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CHARACTERIZATION OF BIODEGRADABLE POLYURETHANE POLYMER BASED ON BENTONITE-CHITOSAN HYBRID PALM OIL AS A CORROSION INHIBITORY AGENT

Sabiila Yasara SA[1], Syafruddin[1]*, Teuku Rihayat[1]
[1]Department of Chemical Engineering, Lhokseumawe State Polytechnic, Lhokseumawe City
*Email: syafruddin@pnl.ac.id

ABSTRACT
Corrosion problems that often occur cause various damages and losses. The coating process has the advantage of being able to protect the metal surface from environmental influences that result in corrosion of the metal. The innovation of combining Polyurethane with Bentonite-Chitosan filler is able to make the polymer have better corrosion resistance. This study aims to see the effect of mixing between Polyurethane and Bentonite-Chitosan filler. The sample formulation used is polyurethane with variations of bentonite and chitosan 1%, 3%, 5%, 7%, 9%. The addition of Bentonite-chitosan filler affects the mechanical properties of the material. Characterization with the addition of Bentonite and Chitosan produces a polymer that has good thermal stability and good corrosion resistance. Test result Fourier Transform Infrared(FT-IR) there are functional groups NH, CH, C=O. Based on test resultsThermogravimetric Analysis(TGA) samplePolyurethane with modified bentonite 9%/chitosan 9% w/w has the best thermal stability among other samples where the sample starts to degrade (on set) at 419.22(oC) and stops degrading (end set) at 521.94 (oC) with a weight loss of -31.156%. Polyurethane samples with 1% bentonite/chitosan 9% w/w modification had lower thermal stability where the sample started to degrade (onset) 312.21 (oC) and stopped degrading (end set) at 391.09 (oC) with a weight loss of -55.729 %. The results of the morphological test using the SEM tool show that the chitosan chains dispersed well into the bentonite interlayer. The corrosion test showed that the addition of bentonite and chitosan affected the corrosion rate, the greater the composition of bentonite and chitosan, the lower the corrosion rates. the best sample with a ratio of Polyurethane/Bentonite/Chitosan 9:9% w/w experienced the smallest corrosion rate of 5.08mpy and a mass loss of 0.1 gram.

Keywords: Biodegradable, Corrosion, Polyurethane, Bentonite, Chitosan

1. INTRODUCTION

Corrosion is a problem that often occurs in the industrial world. Metal corrosion is a serious problem and causes huge economic losses every year in the world[1]Corrosion can cause severe damage to metal facilities, which can cause major economic losses and can threaten personal safety. There are many approaches used to prevent corrosion, organic coatings attract a lot of attention from materials scientists, where organic coatings are usually developed in the form of coating paints. Paint is a general term used to protect and give color to objects. Meanwhile, coating is the process of deposition of coating particles on a metal surface, either electrolytically or non-electrolytically[2]Organic coatings are widely used as physical barriers to inhibit metal corrosion.The coating process has the advantage of being able to protect metal surfaces from environmental influences that cause corrosion of the metal.

Traditional solvent-based coatings that can produce volatile organic compounds (VOCs) that are detrimental to human health and the environment are slowly being replaced by environmentally friendly materials.[3]. Among them, vegetable oil-based polyurethanes, vegetable oil-based polyurethane coatings have proven their capabilities by displaying superior properties such as excellent toughness, abrasion resistance, corrosion and chemical resistance.[4]Recently, polyurethane has received special attention because of its low cost and excellent weather resistance. However, the long-term corrosion resistance performance of polyurethane coatings is weaker than solvent-based coatings, so more development is needed to strengthen the anti-corrosion performance of polyurethane coatings. This can be done by carrying out material engineering or modification.

