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DEVELOPMENT OF CHITOSAN MODIFIED POLYURETHANE COMPOSITE AS A BASE MATERIAL FOR ANTIBACTERIAL COATING PAINT

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ABSTRACT

Polyurethanes are generally made from petroleum-based polyols, but the current state of petroleum is depleting. The availability of petroleum, which is currently decreasing, encourages other parties to look for new alternatives. One alternative that can be used is palm oil. Technological developments that continue to increase are now also a reference for the development of antibacterial polyurethane coating paints which are carried out by adding another filler, namely chitosan. This study aims to determine the effect of variations in the weight of chitosan as an antibacterial agent and to determine the effect of the ratio of polyol and TDI on the quality of the paint analyzed through functional group analysis with Fourier Transform Infra Red (FTIR), morphological analysis of Surface Scanning Electron Microscopy (SEM), Heat resistance test with Thermo Gravimetry Analyzer (TGA), and Bacterial activity test. The analysis process was carried out with variations in the weight of chitosan (0; 2; 3; 4; 5; 6) % w/w and variations in the ratio of polyol and TDI (50:50) %; (40:60)%; (45:55)%. The test results showed that the best polyurethane paint was the variation in the ratio of polyol and TDI 50:50% with 6%w/w chitosan filling. This is because the more chitosan added, the better it will be in inhibiting bacterial activity, and the more polyols, the better the paint quality. The test results showed that the best polyurethane paint was the variation in the ratio of polyol and TDI 50:50% with 6%w/w chitosan filling. This is because the more chitosan added, the better it will be in inhibiting bacterial activity, and the more polyols, the better the paint quality. The test results showed that the best polyurethane paint was the variation in the ratio of polyol and TDI 50:50% with 6%w/w chitosan filling. This is because the more chitosan added, the better it will be in inhibiting bacterial activity, and the more polyols, the better the paint quality.

Keywords: Chitosan, Composites, Polyols, Polyurethanes, TDI

1. INTRODUCTION

1.1 Background

Increased construction activities across the world coupled with increase in urban population have been the major factors driving the growth of the paint manufacturing market. Paint is a product that is widely used by people, especially in construction, because of its important function, namely providing decorative (aesthetic) value. This causes the need and use of paint in society to be quite high. (Supraptiah et al., 2022). The components or materials that make up paint consist of binder (resin), pigment, solvent and additives. Based on the type of resin used, paint consists of various types, namely epoxy paint, polyurethane, acrylic, melamine, alkyd, nitro cellulose, polyester, vinyl, chlorinated rubber, etc.

Polyurethane is a polymer material characterized by the presence of a functional urethane group (NHCOO-) in the main polymer chain. The urethane functional group is formed between compounds containing hydroxyl (OH), often called polyols, and compounds containing isocyanate (-NCO-). Polyurethanes are usually synthesized from petroleum that has been converted into derivatives, such as alkyd resins based on alkyd polyols. The polyol is then allowed to react with various diisocyanates to obtain a polyurethane coating (H. Janik, M. Marzec, 2015).

Polyurethane is a type of paint that has many advantages compared to other types of paint, namely weather resistance, high gloss, hardness and good adhesion to various materials (metal, plastic and wood). Polyurethane is generally made from petroleum-based polyols, but petroleum is currently running low. The currently decreasing availability of petroleum has encouraged other parties to look for new alternatives. One alternative that can be used is vegetable oil such as sunflower oil, castor oil, soybean oil, cottonseed oil and palm oil. In other words, vegetable oils can replace petroleum (petrochemicals) as raw materials in polyurethane production, because they are superior in addition to their abundant availability in nature and are easily decomposed (Chuanjin, H., Qunfeng, C. 2021).

Research on polyurethane coating paint has been carried out by (Teuku Rihayat, Mashura, 2018). Research on castor oil-based polyurethane coating paint with bentonite filler modified with CTAB to montmorillonite (MMT). The addition of purified MMT to castor oil polyurethane coating paint functions as a heat resistant agent.

The research above used castor oil to obtain polyol compounds, but there are only a few polyol compounds in castor oil, so it is necessary to look for new alternatives to replace castor oil. The alternative used is palm oil, because apart from the polyol compounds found in palm oil, palm oil is also quite easy to obtain. The research above also only modifies polyurethane coating paint as heat-resistant paint, while the need for paint always increases every year, so the paint must have very environmentally friendly qualities, especially resistance to bacteria.

The ever-increasing technological developments have now also become a reference for the development of antibacterial coatings that can be used on various devices ranging from furniture, electronics, cars to medical devices. To produce antibacterial coating paint products, modifications need to be made. Modifications are made by adding other fillers to the polyurethane coating paint. The filler in question is chitosan.

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, Coelenterata sp, Annelida sp, Nematoda sp, as well as several fungal groups. The main source is the shell of Crustaceae sp, namely shrimp, lobster, crab and other shelled animals with a chitin content of between 65-70% (Gang, X., Pingya, L., Qiang, D. 2020; Jinbo, Z., Lili , W., Liqun, Z. 2021). By adding chitosan as an alloy in modifying polyurethane, polyurethane can have anti-bacterial properties. According to research results, it shows that intercalation of chitosan through a cation exchange process can increase its antimicrobial activity.

