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The Effect of Titanium Dioxide Nanoparticle Composites as An Antibacterial in Synthesizing Polyurethane Biopolymers

Andi Budirohmi[1]*, Yanti Mustari[1], Paulina Taba[2], Hasnah Nasir[2]

Abstract. In the health sector, the use of polyurethane (PU) as a basic material for the manufacture of medical devices also creates problems related to local and systemic infections. One of the most appropriate ways to overcome this problem is to add titanium dioxide (TiO_2) nanoparticles to the urethane polymer to produce a biodegradable polymer and bacterial decontamination. In synthesizing decontaminating polyurethane bacteria, several characterization techniques were carried out, including polymer test, namely strain and stress, functional group analysis using Fourier Transform Infra-Red (FTIR), and antibacterial test. Based on the results of the FTIR test analysis, shows a change in the functional group. At wave number 1724.36 cm-1, the N-H functional group appears, this absorption is the absorption of the urethane group and TiO_2 is in the range of 513.07 cm-1. Mechanical properties test showed strain (28.92 - 21.88% GL) and young modulus at intervals (5,484-3,268 MPa). and the antibacterial test showed that the inhibitory power of test samples A1 and A4 with resistance diameters of 8mm and 8mm proved to be very effective in killing *E.Coli* bacteria while A1[1], A2[1], A3[1], and A4 killed could not kill *S. Aureus* bacteria inhibitors. The characterization results show that the polyurethane biopolymer can be used as a medical device with bacterial decontamination properties.

Introduction

In the medical field, medical equipment is an inseparable part of modern medical care (Aranguren et al., 2015). In recent years, many new synthetic materials have been developed for the manufacture of medical equipment derived from polyurethanes whose use is temporary or permanent; for example, prostheses, implants, bone changes, artificial heart valves, catheters, blood bags, and other equipment (Nakkabi et al., 2016 and Francolini et al., 2015).

In the field of health, the use of polyurethane (PU) as a basic material for making medical devices also raises problems associated with local and systemic infections (Ioana et al., 2018). When medical equipment is implanted in the body, the biological response of the organism immediately begins with the touch or contact of the surface of the skin with medical equipment, for example in cooling films that are rich in protein, polysaccharides, and cells on the surface of the skin (covering). This plays an important role in the early stages of bacterial biofilm formation, such as changes in the surface properties of medical equipment which can increase the speed of bacterial adhesion to these medical devices (Nakkabi et al., 2016).

Prevention of infection with antibacterial drugs is usually more difficult because infections that occur often result in damage to medical equipment. Therefore, there is a need for new methods to kill bacteria and prevent colonization, one of which is the use of antibacterial polymers as materials for making medical equipment based on bacterial biofilms (Poonsub et al., 2014). Research on the synthesis of antibacterial polymer material has been carried out by several previous researchers (Duan et al., 2016). One-shot polyurethane synthesis method, namely reacting polytetramethylene oxide with isophorone diisocyanate and 1,4-dihydroxybutane as a chain extender

[1]*High School of Health Sciences Gema Insan Makassar Academic, 90134, Makassar, Indonesia;* ***Email: andibudirohmi@gmail.com***
[2]*Department of Chemistry, Faculty of Mathematics and Natural Science, Hasanuddin University, Makassar 90245, Indonesia.*

in tetrahydrofuran solvent, and adding 1,3,5-Tris- (2-hydroxyethyl) hexahydro-1,3,5 -triazine as an antibacterial agent.

The addition of TiO_2 to urethane polymers can also provide antibacterial polymers. As a semiconductor material, TiO_2 degrades the skin-making compounds of *E. Coli* bacteria so that the bacteria are killed.

Besides the antibacterial properties, the addition of TiO_2 and Ag nanoparticle composites can also enhance the functionality and synergy effect of polymers such as the improvement of mechanical, optical, photocatalytic properties (Baama and Sundarjan, 2017), polyurethanes have been successfully synthesized by reacting polytetramethylene ether glycol with toluene diisocyanate and the addition of composite nanoparticles TiO_2 and nanoparticles (Kuan et al., 2019) hydroxyapatite and 1,4-butanediol as chain extenders and 1,4-diazabisiklooktane as the hardener. The use of TiO_2 in the health sector is very useful because it is photocatalytic and can absorb and reflect UV rays so TiO_2 is classified as UV protection in the health field (Razi and Meryam, 2013).

