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Formulation of Polyurethane with Bentonite-Chitosan as Filler Applied to Carbon Steel as an Antibacterial and Environmentally Friendly Paint

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Abstract. The coating material used for the manufacture of polyurethane paint with the addition of bentonite into the matrix can improve thermal capability. The purpose of this study is to produce new material namely hybrid bentonite-chitosan which can be used as a filler for the manufacture of polyurethane paint, chitosan intercalation process into bentonite interlayer and increase the concentration of surfactant against the opening of bentonite interlayer. By varying the CEC of cationic surfactants (0.7 CEC, 1 CEC , and 1.3 CEC) and CEC anionic surfactants (0.1 CEC, 0.2 CEC and 0.3 CEC) to obtain the highest basal spacing, structure, and morphology, several characterization procedures have been carried out. From the results of interlayer bentonite analysis with modification of cationic and anionic surfactants using XRD (X-Ray Diffraction) an increase in basal spacing from 14.18393 Å to 23,00023 Å. While the FTIR (Fourier Transform Infrared) chemical structure of hybrid bentonite-chitosan at a wavelength of 2800 cm-1 shows the C-H group, 1025 cm-1 shows the C-O group and polyurethane in the -OH absorption (3445 cm-1). This study can produce hybrid bentonite-chitosan material as a filler in the manufacture of polyurethane paint.

1. Introduction

Throughout the world, there are an estimated 10 million deaths caused by diseases bacterial infections, of which more than 80% of infections in humans are caused by biofilm formation. Every year in the United States, the costs of tackling diseases caused by bacterial infections reach 25-48 million dollars, more than 60% of these expenditures are used to handle infected medical equipment (Salwiczek, et al., 2014).

Bacterial growth can be inhibited by blocking the occurrence of contact between bacteria and the surface containing substrates that can form biofilms, so that bacterial colonization can be prevented. One way is to coat the surface using anti-bacterial coating paint (Cloutier, 2015).

Paint that is often used as a coating is polyurethane (Pitera, 2017). But the material does not yet have antibacterial abilities. To improve the ability of polyurethane as anti-bacterial paint, modifications can be made through the addition of fillers (Rihayat, 2017).

One type of filler that has antibacterial properties is chitosan. In addition to chitosan, bentonite is also a type of filler commonly used for composite manufacturing. Addition of 5% bentonite to the matrix can increase the thermal composite ability by up to 60% (Yu et al., 2015). The combination of bentonite and chitosan can form a new material, namely hybrid bentonite-chitosan. The merging process can be carried out by chitosan intercalation into bentonite interlayer.

The success of chitosan intercalation into bentonite particles is strongly influenced by the amount of interlayer that can be opened by surfactants. Therefore, the focus of this research is to try to form a hybrid bentonite-chitosan with a combination of Cetyl Trimethyl Ammonium Bromide (CTAB) surfactant and Sodium Dodecyl Sulfate (SDS). The material will be used as a filler in polyurethane paint to improve thermal capability and provide antibacterial properties against polyurethane paint, so it is hoped that paint will be obtained that not only has good thermal strength but is also resistant to bacterial attacks that can be applied to medical devices.

2. Methods

2.1 Materials

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The materials used in this study are polyols based on palm oil (with ingredients such as oleic acid based on palm oil, glycerol), Toluene diisocyanate (TDI), clay from North Aceh (type Na +), cetyltrimethyl ammonium bromide (CTAB) supplied from Fluka , Sodium Deodecyl Sulfate (SDS) is supplied from Fluka, Sulfuric Acid, Hydrogen Perocicide, Glycerol, Methanol, Chitosan, xylene, acetic acid, AgNO3 solution, sodium hydroxide, agar media, staphylococcus aureus bacteria (gram positive) and Escherichia coli bacteria (gram negative).

2.2 Synthesis polyol of palm oil

The process of polyol synthesis from palm oil was carried out in a 250 ml three-neck flask equipped with a mechanical stirrer and using a batch water cooling system. 30 ml H2O2 is added to the rekator, 50 ml CH3COOH is added, 2 ml H2SO4 is stirred at 40-50ºC for 1 hour to form paracetic acid. Then put 10 ml of oleic acid stirred again for 5 hours, the obtained dioxide oil is added 100 ml methanol, 50 ml glycerol, and catalyst H¬2SO¬4 stirred again at 50ºC for 2 hours. Next, it is cooled at room temperature in the filter, so that the molecular sieve does not escape in the reactants. Then the rectum is washed with NaCl solution to remove the remaining unreacted glycerol.