Based on antibacterial testing of chitosan nanoparticles against Staphylococcus aureus and Eschericia coli bacteria, the results showed that the antibacterial ability of chitosan nanoparticles worked more actively in suppressing the growth of Eschericia coli bacteria compared to Staphylococcus aureus. This was proven in research by Suherman et al. (2018), that chitosan has a positive charge. which can bind negative charges from other compounds or play a role in inhibiting bacterial growth because its main property is antibacterial.

The specific aim of this research is to produce polyurethane coating paint through the palm oil synthesis process to produce polyol and add TDI and then modify it with a combination of chitosan which has antibacterial capabilities. Modification of polyurethane with chitosan affects its properties and consequently affects its applications. Chitosan added to the polyurethane matrix very often improves the processing of the composite. Chitosan was chosen because it has antibacterial properties which can provide physical defense to objects coated with polyurethane coating paint from damage caused by the activity of microorganisms.

1.2 Supporting Theories

1.2.1 Paint

Paint is a product that is widely used by the public, especially in the construction of various buildings because of its important function, namely providing decorative (aesthetic) value in addition to providing protection to the building so that the building becomes more beautiful and attractive. This causes the need and use of paint in society to be quite high (Supraptiah et al., 2022). Paint is a liquid that is used to coat the surface of a material with the aim of beautifying, strengthening or protecting the material. After being applied to a surface and drying, the paint will form a thin layer that adheres firmly to the surface. Paint can be attached to the surface in many ways, namely rubbing, smearing, brushing, spraying, etc. The components or materials that make up paint consist of binder (resin), pigment,

a. Binders

A binding agent or binder is a material that binds paint pigment particles together, so that the paint can form a thin, dense layer when used. The binder's job is to glue the pigment particles into the paint film layer and make the paint stick to the surface. The type of binder in a paint formula determines many things about the paint's performance. Binder is made from a material called resin which is usually made from natural or synthetic materials. Paint can be made of Natural Oil, Alkyd, Nitro Cellulosic, Polyester, Melamine, Acrylic, Epoxy, Polyurethane, Silicone, Fluorocarbon, Vinyl, Sellulosic, and others.

b. Pigment

Pigment acts as the main coloring agent in paint. Pigments can be divided into 2, namely organic and non-organic. Non-organic pigments are made from several 5 metals (metal oxides) while organic pigments are made from petroleum (Carbon Based). Pigments can be divided into main pigments and extender pigments. The main pigment provides the paint with coverage and color, while the extender pigment helps strengthen the main pigment.

c. Solvent

Solvent or solvent functions to maintain the viscosity of the paint so that it remains liquid when used, apart from that, it also acts as a dispersing medium. A paint requires a liquid material so that pigment particles, binders and other solid materials can flow. The liquid in a paint is composed of oil solvent and/or diluent. Both are liquids that can dissolve (dissolve) a material. Both are also called thinners because they both have the ability to thin paint to the desired viscosity.

d. Additives

*Additives*is a material added to paint to add properties or properties to the paint so that it can improve the quality of the paint. In addition to liquid, pigment and binder, a paint can contain one or more additives (additional substances) which function to improve performance, and are usually used in very small quantities. This affects the vital features depending on the final use of the paint, especially the flow and leveling capabilities of the paint.

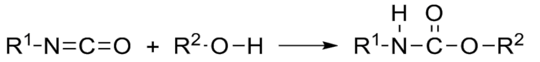
1.2.2 Palm oil

Palm oil isvegetable oilobtained frommesocarptree fruitPalm oil, generally of the species*Elaeis guineensis*and few of the species*Elaeis oleifera*And*Attalea maripa*. Palm oil is naturally red due to its ingredientsalpha and beta-carotenehigh oid. Palm oil is also different fromcoconut oilproduced from the core of the fruitcoconut(*Cocos nucifera*). Palm oil contains 41% saturated fat, palm kernel oil 81%, and coconut oil 86%.

1.2.3 Polyurethane

Polyurethane is generally a polymer compound whose main chain constituent is a urethane group (-NHCOO-). Polyurethane was discovered by Otto Bayer from Germany in 1937 (Claudiane, M., et al. 2019). Research developments in the field of polyurethane are increasing because this material is an important material in various building and pharmaceutical industries and other purposes (Daimei, C., et al. 2021). Polyurethane is usually applied to paint and coatings, the automotive industry, fiber, construction materials, and synthetic leather. Polyurethane is a thermosetting polymer formed from the reaction between diisocyanate compounds and polyfunctional compounds containing a number of hydroxyl functional groups (polyols). So far, polyols are produced from petroleum derivative products, namely ethylene oxide and propylene oxide.

