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ADDITION OF BENTONITE AND CHITOSAN FILLING TO POLYURETHANE COATING PAINT IN AN EFFORT TO INCREASE RESISTANCEAGAINST HEAT AND ANTIBACTERIA

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ABSTRACT

The increasing market demand for polyurethane is due to its various functions, including being used as a coating material, adhesives, elastomers and hard foams.Polyurethane is a polymeric material that contains a functional group (-NHCOO-) in its main chain. In principle, polyurethane can be produced by reacting two reactive materials, polyol and isocyanate. Various researches are intensively carried out to synthesize polyurethane in order to improve the performance of polyurethane.Bentonite and chitosan are widely used as filler materials in polyurethane matrices to retain heat and improve the mechanical properties of polyurethane. The addition of bentonite and chitosan to polyurethane will affect the mechanical properties, thermal properties, and morphological structures which can be seen based on the FTIR test, TGA test, SEM test and Antibacterial test.In this study, variations of Bentonite and Chitosan 5.7.9% will be used, then the mixing process with Polyurethane will be carried out. The results showed that the results of the FTIR analysis showed that the mixing of Polyurethane and bentonite did not affect the wavelength absorption of the Polyurethane functional groups themselves. This was due to the mixing process which took place only physical bonds without chemical bonds. The results of thermogravimetric analysis (TGA) showed changes in the weight of the material when heated and it could be concluded that the best sample was B:K 9%, because it experienced less weight loss. Based on the results of the Morphological Structure test with a Scanning Electron Microscopy (SEM) chitosan chain dispersed well into the bentonite interlayer, as shown by testing using the SEM tool. The results of the antibacterial test showed that the more chitosan and bentonite added, the better the ability to inhibit the growth of Escherichia coli bacteria. In testing the activity of these bacteria it can be seen that chitosan and bentonite are better at inhibiting the growth of Escherichia coli than Staphylococcus aureus.

Keywords: Bentonite, Chitosan, Polyol, Polyurethane, Thermal

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INTRODUCTION

Corrosion problems that often occur in the industrial world make researchers globally begin to take approaches related to corrosion prevention. Corrosion can cause damage to the materials used, such as vehicles and infrastructure[1]. Damage arising from this corrosion phenomenon causes large economic losses and threatens personal safety. Anti-corrosion coatings are considered to be very effective and economical in protecting metal facilities[1]. In recent years polyurethane has become a popular material used in the polymer industry.

Based on data from Fortune Business Insights, in 2020 the global polyurethane market value is USD 56.45 billion and is projected to increase to 81.74 billion in 2028. The increasing market demand for polyurethane is because polyurethane has a variety of functions including being used as a coating material, adhesive material, tough elastomers and foams.

Polyurethane is a polymeric material that contains a functional group (-NHCOO-) in its main chain. In principle, polyurethane can be produced by reacting two reactive materials, polyol and isocyanate. Various researches are intensively carried out to synthesize polyurethane in order to improve the performance of polyurethane. The addition of nanomaterials has received attention because it can improve the physical properties of polyurethane[2].

In this decade, bentonite and chitosan have been widely used as filler materials in polyurethane matrices to retain heat and improve the mechanical properties of polyurethane[3]. Bentonite is a trade term for clay containing monmorillonite. Widely used in the polymer industry, bentonite-coated silicates can play an important role in terms of providing barrier and heat-resistant properties for coating systems.

The addition of chitosan into an alloy in modifying polyurethane can increase the anti-bacterial properties of polyurethane[4]. Intercalation of chitosan through a cation exchange process can increase the antimicrobial activity. Chitosan is a chemical compound derived from the biological substance chitin. Chitin is generally obtained from the skeletons of invertebrate animals from the Arthropoda sp, Mollusca sp, Annelida sp, Nematoda sp, and several groups of fungi.

In this study, variations of Bentonite and Chitosan 5.7.9% will be used, then the mixing process with Polyurethane will be carried out. Where the addition

of bentonite and chitosan can produce a coating paint that has better physical properties, anti-bacterial properties and heat reinforcement. The addition of

bentonite and chitosan to polyurethane will affect the mechanical properties, thermal properties, and morphological structures which can be seen based on the FTIR test, TGA test, SEM test and Anti-Bacterial test.

