Mechanical Properties of Alginate Based Biopolymers as Wound Dressing Material

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Abstract. The utilization of biopolymers has been widely accepted in many areas due to its eco-friendly. Especially in medical care, biopolymers are receiving great attention and are considered as a potential for wound healing. Wound dressing material is one of medical needs and the demand continue to raise. One of the most widely used biopolymers for wound dressing is alginate. To improve alginate properties as wound dressing material, various alginate modifications with nanoparticles or synthetic polymers have been developed. In this paper alginate biopolymer will be modified with ZnO nanoparticles and synthetic polymer, such as poly (ethylene glycol) dimethacrylate (PEGDMA) as one of the candidates of wound dressing material. Alginate can go through swelling and because of its crystallinity is low so that it affects its mechanical properties. In order to increase the compatibility, ZnO needs to be modified with PEGDMA which is crosslink with alginate to strengthen the bonding network of materials. Characterization of alginate-based wound dressing material was performed using FTIR, XRD and SEM. In addition, optimization tests of mechanical and antibacterial resistance properties were performed to meet detailed studies of the effect of ZnO nanoparticles and PEGDMA interpenetrated into alginate to the properties of the wound dressing material.

1. Introduction

Alginate is a linear biopolymer consisting of two monomeric units, namely D-manuronic acid and L-guluronic acid. Alginate is found in all types of brown algae (Phaeophyta) which is one of the main components making up the cell wall. Alginate has a characteristic as wound dressing material because it is non-toxic, biocompatible and biodegradable. In addition, some wound dressing materials use alginate as raw material because its increase the growth of new cell tissue and reduce inflammation, thereby accelerating wound healing. However, alginate has relatively low mechanical resistance and antibacterial properties [1]. Thus, further modifications are needed, for example with nanoparticles or synthetic polymers. ZnO nanoparticle (zinc oxide) is one of the materials that have been widely synthesized into nanoparticles [3,8,9]. This material has potency to be applied in the biomedical field because of its good antibacterial properties.

In this paper, the characterization of ZnO nanoparticles was carried out and modified [3,8] with alginites and synthetic polymers, poly (ethylene glycol) dimethacrylate (PEGDMA) as a candidate for wound dressing material. Alginate can experience swelling and low crystallinity so it affects the mechanical properties. Interpenetration of ZnO nanoparticles into the alginate matrix is able to limit the volume of the alginate polymer chain with the surface of ZnO to improve its mechanical and antibacterial properties. To increase the compatibility, ZnO needs to be modified by synthetic polymers that can cross-link with alginites so that they are able to strengthen the bonding network of
IPN material [3]. The characterization of alginate-based wound dressing material was carried out using FTIR and SEM-EDS. Its mechanical resistance properties were characterized and initial studies on its antibacterial properties was carried out.

2. Material and Methods

2.1. Material

The equipment used in this study are measuring flask, Erlenmeyer flask, measuring cup, funnel, drop pipette, analytical balance, chemical beaker, drip plate, reflux tool set, mechanical stirrer, desiccator, incubator, X-ray diffractometer, Fourier Transform Infrared Spectrophotometer (FTIR), Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM), UV-Vis Spectrophotometer and Instron IX series testing machines. The materials used are sodium alginate, aqua, zinc nitrate hexahydrate (Zn(NO$_3$)$_2$.6H$_2$O), sodium hydroxide, hexamethylene diisocyanate (HDI), ethylene glycol dimethacrylate (EGDMA), dibutyltin dilaurate (DBTDL), nitrogen gas, and Favigraph.

2.2. Methods

Sodium alginate as much as 0.75 grams was dissolved in 100 mL of water, then added 0.25 grams of ZnO and PEGDMA synthesis results with a ratio of 1: 1 to form a gel. Alginate-ZnO-PEGDMA material that has been formed into a membrane is then characterized by FTIR and SEM and tested for its mechanical strength using a Favigraph.

3. Results

3.1. Synthesis and characterization of Alginate-ZnO-PEGDMA

PEGDMA has been used in medical applications, but as a synthetic polymer in wound dressing material, it has never been done. Wang (2016) used synthetic poly (ethylene glycol) methacrylate (PEGMA) synthetic polymers modified with agarose and ZnO to produce wound dressing material [8]. Alginate, ZnO and EGDMA concentrations used in the synthesis of this IPN material were 1 mmol, 4 mmol and 20 mmol. AZP material was obtained from synthesis in the form of white powder as much as 4.9959 grams. The following image of AZP material synthesized is shown in Figure 1:

![Figure 1. Synthesis of Alginate-ZnO-PEGDMA (AZP) IPN material: (a) gel form, (b) powder form, and (c) membrane form.](image-url)

Material characterization was carried out using FTIR and SEM-EDS. The mechanical strength and antibacterial properties were characterized to be studied as wound dressing material. The following is a spectrum of IR Alginate-ZnO (AZ) and Alginate-ZnO-PEGDMA (AZP) synthesis results:
3.2. Synthesis of Alginate-ZnO-PEGDMA (AZP)

Based on the Figure 3, the morphology of AZP material was successfully observed at 10000x and 40000x magnification. ZnO sample particle distribution seems to have non-uniform shape. This is because the whole sample can be said experiencing agglomeration between its constituent components.

Figure 3. Morphology of Alginate-ZnO PEGDMA (AZP) at magnifications of 10000x and 40000x.

SEM imaging results generally describe the synthesis of AZP which has a spherical shape "like a flower" with a gap between the particles looks quite clear. The flower-like form of AZP morphology may be displayed by ZnO nanoparticles, as in a study reported by Mun Lam (2017) regarding the synthesis of Ag-ZnO composite material whose morphology is flower-shaped with several petals growing radially from the center and well dispersed.