Polyurethane is different from most other plastic materials, this is because the polyurethane synthesis process makes it possible to control the properties of the final product. Reactive chemicals are mixed and reacted simultaneously to produce polymers with the desired properties. Polyurethane is synthesized into the final product during the polymerization reaction. Polymerization reactions based on polyisocyanates and polyols containing hydroxy groups with several basic isocyanate compounds and polyols with different molecular masses and functionalities are used to produce a spectrum of polyurethane materials.



$$R^1\text{-}N{=}C{=}O + R^2\text{-}O\text{-}H \longrightarrow R^1\text{-}\overset{H}{N}\text{-}\overset{O}{\underset{}{\overset{\|}{C}}}\text{-}O\text{-}R^2$$

Figure 1.1 General Chemical Structure of Polyurethane

Several types of polyurethane that are traded and are very suitable for their use include:

1. The flexible, low-density foam used in the cushion resists flexing.
2. Rigid, low density foam used for thermal insulation of car dashboards.
3. Elastomer, a soft, solid material used as a gel pad for die grinders.
4. Hard, dense plastics are used as structural materials and electronic instrument materials.

Research on plant-based polyurethane has been carried out from various raw materials such as corn, sweet potato, sago, potato, etc. and has obtained its characteristics, but the mechanical and processing requirements of various applications cannot be met by polyurethane alone. Various efforts have been made to increase mechanical requirements such as mixing polyurethane with other biodegradable polymers or using fillers (Halima, K., Sharif, A. 2019).

1.2.4 Polyol

Polyol compounds used in polyurethane production are generally compounds with a molecular weight in the range of 400-5000 Da, depending on the length of this diol or glycol chain, the properties of the polyurethane change. If the polyol has a low molecular weight, it produces a hard plastic, and if it has a high molecular weight, it creates a flexible elastomer. Reactivity is not the same for all hydroxyl groups Primary alcohols react easily at 25-50° C, while secondary and tertiary alcohols are about 0.3 and 0.005 times less reactive than primary ones.

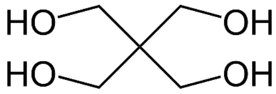


Figure 1.2 Chemical Structure of Pentaerythritol

1.2.5 Isocyanate

The most common diisocyanates are toluene diisocyanate (TDI) and Methylene Bis Diphenylisocyanate (MDI), plus higher oligomers to increase functionality and cross-linking. For resistance to ultraviolet rays and outdoor weather resistance, aliphatic polyisocyanates such as Hexamethylene Diisocyanate (HDI) and hydrogenated MDI (HMDI) are useful, although these aliphatic diisocyanates involve lower polymerization reactivity and much higher costs.

Reaction between diisocyanates, long linear chain polyols, and low molecular weight chain lead towards the production of elastomers. The properties of elastomes are determined primarily by the chain structure, the degree of branching of the polymer intermediates, and the stoichiometric balance of the components. The NCO to OH ratio for optimal mechanical strength is typically 1.0-1.1. When the ratio drops below 1.0, the mechanical strength, hardness, and durability decrease, and the elongation and compression set increase very sharply.

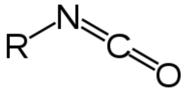


Figure 1.3 Chemical Structure of Isocyanates

1.2.6 Chitosan

Chitosan is a chemical compound derived from the biological material chitin, an organic compound that is abundant in nature after cellulose. This chitin is generally obtained from the skeletons of invertebrate animals from the Arthopoda sp, Mollusca sp, Coelenterata sp, Annelida sp, Nematoda sp, and some fungal groups. The main source is the shell of Crustaceae sp, namely shrimp, lobster, crab and other shelled animals with a chitin content of between 65-70 percent (Jinbo, Z., et al. 2021).

Table 1.1 Sources of Chitin and Chitosan

Type	Chitosan Content
Mushrooms/fungi	5-20%
Squid	3-20%
Scorpion	30%
Spider	38%
Bee	35%
Crab	69%
Shrimp	70%
Silk worm	44%

Shrimp shells contain 20-30% chitin compounds, 21% protein and 40-50% minerals. In the shells of Crustaceae sp, chitin is found as a mucopolysaccharide which binds to inorganic salts, especially calcium carbonate (CaCO3), proteins and lipids including pigments. Therefore, obtaining chitin from shrimp shells involves the processes of separating proteins (deproteination) and separating minerals (demineralization). Meanwhile, to obtain chitosan, the deacetylation process is continued.

Chitosan is a multipurpose chemical in the form of fibers and is a copolymer in the form of thin sheets, white or yellow in color, odorless. Chitosan is a product of chitin deacetylation through a chemical process using sodium hydroxide base or an enzymatic process using the chitin deacetylase enzyme. This fiber is not digested and is not absorbed by the body. The prominent characteristic of chitosan is its ability to absorb fat up to 4-5 times its weight (Halima, K., Sharif, A. 2019).