Experimental

Materials and Methods

Banana weevils were obtained from Sengkang, South Sulawesi, Indonesia, Methylendifenyl diisocyanate (MDI) from (Sigma Aldrich) and, PEG 400 from Merck, and Titanium dioxide (TiO_2) nanoparticles from (Sigma Aldrich), and aquadest.

Procedures

The polyurethane synthesis process is carried out using the one-step process method. Where KBH starch was weighed in 2,5979 g beakers then 10 g of PEG and 1,342 g of TiO_2 nanoparticles were added to a beaker containing starch, then stirred with a magnetic stirrer for 3 hours, at 100 °C, MDI is then added then stirred together for 15 minutes. Polyurethane pre-cure printed in glass molds measuring 4 cm x 5 cm. An illustration of the polyurethane synthesis process can be seen in Figure 1.

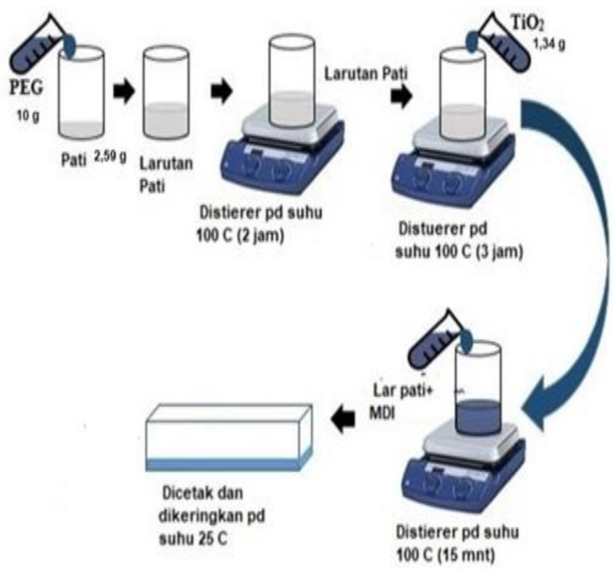

Figure 1. An illustration of the polyurethane synthesis process

Result and Discussion

Test of mechanical properties

To determine the mechanical properties of polyurethane, tensile and strain tests are carried out.

Mechanical properties and stresses of polyurethane polymers derived from PEG 400, MDI, starch KBH % and TiO_2 1% can be seen in Table 1. Polyurethanes synthesized from TiO_2 1% show high stress and small strain and lower modulus of elasticity (Modulus young). This data shows that the polymers obtained are included in the flexible category.While polyurethanes derived from PEG 400, MDI, starch KBH 5%, and TiO_2 1.5% indicate that polyurethanes have large stresses and small strain, and low elastic modulus, this shows that polyurethane polymers are in the very flexible category.

Whereas PU polymers derived from PEG 400, MDI, starch KBH 15%, and TiO_2 2% indicate that these polymers have small stresses and large strains and large elastic modulus, polymers are categorized as rigid polymers.

Synthesis of PU derived from PEG 400, MDI, starch KBH 15%, and TiO_2 2.5% showed that this polymer has small stress and large strain and a large modulus of elasticity then the polymer is categorized as a rigid polymer.

If the mechanical polymer properties have large stress and small strain and the modulus of elasticity (modulus young) is low, the polyurethane polymer is included in the category of very flexible. However, if the polymer has small stress and large strain, and high elastic modulus, it is included in the rigid category (Malik et al., 2013).

The analysis of the mechanical properties of stress and strain shows that polymers derived from PEG 400, MDI, CPC starch, and TiO_2 2% can be applied as medical devices because they have strains at intervals (28.92-21.88% GL) and Modulus Young are at intervals (5.484-3.268 MPa). Polyurethanes that can be applied in the medical field and physiological conditions in the human body must have mechanical qualities that meet the standards. One important mechanical aspect of polymers is strain strength and modulus of elasticity (Budirohmi et al.,2020).

