SEM (Scanning Electron Microscope) from polyurethane products and with the addition of hybrid bentonite-chitosan namely polyurethane paints produced mixed with chemicals and the main ingredients are polyols from palm oil (oleic acid) while small white clumps greyish namely hybrid bentonite-chitosan which has been mixed into polyurethane paint. This study produced a hybrid material of benthic-chitosan as a filler in the manufacture of polyurethane paint.

1. Introduction
Bentonite is a rock term and is part of a group of smectite minerals containing montmorillonite. The main content of bentonite is mineral montmorillonite. Bentonite application has been widely used for fillers, pellets, drilling mud, catalysts and as adsorbents. Currently, it has also been made into several high-value products such as nanomaterials, drugs and chemicals. Bentonite is widely used for the treatment of esophagitis, gastritis, colitis and so on. Bentonite is also used as a raw material for cosmetics due to decontamination, detoxification, as a moisturizer. In addition, with chemical adsorption and
stability, bentonite has been widely used in food processing industries which are closely related to human health and life [8].

Bentonite usually contains a negative charge which allows a cation exchange reaction. This charge comes from one or more of several different reactions. The main contribution of the negative charge is the isomorphic and the dissociation of the open hydroxyl group. The ions that can be exchanged are different ions around the alumina-silica clay minerals.

Ion exchange reactions are stoichiometric and different from absorption or sorption and desorption. Ion exchange is a process whereby the cations usually found in the crystal layer are replaced by cations from the solution. In water, the cations on the surface of the layer become more easily replaced by other cations contained in the solution, known as exchangeable cations.

The use of bentonite as an adsorbent for inorganic compounds such as heavy metal ions because bentonite has cation exchange capacity and has hydrophilic properties on the surface. The chemical properties of the bentonite pore structure generally determine its adsorptive capacity. Because of the ineffective hydrophilic nature of bentonite to absorb organic compounds, to increase its capacity. One of the deficiencies of clay is its hydrophilic nature which can cause agglomeration of clay minerals in a hydrophobic polymer matrix. This deficiency can be overcome by intercalating organic cations such as amino acids or alkyl ammonium to form organoclays that are hydrophobic.

Increasing the basal spacing after the intercalation process can also increase the diffusion capability of the polymer or polymer coating into clay interlayer. Intercalation is based on the exchange of cations found in the layers of clay, such as Na+, K+, and Ca2+. Intercalation into the clay structure resulted in an increase in surface area, basal spacing (spacing of montmorillonite silicate layer), and surface acidity which affected the adsorption power.

This intercalation process can cause clay pores to become larger and homogeneous, and the layers become more stable than before being intercalated. The purpose of intercalation is to: expand the interlayer distance, reduce solid-solid interactions between clays and increase the interaction between clay and matrix.

Organic compounds, bentonite is intercalated with surfactants that can interact with the negative charge present on the surface of the interlayer. Bentonite has a complex chemical surface and arises from its ability to form thixotropic water gels, high water absorption, high surface area, layered structure and high cation exchange capability, and contains crystals of quartz, cristobalite, feldspar, or other compounds [10].

Chitosan which is also called β-1,4-2 amino-2-deoxy-D-glucose is a compound which is slightly soluble in HCl, HNO3, and H3PO4 and is not soluble in H2SO4. Chitosan is non-toxic, biodegradable and polyelectrolytes. Besides, chitosan can easily interact with other organic substances such as proteins. Therefore, chitosan is relatively more widely used in various fields of applied industry and health industry [5]. Chitosan is insoluble in water, organic solvents, also insoluble in alkalis and mineral acids at pH above 6.5. In the presence of a number of acids, it is soluble in water-methanol, water-ethanol, water-acetone, and other mixtures.

Chitosan dissolves in formic acid and acetic acid and according to Peniston in 20% citric acid can also dissolve. Other organic acids also cannot dissolve chitosan, other inorganic acids at a certain pH after being sterilized and heated and citric acid can also dissolve chitosan in a small part after some time will form white sediments that resemble jelly [11].

Resin or binder is a major component in the manufacture of coatings, paints and resins. The function is to glue the existing components and attach the entire material to the surface of a material forming a film. Resins are basically polymers where at room temperature they are liquid, sticky and thick. There are many types of resins, such as natural oil, alkyd, epoxy, polyurethane, polyester, etc [7].

