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Cassava Starch and Nano Zinc Oxide Biodegradable Films as Packaging Materials

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In the mid-20th century polymeric materials were introduced, since then, have gained significant ground in different fields. Their low density, combined with mechanical, thermal, optical, and chemical properties sufficient to meet various needs, has allowed them to replace conventional ceramic and metallic materials. However, the mass adoption of their use, coupled with challenges related to their recovery, degradation, and improper disposal, has led to their accumulation in natural environments. A potential solution lies in the use of biodegradable polymers to replace those still in use today, especially in single-use products. However, this requires improvements in their properties. In this study, films were produced from gelatinized starch formulations with zinc oxide (ZnO) nanoparticles in concentrations ranging from 0% to 1.0% w/w. The obtained films were characterized using Fourier Transform Infrared (FTIR) spectroscopy, tensile strength tests, scanning electron microscopy (SEM), and their biodegradability was assessed in soil (black earth). The results showed that ZnO formulations exhibited lower modulus, lower tensile strength, and higher elongation than plasticized starch films, as well as potential interactions between ZnO nanoparticles and the polymeric matrix, particularly at concentrations of 0.4% w/w and 0.6% w/w. Furthermore, the films containing ZnO showed damage and deterioration in soil at 40°C and humidity levels between 40% and 60%, with monitoring over 52 days. These results allow us to continue the search for additives and formulations that improve the properties of plasticized starch with the purpose of using it as packaging material at an industrial level.

1. Introduction

Polymeric materials have gained widespread acceptance for various applications due to their broad range of properties, low weight, and ease of processing. As a result, their consumption has increased (Montanari et al. 2023). For instance, in 2018, 359 million tons of thermoplastics were produced, with 44% of this amount being used for packaging materials. Of the total production, only 173 tons were collected for recycling (Rai et al., 2021). This leads to the accumulation of thermoplastic polymers in natural environments, causing environmental issues.

Several solutions have been proposed to improve the environmental performance of polymers, some of which involve chemical modifications that introduce functional groups to enhance degradation processes. Others focus on additives that accelerate degradation, such as oxo-degradants (Roy et al., 2011). However, accelerating degradation does not necessarily result in polymer biodegradation, meaning that it does not make the polymer susceptible to being metabolized by microorganisms, which would lead to biomass generation.

Additionally, the use of biodegradable polymers, both natural and synthetic, has been explored. However, these materials do not match the properties of conventional non-biodegradable polymers that need to be replaced (Zhang et al., 2022). This has led to significant research into strategies for improving the properties of biodegradable polymer materials, as Wang et. al., (2022), who used different ratios of plasticizer to improve the mechanical properties of starch films, or Hashem et. al (2023) who added zinc oxide nanoparticles to obtain materials with antimicrobial properties.

A variety of biodegradable polymers from natural sources, such as starch, chitosan, cellulose, and polylactic acid (PLA), as well as fossil-based polymers such as polycaprolactone (PCL), polyvinyl alcohol (PVOH), poly(butylene-adipate-co-terephthalate) (PBAT), poly (glycolic acid) (PGA), and polybutylene succinate (PBS),

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are available (Wu and Mohanty, 2021). Each of these polymers has strengths and weaknesses. Generally, biodegradable polymers are more expensive and less available than conventional polymers; however, they remain the focus of research aimed at improving their properties and processability (Liu et al., 2020). Among these, starch is one of the most studied due to its cost and availability, and its properties can be modified with various additives,

Starch is a natural polymer composed of amylose and amylopectin, found in a wide range of tubers, fruits, and legumes, making it an attractive raw material due to its availability. However, it is a rigid and fragile material whose properties must be modified to be used as packaging. It is crucial to improve its mechanical properties such as tensile strength, chemical stability against contents, processability, stability against microorganisms and barrier properties against oxygen and water vapor are also essential. There are numerous works in the literature that present starch formulations with additives to improve these properties, an example is the use of zinc oxide nanoparticles to reinforce pectin functionalized starch films presented by do Nacimento et al., (2024). The zinc oxide is also used as an antimicrobial agent. Ahmad et al., (2021) prepared composite materials based on cassava starch and observed less microbial growth with the presence of ZnO.