The properties of chitosan such as biodegradability, biocompatibility, non-toxicity and anti-bacterial have become attractive to industry (Chen, L., Jian, B, L. 2017). Chitosan is a poly-(2-amino-2-deoxy-β-(1-4)-D-glucopyranose) with the molecular formula (C6H11NO4)n which can be obtained from complete or partial deacetylation of chitin. Chitosan is a biopolymer whose main content is D-glucosamine and some parts of Nacetyl-D-glucosamine which are bound to β-(1-4) glucoside. Chitosan can be hydrolyzed into its oligomeric form known as chitosan oligamer, where the structure can be seen as follows:

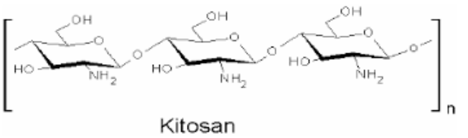


Figure 1.4 Chitosan structure

Most of the polysaccharides that occur naturally such as cellulose, dextran, pectin, alginic acid, agar, carrageenan are neutral or acidic in nature, while chitosan is a polysaccharide that is basic (Halima, K., Sharif, A. 2019).

The biological properties of chitosan include:

1. Biocompatible means that as a natural polymer it has no side effects, is non-toxic, cannot be digested, is easily broken down by microbes (biodegradable).

2. Can bind to mammalian cells and microbes aggressively.
3. Has hemostatic, fungistatic, spermicidal, antitumor, anticholesterol properties.
4. Acts as a depressant in the central nervous system. Based on these two properties, chitosan has unique physical properties, namely that it is easily formed into sponges, solutions, pastes, membranes and fibers which are very useful.

1.2.7 Antibacterial

Antibacterials are substances that can inhibit the growth of bacteria and can kill bacteria that cause infection. Bacteria that cause infection and disease are often found in the environment around us, including bacteria*Staphylococcus aureus*and Escherichia coli which are also Gram positive and Gram negative bacteria which can cause infection or disease in the body (Magani et al., 2020).

The growth of bacteria that cause infection and disease needs to be inhibited with antibacterials. Antibacterials are substances that can inhibit the growth of bacteria and can kill pathogenic bacteria (Paju et al. 2013). Antibacterials are divided into two, namely bacteriostatic which suppresses the growth of bacteria and bactericidal which can kill bacteria (Safitri, 2016).

1.3 Specific Objectives

The specific objectives to be achieved in this research are:

1. To determine the effect of variations in the weight of chitosan as an antibacterial material in the process of making polyurethane coating paint.

To determine the effect of the ratio of polyol and TDI on the quality of polyurethane coating paint.

2. RESEARCH METHODS

Research methodology

2.1 Research Place

This research was conducted at the Laboratory of the Chemical Engineering Department of the Lhokseumawe State Polytechnic.

2.1 Tools and Materials

2.2.1 Tools used

- A set of polyurethane synthesis tools
- *Magnetic stirrer*
- Bath
- *Centrifuge*
- Petri dish
- Filter paper
- Analytical scales
- Fourier Transform Infrared (FTIR) Spectrophotometer
- *Scanning Electron Microscope*(SEM)
- *Thermal Gravimetry Analysis*(TGA)
- Incubator

2.2.2 Materials used

To Make polyurethane

- Oleic acid is based on palm oil
- CH_3COOH glacial acetic acid
- H_2O_2 30%
- H_2SO_4
- *Methanol*
- Glycerin
- Toluene diisocyanate (TDI)

To Make Chitosan

- Shrimp shells
- NaOCl
- NaOH
- HCl

For Paint Testing

- Steel plate 2×1.2 cm
- Paint Cans/Plastic Bottles
- Nutrient Agar

2.3 Experimental Treatment Design

2.3.1 Fixed/Controlled Variable

- Synthesis time : 6 hours
- Synthesis temperature : 40ºC
- Chitosan Particle Size: ±100 mesh

2.3.2 Independent Variable

- Chitosan weight: (0; 2; 3; 4; 5; 6) % w/w
- Comparison of Polyol and TDI: (50:50)%; (40:60)%; (45:55)%

2.3.3 Dependent variable

- Functional group analysis with Fourier Transform Infrared (FTIR) Spectrophotometer
- Morphological analysis with Scanning Electron Microscope (SEM)
- Heat resistance analysis with Thermal Gravimetry Analysis (TGA)
- Test bacterial activity

2.4 Experimental and Testing Procedures

2.4.1 Polyol synthesis

The polyol synthesis process goes through two stages, namely the epoxidation and hydroxylation processes. In the epoxidation stage, there are six stage points:

1. Polyol synthesis was carried out in a 350 ml 3 neck flask equipped with a mechanical stirrer and cooling system.
2. Into the reactor, add 60 ml of glacial CH3COOH and 30 ml of 30% H2O2 slowly while stirring.
3. Through a dropper funnel, 2 ml of concentrated H2SO4 was added and stirred slowly at 30ºC for 1 hour.
4. Next, through a dropper funnel, 100 ml of palm oil oleic acid is slowly added.
5. The temperature was maintained at 30ºC and continued to stir for 3 hours.
6. 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.