Determination of polyols and characteristics of hybrid bentonite-chitosan produced using FTIR (Fourier Transform Infrared) analysis to determine functional groups, XRD (X-Ray Diffraction) to determine the element/compound content (qualitative analysis) and Scanning Electron Microscope to see the morphology of polyurethane products produced by the addition of hybrid bentonite-chitosan filler.
2. Method

2.1. Materials
The materials used in this study were bentonite from Nisam, North Aceh, Methylen Blue (Merck, Germany), aquadest, aquabidest, Sodium Dodecyl Sulfate (SDS), Cetyl Trimethyl Ammonium Bromide (CTAB), AgNO₃ Solution and Sodium Hexamethapospate (NaPO₃)₆.

2.2. Purification of bentonite with cationic and anionic surfactants
Bentonite with a size of 100 mesh as much as 2 grams mixed with 98 ml of aquadest with 0.5 hours at 80ºC. CTAB surfactants are added with 2.5 gram stirred for 2 hours at 80ºC. After cationic surfactant is homogeneous with bentonite, then enter anionic surfactant into bentonite solution which has been homogeneous with cationic surfactant and stir until homogeneous for 1 hour at 80ºC with 1.5 gram. Furthermore, the results of the resulting samples were analyzed using XRD to determine the basal spacing of bentonite after the addition of cationic and anionic surfactants [11].

2.3. Synthesis of bentonite-chitosan hybrids
Bentonite which has a larger basal spacing is added with 1 gram of chitosan. Then bentonite and chitosan are mixed until homogeneous. The resulting suspension is then filtrated using a vacuum pump, the solids produced are then dried and analyzed using FTIR to determine the chemical compound groups of hybrid bentonite-chitosan produced [12].

2.4. Polyol synthesis
30 ml of 30% H₂O₂ was added 100% 50 ml CH₃COOH and concentrated H₂SO₄ as much as 2 ml into 350 ml three-neck flask equipped with thermometer and condenser with stirring speed 200 rpm and process temperature 40-45ºC for 1 hour to make peracetic acid. Then add 100 ml of oleic acid into a three-neck flask containing a mixture of peracetic acid. When heating and stirring takes place, the temperature of the mixture at 45-60ºC for 5 hours. The product is cooled to room temperature and the oil phase separation as oxidized which is then used in the hydroxylation process [13].

2.5. Polyurethane paint synthesis with additional bentonite-chitosan hybrid filler
8.92 ml polyol mixed with 8 ml xylene and heated at 60ºC for 60 minutes. After 1 hour, add hybrid bentonite-chitosan filler into the solution and stir until homogeneous. Once homogeneous, add TDI 0.428 ml drop by drop and wait until it thickens. Then applied directly on the iron plate. Furthermore, it was analyzed using SEM to determine the morphology [13].

2.6. Fourier Transform Infrared (FTIR) analysis
Infrared spectroscopy of nanocomposites obtained by pallet KBr using Shimadzu FTIR Spectrophotometer, to see the hydroxyl groups of the polyols produced.

2.7. X-Ray Diffraction (XRD) analysis
X-Ray Diffraction Shimadzu 6000 for viewing basal spacing from bentonite modified by both cationic and anionic surfactants and hybrid bentonite-chitosan material.

2.8. Scanning Electron Microscope (SEM) analysis
Scanning Electron Microscope to see the morphology of hybrid chitosan bentonite and to see products (polyurethane paint) against anti-bacteria.

3. Result and discussion

3.1. Bentonite preparation with addition of cationic-anionic surfactants
Bentonite clay is widely used in paint. White Bentonite is the material of choice that is widely available around. In water-based paint, sodium or montmorillonium suspend and thicken substances. This
montmorillonite is also used as an emulsifier in water and oil paint formulations. Organoclays can be made specifically with organic compounds to meet different vehicle requirements including varnishes, epoxy resins, and vinyl resins, which are used in paint formulations. These organoclays improve pigment suspension, viscosity, and techotropic control and are very good in non-drip emulsion paints [14]. Bentonite used is from Nisam, North Aceh. This bentonite was previously ground and then sieved to a size of 100 mesh. Before being mixed with surfactant, raw bentonite was first analyzed using XRD to find out the spacing of the interlayer bentonite.

