Enhancing the Mechanical and Water Absorption Properties of PLA/Chitosan Composites by the Incorporation of Zinc Oxide Nanoparticles

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Abstract
The interaction of ZnO (zinc oxide) and CS (chitosan) nanoparticles in improving the mechanical and water absorption properties of nanocomposites (PLA/CS/ZnO) has been investigated. The formation of composites from a polymer (polylactic acid) mixture was carried out through the precipitation method using a water bath at a temperature maintained at 70^{o}C. Five prepared types of samples PA, PPA, BPPA, CPPA, and DPPA were produced in the form of plastic film material using mechanical properties with tensile tools and water absorption test. The results showed that the mechanical properties increased with the addition of ZnO nanoparticles compared to pure PLA and PLA/CH, especially in CPPA (PLA/CS with 2% of ZnO) with the highest tensile strength value of 15 MPa. In line with this, the increase in water absorption was more significant in DPPA (PLA/CS with 4% of ZnO). It has a better absorbability than other samples with the lowest percentage absorption rate of 0.04% to 0.05%. The incorporation of ZnO nanoparticles plays an important role in the main properties of polymer nanocomposites.

Keywords: *polylactic acid, zinc oxide, chitosan, polymer, nanocomposites*

1. Introduction

Over the years, there has been an increasing interest in renewable bio-sourced components to replace petrochemical products (Nonato et al., 2019). Since the concept of chemical macromolecules was introduced, it has been a challenge for polymer scientists to figure out and invent new monomer-to-polymer systems that could form new polymer products accurately, controlling molecular weight and forming more promising material properties (Abbasian et al., 2019; Alam et al., 2019; Velerio et al., 2018). The resulting polymer products can be adapted to the ability of supramolecular induction in aqueous media or interfaces to produce micro or nanostructures with nearly unlimited applications in the fields of pharmaceutical, medical, and biotechnology. Bio-based polymers can play an important role, unlike conventional plastics that cannot help reduce emissions of greenhouse gases (carbon dioxide). A biomaterial is such a substance (other than a drug) or combination of substances, synthetic or natural in origin, which can be used for any period of time, as a whole or a part of a system, which treats, augments, or replaces any tissue, organs or functions of the body (Piekarska et al., 2017).

Polylactic Acid (PLA) is also non-toxic, biodegradable, and biocompatible and possesses good mechanical properties, but it has low impact strength. Therefore, to overcome these weaknesses, PLA can be enhanced properties with the addition of filler material (filler) to form a nano-sized nanocomposite (Bhasney et al., 2020; Jaafar et al., 2018). PLA can be formed through the esterification process of lactic acid obtained from fermentation by bacteria using substrates starches or simple sugars. Other advantages of the PLA are that they are transparent and safe to use in the medical field. The PLA is applied usually for beverage bottles, plastic bottles of chemicals, materials chairs, cutlery, plastic bags, car components, shelves, buckets, and others. The latest application of PLA is in other fields, such as the medical field, among others, are used as artificial leather, sewing thread operations, drug capsules, and tissue engineering because the body can absorb it (Midya et al., 2019; Rihayat et al., 2014; Suryani et al., 2017).

Chitosan (CS) is a quite unique bio-based polymer. Its intrinsic properties are highly singular and valuable with no actual petrochemical equivalent. These inherent characteristics of CS make itself directly exploitable (Bahremandi et al., 2019; Hooda, 2017). Chitosan compound is derived from chitin biological material – an organic compound that is abundantly available in nature like cellulose. It is a fiber-shaped multipurpose chemical and a sheet-shaped copolymer thin, white or yellow, odorless. Blending the CS with other biodegradable polymers, for example, poly(ε-caprolactone) (PCL) has been carried out to modify its water sensitivity properties(Boura-theodoridou et al., 2020; Rihayat et al., 2018).