In this decade, polyurethane (PU) has become one of the most popular materials in the world[5]. Polyurethane is an important division of synthetic polymers that is widely used in biomedical applications and various industries, especially the motor vehicle industry. Products that contain polyurethane include synthetic resins, furniture coatings, construction materials, paints, elastomers, synthetic leather and paints. As has been mentioned, polyurethane is one of the polymers used as raw material for making coating paints. However, polyurethane has a coating system stability and low thermal barrier properties[6]To improve the physical properties of polyurethane (thermal and stretch resistance), modifications are made by adding filling materials or fillers including bentonite and chitosan.[8]Polyurethane is generally a polymer compound whose main chain constituent is a urethane group (-NHCOO-)[9]The urethane group -NH-COO- is an ester of carbamic acid, which is a hypothetical unstable (and impossible to obtain under normal conditions) acid (R-NHCOOH). To synthesize urethane groups, various methods can be used, but the most appropriate is the reaction between isocyanate and alcohol. Polyurethanes can be crystalline solids, segmented solids, amorphous glasses, orviscoelastic solids. The properties of linear polyurethane are also highly dependent on temperature and humidity.

Research Urgency

Recently bentonite has become very popular in the paint industry. Bentonite is a trade term for clay containing montmorillonite.The use of clay itself is widely used in the polymer industry. Based on previous research in the field of polyurethane nanocomposites, it was found that to increase the heat resistance of polyurethane materials, bentonite was added to the polyurethane coating.[5]The addition of bentonite nanocomposite filler shows an increase in the mechanical and temperature properties of polyurethane. Clay itself is widely used in the polymer industry. Clay coated silicate can play an important role in terms of providing barrier and heat resistant properties to coating systems. The main content of bentonite is the mineral montmorillonite (80%) with the chemical formula ($Al2O3.4SiO2.X\ H2O$). It has color variations ranging from white to yellow, to olive green, deposited in various fresh waters and marine basins, characterized by moderate environmental and climatic conditions. The bentonite sheet structure consists of 2 tetrahedral layers composed of the main element SIlica (O and OH) flanking one octahedral layer composed of the element M (O and OH) (M= Al, Mg, Fe).

By adding chitosan which is an alloy in modifying polyurethane, polyurethane can have anti-bacterial properties. According to research results which show that intercalation of chitosan through a cation exchange process can increase its antimicrobial activity. Chitosan is a chemical compound derived from the biological material chitin. Chitin is generally obtained from the skeletons of invertebrate animals from the Arthopoda sp, Mollusca sp, Annelida sp, Nematoda sp, and some fungal groups. Chitosan is a multifunctional chemical in the form of fibers and is a copolymer in the form of thin sheets, pink or yellow in color, odorless. Chitosan is a poly -(2-amino-2-deoxy-β-(1-4)-D-glucopyranose) with the molecular formula ($C6H11NO4$) which can be obtained from complete or partial deacetylation of chitin.

Some research that has been carried out previously is:[10]Making polyurethane films is done by modifying the manufacture of palm oil-based polyurethane which is mixed with arganoclay at room temperature for 10 minutes, then adding diphenylmethane diisocyanate (MDI) isocyanate and stirring for 5 minutes to get a homogeneous mixture. Based on the test results, it was found that palm oil polyurethane coatings with the addition of montmorillonite (MMT) insulation experienced an increase in heat compared to polyurethane without the addition of montmorillonite. The addition of montmorillonite (MMT) can increase the adhesion of polyurethane paint coating applications and also increase the gloss index of the paint layer surface.[5]carried out the synthesis of polyurethane with the addition of bentonite filler, chitosan as a heat resistant property in the coating material obtained at a temperature of 500°C while the addition of B:K 2.5:2.5% w/w was obtained at a temperature of 580°C.

In this research, polyurethane will be made using oleic acid based on palm oil with the addition of bentonite-chitosan filler in order to increase its heat-resistant and anti-bacterial properties. Oleic acid in palm oil will be used as a source of polyol to produce polyurethane. The characteristics carried out are assessed in terms of functional group analysis, bacterial activity analysis, and heat resistance analysis.