3.1.1. X-Ray Diffraction (XRD) analysis
X-Ray Diffraction is one of the characterizations that use x-rays, x-ray scattering is produced if an electron metal is fired by electrons at high speed in a vacuum tube. A crystal can be used to diffract x-ray beam due to the order of x-ray wavelengths almost the same or smaller with the order of the distance between atoms in a crystal.

From Figure 1, the basal spacing of raw bentonite is 14,18393 Å. Then the raw bentonite was mixed with Cetyl Trimethyl Ammonium Bromide (CTAB) cationic surfactant stirred for 2 hours and then the mixture of anionic Sodium Dodecyl Sulfate (SDS) surfactant was added for 1 hour. The results of these two types of surfactants were then washed to remove surfactants contained in the interlayer of bentonite using aquadest. To test whether the surfactant has been lost from the bentonite solution, AgNO3 solution was used which was dripped into surfactant water, if the water turned grey then it still contained surfactants, therefore it is necessary to re-wash with aquadest.

3.2. Bentonite-chitosan hybrid synthesis
After obtaining bentonite with the highest basal spacing, chitosan is then intercalated into the bentonite interlayer. The intercalation process lasts for 60 minutes under stirring conditions until both solutions are homogeneous. Then filtered using a vacuum pump to clean the filtrate and solids produced then dried to remove the water content and analyzed using FTIR and SEM.

3.2.1. Fourier Transform Infrared (FTIR) analysis
Chitosan has the properties of biocompatibility and its positive charge, while bentonite has a high specific surface area and a negative charge. Composites consisting of chitosan and bentonite can be considered as a type of polyelectrolyte complex and have several beneficial properties in biomedical applications. Bentonite has no anti-bacterial activity, but a double performance of bacteria that absorb and kill bacteria when chitosan chains interact with bentonite layers (Cabuk, 2016).
The FTIR spectrum in figure 2. shows all expected characteristic peaks arising from the presence of chitosan and bentonite and that could be evidence of composite formation. Chitosan: -OH group at Wavelength 3250 cm⁻¹, N-H at 3545 cm⁻¹, C = O at wavelength 1681 cm⁻¹, C-H group at Wavelength 2810 cm⁻¹. Bentonite: -OH group at Wavelength 3435 cm⁻¹, Si-O group at Wavelength of 1161 cm⁻¹ and Al-O and Si-O groups at Wavelength 820 cm⁻¹. Aliphatic C-H Cluster at 2815 cm⁻¹ Wavelength and 1125 cm⁻¹ Wavelength indicates the presence of a C-O group. This phenomenon shows that ionic exchange reactions occur between chitosan and bentonite and consequently chitosan is dispersed into the interlayer of bentonite [15].

3.2.2. Scanning Electron Microscope (SEM) analysis. Testing using an SEM tool shows that chitosan chains are well dispersed into bentonite interlayer. The formation of composite flocculation can be attributed to the interaction of the hydroxylated edges of the silicate layer between the hydroxylated edge groups of silicates and chitosan chains [15]. The SEM image of hybrid bentonite-chitosan as shown in figure 3 is a small white surface which is chitosan which has been dispersed on the bentonite surface.

3.3. Polyol
The polyol used in this study is natural polyol derived from vegetable oil. Vegetable oil does not contain hydroxyl groups, but on average has a double bond, one of which is oleic acid. This double bond is converted into an epoxy group at atmospheric pressure through an epoxidation reaction which is then followed by a hydroxylation process to form a hydroxyl group. At the epoxidation stage, oil is reacted
with peracetic acid to form epoxide compounds, peracetic acid is a material that is difficult to obtain and dangerous, therefore the use of peracetic acid is made in situ by reacting H2O2 and CH3COOH with H2SO4 catalyst in palm oil to produce oxidized oil (epoxide compound). Then proceed to the hydroxylation process where the oxidized oil is reacted with a mixture of alcohol (methanol and isopropanol), catalyst and water to form a hydroxyl group from the opening of the epoxide ring [16].

3.3.1. Fourier Transform Infrared (FTIIR) analysis. The raw materials used and the resulting polyol products were tested quantitatively by analyzing using Fourier Transform Infrared (FTIR) to determine the presence of molecular groups, in this case the presence of hydroxyl groups.