EXPERIMENTAL

2.1 Material

The materials used in this study consisted of 3 types, namely materials for polyurethane, materials for bentonite, and materials for chitosan. The ingredients for making polyurethane are oleic acid based on palm oil, galcial acetic acid CH3COOH, H2O2 30%, H2SO4, Methanol, Glycerin, Xylene and Diisocyanate toluene (TDI). The ingredients for making bentonite are Aquadest, Bentonite, Cetyl trimethyl ammonium bromide (CTAB) and AgNO3. While the materials used to make chitosan are shrimp shells, NaOCl, NaOH, HCl.

2.2 Methodology

2.2.1 Polyol synthesis

The polyol synthesis process goes through two stages of the process, namely the epoxidation and hydroxylation processes. In the epoxidation stage there are six steps starting from polyol synthesis in a 350 ml 3 neck flask equipped with a mechanical stirrer and cooling system, then 60 ml of glacial acetic acid (CH3COOH) and 30 ml of 30% hidrogen peroksida (H2O2) are added slowly while stirring. Through the dropper funnel, 2 ml of concentrated asam sulfat (H2SO4) was added and stirred slowly at 30°C for 1 hour. Then, slowly add 100 ml of palm oil oleic acid through the dropper funnel. The temperature was maintained at 30ºC and continuously stirred for 3 hours. The result of the reaction is an oleic acid epoxidized compound which is cooled to room temperature and the separation of the oil phase as epoxidized oil[5].

The hydroxylation stage was divided into four stages, namely 100 ml of methanol added 50 ml of glycerin, 2 ml of concentrated Hidrogen peroksida (H2SO4) catalyst and 5 ml of water into a 350 ml three-neck flask, heated to a temperature of 40ºC. Then the mixture was added to the epoxidized oil solution and stirred at 50°C for 2 hours. Then cooled to room temperature and transferred

to a separating flask to separate the polyols formed and then stored in glass bottles. Then analyzed with FTIR to determine the OH groups in polyols.

2.2.2 Refining and Opening of the Bentonite Interlayer

Weigh as much as 20 grams of bentonite and then grind it using a crusher. Filtering was carried out using a 100 µm sivetray. As much as 18.2 grams of cetyltrimethyl ammonim bromide (CTAB) was dissolved in 250 mL of distilled water, the solution was heated at 80□ for 1 hour. As much as 20 grams of bentonite dissolved with 250 mL of distilled water. The bentonite dispersion solution was added to the CTAB solution and stirred for 1 hour. The bentonite was filtered and washed with distilled water several times until no bromide was present. The filtrate was tested by 1 M AgNO3 test until a white precipitate formed. Bentonite is put in the oven at 60□ to dry.

2.2.3 Synthesis of Chitosan

100 grams of shrimp skin cleaned with boiled water for 1 hour. Then the shrimp shells were washed and dried at 60oC for 2 hours in the oven. Then the dried shrimp shells are ground into powder. Demineralization of shrimp shell powder using HCl with a concentration of 0.25M – 2M (ratio 1:10 (w/v)) by heating at 60-70ºC for 4 hours at a speed of 500 rpm, then bleaching with NaOCl and 5% NaOH to produce chitosan.

2.3 Sample Preparation

Prepare 3 containers for mixed samples of polyurethane, bentonite and chitosan. Mix polyurethane, bentonite and chitosan (total weight = 30g). There are four steps to make the polyurethane-bentonite-chitosan coating, namely mixing polyol, bentonite, chitosan and then TDI into a glass beaker, stirring with a magnetic stirrer at 200 rpm for 1 hour. In this procedure, amounts of bentonite and chitosan were used, respectively 5, 7, and 9 weight percent (%wt). The resulting polyurethane is then cooled to room temperature. Furthermore, the chemical structure of polyurethane, bentonite, and chitosan paints was analyzed using FTIR, surface shape analysis using SEM, heat resistance test and antibacterial test.

2.4 Characterization Techniques

2.4.1 Functional group analysis with Fourier Transform InfraRed (FTIR)

FTIR is used to analyze the characterization of polymeric materials and analysis of functional groups. The sample will be crushed with KBr using a Shimadzu FTIR spectrophotometer.

2.4.2 Analysis of thermal properties by thermogravimetric analysis (TGA)

In principle, this method measures the mass loss of a material when it is heated from room temperature to a high temperature of about 900□ with a heating rate of 20□.

