Jurnal Reaksi (Journal of Science and Technology)
Jurusan Teknik Kimia Politeknik Negeri Lhokseumawe
Vol. 21 No.02, December 2023 ISSN 1693-248X

DEVELOPMENT OF CHITOSAN-FILLED POLYURETHANE COMPOSITES AS ANTIBACTERIAL COATING PAINT

Nurlaili[1]
[1]Mechanical Engineering, Lhokseumawe State Polytechnic, Jl. Banda Aceh-Medan Km. 280.3, Buketrata, Mosque Punteut, Blang Mangat, Lhokseumawe City, Aceh 24301, Indonesia
*E-mail: nurlaili@pnl.ac.id

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 through 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 (2; 3; 4) % w/w). The test results showed that the best polyurethane coating paint was with a variation of 4% w/w chitosan filling. This is because the more addition of chitosan, the better it will be in inhibiting bacterial activity.

Keywords : *Chitosan, Composites, Polyols, Polyurethanes, TDI*

1. INTRODUCTION

Increased construction activity worldwide coupled with increasing urban populations have been the main factors driving the growth of the paint manufacturing market. Paint is a product that is widely used by the community, especially in construction because of its important function, which is to provide decorative (aesthetic) value. This causes the need for and use of paint in society is quite high. (Supraptiah et al., 2022). Components or paint constituents consist of binders (resins), pigments, solvents and additive materials. 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 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). 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 vegetable oil such as sunflower oil, castor oil, soybean oil, cottonseed oil, and palm oil. In other words, vegetable oil can replace petroleum (petrochemicals) as a raw material in polyurethane production, because it is superior in addition to its availability in nature which is abundant and easy to decompose (Chuanjin, H., Qunfeng, C. 2021).

Technological developments that continue to increase are now a reference for the development of antibacterial coatings that can be used in various devices ranging from furniture, electronics, cars to medical devices. To produce antibacterial coating paint products need to be modified. Modification is done by adding other fillers to the polyurethane coating paint. The filler in question is chitosan.

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, Coelenterata sp, Annelida sp, Nematoda sp, and some of the mushroom groups. As 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). With the addition of chitosan as an alloy in modifying polyurethane, it can have anti-bacterial properties in polyurethane. According to the results of the study showed that the intercalation of chitosan through the cation exchange process can increase the antimicrobial activity.

Antibacterial is a substance that can inhibit the growth of bacteria and can kill bacteria that cause infection. Bacteria that cause infection and disease are commonly found in the environment around us, including Staphylococcus aureus and Escherichia coli bacteria which are also Gram-positive and Gram-negative bacteria that 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 bacterial growth 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).

Based on the 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 the study of Suherman et al. (2018), that chitosan has a positive charge which can bind the negative charge of other compounds or play a role in inhibiting the growth of bacteria because its main nature is antibacterial.

2. MATERIALS AND METHODS

2.1 Ingredients

The materials used in this study consisted of 2 types, namely materials for polyurethane and materials for chitosan. The ingredients for making polyurethane are oleic acid based on palm oil, galcial acetic acid CH_3COOH, H_2O_2 30%, H_2SO_4, Methanol, Glycerin, Xylene and Diisocyanate toluene (TDI). While the materials used to make chitosan are shrimp shells, NaOCl, NaOH, and 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 CH_3COOH and 30 ml of 30% H_2O_2 are added slowly while stirring. Through the dropper funnel, 2 ml of concentrated H_2SO_4 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.

The hydroxylation stage was divided into four stages, namely 100 ml of methanol added 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 40ºC. Then the mixture was added to the epoxidized oil solution and stirred at 50°C for 2 hours. Then cooled at room temperature and transferred to a separating flask to separate the polyols formed and then stored in glass bottles.

2.2.2 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 2 containers for mixed samples of polyurethane and chitosan. Mix polyurethane and chitosan (total weight = 20g). There are 3 stages in the manufacture of polyurethane-chitosan coatings, namely mixing polyol and chitosan and then TDI into a glass beaker, stirring with a magnetic stirrer at 200 rpm for 1 hour. In this procedure a number of chitosan was used as much as 2, 3, and 4 weight percent (%wt). The resulting polyurethane is then cooled to room temperature. Furthermore, the surface shape was analyzed using SEM, heat resistance test and antibacterial test.

2.4 Characterization techniques

2.4.1 Analysis of thermal properties by thermogravimetric analysis (TGA)

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

2.4.2 Morphological analysis of surface 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 about 20 µm from the surface. The surface image obtained is a photograph of all the protrusions, indentations and holes on the surface.