Table 1. Test the mechanical properties of polyurethane synthesized from KBH, PEG 400, MDI and TiO_2 starch with concentrations (1%, 2%, 3% and 4%)

No	Polymer Composition	Modulus Young (Kpa)	Stress (Kpa)	Strain % GL
1	PU+ Starch KBH+ TiO_2 1%	39.21-4244.50	7.64-191.10	13.64-26.41
2	PU+ Starch KBH+ TiO_2 1,5%	817.43-3183.60	39.63-76.14	3.76-7.77
3	PU+ Starch KBH+TIO_2 2 %	3267.90-483.70	214.54- 333.30	21.88-28.92
4	PU+ Starch KBH+TIO_2 2,5 %	2014.40-562.92	6.77-8.613	177.47-211.70

Fourier Transform Infra Red (FTIR) Test

The composition of functional groups was found in polyurethanes synthesized from PEG 400, MDI starch KBH 15% and TiO_2 2.5% can be analyzed by FTIR spectroscopy can be seen in (Figure 1). Polyurethanes were synthesized from PEG, MDI, KBH starch and TiO2 with variations of concentrations (1%, 1.5%, 2%, and 2.5%) of the weight of the polymer (Malik et al*.,* 2014 and Andi Budirohmi et al., 2020).

Polyurethanes synthesized from 2.5% TiO_2 showed the absorption band of the O-H group at wave number 3444.9 cm^{-1} and in the range of wave number 2918.7 cm^{-1}, there seemed visible saturated C-H functional groups. A wavenumber 1724.5 cm^{-1} the N-H function group appears this absorption is the absorption of the urethane group. Wavenumber 1516.72 cm^{-1} shows the group C = O group and the range of numbers 1107.1 cm^{-1} shows the C-O group. The peak of band absorption at wave number 513.81 cm^{-1} shows the group of TiO_2 functional groups.

Polyurethanes synthesized from TiO2 2% showed the absorption band of the O-H group at wave number 3444.4 cm^{-1} and in the range of wave number 2918.3 cm-1 there appeared to be a saturated C-H function group. A wavenumber 1724.3 cm^{-1} the N-H functional group appears, this absorption is the absorption of the urethane group. Wavenumber 1516.05 cm^{-1} shows the group C = O group and the range of numbers 1107.20 cm^{-1} shows the C-O group. The peak of the band's absorption at wave number 513.51 cm^{-1} shows the group of TiO_2 functional groups.

Polyurethanes synthesized from 1.5% TiO_2 showed the absorption band of the O-H group at wave number 3443.4 cm^{-1} and in the range of wavenumbers, 2902.8 cm^{-1} there appeared to be a saturated C-H function group. At the wave number 1724.16 cm^{-1}, the N-H functional group appears, this absorption is the absorption of the urethane group. Wavenumber 1516.01 cm^{-1} shows the group C=O group and the range of numbers 1105.20 cm^{-1} shows the C-O group. The peak of band absorption at wave number 513.03 cm^{-1} shows the group of TiO_2 functional groups.

Polyurethanes synthesized from TiO_2 1% showed the absorption band of the O-H group at wave number 3443.0 cm^{-1} and in the range of wave number 2902.0 cm^{-1}, there seemed visible saturated C-H functional groups. A wavenumber 1722.43 cm^{-1} the N-H functional group appears, this absorption is the absorption of the urethane group. Wavenumber 1515.01 cm^{-1} shows the group C=O group and the range of numbers 1100.20 cm^{-1} shows the C-O group. The peak of the absorption band at the wave number 512.8 cm^{-1} shows the group of TiO_2 functional groups.

The data obtained show that the increasing concentration of TiO_2 in polyurethane synthesis also increases its mechanical properties, which are characterized by an increase in the intensity of urethane groups (N-H, C=O, and C). PU antibacterial test synthesized from PEG 400, MDI, starch banana kepok and TiO_2 with concentrations of 1% and 1.5%.

Antibacterial test results using the diffusion method for PU derived from PEG 400, MDI, starch KBH and 1% TiO_2 can be seen in (Figure 2). The data obtained showed that the test samples (A1 and A4) were effective in killing *E. Coli* bacteria, with an inhibition zone of each resistance (8 mm), whereas the test samples (A2, and A3) it could not kill *E. Coli* bacteria (gram-negative) because the inhibition zone of each resistance (0 mm), and the control (+) shows a diameter of resistance of 7 mm in *E. Coli* bacteria and the inhibition zone of the resistance in control (-) is 30 mm. Looks at the test samples ($A1^1$, $A2^1$, $A3^1$, and $A4^1$) cannot kill *S. Aureus* (gram-positive) bacteria because of the diameter of each resistance (0 mm). Whereas the control (+) diameter of the resistance is (0 mm) and the control (-) inhibition zone is (7 mm).