The hydroxylation stage can be divided into four stages, namely:

1. A total of 100 ml of methanol was added with 50 ml of glycerin, 2 ml of concentrated H2SO4 catalyst and 5 ml of water into a 350 ml three-neck flask, heated to a temperature of 40ºC.
2. The epoxidized oil solution was added to the mixture into a three-neck flask, stirred at a temperature of 50ºC for 2 hours.
3. 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.
4. Next, it was analyzed using FTIR to determine the OH groups in the polyol.

2.4.2 Chitosan Synthesis

1. Clean 100 grams of shrimp shells with boiled water for 1 hour.
2. Then the shrimp shells were washed and dried at 160 oC for 2 hours in the oven.
3. Then the dried shrimp shells are ground into powder. The demineralization stage of shrimp shell powder uses HCl with a concentration of 0.25M – 2M (ratio 1:10 (w/v)) by heating at a temperature of 60-70ºC for 4 hours at a speed of 500 rpm
4. Then bleached with NaOCl and 5% NaOH to produce chitosan.

2.4.3 Manufacture of polyurethane coating paint*Hybrid*chitosan

There are four stages in making polyurethane-chitosan coatings, namely:

1. Mix polyol, chitosan and then TDI in a glass beaker, stir with a magnetic stirrer at a speed of 200 rpm for 1 hour.

2. In this procedure, the amount of chitosan used is 2, 3, 4, 5 and 6 percent by weight (%wt), respectively. The resulting polyurethane is then cooled to room temperature.
3. Next, the chemical structure of polyurethane and chitosan paint was analyzed using FTIR.
4. Surface shape analysis using SEM and antibacterial analysis using a bacterial test kit.

2.4.4 Characterization of Research Results

2.4.4.1 Functional group analysis with*Fourier Transform Infrared*(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 obtained in the mid-infrared region (4000-400 cm-^{1}) at room temperature (Mounia, A., et al. 2018).

2.4.4.2 Morphological analysis with*Surface Scanning Electron Microscopy*(SEM)

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 (Milena, S., et al. 2019). The surface image obtained is a photograph of all the protrusions, indentations and holes on the surface.

2.4.4.3 Heat resistance analysis with Thermo Gravimetry Analyzer (TGA)

Heat resistance analysis was carried out using a Shimadzu DTG-60 instrument. The sample was weighed with a mass of mg and heated at room temperature to 800℃ with a heating rate of 20℃/min. The analysis was carried out by increasing the sample temperature gradually and determining the weight loss with changes in temperature. All specimens were tested under a flow of nitrogen gas (Teuku Rihayat, Mashura 2018).

2.4.4.4 Bacterial Activity Test

To determine the effect of adding chitosan as an antibacterial, it was analyzed using the halo zone method, namely:

1. Cultivate bacteria on solid NA media in petri dishes.
2. Then each plate that has been smeared with polyurethane is placed on the surface of the media.
3. Done aseptically in laminar flow
4. Samples were incubated for 24 hours at 37ºC. Observe the colony shape and activity of the microbes.
5. Observations were made during the incubation period.

The bacterial inhibitory activity of the plate on bacterial growth was measured based on the area of the clear zone formed around the membrane. As reported by (Marzec, M, J., et al. 2021) antibacterial activity on polyurethane plates using Staphylococcus aureus and Eschericia coli bacteria.

3. RESULTS AND DISCUSSION

3.1 Research Results

Table 3.1 Data from bacterial activity test results

Code Sample	PU (%)	Polyol: TDI (%)	Chitosan Weight (%w/w)	Obstacle zone (mm)
1	100	50:50	0	2.75
2	98	50:50	2	5.75
3	97	50:50	3	8.5
4	96	50:50	4	10.5
5	95	50:50	5	13.5
6	94	50:50	6	15
7	100	40:60	0	1
8	98	40:60	2	3.75
9	97	40:60	3	7.5
10	96	40:60	4	9.75
11	95	40:60	5	11.5
12	94	40:60	6	12.5
13	100	45:55	0	2
14	98	45:55	2	5

15	97	45:55	3	8
16	96	45:55	4	10
17	95	45:55	5	12
18	94	45:55	6	13.25

Table 3.2 Data from Functional Group Analysis with Fourier Transform Infra Red (FTIR) Spectrophotometer

Sample Code	Wave number (cm-1)	Functional groups
Polyurethane resulting from CPO synthesis	1458.39	C=O in
	1537.60	Allophanate
	1646.25	C=C aromatic
	1744.56	C=C alkene
	2250-2300	C=O in Urethane
	2357.52	-NCOs
	2853.27	CO2
	2924.60	Methylene (-CH2-)
	3465.59	Symmetric CH3 Alkane Secondary NH Stretch
5	1718.58	C=O
	2937.59	CH
	3614.6	NH
6	1716.65	C=O
	2937.59	CH
	3614.6	NH
18	1718.58	C=O
	2941.44	CH
	3618.46	NH

Table 3.3 Data from heat resistance analysis using Thermal Gravimetry Analysis (TGA)

Sample code	Thermal Resistance (ºC)
5	392.82
6	446.96
18	312.78

3.2 Discussion

From the results of the research data carried out, the results and description of the discussion were obtained as follows:

3.2.1 Bacterial Activity Test Results

In testing antibacterial activity, 15 mL of Nutrient Agar (NA) medium was put into a petri dish and then allowed to solidify. After solidifying, 1 dose of bacteria was taken, then scratched evenly on the surface of the medium, then inserted into each steel plate which had been smeared with polyurethane paint on the surface of the medium. Then the cup was incubated at 37°C for 1x24 hours, this is the optimum temperature and time for bacterial growth. Next, the diameter of the clear formed is observed and the diameter of the inhibitory area is measured with a caliper.

