

Characterization of composite bioplastic from Cassava starch with titanium dioxide and zinc oxide

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This study focused on bioplastics and composite bioplastics with incorporated ZnO and TiO₂. The ZnO gave a film more transparent than that made with TiO₂. The effects of these additives on physical and mechanical properties, biodegradability, surface morphology, and thermal properties of the films were investigated. The functional groups O-H, C-H, C=O, and C-O in the bioplastic and the composites were confirmed by FT-IR. The addition of ZnO and TiO₂ could increase thermal stability. The composites exhibited higher tensile strength than the control bioplastic film. The bioplastic film was 100% biodegradable compared to 14.71% and 14.59% for ZnO and TiO₂ containing bioplastic films, respectively.

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1. Introduction

Pollution from plastics is a global crisis with impacts on ecosystems, biodiversity, climate, marine economies, and human health. In the last decades there has been an increasing interest in the development of bioplastics to reduce the environment problems. Biopolymers are raw materials that are inexpensive, abundant, and biodegradable. One major source of biopolymers is cassava starch that can be degraded easily. Cassava starch has 83% amylopectin and 17% amylose [1] type of starch, and remains inexpensive and easy to access. Studies have reported that biodegradable plastics can be made from cassava starch [2, 3]. However, these bioplastics from cassava starch have disadvantages, namely poor mechanical properties and high water affinity [4]. In recent years, the metal oxides, ZnO, SiO₂ and TiO₂ have been widely used in various applications, including cosmetics, dye degradation, and pharmaceuticals [5-7]. Metal oxide particles as fillers have tended to improve the performance of bioplastic film composites. Prior research indicates that bioplastics with ZnO have potential to become active packaging materials [8]. Besides, TiO₂ nanoparticles in chitosan bioplastic improved mechanical properties and biocompatibility [4, 9]. Therefore, the aim of the present work was to know assess the effects of the inorganic particles ZnO and TiO₂ in cassava starch based bioplastic films. The physical properties, thermal stability, and biodegradability of composite bioplastic films were investigated.

2. Experimental

2.1. Synthesis of bioplastics

A suspension of 0.5%w/v TiO₂ or ZnO in distilled water was sonicated for 30 min (solution A). 100 mL of distilled water, 10 grams of cassava starch and 2.4 mL glycerol were mixed and stirred at 500 rpm for 30 min (solution B). The solutions A and B were mixed and heated at 85 °C. The blend was centrifuged for 2 min at 200 rpm and poured onto a plate (21 x 21 cm) then dried in an oven at 45 °C temperature for 10 hours. Finally, the sample was left at room temperature for 24 hours. Control films were prepared similarly but without adding TiO₂ or ZnO.

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2.2. Physical and chemical properties of bioplastics

Thickness of bioplastics was measured by using a Micro Thickness micrometer. Five different random locations were measured and the average is reported [10]:

$$\text{Thickness} = \frac{\text{sum of measured values}}{5} \quad (1)$$

To determine the moisture content, the weight of bioplastic film was taken precisely, and this was repeated after heating at 105 °C for 3 hours. The moisture on wet basis was calculated as follows [11]:

$$\text{Moisture content (\%)} = \frac{w_1 - w_2}{w_1} \times 100 \quad (2)$$

where w_1 is the initial weight of bioplastic and w_2 is its final dry weight.

Density of the bioplastic films was calculated using weight and dimensions as follows [12]:

$$\text{Density} = \frac{M}{A \times D} \quad (3)$$

here, density is in g/cm^3 , M is the mass (g), A is the area (cm^2) and D is the thickness of bioplastic. Swelling was investigated by placing the bioplastic film in a container having 10 mL of distilled water, for 24 hours. Then the film was removed from the container, surface was dried by wiping, and it was weighed to measure the wet weight. Swelling percentage was calculated as follows [11]:

$$\text{Swelling percentage} = \frac{w_2 - w_1}{w_1} \times 100 \quad (4)$$

where, w_1 is the dry weight of bioplastic and w_2 is its wet weight.