2.RESEARCH OBJECTIVES, BENEFITS AND LIMITATIONS

This research can be a solution to the problems caused by corrosion problems, so that renewable resource-based coating paint is produced which has anti-bacterial and anti-corrosion properties by using palm oil-based polyurethane polymers which are strengthened by the addition of Bentonite and Chitosan replacing petrochemical polymers in the paint industry so that can be applied to coating paint manufacturing factories which currently use petroleum materials which are becoming scarce and are not environmentally friendly as raw materials. The use of palm oil-based polyurethane polymer reinforced with the addition of Bentonite and Chitosan has shown many improved properties in previous polymer studies, especially increased thermal and anti-bacterial properties. The coating paint industry requires good thermal properties to prevent corrosion at high temperatures and good anti-bacterial properties to prevent the growth of bacteria that can be harmful to health. So the coating paint produced from this research has better conventional value than the coating paint previously available.

3. RESEARCH METHODS

3.1 Materials

The materials used in this research consisted of 3 types, namely polyurethane based on palm oil, bentonite and chitosan.

3.2 Methodology

3.2.1 Purification and Opening of Bentonite Interlayer

Weighed 20 grams of bentonite and then ground it using a crusher. Filtering was carried out using a 100 size sivetrayɥm. A total of 18.2 grams of cetyl trimethyl ammonim bromide (CTAB) was dissolved in 250 mL of distilled water, the solution was heated at 80 °C for 1 hour. A total of 20 grams of bentonite was dissolved in 250 mL of distilled water. The bentonite solution dispersion was added to the CTAB solution and left for 1 hour. The bentonite is filtered and washed with distilled water several times until there is no more bromide. The filtrate was tested by dropping 1 M AgNO3 until a white precipitate formed. The bentonite is put into the oven at 60°C to dry.

3.2.2 Polyol Synthesis

The polyol synthesis process goes through two process stages, namely the epoxidation and hydroxylation processes. Polyol synthesis was carried out in a 350 mL 3-neck flask equipped with a mechanical stirrer and cooling system. 60 mL of glacial CH_3COOH and 30 mL of 30% H_2O_2 were added into the reactor slowly while stirring. Through a dropper funnel, 2 mL of concentrated H_2SO_4 was added and stirred slowly at temperature. 30°C for 1 hour. Next, through a dropper funnel, 100 mL of palm oil oleic acid is slowly added. The temperature is maintained at 30°C and continued to stir for 3 hours. The reaction result is an oleic acid epoxidation compound, which is cooled to room temperature and the oil phase is separated as epoxidized oil which will then be used in the hydroxylation process. In the hydroxylation stage, 100 mL of methanol was added with 50 mL of glycerin, 2 mL of concentrated H_2SO_4 catalyst and 5 mL of water into a 350 mL three-neck flask, heated to a temperature of 40°C. The epoxidized oil solution was added to the mixture into a three-neck flask, stirred at 50°C for 2 hours. Next, it was cooled to room temperature and transferred to a separating flask to separate the polyol formed and then stored in a glass bottle.

3.3 Sample Preparation

Mix polyol, bentonite, chitosan and then TDI into a glass beaker and stir using a magnetic stirrer at a speed of 200 rpm for 1 hour. In this procedure, amounts of bentonite and chitosan are used at 1, 3, 5, 7, and 9 percent by weight (%wt). The resulting polyurethane was then cooled to room temperature. Next, the chemical structure of polyurethane paint, bentonite and chitosan was analyzed using FTIR and the heat resistance analysis of the coating was analyzed using TGA and surface shape analysis using SEM.

3.4 Functional group analysis using Fourier Transform Infra Red (FTIR)

FTIR is used to analyze the characterization of polymer materials and functional group analysis. The synthesized polyurethane samples were crushed using mortar equipment. Samples were crushed with KBr using a Shimadzu FTIR spectrophotometer. Spectra were obtained in the mid-infrared region (4000-400 cm-1) at room temperature.

3.5 Analysis of thermal properties using thermogravimetric analysis (TGA)

In principle, this method measures the reduction in material mass when heated from room temperature to high temperature which is usually around 900ºC with a heating rate of 20ºC/minute. The TGA tool is equipped with a micro balance in it so that the sample weight can automatically be recorded and presented in a graphic display.