Antibacterial test on the test samples (B1, B2, B3 and B4) showed that the inhibition zone were 7, 0, 10, and 9 mm respectively, based on the measurement of the inhibition zones (B1, B3 and B4) effectively killing *E.Coli* bacteria. The control (+) shows the diameter of the obstacle (30 mm) and the control (-) the inhibition zone of the obstacle (0 mm). Whereas the test samples ($B1^1$, $B2^1$, $B3^1$, and $B4^1$) cannot kill *S.Aureus* bacteria because of the inhibition zone of each resistance (0 mm). Data from positive and negative controls show that the inhibition zone on the dick (+) is 7 mm and the diameter of the control (-) is 0 mm. PU inhibition is effective against *E. Coli* bacteria due to the effect of adding TiO_2 into polyurethane biopolymers. Titanium dioxide functions as a semiconductor material, which can degrade the skin making compounds of *E. Coli* bacteria so that the bacteria are killed (Budirohmi et al., 2020).

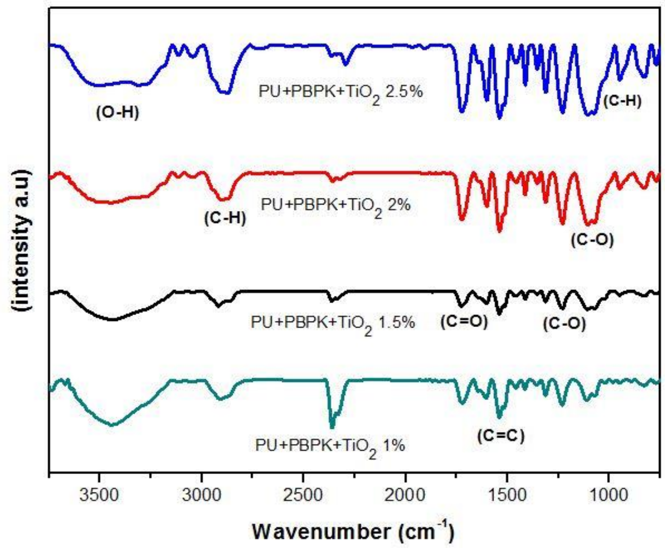

Figure 1. FTIR Polyurethane Test Results were synthesized from PEG 400, MDI, KBH Starch and TiO_2 (1%, 1.5%, 2% and 2.5%)

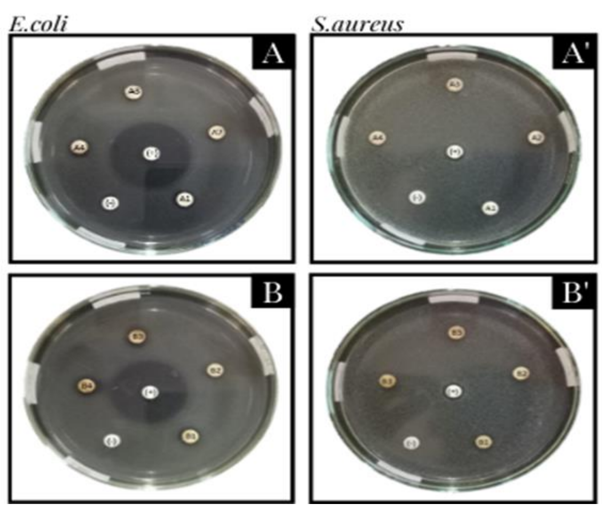

Figure 1. Antibacterial test of PU with diffusion method so that polyurethane derived from PEG 400.MDI material, KBH starch TiO_2 (1% and 1.5%)

Conclusion

The results of the analysis of the mechanical properties of stress and strain show that polymers derived from PEG 400, MDI, CPC starch, and TiO_2 2% can be applied as medical devices because they have strain at intervals (28.92-21.88% GL) and Young modulus which is at intervals (5,484-3,268 MPa). The results of the FTIR test analysis showed that changes in functional groups in the wavenumber 1724.3 cm^{-1} appear to be N-H functional groups, this absorption is the absorption of urethane groups and TIO_2 is in the range of 472 cm^{-1}.

The antibacterial test showed that the inhibition of the C3 and C4 test samples with 15mm and 13mm inhibition diameters proved to be very effective in killing *E. coli* bacteria while the $C1^1$ and $C4^1$ test samples with 8 mm and 9 mm inhibition diameters proved to be effective in inhibiting S.aureus bacteria. The results of the characterization show that polyurethane biopolymers can be used as medical devices that are bacterial decontamination properties and are biodegradable.

Conflict of Interest

The authors declare that there is no conflict of interest.

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