Additionally, starch formulated with plasticizers and subjected to high shear stresses in single-screw or twin-screw extrusion processes becomes thermoplastic starch, which is already used to produce biodegradable films. Nevertheless, the need to further improve the processability and properties of starch to expand its range of applications and reduce costs is evident in the growing body of research on the subject (Bangar et al., 2021).

This study proposes formulations of gelatinized starch plasticized with glycerol, with varying zinc oxide content, as a potential additive to improve the starch's performance against microorganisms. The goal is to develop packaging materials that maintain their biodegradability while allowing for a reasonable usage period before microbial degradation.

2. Experimental

2.1. Preparation of Gelatinized Starch Films

For the preparation of biodegradable films with zinc oxide, cassava starch (Produsur) and glycerol (Merck) were used. The zinc oxide was synthesized in the Chemistry Laboratory at ECCI University through coprecipitation reactions in methanol, yielding quasi-spherical nanoparticles with sizes between 5 and 35 nm (Suárez and León, 2022). To prepare the films, gelatinized starch solutions were prepared, and ZnO nanoparticles were dispersed using an Ultra-Turrax T 18 at 15,000 rpm. The mixture was then poured into a non-stick metal tray and placed in an oven at 50°C for 24 hours or until the film weight became constant. Nanocomposite films were obtained with a matrix of gelatinized cassava starch and ZnO nanoparticle contents of 0%, 0.2%, 0.4%, 0.6%, 0.8%, and 1.0% w/w, labeled F1, F2, F3, F4, F5, and F6, respectively. The films, produced in triplicate, had a whitish, uniform appearance with a thickness of 50 µm ± 5 µm and were cut according to the requirements for the various tests they underwent.

2.2. Characterization of the Films

2.2.1. Fourier Transform Infrared (FTIR) Spectroscopy

Infrared spectra were obtained using a Bruker ALPHA 1 spectrometer, in the rage of 400 to 4000 cm^{-1}.

2.2.2. Tensile Strength of the Formulations

Tensile properties of the films were tested using a Shimadzu universal testing machine with a 5 kN load cell. The procedure followed ASTM D 882 standard, using five samples of each formulation with dimensions of 12.5 mm width and 125 mm length. The testing speed was 5 mm/min.

2.2.3. Morphology of the Formulations

Scanning electron microscopy (SEM) of the samples was conducted using a Phenom ProX - Phenom World microscope at 5 kV, with magnifications ranging from 1000X to 10,000X. The samples were coated with a thin gold layer using a TED PELLA C 6390 equipment.

2.2.4. Biodegradability

For biodegradability testing, sample preparation and biodegradation conditions followed the ASTM D 5338 standard, it involved mixing 100 g of commercial compost with 1 g of sample formulation, then transferring the mixture to a 600 mL bioreactor. The bioreactors were filled to three-quarters of their capacity to allow for periodic manual agitation. They were then placed in a controlled environment chamber at 55°C ± 5°C with 58% ± 7% humidity. The tests were conducted in triplicate for each formulation, as well as for positive and negative controls. The positive control used 100% cellulose films manufactured by Lion Rolling Circus, and the negative

control used 50 microns thick polyethylene film without pro-oxidant agents, extruded on the blown film extrusion machine of the ECCI University Plastics Workshop, using Esenttia P 2220 AD low-density polyethylene (LDPE) as raw material. Samples were monitored biweekly for changes in appearance and weight loss.

3. Results and discussion

3.1. Preparation of Gelatinized Starch and Zinc Oxide Nanoparticles

The following images show the gelatinized starch films obtained from the proposed formulations, along with the results of infrared spectroscopy, morphology, tensile strength, and compost biodegradability behavior tests. Figure 1 illustrates the obtained films.