3.6 Surface scanning electron microscopy (SEM) morphological analysis

A tool 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 examination and analysis of the surface of a specimen, the data or appearance obtained is data from the surface or layer which has a thickness of around 20 μm from the surface. The surface image obtained is a photograph of all the protrusions, indentations and holes on the surface.

3.7 Corrosion Test

Conducted to determine the effect of adding anti-corrosion paint to steel plates. Steel plates that are not coated with coating paint and steel plates that are coated with coating paint will be placed in a corrosive environment for 2 months. Observations are made every day to determine changes that occur in the steel plate.

4. RESULTS AND DISCUSSION

4.1 Characterization of Fourier Transform Infra Red (FT-IR)

Fourier Transform Infrared(FT-IR) is used to determine the functional group bonds contained in polyurethane paint that has been modified by adding chitosan bentonite filler. The purpose of FT-IR analysis on polyurethane paint samples is to determine the wavelength and characteristic peaks in the sample. Each functional group has a specific characteristic peak. The FT-IR spectrum is presented in figures 3.1, 3.2 and 3.3

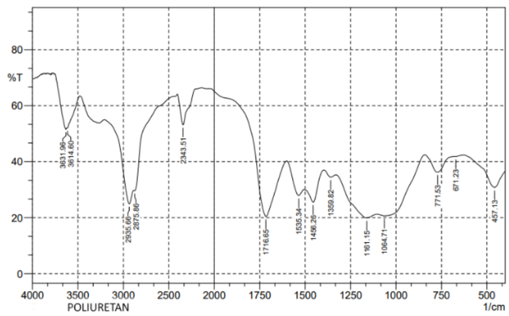


Figure 4.1FT-IR Spectrum of Polyurethane

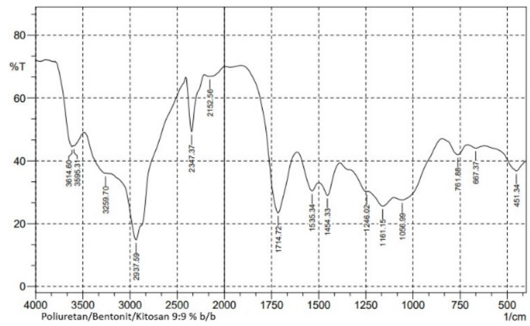


Figure 4.2Polyurethane/Bentonite/Chitosan FT-IR Spectrum 9:9 % w/w

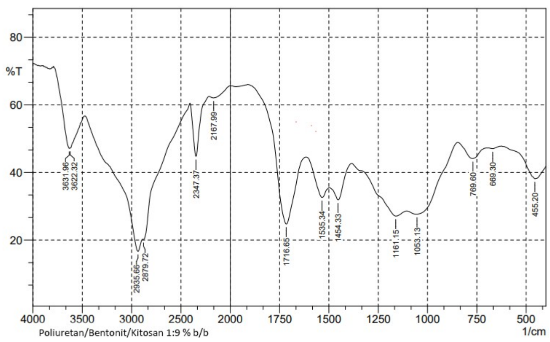


Figure 4.3FT-IR Spectrum of Polyurethane/Bentonite/Chitosan 1:9 % w/w

The results of FT-IR analysis show that the formation of NH urethane groups in polyurethane compounds is indicated by the NH absorption wave number which is wide at 3631.94 cm-1. The wave absorption of 2935.66 cm-1, 1716.65 cm-1 shows the CH and C=O groups. In polyurethane that has been modified with the addition of 9% bentonite and 9% chitosan and the results of FT-IR analysis show the formation of NH urethane groups at an absorption wave number of 3614.60 cm-1. The CH wave absorption at 2935.66 cm-1 and 1716.65 cm-1 shows the C=O wave absorption. In Figure 3.3 with a comparison sample of polyurethane that has been modified with the addition of 1% bentonite and 9% chitosan, it shows the characteristic wave number areas of 3631.96 cm-1, 2935.66 cm-1 and 1716.65 cm-1 indicating the NH group, CH and C=O. The detected functional groups represent the functional groups of polyurethane (-NHCOO-).