Thermal stability is an essential characteristic of a bioplastic. A FRITSH Mettler Toledo, HT 3000 was used for TGA analysis of the bioplastic films over the temperature range from 30 °C to 500 °C, with heating at the rate of 5 °C/min. The FT-IR spectra of the bioplastic films were recorded using an FT-IR instrument (Fourier Transform Infrared Spectrometer, Perkin Elmer) in range 4,000-400 cm^{-1} . Tensile strength was measured with a universal testing machine following the standard ASTM D638. Bioplastic film sample of 15x15 cm size were used to determine the mechanical properties. Scanning electron micrographs of the bioplastic films were obtained using SEM Quanta (Scanning Electron Microscope Thermo Fisher Scientific-Quanta 400).

2.3. Biodegradability test

Biodegradability behavior of the bioplastics was determined using soil burial in a degradation test. The bioplastic films were placed in the soil at 8 cm depth. The degradation rate during the soil burial test was calculated from weight loss of the samples over 15 days as follows [12]:

$$\text{Weight loss \%} = \frac{w_1 - w_2}{w_1} \times 100 \quad (5)$$

where w_1 is the initial weight and w_2 is the final weight of bioplastic after degradation.

3. Results and discussion

3.1. Synthesis of bioplastics

The physical appearances of cassava bioplastic and composite bioplastics are shown in Fig. 1. The cassava bioplastic film (BP) was smooth and transparent, whereas the composite bioplastics (BP_ZnO and BP_TiO₂) were not transparent. Also, the tints of cassava films with ZnO and TiO₂ were respectively slightly yellowish and white.

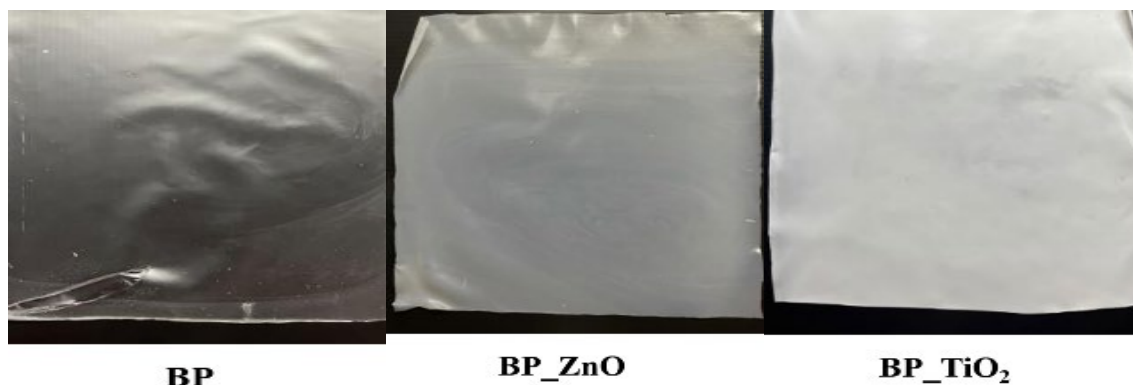


Fig. 1. The appearances of the cassava bioplastic and the composite bioplastics as thin films.

3.2. Thickness and density

The total content of components used to prepare bioplastics will affect the physical and mechanical properties of a bioplastic film [13]. The film thicknesses were averaged from 5 different points measured with Micro Thickness micrometer. The results reveal that the thickness of the film increased on adding particles (TiO₂ or ZnO₂). Thicknesses, and densities of the bioplastic films are shown in Table 1. ZnO bioplastic had the largest thickness, superior to those of the control and the TiO₂ filled bioplastic. This might be associated with the particle size of the added material [14]. Besides, the particles had a large specific surface and surface energy. They could have strong interactions with the starch and increase the viscosity in molding stage of the film preparation, causing thicker film. The bioplastic films showed increased density with added filler.

Table 1. Thickness and density of bioplastic films.