(a) (b) (c) (d) (e) (f) (g)

Figure 1. Digital images of gelatinized starch and zinc oxide nanoparticle nanocomposite films on a piece of printed paper. (a) Piece of printed paper (b) F1: Gelatinized starch, (c) F2: Gelatinized starch with 0.2% w/w ZnO, (d) F3: Gelatinized starch with 0.4% w/w ZnO, (e) F4: Gelatinized starch with 0.6% w/w ZnO, (f) F5: Gelatinized starch with 0.8% w/w ZnO, (g) F6: Gelatinized starch with 1.0% w/w ZnO.

Figure 1 shows that films were obtained from formulations F1 to F6, which exhibited uniformity, translucency, and no visible aggregates to the naked eye, other authors as Zhang et al., (2022), have obtained similar starch films. However, the SEM images of the film surfaces (Figure 2) reveal what could be interpreted as ZnO aggregates. In Figure 2, F1 shows a uniform surface with a smooth morphology, without the presence of a second phase. In F2, small aggregates are observed protruding from the matrix, but they appear to have partial adherence to the matrix. In formulations F4 and F6, micron-sized protrusions are visible, which may correspond to ZnO aggregates. For F4, there appears to be poor adhesion between the aggregate and the starch polymer matrix, with phase separation observed. Formulation F3 showed similar behavior. In contrast, in F6, the matrix seems to partially adhere to the aggregate, like what was observed for F2 and F5. This could be related to differences in the interaction between ZnO and the starch matrix, depending on the concentration. These differences in phase interaction seem to also affect the FTIR and tensile strength results.

3.2. Tensile strength of the films

Table 1 presents the tensile strength properties of the prepared formulations. Wang et al., 2022, obtained values in the same magnitude order for tensile strength and elongation at break for similar starch films. According to Table 1, F1 is the film with the highest rigidity and tensile strength, as well as the lowest elongation, along with F2, suggesting that nano ZnO is acting as a plasticizer. A similar effect was observed by do Nacimento et al., (2024) and it was explained by the disruption of the polymer - polymer hydrogen bonds caused by the ZnO. This may be due to its small molecular size, which separates the starch chains and reduces their interactions, thereby supporting the glycerol used as a plasticizer in all the formulations. On the other hand, F4 films exhibit the lowest tensile strength and the highest elongation. The best combination of tensile strength and elongation could be F3, considering the cost of the formulation. This particular behavior of F3 and F4 coincides with the phase separation observed for these formulations in the SEM images.

Table 1: Maximum stress and strain at maximum stress for formulations F1 to F6.

Formulation	$\sigma_{máx} \pm \Delta\sigma_{máx}$ (N/mm²)	$\varepsilon_{\sigma máx.} \pm \Delta\varepsilon_{\sigma máx}$ (%)
F1	1,82 ± 0,17	118 ± 14
F2	1,11 ± 0,08	103 ± 13
F3	1,19 ± 0,10	193 ± 11
F4	0,76 ± 0,13	217 ± 7
F5	1,06 ± 0,06	136 ± 9
F6	1,41 ± 0,12	148 ± 25