Based on the analysis results, it can be seen that the functional groups of polyurethane and polyurethane that have been modified by adding bentonite-chitosan do not change the functional groups. Mixing polyurethane with bentonite and chitosan does not change or affect the absorption of the functional group wavelengths of the polyurethane. This is because the mixing process takes place without changes in chemical bonds, only physical changes occur.

4.2 Thermogravimetric Analysis (TGA) Analysis Results

Thermogravimetric Analysis(TGA) is a tool used to quantitatively determine the thermal stability and mass loss of polyurethane samples that have been modified with the addition of bentonite and chitosan. Thermal stability is an important parameter for the selection and use of materials. The results of characterizing the properties of polyurethane paint using Thermogravimetric Analysis (TGA) can be seen in the following image

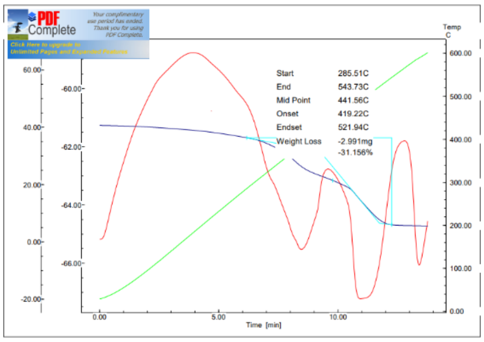


Figure 4.4Chart*Thermogravimetric Analysis Polyurethane/ Bentonite/ Chitosan 9:9 % w/w*

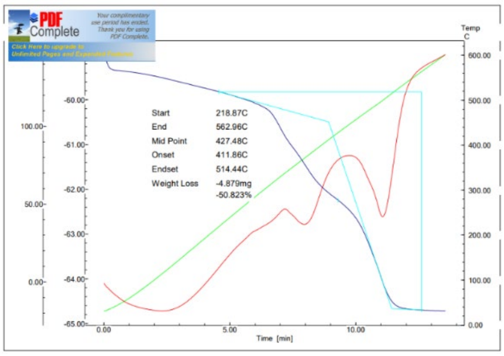


Figure 4.5Chart*Thermogravimetric Analysis Polyurethane/Bentonite/Chitosan 9:1 % w/w*

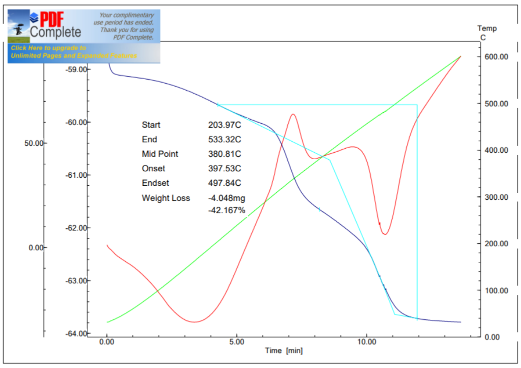


Figure 4.6Chart*Thermogravimetric Analysis Polyurethane/Bentonite/Chitosan 5:5 % w/w*

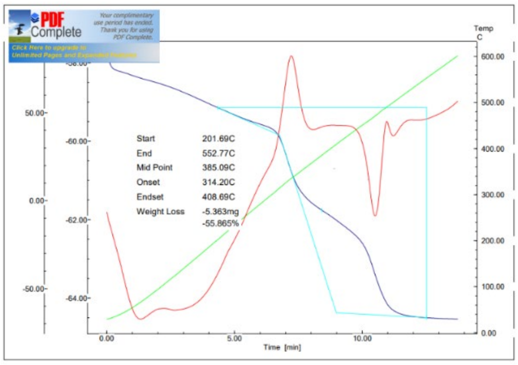


Figure 4.7Chart*Thermogravimetric Analysis Polyurethane/Bentonite/Chitosan 3:1 % w/w*