Table 3.4 Data from Bacterial Activity Test Results

Sample	Test Bacteria	Vertical Clear Zone (mm)	Horizontal Clear Zone (mm)	P Plate (mM)	L. Plate (mm)	Obstacle zone (mm)
1	S.A	23	14.5	20	12	2.75
2	EC	25.5	18	20	12	5.75
3	S.A	28	21	20	12	8.5
4	EC	30	23	20	12	10.5
5	S.A	33	26	20	12	13.5
6	EC	34	28	20	12	15
7	S.A	21	13	20	12	1
8	EC	24	15.5	20	12	3.75
9	S.A	27	20	20	12	7.5
10	EC	29.5	22	20	12	9.75
11	S.A	31	24	20	12	11.5
12	EC	32	25	20	12	12.5
13	S.A	22	14	20	12	2
14	EC	25	17	20	12	5
15	S.A	27.5	20.5	20	12	8
16	EC	30	22	20	12	10
17	S.A	31.5	24.5	20	12	12
18	EC	32.5	26	20	12	13.25

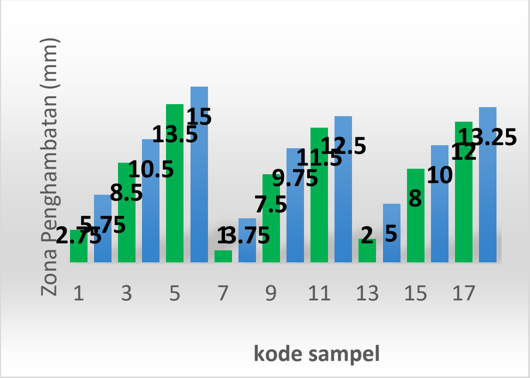


Figure 3.1 Graph of Bacterial Activity Test results

Based on the results of the data in table 3.4 and figure 3.1, antibacterial activity testing resulted in the average diameter of the inhibition zone for Staphylococcus aureus bacteria in the PU 50:50% K 0% sample being 2.75 mm; PU 50:50% K 3% of 8.5 mm; PU 50:50% K 5% of 13.5 mm; PU 40:60% K 0% by 1 mm; PU 40:60% K 3% by 7.5 mm, PU 40:60% K 5% by 11.5 mm, PU 45:55% K 0% by 2 mm, PU 45:55% K 3% by 8 m, and PU 45:55% K 5% by 12 mm. These results indicate that the more chitosan added, the better its ability to inhibit the growth of Staphylococcus aureus bacteria. Meanwhile, the average diameter of the inhibition zone in the Escherichia coli bacteria test with the 50:50% K 2% PU sample was 5.75 mm; PU 50:50% K 4% of 10.5 mm; PU 50:50% K 6% of 15 mm; PU 40:60% K 2% by 3.75 mm, PU 40: 60% K 4% by 9.75 mm, PU 40:60% K 6% by 12.5 mm, PU 45:55% K 2% by 5 mm, PU 45:55% K 4% by 10 mm, and PU 45:55 % K 6% is 13.25 mm. These results also show that the more chitosan added, the better its ability to inhibit the growth of Escherichia coli bacteria. In testing bacterial activity, it can be seen that polyurethane with a concentration of 50:50% is better at inhibiting bacterial growth than other concentrations.

3.2.2 Results of Functional Group Analysis with Fourier Transform Infra Red (FTIR) Spectrophotometer

Infrared spectroscopy is a tool that can be used to analyze chemical compounds. The mid-infrared region (4000 – 400 cm-1) is related to the vibrational energy transition of the molecule which provides information about the functional groups in the molecule. The resulting spectrum is in the form of absorbance and transmittance which is the fingerprint of the molecule being analyzed. Each fingerprint region of a sample marks only 1 molecular structure in the same IR spectrum. The FT-IR spectra can be shown in figures 3.2, 3.3 and 3.4.