Zinc oxide nanoparticles (ZnO) have been known to be environmentally friendly and multifunctional. Inorganic additives that could be considered as nanofillers for various polymers providing properties like antibacterial effect or intensive ultraviolet absorption (Bombonatti et al., 2019). ZnO formed as powder and insoluble in water like an inorganic compound. ZnO can be used as an additive for materials such as rubber, plastics, ceramics, etc. ZnO has a high capacity and thermal conductivity, and also a high melting temperature. ZnO nanostructures have some morphology, including nanowires, nanorods, and tetrapods(Heydari-majd et al., 2019; Rihayat et al., 2017; Tsou et al., 2018). Numerous studies have been done on the physical, mechanical, and morphology of the mixture of PLA/CS.However, no single research has been focused on the blending of PLA/CS/ZnO NPs, its mechanical properties, and its morphological characterization.

This study thus aimed to produce a composite Polylactic (PLA)/CS by adding the concentration of ZnO nanoparticles in several variations of ZnO. ZnO synthesis using the method of direct precipitation through direct mixing sol-gel forming solution that is simple and low-cost. Furthermore, ZnO nanoparticles are used as a nontoxic material supporting the formation of polymer composites PLA/CS/ZnO on a few variations aiming to increase the essential properties of polymer composites, such the thermal, mechanical and water absorption properties as the novelty and focus of this paper. Several methods of characterization were performed using tensile tools and water absorption test.

2. Method

Materials

Some of the chemicals used for the formation of ZnO nanoparticles and composites in this experiment used analytical reagents (99.9% pure). The polymer material Polylactic Acid (PLA) grade (3001D) in the form of pellets derived from Nature Work LLC, USA to type with a melting point of 190 °C and 1.24 g/cm of specific gravity. Zinc acetate dihydrate (CAS. 5970-45-6) was supplied from Merck. NaOH (sodium hydroxide) (CAS. 1310-73-2) pellets were obtained from Merck. Ethanol (CAS. 64-17-5) was supplied by Sigma-Aldrich, and chloroform (CAS. 67-66-3) was used as a solvent. Chitosan (CS)C3646 was used by commercial types of Sigma-Aldrich as an additional ingredient for fillers and reinforcing.

Procedure

1. The Preparation of ZnO Nanoparticles

A total of 0.25 M solution of zinc acetate dihydrate ($Zn(CH_3CO_2)•2H_2O$) was prepared with deionized water by dissolving it. Then, 0.8 M of NaOH was added to the solution of zinc acetate dihydrate. The solution was then stirred continuously at 25 °C for about 2 hours (Salim et al., 2018) until white precipitation was formed because of the reaction of NaOH and zinc acetate dihydrate. Once it was formed, it was filtered and washed with ethanol and water to remove residual sodium hydroxide. The precipitate was then dried for about 24 hours at 50 °C in the oven.

2. The Preparation of ZnO Nanoparticles

Which will be formed as a composite test sample is divided into five types. Those are PA (pure PLA), PPA (PLA and Chitosan), and BPPA, CPPA, and DPPA (composites with ZnO nanoparticles loading) at different variations. There were 2%, 3% and 4% of ZnO nanoparticles addition, respectively. PLA polymer film composite formation was carried out by mixing 20 grams of PLA pellet with 15% solution of chloroform to dissolve to form a viscous liquid with the mixing process in a water bath at 70 °C (Wirjosentono et al., 2015). Subsequently a solution of baking or printed with a petri dish with a thickness of about 0.1 mm and dried for 24 in order to evaporate the chloroform as solvent. After the completion of the first sample, followed by the formation of PLA/CS wherein 20 grams of PLA mixed with 5% of CS by the same method as before using chloroform solvent until all the ingredients are fully soluble, then printed with the same thickness on a baking sheet. Likewise, the PLA/CS/ZnO sample, each of BPPA, CPPA, and DPPAwas mixed with 20 grams of PLA, 5% of CS, and 2%, 3%, and 4% of ZnO nanoparticles in the same solvent and at the same operating conditions. The solution was then stirred at 60 °C until the handler to dissolve completely. Next, the sample was left for 24 hours to remove the solvent and peeled from the mold to test the test in the form of tensile and moisture absorption.