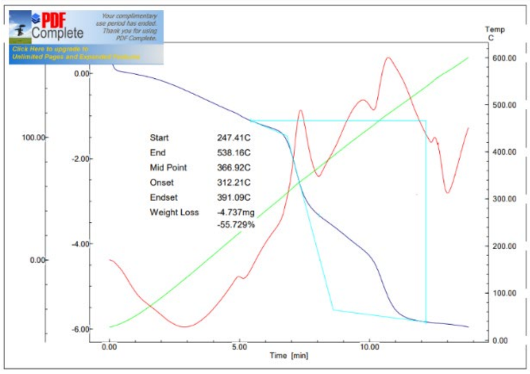


Figure 4.8Thermogravimetric Analysis Graph for Polyurethane/Bentonite/ Chitosan 1:3 % w/w

The TGA graph above shows that all samples experience single decomposition where on set and end set only occur once. Of the five best samples tested using Thermogravimetric Analysis (TGA), Graph 3.4 shows that the Polyurethane sample with 9% bentonite/9% chitosan modification has the best thermal stability among the other samples, where the sample begins to degrade (onset) at a temperature of 419.22(oC) and stopped degrading (endset) at a temperature of 521.94 (oC) with a weight loss of -31.156%. Polyurethane samples with 1% bentonite / 9% chitosan modification have lower thermal stability where the sample starts to degrade (onset) at 312.21 (oC) and stops degrading (endset) at a temperature of 391.09 (oC) with weight loss -55.729%.

This shows that the addition of bentonite and chitosan can increase thermal stability. Based on the principle of Thermogravimetric Analysis (TGA), the sample with the highest degradation (onset) and degradable (endset) temperature is the sample with the best thermal stability[11].In this research, Polyurethane/Bentonite 9%/Chitosan 9% is the sample that has the best thermal stability because it has the highest degradation temperature (onset) and degradation temperature (endset).

4.3 Morphological Structure Test Results using Scanning Electron Microscopy (SEM)

SEM testing aims to support the best sample results which aims to support the best sample results taken from the TGA test. The samples tested were the best samples with variations of 9% Bentonite: 9% chitosan.

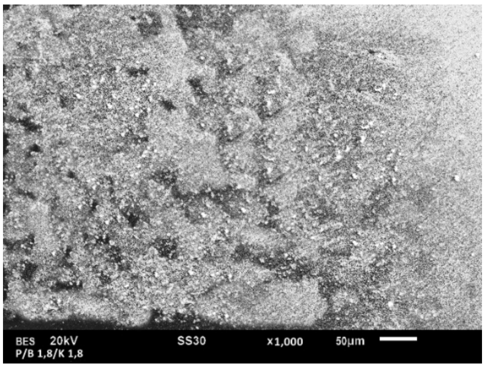


Figure 3.9SEM Test Results for Polyurethane/Bentonite/Chitosan 9:9 % w/w

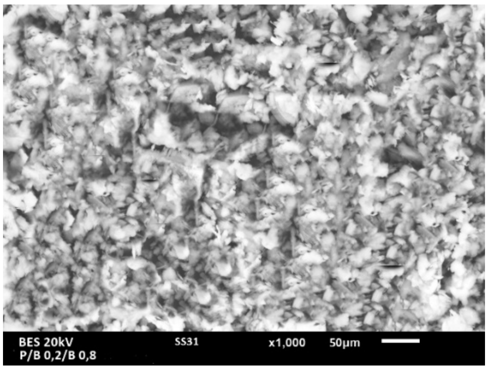
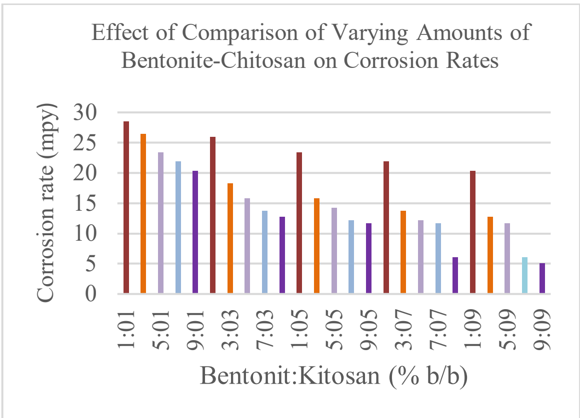