2.4.3 Scanning Electron Microscopy (SEM)

An instrument that forms a microscopic image of the surface of a specimen. An electron beam with a diameter of 5-10 nm is directed at the specimen. The SEM technique is basically an inspection and analysis of the surface of the specimen, the data or display obtained is data from the surface or layer which has a thickness of sabout 20 µm from the surface. The surface image obtained is a photograph of all the protrusions, indentations and holes on the surface.

2.4.4 Antibacterial test

To determine the effect of adding chitosan as an antibacterial, it was analyzed using the halo zone method, namely cultivating bacteria on solid NA media in petri dishes. Then each plate that has been smeared with polyurethane is placed on the surface of the media. Done aseptically in laminar flow. Samples were incubated for 24 hours at 37ºC. Colony shape and microbial activity were observed. Observations were made during the incubation period. The bacterial inhibition activity of the plate against bacterial growth was measured based on the area of the clear zone formed around the membrane.

RESULTS AND DISCUSSION

3.1 Functional group analysis with Fourier Transform InfraRed (FTIR)

The results of FT-IR analysis have shown the formation of NH urethane groups in polyurethane compounds of palm oil, the reaction lasted for 6 hours at 80oC as evidenced by the absorption of the NH wavenumber which widened at 3631 cm-1 cm-1 . The results of measuring the wavelength of the NH group in the previous study were 3300cm-1 [9], 3311 cm-1 , 3315 cm-1 , 3316 cm-1 [6], 3345cm-1. Meanwhile the absorption wave number of the C=O urethane group widened at 1716.65 cm-1 , in the previous study 1720 cm-1 [10], 1652.95 [7], while the CH group at absorption was 2935.66 cm-1 and in the previous study 2924.10 cm-1. Based on the analysis results, it can be seen that the functional groups of pure PU, PU/Bentonite, PU/Chitosan, and PU/B/K nanocomposites did not change functional groups. Mixing PU with bentonite and chitosan does not affect the wavelength absorption of the polyurethane functional group itself, the same as the results of previous studies on FTIR analysis of PU, PU-plasma, PU-

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AAm, PU-CH-0.5, and PU-CH-2.0, PUh and Pre-Puh. This is due to the process of mixing bentonite and chitosan with polyurethane which occurs only in physical

bonds, not chemical bonds. So, there is no change in chemical bonding that occurs so that the wavelength absorption of the PU/B/K nanocomposite functional groups that are detected does not change. This is due to the process of mixing bentonite and chitosan with polyurethane which occurs only in physical bonds, not chemical bonds. So, there is no change in chemical bonding that occurs so that the wavelength absorption of the PU/B/K nanocomposite functional groups that are detected does not change. This is due to the process of mixing bentonite and chitosan with polyurethane which occurs only in physical bonds, not chemical bonds. So, there is no change in chemical bonding that occurs so that the wavelength absorption of the PU/B/K nanocomposite functional groups that are detected does not change[8].

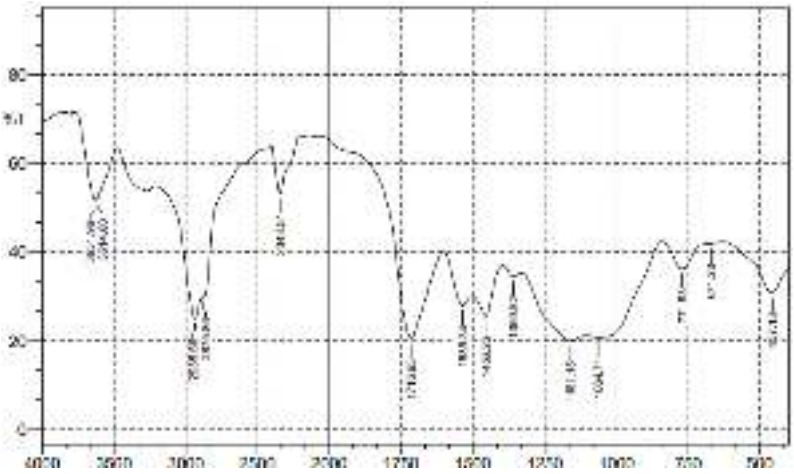

Figure 3.1 FT-IR analysis of PLA/coir/bentonite composites

3.2 Analysis of thermal properties by thermogravimetric analysis (TGA)

Loss of mass on thermal testswith thermogravimetric analysis (TGA) occurs due to the decomposition process. Thermogravimetric analysis (TGA) can be used to characterize any material that exhibits a change in weight when heated, and to detect phase changes due to decomposition processes. Thermal test results with thermogravimetric analysis (TGA) on sample B:K 5%, onset starts at 392.82ºC and endset is 497.46ºC with weight loss -63.875%, at B:K 7% onset starts at 446.96ºC and the endset is 504.01ºC with a weight loss of -53.698%, and B:K 9%, the onset starts at 312.78ºC and the endset is 403.25ºC with a weight loss of -65.729%. So it can be concluded that the best sample is B:K 6%, because it experiences less weight loss.