From Figure 4, the results of the polyol are synthesized from oleic acid, the group obtained is the hydroxyl group at wavelengths 3240 - 3640 cm⁻¹ [16]. O-H bond at Wavelength 3210.25 cm⁻¹, C-H bond at Wavelength 2856.87 cm⁻¹ and C = O bond at Wavelength 1610.86 cm⁻¹.

3.4. Addition of polyurethane hybrid filler bentonite-chitosan

Polyurethane is a group of special polymeric materials that are basically different from most other types of plastic. Polyurethanes can be combined into various items such as paints, liquid coatings, elastomers, insulators, elastic fibers, foams, and others. The urethane group is the main repetition unit of polyurethane, resulting from the reaction between alcohol (O-H group) and isocyanate (-NCO group). Polyurethane also contains other groups such as ethers, esters, urea and some aromatic compounds.

The nanocomposite polymer is a class of hybrid material composed of a matrix of organic polymers with dispersed inorganic materials, which have at least one dimension in the nanometer range. On this scale, the large surface area of the filler, even at very low concentrations can significantly change the macroscopic nature of the polymer and contribute many new characteristics to the polymer, such as increased modulus and strength, heat resistance and decreased gas permeability and flammability [4].

Bentonite can provide properties such as high thermal stability, lightweight, better compressive strength and good fire resistance properties to several polymeric systems. However, it was observed that the hydrophilic nature of bentonite often caused poor interface adhesion between the polymer matrix and nano clay filler, but for this study, the properties of the bentonite itself had changed to hydrophobicity resulting in interface matrix adhesion. Modification of polyurethane with chitosan can help release antibacterial agents [7]. Thermosensitive polyurethane membranes modified with chitosan were found to be antibacterial against P. Aeruginosa and S. Aureus and showed that polyurethane-coated chitosan was non-toxic, biocompatible and safe [9].

Polyurethane synthesis was carried out by mixing polyols with their fillers, namely hybrid bentonite-chitosan produced before stirring until homogeneous (about 60 minutes) then add Toluene Diisocyanate
(TDI) little by little and add solvents, then stirred again at 200 rpm to homogeneous. The results of polyurethane paint are then applied on the surface of the cleaned plate, and wait until it dries. Then characterization was performed using SEM to see the functional groups contained in the polyurethane paint produced and the morphology of the plate that had been applied with polyurethane paint.

3.4.1. Scanning Electron Microscope (SEM) analysis. The morphology of polyurethane nanocomposite with the addition of hybrid bentonite-chitosan filler was analyzed using SEM (Scanning Electron Microscope) at room temperature. SEM fractography results showed that chitosan chains were intercalated well into bentonite interlayer [13].

![SEM Analysis](image)

**Figure 5.** Results of SEM analysis of polyurethanes with chitosan bentonite hybrid filler.

The fractography results of SEM in Figure 5, are surfaces that tend to be darker, namely iron plates that have been applied with polyurethane paint, polyurethane paints produced mixed with chemicals and the main ingredients are polyols from palm oil (oleic acid) while small white clumps greyish namely hybrid bentonite-chitosan which has been mixed into polyurethane paint.

4. Conclusion
Bentonite is part of the smectite group containing montmorillonite. The application of bentonite has been widely used for fillers, pellets, drilling mud, catalysts and as adsorbents. Besides bentonite, chitosan can also be used for fillers and is antibacterial. Combining the two materials obtained a new material, namely hybrid bentonite-chitosan which has thermal resistance and antibacterial properties which are then synthesized into polyurethane. The characterization carried out in this study was using X-Ray Diffraction (XRD), Fourier Transform Infrared (FTIR) and Scanning Electron Analysis Microscope (SEM).

Acknowledgement
The Author would like gratefully and acknowledgement thanks to Directorate of Student Affairs and Education Ministry of Research Technology and Higher Education of Indonesia and Politeknik Negeri Lhokseumawe.

References
[1] Alves, Jefferson Lopes., Paulo de Tarso Vieira e Rosa., Ana Rita Morales., 2017; Evaluation of Organic Modification of Montmorillonit With Ionic and Nonionic Surfactants. Applied Clay Science, Vol.150. Pp: 23-33
[2] Chatel, Gregory., Liudmila Novikova., Sabine Petit., 2016; How Efficiently Combine
Sonochemistry and Clay Science. Applied Clay Science. Vol.119, Pp: 193-201.