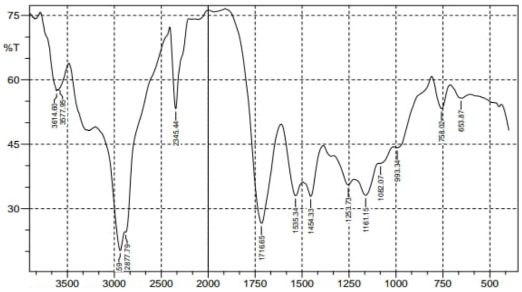


Figure 3.2 FTIR Spectra of PU 50:50% K 5%

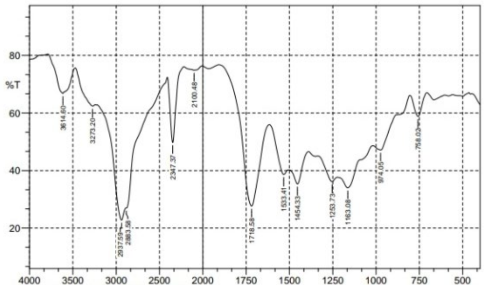


Figure 3.3 FTIR Spectra of PU 50:50% K 6%

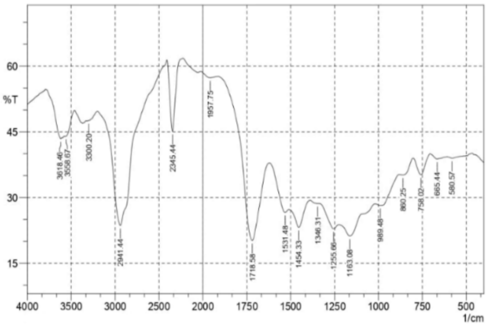


Figure 3.4 FTIR Spectra of PU 45:55% K 6%

FT-IR is a widely used method to investigate intermolecular interactions and phase behavior between polymers. In Figure 3.2, the sample is a mixture of polyurethane and 5% chitosan, showing the characteristic wave number areas of 1718.58 cm-1, 2937.59 cm-1 and 3614.6 cm-1 which indicate the C=O, CH and NH groups. In Figure 3.3, a sample of a mixture of 6% polyurethane and chitosan shows the characteristic wave number areas of 1716.65 cm-1, 2937.59 cm-1 and 3614.6 cm-1 which indicate the C=O, CH and NH groups. In Figure 3.4 with a sample in the form of a mixture of polyurethane and 6% chitosan as a comparison, it shows the characteristic wave number areas of 1718.58 cm-1, 2941.44 cm-1, and 3618.46 cm-1 which indicate the C=O, CH, and NH.

3.2.3 Results of Heat Resistance Analysis using Thermal Gravimetry Analysis (TGA)

Thermal degradation testing using the TGA (Thermo Gravimetric Analysis) tool aims to qualitatively determine the thermal stability of a mixture of PU (polyol and TDI) and chitosan. TGA is a technique used to study thermal stability/decomposition of composite matrices. The thermal stability of fibers is a very important parameter for the processing and use of materials. This test is based on changes in sample weight due to heating from room temperature to high temperatures, usually reaching hundreds of degrees Celsius, so that the sample will experience a reduction in mass (degradation) due to burning at a certain temperature. The process of mass loss occurs due to the decomposition process, namely the breaking of chemical bonds.

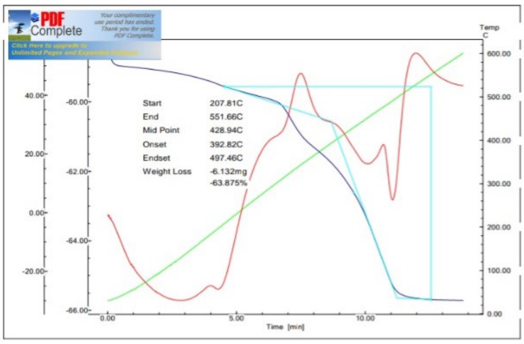


Figure 3.5 TGA graph of temperature for PU 50:50% K 5% sample

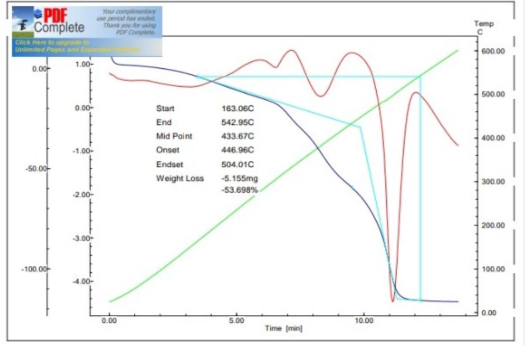


Figure 3.6 TGA graph of temperature for PU 50:50% K 6% sample

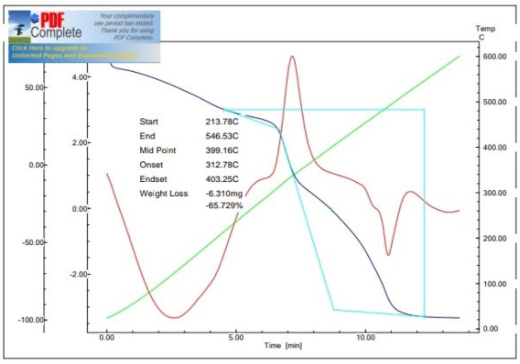


Figure 3.7 TGA graph of temperature for PU 45:55% K 6% sample

The graph above is a plot of the decrease in mass on the y-axis and the increase in temperature on the x-axis. The graph shows that all samples experienced a single decomposition because onset and endpoint only occurred once. Onset is the temperature at which the sample begins to degrade thermally and endset is the temperature at which the sample retains its mass from the combustion reaction. Weightloss is the amount of weight lost. This graph is a comparison of the 3 best samples based on the results of bacterial activity tests, with the composite degradation temperature in this study ranging from 312-504ºC. Where in the PU 50:50% K 5% sample, the onset starts at a temperature of 392.82ºC and the endpoint is 497.46ºC with a weight loss of -63.875%, in the PU 50:50% K 6% the onset starts at a temperature of 446.96ºC and the endpoint is 504 .01ºC with weight loss -53.698%, and PU 45: 55% K 6% onset starts at a temperature of 312.78ºC and the endpoint is 403.25ºC with a weight loss of -65.729%. So it can be concluded that the best sample is PU 50:50% K 6%, because it experiences less weight loss.