3. Characterization

3.1. Mechanical Test

The tensile test was conducted to measure the strength of asubstance/material by providing a load of coaxial style. Tensile properties included strength, modulus, and elongation at break solving pure PLA films and composite films mix was determined by using Shimadzu Universal Testing Machine. It used a set capacity of 10 kN, based on ASTM D882. It was done under the mode voltages on a single strain rate of 10 mm/min at room temperature and the result was taken as the average of four tests. Standardized test specimens, uniaxial loading was done so that the test specimen stretched and became long until it broke.

3.2. Water Absorption Properties

Water absorption test was carried out by preparing a 6 mm ball-shaped sample according to ASTM D570. Furthermore, the samples were dried at 60 °C for 1 hour and cooled in a desiccator. The sample was weighed immediately after being rotated and immersed in deionized water at room temperature for about 24 hours. After completing it, the sample was transferred in a dry state and weighed. After that, the same treatment again was repeated. The samples were prepared to go back into the air and weighed again for ten days. Water absorption is expressed as the increase in weight percent and is calculated according to the formula shown below:

$$\text{Water absorption (\%)} = (W2-W1)/W1 \times 100\% \quad (1)$$

4. Results and Discussions

Mechanical Properties

The composite PLA/CS/ZnO nanoparticles have been formed then tested the mechanical properties, such as tensile strength levels through coaxial force provided by the tensile test equipment to reach the maximum limit of up disconnected. Tensile modulus, tensile strength and elongation at break time composite PLA, PLA/CS and PLA/CS/ZnO determine the optimal degree of dispersion and good interaction between the components.

Figure. 1 (a) describes the value tensile strength of each sample PA, PPA, BPPA, CPPA and DPPA. Based on these graphs, it can be seen that the addition of CS and ZnO filler showed improved mechanical properties of the polymer when compared to pure polymer without mixing (PA). PA had a tensile strength of 14 MPa which declined after CS was added. However, the addition of ZnO nanoparticles further increased the tensile strength, as reported in previous studies (Zare & Rhee 2019; Rahman, Islam & Shu 2018). BPPA is the most significant variation value tensile strength of 15 MPa compared with CPPA and DPPA composites with a tensile strength of only 12.5 and 13 MPa, the same thing was also found in other studies using ZnO concentrations of 2% producing the best mechanical value (Agusnar et al., 2018). This pattern of results tells us that the strong nature of the attraction decreases modulus because the unideal amount of ZnO is mixed. This decrease in tensile strength is due to the formation of intramolecular hydrogen bonds due to the portion of one of the excess materials; thus, there is a split in the mixed matrix. A similar explanation occurs in the modulus results.