2.3 Purification of Bentonite with Cationic and Anionic Surfactants

Bentonite with a size of 100 mesh as much as 2 grams was mixed with 98 ml of demineral for 0.5 hours at a temperature of 80 ° C. CTAB surfactant was added with varying CEC concentrations, namely (0.7 CEC, 1 CEC and 1.3 CEC) stirred for 2 hours at 80 ° C. After the cationic surfactant is homogeneous with bentonite, then enter the anionic surfactant into the bentonite solution which has been homogeneous with cationic surfactant and stir until homogeneous for 1 hour at 80 ° C with varying CEC concentrations namely (0.1 CEC, 0.2 CEC and 0.3 CEC). Furthermore, the results of the resulting samples were analyzed using XRD and FTIR to determine the crystal structure and functional groups of bentonite after being modified with surfactants.

2.4 Synthesis of Bentonite-Chitosan Hybrids

Bentonite which has a larger basal spacing is added with 1 gram of chitosan. Furthermore, 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 the hybrid bentonite-chitosan produced.

2.5 Processing of Polyurethane Paint with Additional Bentonite-Chitosan Hybrid Filler

Polyol 8.92 ml 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 morphology.

2.6 Spectroscopy Fourier Transform Infra Red (FTIR) Analysis

Fourier Transform Infra Red analysis is used to identify chemical compounds from organic and inorganic materials, and can also analyze solids, solutions and films. The results of the analysis obtained are in the form of data in the form of a spectrum of wavelengths from the samples that have been analyzed.

2.7 X-Ray Difraction (XRD)

XRD analysis was used to identify the magnification of benthic basal spacing after the addition of cationic surfactants and anionic surfactants. The results of the analysis are in the form of basal spacing data (in units of Å).

2.8 Scanning Electron Microscopy (SEM)

SEM is used to determine the shape and change of the surface of a material. In principle, if there is a material change from the surface, the material has undergone a change in energy. Energy can be emitted, reflected and absorbed and converted into other electromagnetic wave functions and can be read on SEM

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images.

2.9 Antimicrobial Activity

The antibacterial activity of polyurethane paint was tested with gram positive bacteria (Staphylococcus Aureus) and gram negative bacteria (Escherichia Coli).

3. Result and Discussion

CEC or called cation exchange capacity (CEC) is a component of soil to absorb and exchange / release back soil solutions (Zuber, 2010). One of the CEC tests is the methylene blue method. Methylene blue powder when mixed with water and identified by chemical formula: C16H18N3SCl. When mixed with clay (bentonite), the chloride ion in the solution of methylene blue is replaced by cation in clay. The amount of methylene solution adsorbed varies according to the number of minerals and types of clay (Turoz, 2011).

The mixture made by adding 5 ml of methylene blue solution to the clay solution is stirred to 200 rpm, after 1 minute a number of mixtures are taken with a dropping pipette and deposited on filter paper. Generally, the filter paper looks circle but there are no blue shadows around it (this means the test is negative). To get a positive test, repeat the previous step until it appears that the last drop has a bright blue circle around dark blue (meaning the test is positive) this is called halometric.

As shown in figure 1, this shows that there is an excessive amount of methylene blue which is no longer adsorbed by clay which remains in suspense. At this point there is no addition of methylene blue, that's where the halometric formation is. Therefore, the results of the determination of benthic CEC using methylene blue methode obtained the CEC value of North Aceh bentonite which was equal to 95.2 meq/100 grams.

Bentonite clay is widely used in paint. White Bentonite is the material of choice available around a lot. In water-based paint, sodium or montmorillonium suspends and thickens 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 the requirements of different vehicles including varnishes, epoxy resins, and vinyl resins, which are used in paint formulations. These organoclays improve pigment suspension, viscosity and technrophy control and are very good in non-drip emulsion paints (Rihayat. et al. 2017).

