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The Effect of Concentration of Titanium Dioxide Nanoparticles on Their Antibacterial Activity in the Synthesis of Polyurethane Biopolymers

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Abstract
In the health sector, the use of polyurethane (PU) as a basic material for medical devices still causes problems related to local and systemic infections. One of the most appropriate ways to overcome this problem is to synthesize PU biopolymer with titanium dioxide (TiO_2) nanoparticles. The use of nano-shaped materials in this synthesis has many advantages, including being easier to synthesize and being antibacterial. Meanwhile, starch is the result of isolation from banana weevils, where banana weevils are agricultural waste that has not been utilized properly. Particle size and the use of agricultural waste are a form of modification and innovation in PU synthesis, as well as a novelty in the development of this research. In PU synthesis, several characterization techniques are carried out, including polymer tests, namely strain and stress, functional group analysis using (Fourier Transform Infra-Red), and antibacterial tests. Based on the results of the FTIR test analysis, it show that at a wave number of 1724.36 cm^{-1}, the N-H functional group is visible, and the absorption of urethane and TiO_2 groups is in the range of 513.07 cm^{-1}. The mechanical properties test shows the strain (28.92 - 21.88% GL) and young's modulus in the interval (5.484-3.268 MPa). The antibacterial test showed that the inhibitory power of test samples A1 and A4 with diameters of 8 mm and 8 mm proved to be very effective in killing *E. Coli* bacteria, while test samples A1¹, A2¹, A3¹, and A4 were not able to kill *E. Coli* bacteria. *S. Aureus*. bacteria. The characterization results show that PU biopolymer can be used as a basic material for making bacterial decontaminant medical devices.

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INTRODUCTION

In the medical field, medical equipment is an inseparable part of modern medical care (Nakkabi et.al, 2016) In recent years, many new synthetic materials have been developed for the manufacture of medical equipment derived from PU whose use is temporary or permanent; for example, prostheses, implants, bone changes, artificial heart valves, catheters, blood bags, and other equipment (Francolini et al,2016 & Changhua et al, 2023).

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 (Adnan A et al, 2022& Nandini et al, 2017). 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), (Ghazal K et al, 2020). 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 (Angiolillo DJ et al, 2007 & Andi Budirohmi et al, 2020).

Prevention of infection with antibacterial drugs is usually more difficult because infections that occur often result in damage to medical equipment (Vignesh K et al,2021). 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 (Baama, K et al,2017). Research on the synthesis of antibacterial polymer material has been carried out by several previous researchers (Adnan A et al, 2022). One-shot PU synthesis method, namely reacting polytetramethylene oxide with isophorone diisocyanate and 1,4-dihydroxybutane as a chain extender 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 (Baama K et al, 2017). As a semiconductor material, TiO_2 degrades the skin-making compounds of *E. Coli* bacteria so that the bacteria are killed (Baama K et al, 2017& Quan X et al,2022).

Research on the synthesis of antibacterial polymer materials has been carried out by several previous researchers (Adnan et al, 2020 & Salman M et al,2021) Apart from antibacterial properties, the addition of TiO_2 and Ag nanoparticle composites can also increase the functionality and synergy effects of polymers such as improving mechanical, optical, and photocatalytic properties (Aranguren M.I et al., 2015 & Ioanna et al, 2018). PU has been proven to be successfully synthesized by reacting polytetramethylene ether glycol with toluene diisocyanate as well as adding a composite of TiO_2 nanoparticles and nanoparticles (Duan J.H, et al 2016 & Kuan N.C et al, 2019). Hydroxyapatite and 1,4-butanediol as chain extenders and 1, 4-diazabicyclooctane as the hardener. The use of TiO_2 in the health sector is very beneficial because it is photocatalytic and can absorb and reflect UV rays so TiO_2 is classified as UV protection in the health sector (Malik S et al, 2014 & Ping Wang et al, 2019).

METHOD

Equipment and Materials

Beaker, Stirrer, Analytical Balance, Paper, 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.

Research Procedure

The PU synthesis process is carried out using the one-step process method (Nakkabi et al, 2015). Where KBH starch was weighed in 2,598 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^o C, MDI is then added then stirred together for 15 minutes. Polyurethane pre-cure printed in glass molds measuring 4 cm x 5 cm (Andi Budirohmi, et al 2020). An illustration of the PU synthesis process can be seen in Figure 1.