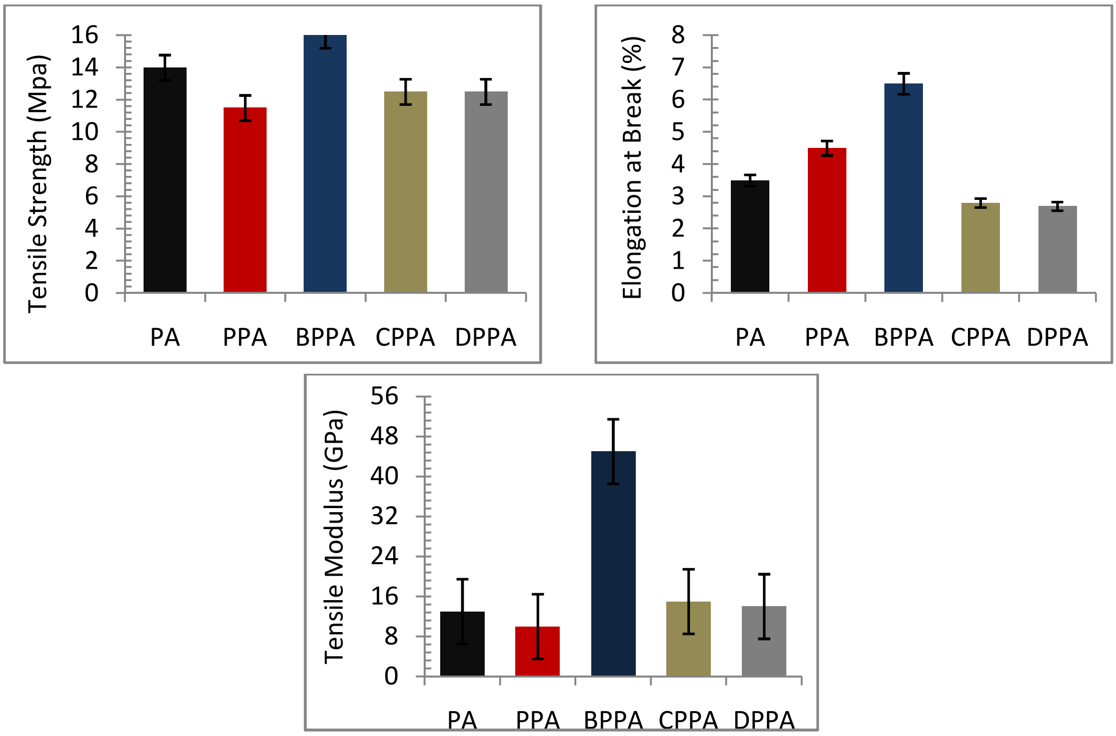

Figure 1. (a) Tensile Strength, (b) Tensile Modulus, (c) Elongation At Break of Various Composites

Based on the modulus shown in Figure. 1 (b), the pattern of the results shows a similarity to the robust nature of the attraction which the PPA experience modulus decreased compared to PA, from 13 MPa to 10 MPa. Both CS and PLA formed intermolecular hydrogen of chitosan and C=O of PLA, leading to a composite tensile strength of PPA weakened, most likely caused by the formation of an intramolecular hydrogen bond between the molecules that are not hydrogen bond, which leads to a phase separation between the two main components (Agusnar et al., 2018). BPPA is still the most excellent composition at 45 MPa with the modulus value being almost 2 times higher than PA.

Figure 1(c) describes chart elongation at break. PA and other composite samples increased with the addition of CS that constant in the composite PPA of 2.5% and increased again with the presence of ZnO nanoparticles, as reported by Ponamma et al., (2019). BPPA is the greatest variation breaking the extension value of 5.5%. However, this is not consistent in ZnO nanoparticle composites by weight of as much as 4%.

In previous research, uniform dispersion between polymer matrix and filler material which is highly compatible will produce a good interaction leading to increased mechanical properties and thermal stability of the composite (Wang et al., 2019). Improving composite mechanical properties supported by the main controller tensile strength that is the effectiveness of reinforcement properties to facilitate the effective stress transfer at the interface of matrix and filler. In this experiment, ZnO nanoparticles act as an amplifier nanoscale resulting in the strain transfer between matrix and filler. However, the composite tensile strength decreased when the amount of ZnO nanoparticle increased to 4% by weight. Similar to the results of modulus and elongation at break of the weakest in the same sample due to the ring structures in CS and PLA. Intermolecular hydrogen bonds were formed by NH2, OH, and C=O, which mainly inhibited the movement of molecular chains. When ZnO nanoparticle was incorporated, the hydrogen bonds between molecules were weakened, and new hydrogen bonds were formed between PLA, CH, and ZnO nanoparticle. These facilitated the rotation and movement of the chain molecules so that its mechanical properties when the composite becomes brittle once doping with ZnO nanoparticle excess.

Water Absorption

The water absorption properties of these materials were based on the amount of water reduced in a trial established over ten days. The patterns of water absorption of the tested materials is shown in Figure 2.