Bentonite used is derived from Nisam, North Aceh. This bentonite was first crushed and then sifted to a size of 100 mesh. Before mixing with surfactants, raw bentonite was analyzed using XRD to find out d-spacing from bentonite interlayer.

Table 1. Observation Results XRD Interlayer Basal Spacing Bentonit from Surfactant CEC Value Variations

CEC Surfaktan		**Analisa**
Kationik (CTAB)	**Anionik (SDS)**	**XRD (d-spacing (Å))**
0,7	0,1	15,11134
	0,2	15,27891
	0,3	16,29728
1	0,1	18,51769
	0,2	19,11531
	0,3	19,17534
1,3	0,1	20,18793
	0,2	21,98631
	0,3	23,00023

Before modification using a surfactant, the basal spacing was 14.18393 Å, then increased after adding the surfactant to 23,00023 Å.

X-Ray Diffraction is one of the characterizations that uses x-rays, x-ray scattering is produced if a metal electrosa is fired with electron-electrons at high speed in a vacuum tube. A crystal can be used to diffract x-ray files due to the order of x-ray wavelengths almost equal to or smaller with the order of distances between atoms in a crystal.

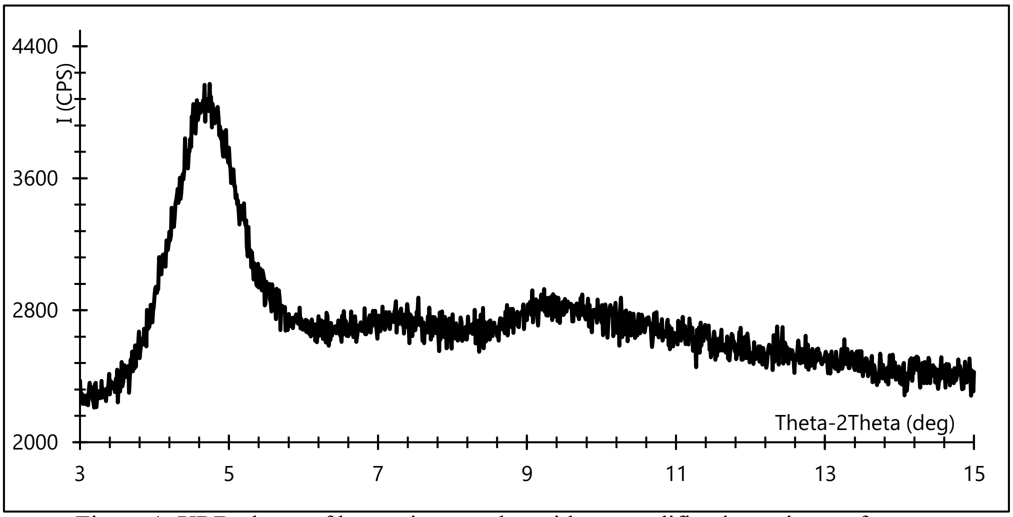

Figure 1. XRD charts of bentonite samples without modification using surfactants

From Figure 2, raw bentonite basing specs were obtained, namely 14.18393 Å. Then the raw bentonite was mixed with cationic surfactant Cetyl Trimethyl Ammonium Bromide (CTAB) stirred for 2 hours and then the mixture was added with anionic surfactant Sodium Deodecyl Sulfate (SDS) stirred for 1 hour. The results of the two types of surfactants were then washed to remove surfactants contained in the bentonite interlayer using distilled water, to test whether the surfactant had disappeared from the bentonite solution then AgNO3 solution was dropped into surfactant water, if the water turned gray then it was still contained surfactants, therefore it is necessary to wash again with distilled water.

Then the solid free of the surfactant is filtered with a vacuum pump to separate the solid from the remaining liquid. Solids are obtained than in the oven at 150ºC to dry. Then it was crushed again until smooth and then analyzed again with XRD to see the increase in d-spacing and SEM to observe the morphological structure of the bentonite obtained.