Samples	Thickness (nm)	Density (g/cm ³)
BP	0.240±0.01	1.24±0.13
BP_ZnO	0.294±0.02	1.56±0.16
BP_TiO ₂	0.274±0.01	1.40±0.11

3.3. Moisture content and water swelling

The moisture content results are exhibited in Figure 2(a). The control films had higher moisture contents (16.31%) than the composite films (12.90-10.26%). The chemical properties of the fillers might have played a major role in the moisture content of bioplastics. Decreased moisture is attributed to the hydrogen bonds between the starch matrix and ZnO or TiO₂ using them up and reducing binding with free water molecules [15]. These interactions decrease the number of available hydroxyl groups, which makes the films water resistant. This is in line with another study in which ZnO particles were able to increase hydrophobicity of the films because of the hydrophobic character of ZnO [16]. The effects of TiO₂ and ZnO particles on water swelling of bioplastic film are shown in Fig. 2(b). The results show a reduced water swelling of bioplastic film when a metal oxide was added. The bioplastic without metal oxide exhibited the most swelling. This is consistent with a prior study that demonstrated decreased water swelling [17].

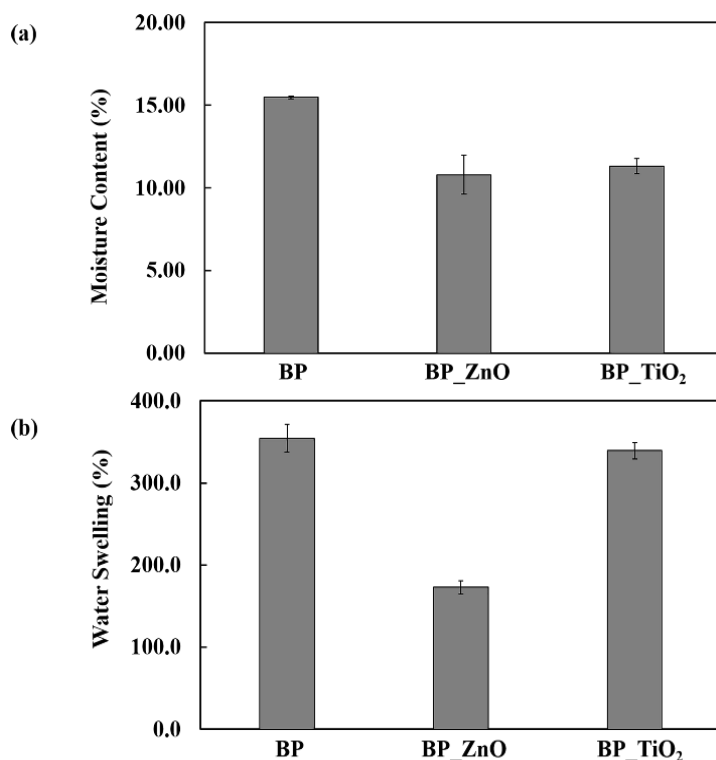


Fig. 2. Percentage moisture content (a), and swelling percentage of BP, BP_ZnO and BP_TiO₂ films (b).

3.4. FT-IR analysis

The FT-IR spectra of films at over 4000-400 cm^{-1} are presented in Fig. 3. The spectrum of the control film revealed stretching of O-H groups at 3325 cm^{-1} , symmetric and asymmetric vibrations of the C-H groups at 2931 cm^{-1} , stretching of C=C groups at 1653 cm^{-1} , and stretching of CH₃ groups around 1455 cm^{-1} for the control film without any filler. For the composite films with ZnO and TiO₂ fillers, stretching of O-H groups was observed at 3307 and 3305 cm^{-1} , respectively. This shift to lower wavenumber from 3325 cm^{-1} was due to an increase in the number of hydrogen bonds with TiO₂/ZnO for hydroxyl groups in cassava starch. The shift in the C-H stretching absorption band from 2931 cm^{-1} of control film to 2929 cm^{-1} with TiO₂ and to 2926 cm^{-1} with ZnO is attributed to the electrostatic interactions between TiO₂/ZnO and starch [18].