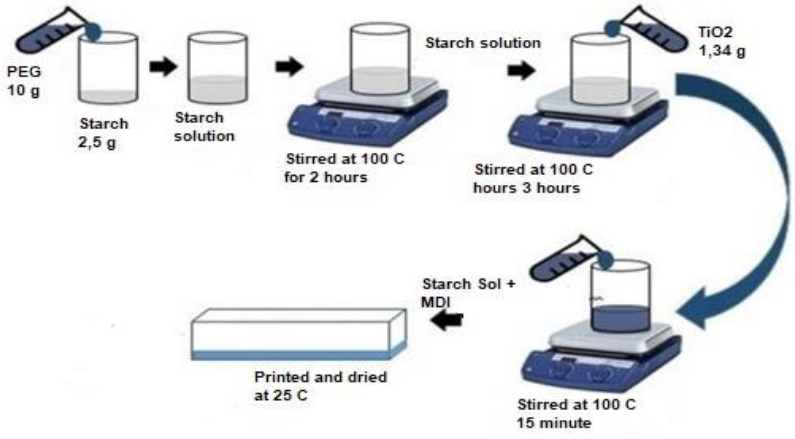

Figure 1. An illustration of the PU synthesis process

RESULTS AND DISCUSSION

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

Table 1. Test the mechanical properties of PU synthesized from KBH 15%, PEG 400, MDI and Nanoparticles TiO_2 starch with concentrations (1%, 2%, 3% and 4%).

No	Polymer Composition	Modulus Young (Kpa)	Stress (Kpa)	Strain % GL
1	PU+ KBH Starch+TiO_2 1% Nanoparticles	39.21-4244.50	7.64-191.10	13.64-26.41
2	PU+ KBH Starch+ TiO_2 1,5% Nanoparticles	817.43-3183.60	39.63-76.14	3.76-7.77
3	PU+KBH Starch+ TIO_2 2 % Nanoparticles	3267.90-483.70	214.54- 33.30	21.88-28.92
4	PU+ KBH Starch + TIO_2 2,5 % Nanoparticles	2014.40-562.92	6.77-8.613	177.47-11.70

Mechanical properties and stresses of PU polymers derived from PEG 400, MDI, starch KBH % and TiO_2 1% nanoparticles can be seen in Table 1. Polyurethanes synthesized from TiO_2 1% nanoparticles 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 (Andi Budirohmi et al, 2020 &Yuemei C, et al, 2016). While PU derived from PEG 400, MDI, starch KBH, and TiO_2 1.5% nanoparticles indicate that PU have large stresses and small strain, and low elastic modulus, this shows that PU polymers are in the very flexible category (Andi Budirohmi et al, 2020).

Whereas PU polymers derived from PEG 400, MDI, starch KBH 15%, and TiO_2 2% nanoparticles 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% nanoparticles 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(Andi Budirohmi et al, 2020).

If the mechanical polymer properties have large stress and small strain and the modulus of elasticity (modulus young) is low, the PU 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 (Andi Budirohmi et al,2020 & Xiao-wei et al, 2020).

The analysis of the mechanical properties of stress and strain shows that polymers derived from PEG 400, MDI, CPC starch, and TiO_2 2% nanoparticles 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 (Poonsub, T, et al, 2014 & Andi Budirohmi et al, 2020).

PU functional group test of PEG 400, KBH Starch 15 %, MDI, and TiO_2 nanoparticles with Fourier Transform Infra Red (FTIR) Test

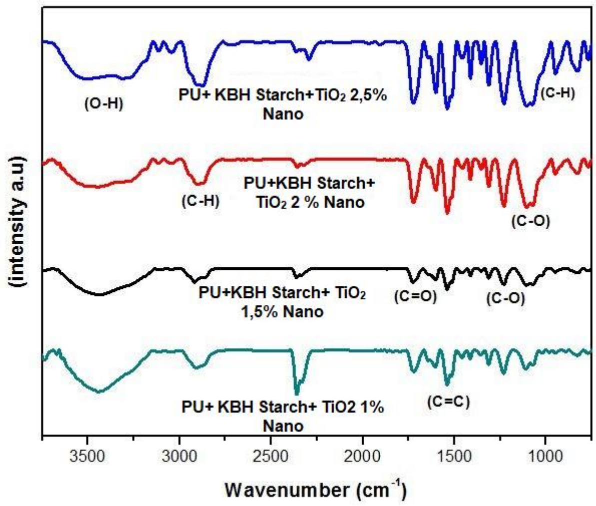

Figure 2. FTIR Polyurethane Test Results were synthesized from PEG 400, MDI, KBH Starch and TiO_2 nanoparticles (1%, 1.5%, 2% and 2.5%)

The composition of functional groups was found in PU synthesized from PEG 400, MDI starch KBH and TiO_2 2.5% nanoparticles can be analyzed by FTIR spectroscopy can be seen in (Figure1). Polyurethanes were synthesized from PEG, MDI, KBH starch and TiO_2 nanoparticles with variations of concentrations (1%, 1.5%, 2%, and 2.5%) of the weight of the polymer (Andi Budirohmi et al, 2020).

Polyurethanes synthesized from 2.5% TiO_2 nanoparticles 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 (Yuemei C et al 2016; Andi Budirohmi et al, 2020). 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 (Andi Budirohmi et al, 2020& Salman M et al ,2021).