Figure 3.10SEM Test Results for Polyurethane/Bentonite/Chitosan 1:9 % w/w

Tests using SEM showed that the chitosan chains were well dispersed into the 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 the silicate and the chitosan chains.(Rihayat et al., 2019). Figure 3.9 shows the surface structure of a sample where the chitosan contains a mixture of bentonite and chitosan. The darker surface is an iron plate that has been applied with polyurethane with the addition of bentonite-chitosan filler. Figure 3.9 shows that the sample is homogeneous and no agglomeration occurs. In samples with a Polyurethane/Bentonite/Chitosan ratio of 1:9 % w/w, it shows that the sample surface is not homogeneous, where agglomeration occurs in the sample so that the sample surface appears uneven.

4.4 Corrosion Test

Corrosion is the main thing to be reviewed in this research. Corrosion tests were carried out to determine whether variations in the amount of bentonite and chitosan were able to minimize the occurrence of corrosion. Corrosion testing in this research uses the mass loss method to calculate the amount of mass lost due to corrosion. In this study, the samples to be tested were not directly contacted with media that cause corrosion such as HCL or H2SO4 solutions, the samples to be tested were left in an open environment for two months. The aim is to see in the real environment whether steel plates that have been coated with the addition of varying amounts of bentonite-chitosan can affect the corrosion rate. The following is a graph of the comparative effect of variations in the amount of bentonite-chitosan on the corrosion rate.



From the graph above it can be concluded that the amount of bentonite-chitosan contained in polyurethane paint affects the corrosion rate. This is because the addition of bentonite and chitosan fillers can act as reinforcing materials thereby increasing the mechanical and physical properties of polyurethane, which based on the graph above shows that the greater the amount of bentonite and chitosan can reduce the corrosion rate. In this study, the largest mass loss experienced a Bentonite - Chitosan ratio of 1:1% w/w, namely 0.56 grams with a corrosion rate of 28.48 mpy. The sample with a Bentonite-Chitosan ratio of 9:9%w/w experienced mass loss of at least 0.1 with a corrosion rate of 5.08 mpy. This shows that the greater the amount of bentonite and chitosan contained in polyurethane is able to reduce the rate of corrosion on steel plates. Based on the corrosion resistance level table, all samples tested had a good level of corrosion resistance, where the corrosion rate for each sample was 5-50 mpy.

CONCLUSION

The best results were obtained from the composition Polyurethane/Bentonite/Chitosan 9:9 % w/w. This shows that increasing the amount of bentonite and chitosan can increase the reinforcement, thermal stability and mechanical properties of the coating material. FT-IR testing shows the presence of NH, CH, C=O groups which represent the functional groups of polyurethane (NHCOO-). The FTIR test results show that mixing polyurethane and bentonite does not have an impact on the wavelength absorption of the polyurethane functional groups, this is because the mixing process only occurs physical changes. In the Thermogravimetric Analysis (TGA) test, the sample underwent single decomposition and showed the best results for the Polyurethane/Bentonite/Chitosan 9:9% w/w sample where the sample began to degrade at a temperature of 419.22(oC). SEM testshows that the chitosan chains are well dispersed into the bentonite interlayer.

Corrosion tests show that the addition of bentonite and chitosan affects the corrosion rate, the greater the composition of bentonite and chitosan can reduce the corrosion rate. The sample with a Polyurethane/Bentonite/Chitosan composition of 9:9 % w/w was the best sample where the sample experienced the smallest corrosion rate, namely 5.08 mpy and a mass loss of 0.1 gram.

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