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

SEM testing as an additional test in this research aims to support the best sample results taken from the main bacterial activity test. The samples tested were sample codes 5,6 and 18. This test aims to see the morphological structure of polyurethane with chitosan filling using a microscope that relies on electron beams to describe the surface shape of the material being analyzed. The following is an image of the results of analysis under an electron microscope (SEM).

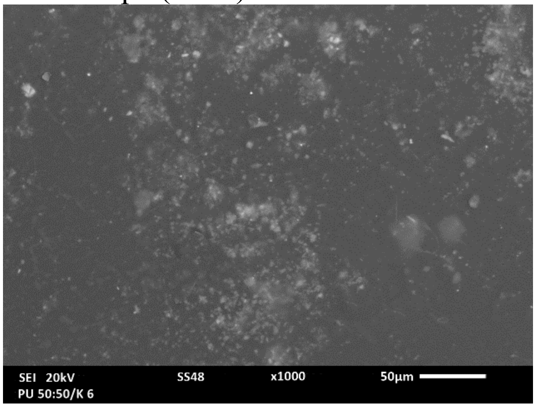


Figure 4.8 SEM test results PU 50:50% K 6%

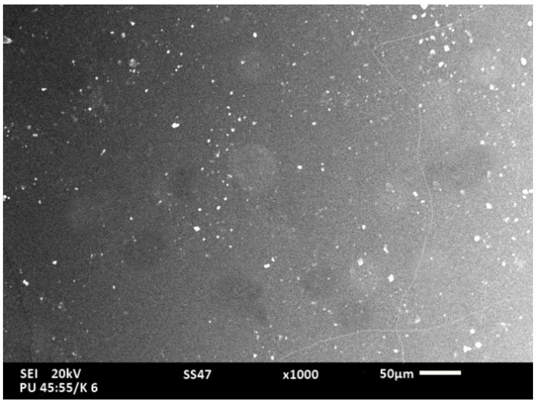


Figure 4.9 SEM Test Results PU 45:55% K 6%

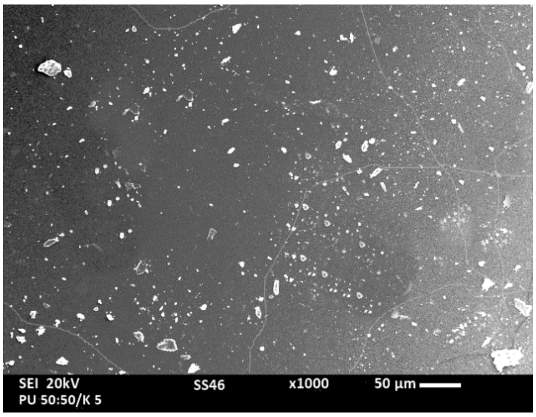


Figure 4.10 SEM Test Results PU 50:50% K 5%

Shown is an SEM photo of a mixture of polyurethane paint and chitosan that has been dried naturally. The image above shows the surface structure of the three samples which shows several differences in their surface structure at a magnification of x100. The PU 50:50% K 6% sample has a smoother surface and the pores of the solid particles are less visible compared to the PU 50:50% K 5% and PU 45:55% K 6% samples which show some lumpy shapes. and large pores. The greater the mole ratio between polyol and isocyanate, the larger the cell diameter.

Research results should be written clearly and concisely. The discussion describes the results based on research methods and data analysis results. Research results can be described in the form of tables or images.

4. CONCLUSION

4.1 Conclusion

Based on the observation data made and the discussion that has been described, it can be concluded as follows:

1. Based on the results of the bacterial activity test, it was found that the more chitosan added as a polyurethane coating paint filling, the better it would be at inhibiting bacterial growth, meaning that variations in the weight of chitosan had an effect on the polyurethane coating paint to inhibit bacterial growth.
2. Based on the analysis results from several tests, it shows that the ratio of polyol and TDI has an effect on paint quality. This can be proven from morphological analysis which shows that the ratio of 50:50% is better than the ratio of 40:60% and 45:55%.

4.2 Suggestions

In further research, additional analysis should be carried out such as a viscosity test to further ensure the effect of the comparison of polyol and TDI. The conclusion contains the results of the research and discussion as well as suggestions for improving the research that has been carried out which refers to practical actions, the development of new theories, especially those related to the results. study.

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