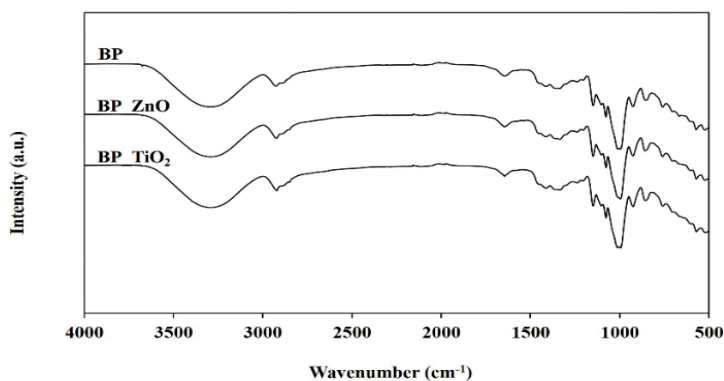


Fig. 3. FT-IR spectra of BP, BP_ZnO and BP_TiO₂ films.

3.5. Thermogravimetric analysis

Thermal stability of bioplastic film was investigated by thermogravimetric analysis. The weight loss thermograms of the films are shown in Fig. 4. The degradation of bioplastic film had 2 stages in the following ranges: (i) 50-220 °C, and (ii) 200-500 °C. In the initial stage (i), the moisture from the surface or interior of the films was lost and the thermal decomposition was associated with evaporation or interior of the films was lost and the thermal decomposition was associated with evaporation or dehydration and with low molecular volatile compounds in the films. The second stage (ii) was caused by thermal degradation of hydroxyl groups and decomposition and depolymerization of starch carbon chains [19]. The responses of BP, BP_TiO₂ and BP_ZnO had 50% weight losses at 305 °C, 314 °C and 310 °C, respectively. The results indicate that the thermal stability of bioplastic films improved with TiO₂ and ZnO fillers compared to the control bioplastic film without additives. The effects on thermal stability indicate strong interactions between starch molecules and the additives [20]. From the thermal stability results it can be concluded that the weight loss was 90% for control film, 85% for BP_TiO₂, and 88% for BP_ZnO over the range 50-500 °C.

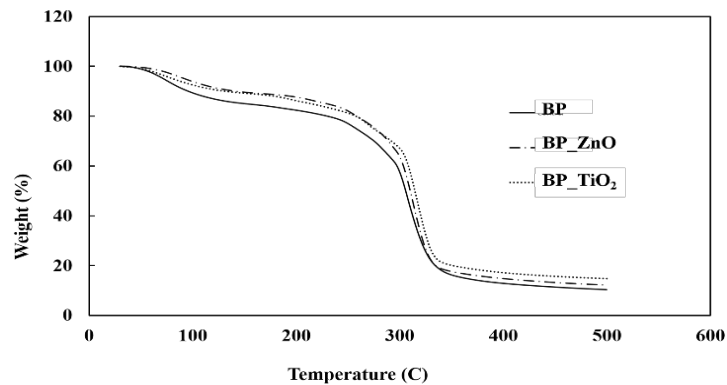


Fig. 4. TGA curves of BP, BP_ZnO and BP_TiO₂.

3.6. Tensile response

Tensile strength was measured to indicate the strengths of the films, as the ultimate force before breaking depends on the type of additive in bioplastic. Fig. 5 summarizes tensile strengths of the control bioplastic and the filled composites. The tensile strength at break of BP_ZnO (7.63 MPa) films was lower than those of BP (7.88 MPa) and BP_TiO₂ (8.48 MPa). This is because ZnO and TiO₂ will capture electrons from hydroxyl groups in the polymer [21]. The elongations at break of the bioplastics were 73% for BP, 62% for BP_ZnO and 26% for BP_TiO₂. The composite bioplastics had greater mechanical strength than the control bioplastic due to the hydrogen bonds and electrostatic interactions between hydroxyl groups of starch and Zn²⁺ or Ti²⁺ ions in the filled bioplastic films. The tensile strengths of the films agree with the findings of Amin *et al.* [18] who reported that bioplastics and TiO₂ filled bioplastic had tensile strength of 3.55 MPa and 3.95 MPa and maximal elongations by 88 % and 62.5 %, respectively.