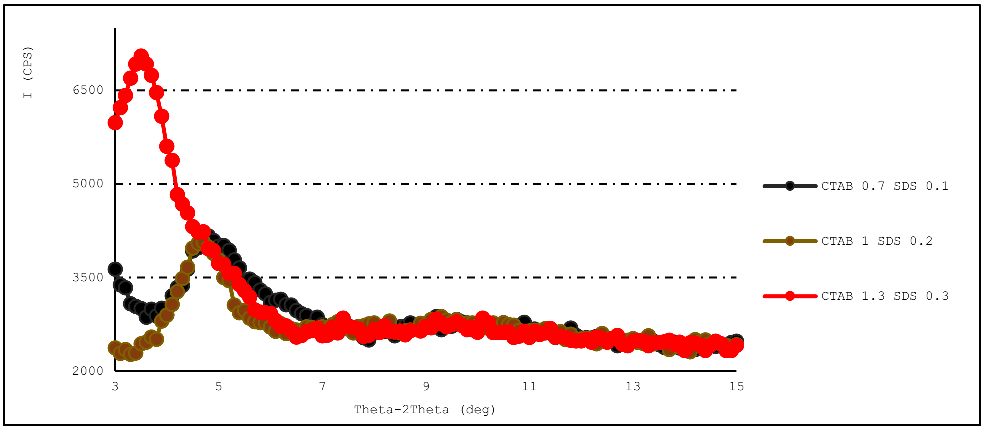

Figure 2. XRD graph of bentonite samples after surfactant intercalation

From Figure 3, the modified basal spacing of bentonite was obtained using cationic and anionic surfactants, namely at CTAB 0.7 CEC and SDS 0.1 CEC, d-spacing was 15.11134 Å, on CTAB 1 CEC and SDS 0.2 CEC, d-spacing was obtained, 19,11531 Å, on CTAB 1.3 CEC and SDS 0.3 CEC, d-spacing is 23,00023 Å.

Thus, the highest d-spacing is the addition of CTAB 1.3 CEC surfactant and SDS 0.3 CEC which is 23,00023

Å. The intercalation mechanism between positively charged CTAB and interlayer of bentonite is negatively charged through cation exchange. When SDS is added, interlayer bentonite increases (Liao, 2016).

After analyzing using XRD, an analysis was then performed using FTIR to determine the functional groups of bentonite and chitosan after addition of surfactants.

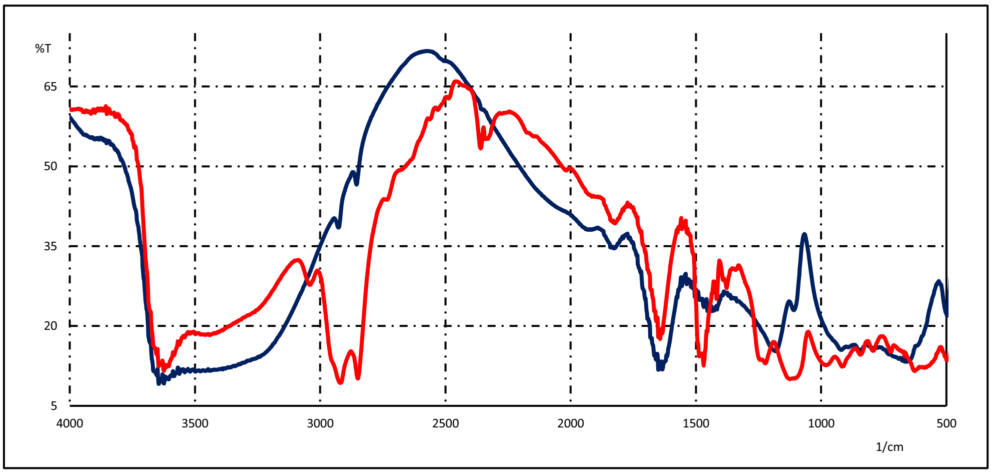

Figure 3. FTIR graph of bentonite samples before being modified with surfaces and after modification

From figure 1, bentonite samples before modified surfactant obtained O-H group whose wavelength was 3510 cm-1 and after addition of O-H group surfactant decreased to 3501 cm-1 showed that the surfactant intercalation into bentonite interlayer resulted in the nature of the bentonite becoming hydrophobic. After the modified bentonite Br-H group was identified which identifies CTAB at a wavelength of 3019 cm-1, whereas to identify SDS that is in the SH group at Wavelength 3419 cm-1, the SO group is Wavelength 1230 cm-1 and CH group in Length wave 1098 cm-1.