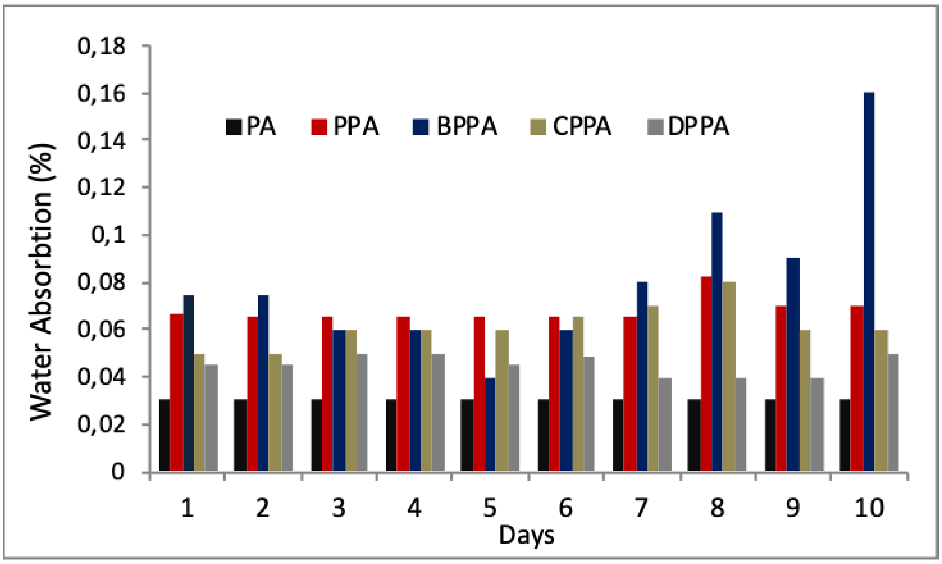

Figure 2. Water Absorption Properties of PA, PPA, BPPA, CPPA and DPPA

It was found that the water absorption increased and decreased randomly on PA, PPA, BPPA, CPPA, and DPPA as a different amount of water was absorbed by the composites. From Day 1 to Day 10, pure PLA did not show any signs of moisture absorption because of its hydrophobic properties, making the value remain constant.

Different results were shown in the PPA capable of absorbing 0.045% to 0.062% water because of CS's high moisture-sensitivity. To enhance their compatibility, PLA can be modified (e.g., with plasma treatment) in order to modulate its hydrophobicity. After blending with CS, the water absorption of the PPA composite showed an increment in water absorption. Similar test results were also reported by other studies that PLA composite absorption value reached 0.06% within two days (Rihayat & Suryani, 2013).

The incorporation of ZnO nanoparticles into the BPPA, CPPA, and DPPA showed the water absorption of different percentages during the test period. DPPA showed the lowest value of water absorption, ranging from 0.04% to 0.05%. This implies that the incorporation of a 4 wt% ZnO nanoparticle can enhance the composite with better water barrier properties compared to BPPA and CPPA that are higher in water absorption properties. CPPA blend composite showed a decrement in water absorption content compared to the BPPA blend composite with the value ranging from 0.055% to 0.08%. This implies that the incorporation of 3 wt % ZnO NPs with PPA can enhance the composite with better water barrier properties than BPPA. Regarding the BPPA blend composite, an even higher decrement in water absorption content ranging from 0.08% to 0.16% was shown in Figure 2.

Therefore, it can be concluded that PLA/CS/ZnO NPs composites possessed good water barrier properties and the property is more pronounced with higher ZnO nanoparticle loading, this is also reported in other studies (Rihayat & Suryani, 2013). It can be tailored to the needs and specific applications that will be used.

5. Conclusions

The effects of ZnO nanoparticles and CS (Chitosan) on improving the mechanical properties and water absorption of nanocomposites (BPPA, CPPA, and DPPA) were investigated. The results showed that CS and ZnO play an important role in increasing the properties of polymer composites. The mechanical properties increase more significantly with the addition of CS and ZnO particles rather than with pure PLA (PA) or PLA/CS (PPA) only, indicated by the samples of BPPA with the highest values of tensile strength and tensile modulus being 15 MPa and 45 MPa, respectively. On the other hand, other composite samples CPPA and DPPA experienced a decrease in the mechanical value due to the influence of ZnO component excess. Meanwhile, the water absorption test revealed that DPPA has a better absorption ability than that of other samples with the lowest percentage absorption rate of 0.04% to 0.05%. during the test day.

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