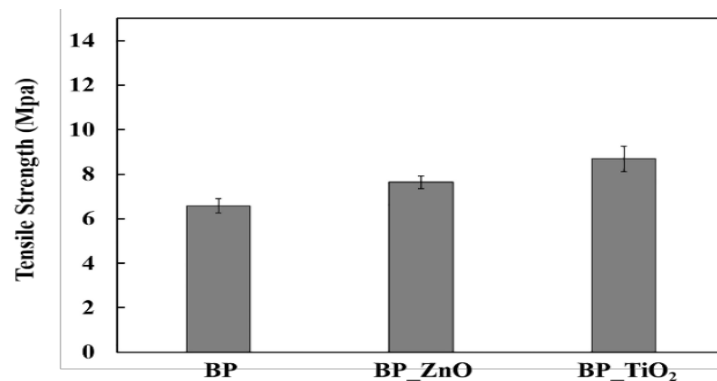


Fig. 5. The tensile strengths of BP, BP_ZnO and BP_TiO₂ films.

3.7. Scanning electron microscopy

Fig. 6. presents SEM images of BP, BP_ZnO (c-d) and BP_TiO₂ (d-e) films. Left and right panels correspond respectively to 2000x and 5000x magnifications. A homogeneous distribution of the filler within the starch matrix can result in enhanced physical properties in nanocomposite films. The bioplastic and composite bioplastic films exhibit dispersed solids within a continuous matrix. Surface morphology consist of granules, which corresponds to remnant solids from the gelatinization of starch granules [18]. The surface of BP_ZnO (2000x) presents small spherical particles fairly distributed with some agglomerates. Theses clusters (Fig.6(d)) might be agglomerated during bioplastic formation because no aggregation was found in BP and BP_TiO₂. Besides, Zn–O–Zn bonds are formed between the particles owing to the presence of water molecules, resulting in hard agglomeration. The surface of BP_TiO₂ is smoother compared to the control film. This is attributed to good dispersion of the additive.