The morphology of nanocomposites was investigated by Scanning Electron Microscopy (SEM) at room temperature. A high-resolution microscope operated at an accelerated 20 kV voltage was used for SEM to observe the surface of the material such as nanofiller agglomeration and its distribution. SEM of the sample surface was cut using an ultramicrotome equipped with a diamond knife at 100ºC and then coated with platinum. In principle, if there is a material change from the surface, the material has undergone an energy change. Energy can be emitted, reflected and absorbed and converted into other electromagnetic wave functions that can be read on SEM photographs.

SEM has an electron gun that produces electrons at an accelerated voltage of 2-30 kV. The electron beam is passed on several electromagnetic lenses to produce an image measuring <10 nm in the sample displayed in the form of a photographic film.

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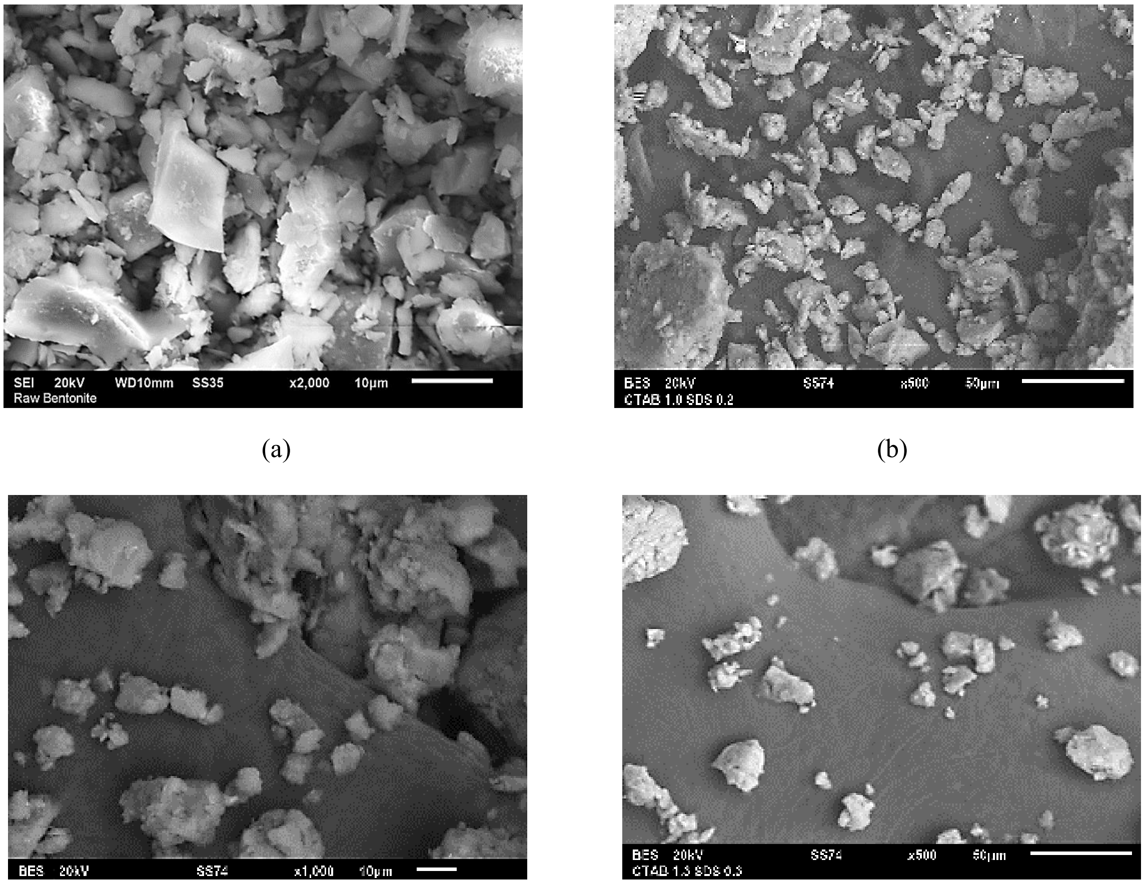

(a) (b)

(c) (d)

Figure 4. SEM analysis of crude bentonite (a), bentonite modification CTAB 0.7 CEC and SDS 0.1 CEC (b), bentonite modification CTAB 1 CEC and SDS 0.2 CEC (c) and bentonite modified CTAB 1.3 CEC and SDS 0.3 CEC (d)

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.