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3.3 Morphological analysis of surface scanning electron microscopy (SEM)

The results of the Morphological Structure Test with Scanning Electron Microscopy (SEM), the chitosan chains were well dispersed into the bentonite interlayer, as shown by testing using the SEM tool. The interaction between the

hydroxylated silicate edge groups and the chitosan chains can be associated with the formation of composite flocculation. The surface structure of the sample consists of a mixture of chitosan and bentonite iron plates coated with polyurethane with bentonite-chitosan filler giving a darker surface. There is no agglomeration in the sample[9].

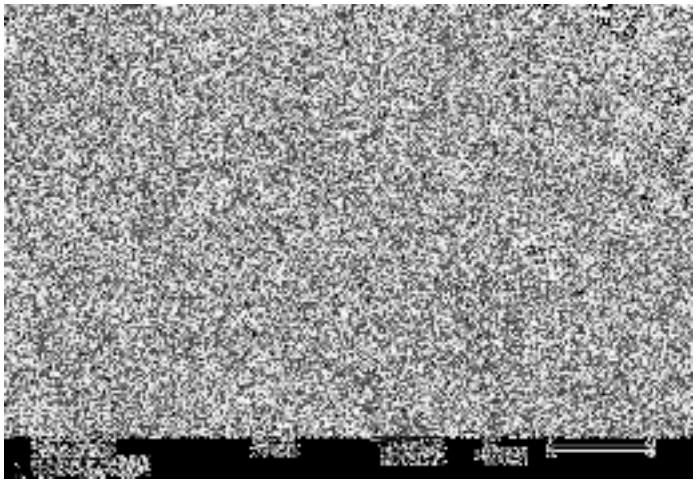

Figure 3.4 Typical SEM micrographs of sample

3.4 Antibacterial test

Antibacterial is a substance that can inhibit the growth of bacteria and can kill bacteria that cause infection. Staphylococcus aureus and Escherichia coli are Gram-positive and Gram-negative bacteria that can cause infections or diseases in the body [10]. Antibacterial activity testing obtained data on the diameter of the inhibition zone for Staphylococcus aureus bacteria in the B:K 5% sample of 3.75 mm; B:K 7% by 8.5 mm; B:K 9% by 13.5mm. These results indicate that the more chitosan and bentonite added, the better the ability to inhibit the growth of Staphylococcus aureus bacteria. While the average diameter of the inhibition zone in the Escherichia coli bacteria test with 5% B:K samples was 5.75 mm; B:K 7% by 10.5 mm; B:K 9% by 15 mm. These results also indicate that the more chitosan and bentonite added, the better the ability to inhibit the growth of Escherichia coli bacteria. In testing the activity of these bacteria it can be seen that chitosan and bentonite are better at inhibiting the growth of Escherichia coli than Staphylococcus aureus.

CONCLUSION

The results of thermogravimetric analysis (TGA) show changes in the weight of the material when heated. Thermal test results using thermogravimetric analysis (TGA) on sample B:K 5%, onset starts at 312.78ºC and endset is 403.25ºC with weight loss -65.729%, at B:K 7% onset starts at 392.82ºC and the endset is 446.96ºC with a weight loss of -63.875% and B:K 9%, the onset starts at 446.96ºC and the endset is 504, 01ºC with a weight loss of -53.698%, so it can be concluded that the best sample is B:K9%, because it experiences less weight loss. Based on the results of the Morphological Structure test with a Scanning Electron Microscopy (SEM) chitosan chain dispersed well into the bentonite interlayer, as shown by testing using the SEM tool. The interaction between the hydroxylated silicate edge groups and the chitosan chains can be associated with the formation of composite flocculation. The results of the Anti-Bacterial Test showed that the more chitosan and bentonite added, the better the ability to inhibit the growth of Escherichia coli bacteria. In testing the activity of these bacteria it can be seen that chitosan and bentonite are better at inhibiting the growth of Escherichia coli than Staphylococcus aureus.

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