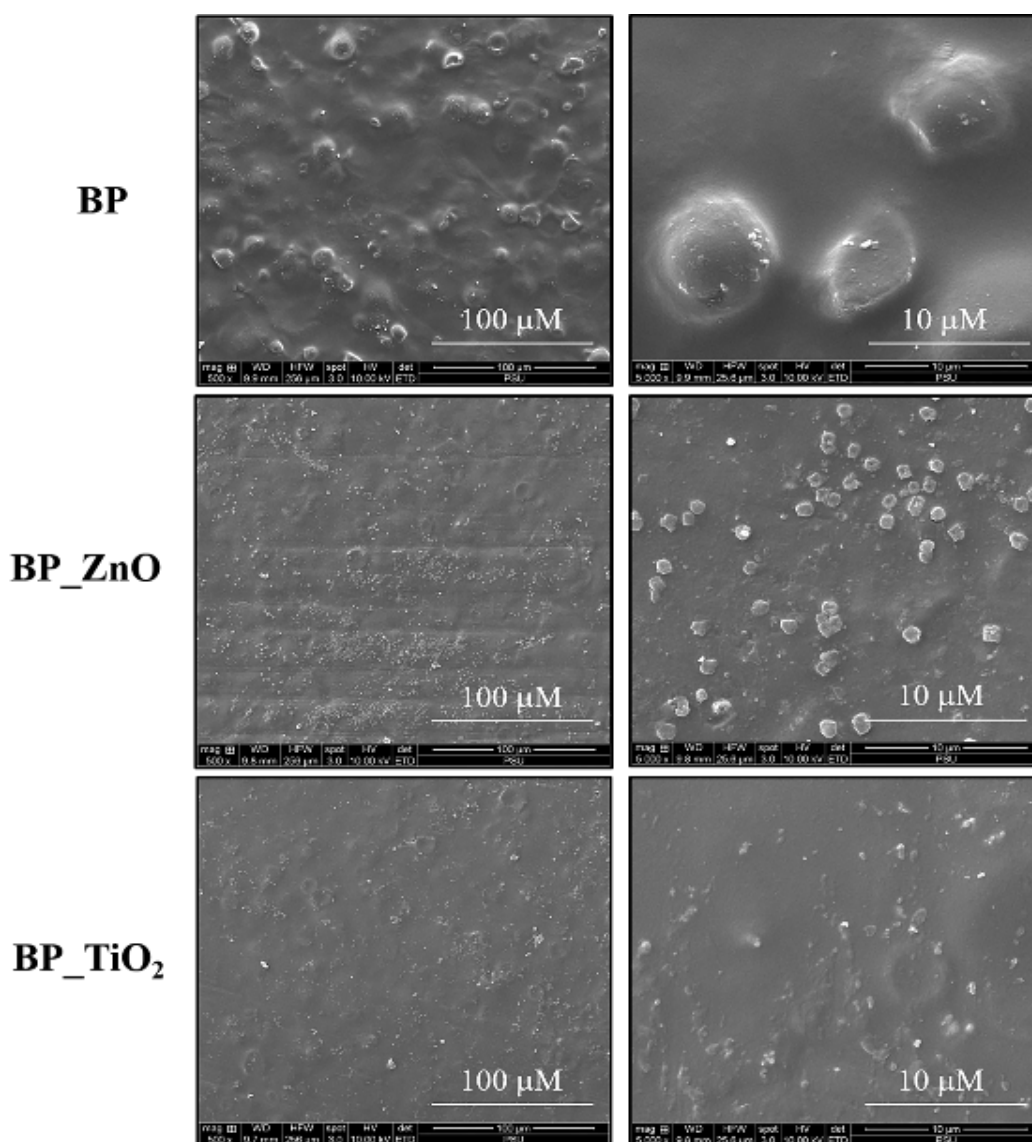


Fig. 6. SEM images of the BP, BP_ZnO and BP_TiO₂ films.

3.8. Biodegradability test

The degradation of bioplastic films was assessed from mass losses during the observation period of 15 days. Fig. 7 shows the degradation of the produced bioplastic films. The degradation trend for all bioplastics starts with an increase in weight, then decreasing

weight until 15 days. This is due to the films initially absorbing moisture from the soil. After 12 days, the control film had lost 63.50% of its weight while the filled composite bioplastic films showed weight losses of 9.52% and 11.07% for BP_TiO₂ and BP_ZnO, respectively. The weight loss continued as time passed and a 100% weight loss was observed for the control film after 15 days because the cassava starch had hydroxyl groups (OH). They can initiate hydrolysis reactions when absorbing water from the soil [12]. The composite bioplastic films exhibited weight losses of 14.71 (ZnO) and 14.59% (TiO₂) after 15 days. This results show that the metal oxides (ZnO and TiO₂) in the film inhibited degradation in the soil. ZnO and TiO₂ can give low hydrophobicity to bioplastic films. In addition, ZnO will make hydrogen peroxide, that is active against microbial cells. Similar findings were reported by Padmavathy et al. [22], Amin et al. [18] and Threepopnatkul et al. [23].

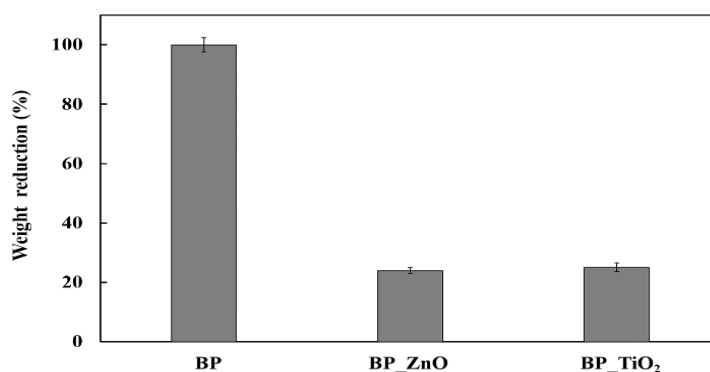


Fig. 7. Biodegradation of BP, BP_ZnO and BP_TiO₂.

4. Conclusion

Based on the results obtained, it is concluded that the metal oxides ZnO and TiO₂ as individual fillers played an important role affecting the physical and mechanical properties of cassava starch films. The moisture contents of the composited films were decreased from the control film without filler. The composite bioplastic films were stronger than the control film with increased tensile strength and reduced elongation at break. Result from TGA indicated that the composite bioplastic films had improved heat stability over the control film. Besides, the biodegradation of bioplastic films was decreased when ZnO and TiO₂ were added. This was due to ZnO and TiO₂ exhibiting antimicrobial properties that slow down the natural degradation.

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