3.1 Fourier Transform Infrared (FTIR)

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 antibacterial activity, but a double performance of bacteria that absorb and kill bacteria when chitosan chains interact with bentonite layers.

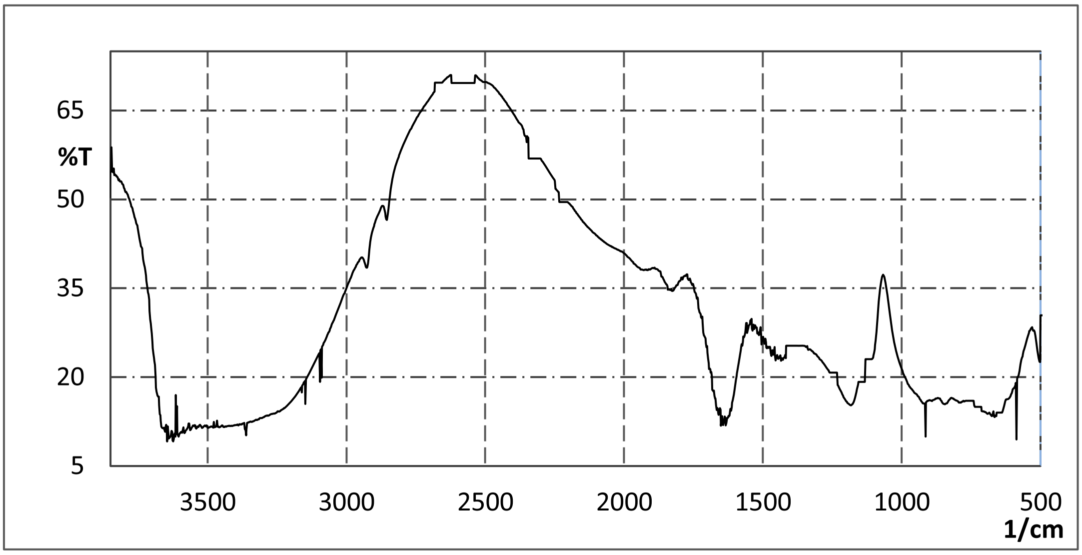

Figure 5. FTIR spectrum of Hybrid Bentonite-Chitosan

The FTIR spectrum in Figure 5. 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 3300 cm-1, N-H at 3500 cm-1, C = O at wavelength 1672 cm-1, C-H group at Wavelength 2800 cm-1. Bentonite: -OH group at Wavelength 3430 cm-1, Si-O group at Wavelength 1060 cm-1 and Al-O and Si-O groups at Wavelength 800 cm-1.

Aliphatic C-H Cluster at 2800 cm-1 Wavelength and 1025 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 (Cabuk, 2016).

3.2 Scanning Electron Microscopy (SEM)

Testing using a 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 (Rihayat, 2015).

SEM images of hybrid bentonite-chitosan as shown in figure 6. A small white surface, chitosan which has been dispersed on the surface of the bentonite.

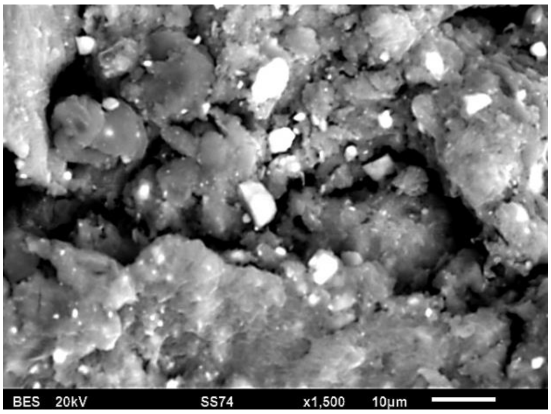

Figure 6. SEM analysis of hybrid bentonite-chitosan samples

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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.