Polyurethanes synthesized from TiO_2 2% nanoparticles 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 (Andi Budirohmi et al, 2020).

Polyurethanes synthesized from 1.5% TiO_2 nanoparticles 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 (Andi Budirohmi et al, 2020).

Polyurethanes synthesized from TiO_2 1% nanoparticles 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 (Andi Budirohmi et al, 2020).

The data obtained show that the increasing concentration of TiO_2 nanoparticles in PU synthesis also increases its mechanical properties, which are characterized by an increase in the intensity of urethane groups (N-H, C = O, and C). Polyurethanes antibacterial test synthesized from PEG 400, MDI, starch KBH and TiO_2 nanoparticles with concentrations of 1% and 1.5% (Andi Budirohmi et al, 2020).

The results of the antibacterial test using the zone of inhibition method for PU sourced from PEG 400, MDI, BPK starch and 1% and 2.5% TiO_2 nanoparticles 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 their respective inhibitions (8 mm), while the test samples (A2 and A3) were unable to kill *E. Coli* bacteria (gram-negative), because of their respective inhibition (0 mm), and in the control (+) the inhibition diameter was 7 mm in *E. Coli* bacteria and in the control (-) the inhibition diameter was 30 mm. It can be seen that the test samples ($A1^1$, $A2^1$, $A3^1$, and $A4^1$) could not kill *S. Aureus* (gram-positive) because of their respective inhibition diameters (0 mm). (Andi Budirohmi et al, 2020) While the control (+) has a resistance diameter (0 mm) and the control (-) has a resistance diameter (7 mm) (Nursin et al, 2019; Andi Budirohmi et al, 2020).

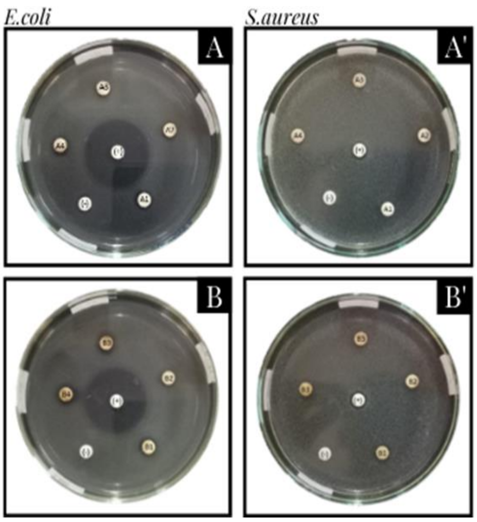

Figure 2. Antibacterial test of PU with diffusion method so that PU derived from PEG 400.MDI material, KBH starch TiO_2 nanoparticles (1% and 1.5%)

Antibacterial test on test samples (B1, B2, B3, and B4) showed inhibition diameters of 7, 0, 10, and 9 mm, respectively, based on measurements of the inhibition of the test samples (B1, B3, and B4) effectively killing *E.Coli* bacteria. control (+) indicates the diameter of the obstacle (30 mm) and control (-) indicates the diameter of the obstacle (0 mm). While the test samples (B1¹, B2¹, B3¹, and B4¹) could not kill *S.Aureus* bacteria because of their respective inhibition diameters (0 mm). The data showed that the positive and negative controls each had a diameter of (+) 7 mm and the control (-) had a diameter of 0 mm. The data obtained, it shows that PU effectively kills *E. Coli* bacteria due to the effect of adding TiO_2 nanoparticles in the synthesis(Andi Budirohmi et al, 2020). Titanium dioxide functions as a semiconductor material, which can destroy the skin-forming compounds from *E. Coli* bacteria so that the bacteria die (Husnul H , 2018; R.Ariessanty et al, 2020).

CONCLUSION

The results of the analysis of the mechanical properties of stress and strain show that the polymer derived from PEG 400, MDI, KBH starch, and TiO_2 2% can be applied as a medical device because it has a strain in the interval (28.92 – 21.88% GL) and a high young's modulus. tall. is in the interval (5,484-3,268 MPa). The results of the FTIR test analysis show that changes in functional groups at the wave number 1724.3 cm^{-1} appear to be the N-H functional group, this absorption is the absorption of the urethane group and TIO_2 is in the range of 472 cm^{-1}.

The antibacterial test showed that the inhibitory power of test samples C3 and C4 with inhibitory diameters of 15 mm and 13 mm proved to be very effective in killing *E. Coli* bacteria, while test samples C1¹ and C4¹ with inhibitory diameters of 8 mm and 9 mm proved effective in inhibiting *S. Aureus* bacteria. . The characterization results show that PU biopolymer can be used as a medical device that has bacterial decontamination properties and is biodegradable. The use of nano-shaped materials and banana hump starch is new in the synthesis of PU biopolymers.

RECOMMENDATIONS

Orders for chemicals from distributors take too long to send the goods. Advice to speed up delivery.

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