[3] Chen, Daimei., Jian Chen., Xinlong Luan., Haipeng Ji., Zhiguo Xia., 2011; Characterization of Anion-Cationic Surfactants Modified Montmorillonite and its Application for the Removal of Methyl Orange. Chemical Engineering Journal. Vol.171. Pp: 1150-1158.

[4] Clouttier, M., D. Mantovani and F. Rosei., 2015; Antibacterial Coatings: Cpplenges, Perspectives, and Opportunities. Trends in Biotechnology. Vol.33. No.11.

[5] Dewi, Ni Putu Widyat Tironika., Nengah Simpen., I Wayan Suarsa., 2017; Modifikasi Lempung Bentonite Teraktivasi Asam Dengan Benzalkonium Klorida Sebagai Adsorben Zat Warna Rhodamine B. Universitas Udayana, Bukit Jimbaran. Vol.11. Pp: 75-81.

[6] Flach, Carl Fredrick., Chandan Pal., Carl Johan Svensson., Erik Kristiansson., Marcus Ostman., dkk. 2017; Does Antifouling Paint Select for Antibiotic Resistance. Science of the Total Environment.

[7] Liu, Guifeng., Guomin Wu., Shuping Hou., Can Jin., Zhenwu Kong., 2017; Synthesis and Properties of Non-Isocyanate Polyurethane Coatings derived from Cyclic Carbonate-Functionalized Polysiloxanes. Progress in Organic Coatings. Vol.112. Pp: 169-175.

[8] Pilch-Pitera, Barbara., Lukasz Byczynski., Bogdan Mysliwiec., 2017; Synthesis and Surface Modification of Polyurethanes with Chitosan for Antibacterial Properties. Carbohydrate Polymers. Vol.112. Pp: 39-47.

[9] Rahman, Arif., Yateman Arryanto., Sutarno., Ariadne L. Juwono., Seto Roseno., 2015; Sintesis dan Karakterisasi Organolempung Dari Bentonit Indonesia. Jurnal Fisika dan Aplikasinya. Vol,16. No.1.

[10] Salwiczek, Mario., Yue Qu., James Gardiner., dkk, 2014; Emerging Rules for Effective Antimicrobial Coatings. Trends in Biotechnology. Vol. 32. No. 2.

[11] Yu, Qian., Zhaoqiang Wu., Hong Chen., 2015; Dual-Function Antibacterial Surface for Biomedical Applications. Acta Biomaterialia. Vol.16. Pp: 1-13.

[12] Turoz, M., Hasan, T., 2011: The Use of Methylene Blue Test for Predicting Swell Parameters of Natural Clay Soils. Scientific Research and Essay. Vo. 6 (8). Pp: 1780-1792.

[13] Martinez., J.M., Volzone, C., Garrido., L.B., 2017: Evaluation of Polymeric Al-Modified Bentonite for its Potential Application as Ceramic Coating. Applied Clay Science. Vol. 140. Pp 20-27.

[14] Rihayat, T., Suryani., Zaihmahwati. 2014. Preparation and properties and application of renewable source (palm oil polyol) based polyurethanes coatings and its thermal stability improvement by clay nanocomposites. Advanced Materials Research. Vol.887-888. Pp.566-569.

[15] Rihayat, T., Salim, S., Zaini, H., Salmiyiah., Rahmawati, C.A., Kurniati., Irawan, Y., Zaimahwati. 2017. Synthesis, Characterization and Microbial Protection of Palm Oil Based Polyurethane / Bentonite / Chitosan as Paint and Coating Material. International Conference on Sustainable and Renewable Energy Engineering.

[16] Teuku, R., Suryani., Teuku, F., Harry, A., Wirjosentono., Syafruddin., Helmi., Zulkifli., Pocut, N, A., Muhammad, S. 2017. Mechanical properties evaluation of single and hybrid composites polyester reinforced bamboo, PALF and coir fiber. IOP Conference Series: Materials Science and Engineering. Vo.334

[17] Rihayat, T., Suryani., Satriananda., Ridwan., Nurhani,., Putra, A., Audina, N., Yunus, M., Sariadi., Safari., Jalal, R., Khan, N,S, P., Saifuddin. 2018. Influence of Coating Polyurethane with Mixture of Bentonite and Chitosan Nanocomposites. International Seminar on Chemistry. Vol. 2049