Nanocomposite polymers are a class of hybrid materials composed of matrix organic polymers with dispersed inorganic materials, which have at least one dimension in the nanometer range. At 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 flameability (Zuber, 2010).

Bentonite can provide properties such as high thermal stability, light weight, 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 nanoclay 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. 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 (Kara, 2014).

Polyurethane synthesis is carried out by mixing the polyol with its filler, namely hybrid bentonite-chitosan produced before stirring until homogeneous (about 60 minutes) then add Toluene Diisosianate (TDI) little by little and add solvent, then stir again at a speed of 200 rpm until homogeneous. The results of polyurethane paint are then applied over the cleaned plate surface, and wait until it dries. Then characterization using SEM to see the functional groups contained in the polyurethane paint produced and the morphology of the plate that has been applied with polyurethane paint.

The morphology of polyurethane nanokomposite with the addition of hybrid bentonite-chitosan filler was analyzed using SEM (Scanning Electron Microscope) at room temperature. SEM fractionography results showed that chitosan chains were intercalated well into bentonite interlayer (Cabuk, 2016).

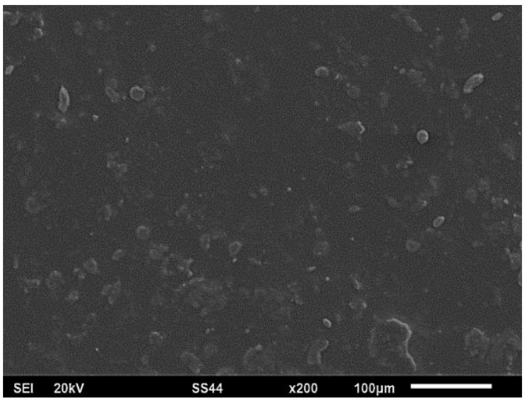

Figure 7. SEM Analysis Results of Polyurethanes with Hybrid Bentonite-Chitosan Filler

SEM fractography results in figure 5. namely darker-tended surfaces namely iron plate that has been applied with polyurethane paint, polyurethane paint produced mixed with chemicals and the main ingredient is polyol from palm oil (oleic acid) while small colored lumps grayish white which are hybrid bentonite-chitosan which has been mixed into polyurethane paint.

Fractography from the results of SEM analysis in Figure 4.3, we can see that the surface is getting smaller and smaller. In figure (a) the raw bentonite (without modification) the resulting fractography is crystalline and has a larger size. In figure (b), (c) and (d) modified bentonites show cationic and anionic surfactants that have been dispersed into the bentonite interlayer and are smaller in size compared to raw bentonite.

3.3 Antimicrobial Activity

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 antibacterial activity, but a dual performance of bacteria that absorbs and kills bacteria when chitosan chains interact with bentonite layers (Flach, 2017).

Chitosan can show antibacterial activity in acid solutions because of the presence of protonated amino groups. Bentonite has no antibacterial activity because of the negative surface charge that indicates its anionic structure. By increasing the concentration of chitosan as an antibacterial agent in the composite structure, hybrid bentonite-chitosan shows antibacterial activity in a specific way against gram positive and gram-negative bacteria.

In particular, the positively charged group on the chitosan structure shows high antibacterial actovotas against gram negative than gram positive bacteria because their murine walls are thinner, allowing faster absorption of ions in the cell.

There are several mechanisms proposed to describe bacterial inhibition by various composites in the literature: this is the adhesion of nanoparticles to the surface of bacteria, changing the nature of the membrane, penetrating inside bacterial cells, and producing DNA damage. One of these mechanisms can be considered for the anti-bacterial activity of hybrid bentonite-chitosan composites. It should be noted that chitosan-based materials can cause cell death by disrupting microbial cell walls by electrostatics.

4. Conclusion

Bentonite CEC obtained using a halometric method is equal to 95.2 meq / 100 grams. Basal spacing from North Aceh bentonite before the addition of surfactant was 14.18393 Å, and increased after it was modified with CTAB surfactant at 1.3 CEC and SDS 0.3 basal CEC spacing obtained at 23,00023 Å.

The results of FTIR analysis on hybrid bentonite-chitosan samples obtained by the aliphatic CH group at a wavelength of 2800 cm-1 and wavelength of 1025 cm-1 showed the presence of CO groups.

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