2.4.3 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. The bacterial inhibition activity of the plate against 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. In testing the antibacterial activity, 15 mL of Nutrien Agar (NA) medium was put into a petri dish and then allowed to solidify. After solidifying, 1 ose of bacteria was taken, then scratched evenly on the surface of the medium, then each steel plate that had been smeared with polyurethane paint was inserted into the media surface. Done aseptically in laminar flow. Then the cup was incubated at 37°C for 1x24 hours, this is the optimum temperature and time for bacterial growth. Furthermore, the diameter of the clear formed was observed and the diameter of the inhibition area was measured with a caliper.

3. RESULT AND DISCUSSION

3.1 Analysis of thermal properties by thermogravimetric analysis (TGA)

The process of mass loss in the thermal test occurs due to the decomposition process. The results of thermogravimetric analysis (TGA) of pure polyurethane and chitosan-filled polyurethane can be used to characterize any material that shows a change in the weight of the material when heated, and to detect phase changes due to the decomposition process. For Polyurethane/Chitosan in the 2%w/w sample the onset starts at 312.78ºC and the endset is 403.25ºC with a weight loss of -65.729%, in the 3%w/w sample the onset starts at 392.82ºC and the endset is 497.46ºC with weight loss -63.875%, and in the 4%w/w sample 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 the 4% w/w sample, because it experiences less weight loss. This proves that the addition of chitosan has increased the thermal stability. The increase in degradation temperature is due to the stronger the melt bond between the polymer and filler so that the decomposition of the material becomes slower and difficult to break.

3.2 Morphological analysis of surface scanning electron microscopy (SEM)

The surface structure of the three samples showing some differences from the surface structure with x100 magnification. The 4%w/b sample has a smoother surface and less visible pores from the solid particles compared to the 2 and 3%w/w samples which show several lumpy shapes and large pores.

3.3 Antibacterial test

Based on the results of the antibacterial activity test data, it was obtained that the average diameter of the inhibition zone for Staphylococcus aureus and Escherichia coli bacteria in the 2% w/w sample was 10.5 mm; the 3%w/b sample was 13.5 mm and the 4%w/b sample was 15mm. These results indicate that the more chitosan added, the better the ability to inhibit bacterial growth.

4. CONCLUSION

The addition of chitosan has increased the thermal stability. The increase in degradation temperature is due to the stronger the melt bond between the polymer and filler so that the decomposition of the material becomes slower and difficult to break.

Based on the results of the bacterial activity test, it was found that the more chitosan added as a filler in the polyurethane coating paint, the better it would be in inhibiting bacterial growth, meaning that variations in the weight of chitosan had an effect on the polyurethane coating paint to inhibit bacterial growth.

REFERENCE

Chuanjin, H., Qunfeng, C. 2021. Composite Science and Technology. Learning from Nacre: Constructing Polymer Nanocomposites. Vol. 150. Pages: 141-166.

Gang, X., Pingya, L., Qiang, D. 2020. Applied Clay Science. Investigation of The Inhibition Mechanism of The Number of Primary Amine Groups of Alkylamines on The Swelling of Bentonite. Vol. 136. Pg: 43-50.

Jinbo, Z., Lili, W., Liqun, Z. 2021. Polymers. Overview of Polymer Nanocomposites: Computer Simulation Understanding of Physical Properties. Vol. 133. Pages: 272-287.

Magani et al., 2020. Journal of Bios Logos. Antibacterial Test of Chitosan Nanoparticles on the Growth of Staphylococcus aureus and Escherichia coli Bacteria. (Antibacterial Test of Chitosan Nanoparticles against Staphylococcus aureus and Escherichia coli). Vol.10 No.1.

Marzec, M, J., Kuciriska, L., Klaszczyriska, H., Janik. 2021. Materials Science and

Engineering. Development Of Polyurethanes For Bone Repair. Vol. 80. Pg: 736-747.

Rihayat, T., Mashura. 2018. Journal of Reaction Science and Technology. Castor oil and bentonite based polyurethane coating for heat resistance. Vol. 16, No. 2.

Safitri Air Force. 2016. Antibacterial Activity of Lobster Shell-Based Chitosan Nanoparticles against Staphylococcus aureus and Staphylococcus epidermidis Bacteria. FPIK IPB. Bogor.

Suherman, B., Muhdar, L. & Sisilia, TDR 2018. Potential of Vannemei shrimp (Litopenaeus vannamel) shell chitosan as an antibacterial against Staphylococcus epidermidis, Pseudomonas aeruginosa, Propionibacterium agnes, and Escherichia coli using the paper disc diffusion method. Journal of Pharmaceutical Media. 14(1), 124-125

Supraptiah et al., 2022. Utilization of Pineapple Leaf Fiber as Filler in Making Environmentally Friendly Paint. Research Journal of Chemical Engineering Department: Sriwijaya State Polytechnic.

Paju N, Yamlean PV, Kojong N (2013). Effectiveness Test of Binahong Leaf Extract Ointment (Anredera cordifolia Steenis) on Rabbits (Oryctolagus cuniculus) Infected with Staphylococcus aureus Bacteria. Pharmacon 2(1):51–61.