3.3. Synthesis and characterization of Alginate-ZnO-PEGDMA

Analysis of mechanical resistance properties was studied to determine the performance of the material. The instrument used in the analysis of the nature of this resistance was used Favigraph with a distance of 2.5 mm and a tensile speed of 10 mm/minute. The samples tested were 2, namely Alginate-ZnO
(AZ) and Alginate-ZnO-PEGDMA (AZP). The sample was in the form of gel that has been dried into a thinly cut film with a length of 3 cm and a width of 0.2 cm. The following is an illustration of the sample to be tested for its mechanical strength.

![Sample Illustration](image)

Figure 4. AZ (Alginate-ZnO) and AZP (Alginate-ZnO-PEGDMA) samples to be tested for mechanical strength.

AZP material has the tensile strength value that is closest to the average value of the mechanical resistance properties of AZP material. We plot the linear lines, \( x \) (E yield) and \( y \) (F yield) at the points of 0.96 and 300.58. Then, the value of tensile strength and elasticity were obtained and has been converted to 26.27 MPa.

| Number of Sample | Tensile Strength (MPa) | Elasticity (MPa) |
|------------------|------------------------|-----------------|
| 1                | 20.47                  | 2477.19         |
| 2                | 20.60                  | 2726.81         |
| 3                | 22.97                  | 1839.88         |
| 4                | 26.63                  | 2785.78         |
| 5                | 26.84                  | 2215.83         |
| 6                | 27.65                  | 1900.54         |
| 7                | 28.53                  | 1890.13         |
| 8                | 29.79                  | 2873.97         |
| 9                | 32.99                  | 1687.53         |

The converted elasticity values can be obtained by making a linear line plot so that the E yield and F yield can be determined. AZP material with sample is the closest to its elasticity value with an average AZP material elasticity value of 2266.40 MPa. The elasticity value was obtained by dividing the value of the tensile strength by the value of E yield. AZP material (E yield, F yield) linear line plot with sample code 5 is at 1.21 and 302.92. After the tensile strength value is converted into MPa units, then the AZP material elasticity value is obtained with sample code 5 of 2215.83 MPa.

4. Discussion

4.1 Synthesis and characterization of Alginate-ZnO-PEGDMA
Based on Table 2, the characterization with fitr for alginate-ZnO (AZ) and alginate-ZnO-PEGDMA (AZP) shows strong and wide absorption for oh groups which are seen at wave number 3427.51 cm⁻¹.
and when there is interaction with pegdma a wave number shifted to \( 3450.65 \text{ cm}^{-1} \). The presence of significant pegdma can be seen in coo- uptake at wave number \( 1726.29 \text{ cm}^{-1} \), while its interaction with az material which is indicated by shifting some of its main peaks can be described as follows, the \( \text{c = c} \) alkene peak of the az material experiences a shift in the wave number and decreases its intensity at the wave number \( 1635.64 \text{ cm}^{-1} \) which indicates that PEGDMA has interacted with az. The presence of pegdma influences the absorption of oh groups in AZ material as a result of interactions between az molecules with PEGDMA at wave numbers of \( 1460.11 \text{ cm}^{-1} \) and \( 1386.75 \text{ cm}^{-1} \). The interaction of pegdma with AZ material is more dominant in shifting the wave numbers of important groups of AZ material such as the coc ether uptake from wave number \( 1095.57 \text{ cm}^{-1} \) to \( 1261.45 \text{ cm}^{-1} \), then the wavelength for ZnO absorption shifts to \( 1161.15 \text{ cm}^{-1} \) [3].

| Number of Waves (cm\(^{-1}\)) | Identification |
|---------------------------------|----------------|
| \( 3450.65 \) | O-H |
| \( 2956.87-2989.66 \) | CH alkane |
| \( 1726.29 \) | C-O-O- |
| \( 1635.64 \) | C=C alkene |
| \( 1386.75; 1460.11 \) | O-H |
| \( 1261.45 \) | C-O-C ether |
| \( 1161.15 \) | ZnO |

In general, the azp particle size distribution produced varies with a range of 105-171 nm. Vasquez et al (2016) state that particles having a diameter <1.000 nm can be accepted as nano-sized carriers that can be used in the pharmaceutical industry. The process of material synthesis using natural materials is greatly influenced by the concentration used [3,8]. The greater the concentration of alginate used, the greater the average AZP particle size produced. because the more the concentration of alginate, the more functional groups available to reduce metal ions, which then produce a large number of particles formed so that the distance between particles is smaller, thus allowing interactions between particles to form particles with a larger size.

4.2 Mechanical properties of Alginate-ZnO-PEGDMA material

Table 1 shows the tensile strength and elasticity data of AZP material. The tensile strength of AZP material is increasing with a relatively irregular increase between one sample code sheet and the next sample code. The increase in tensile strength values lasted until the code snippet of sample 9, meaning that the AZP material samples used in testing the mechanical properties of this sheet were 9 sheets. Unlike the tensile strength values, AZP material elasticity data display random values on each sheet. There are even several sheets of samples that are significantly different. The difference in tensile strength values between the sample sheets can also be caused by the inhomogeneity that occurs in AZP material dispersion [8].

5. Conclusions

ZnO nanoparticles have been successfully synthesized and characterized. Their particle size was determined so that they can be modified with alginate and poly (ethylene glycol) dimethacrylate (PEGDMA) and can be used as wound dressing material. Alginate-ZnO-PEGDMA (AZP) material has been successfully synthesized and characterized. Its mechanical resistance and antibacterial properties have been characterized. The study of mechanical properties was confirmed through tensile strength and elasticity of 26.28 MPa and 2,266.41 MPa, respectively.
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