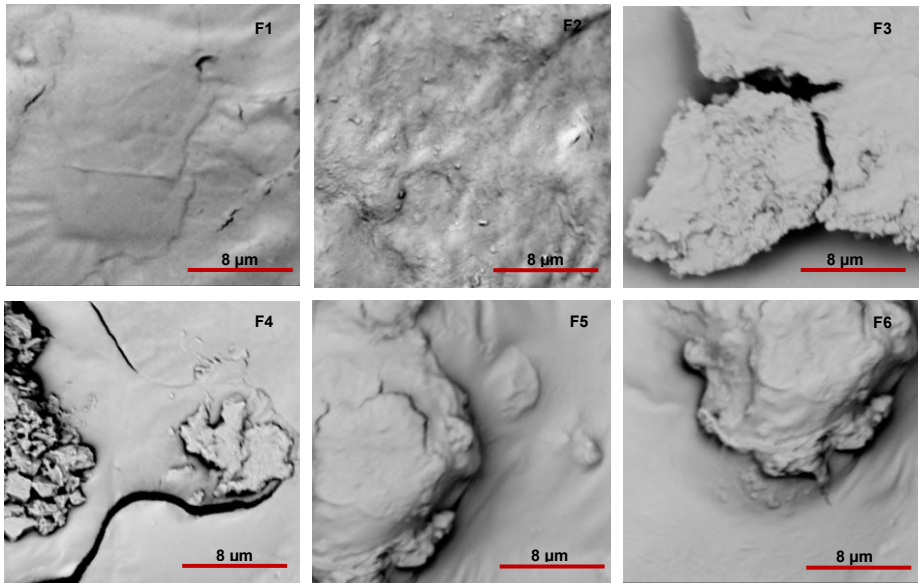

Figure 2. Morphology of the front surface and cross-sectional view of the sample for formulations F1 to F6, obtained at 5 kV and 10,000X magnification.

3.3. FTIR Spectroscopy

Figure 3 shows the infrared spectra obtained from the samples of formulations F1 to F6. It can be observed that, in general, all the formulations exhibit signals at the expected wavelengths for starch, characterized by a peak between 3500 and 3100 cm^{-1}, corresponding to the stretching of the OH bond, as well as deformation peaks for the C-OH bond around 1340 cm^{-1} (do Nacimento et al., 2024). The next group of signals around 3000 cm^{-1} to 2850 cm^{-1} can be associated with the stretching of the C-H bond. Similarly, around 1400 cm^{-1}, signals corresponding to C-H bond deformation are observed (do Nacimento et al., 2024). The peak around 1600 cm^{-1} is associated with water molecules adsorption (Vaezi et al., 2019). The bands between 1300 cm^{-1} to 1400 cm^{-1} could be attributed to C-OH stretching (do Nacimento et al., 2024). The peaks around 1100 cm^{-1} can be attributed to symmetrical and asymmetrical stretching of the $-CH_2$ and $-CH_3$ (do Nacimento et al., 2024), and those around 700 cm^{-1} are characteristic of C-O-C bonds asymmetrical stretching (do Nacimento et al., 2024).

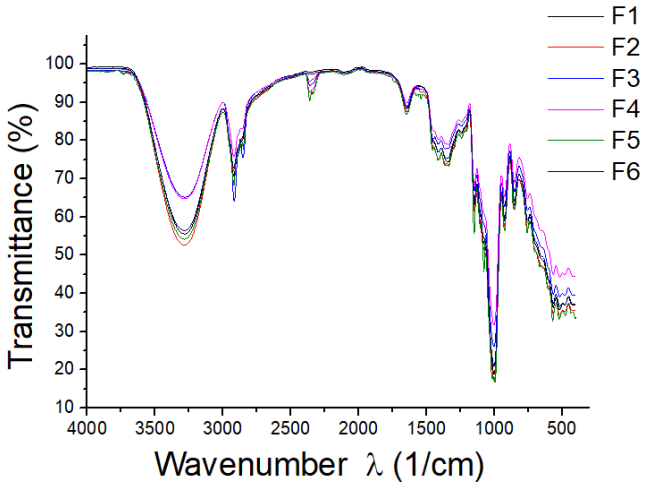

Figure 3. Infrared spectrograms of the obtained samples.

Similar infrared spectra have been obtained by other authors as Congying et al., (2024). A slight shift in the peak corresponding to the stretching of the OH bond is also observed, which is located at 3284 cm^{-1} for the plasticized starch and for the formulations with 0.4% w/w and 0.6% w/w nano ZnO, F3 and F4 respectively, while for the other formulations, it is at 3288 cm^{-1}. This could be an indication of a possible interaction between

the nano ZnO and the starch matrix and may explain the trends observed in the mechanical properties, particularly tensile strength, exhibited by formulations F1 to F6. Other authors as Vaezi et al., (2019), da Silva et al., (2023) and do Nacimento et al., (2024), have reported that the hydrogen bonds between zinc oxide and polysaccharides modify the FTIR spectra.

3.4. Soil degradation behavior

Figure 4 shows the monitoring of the degradative behavior of the samples from formulations F1 to F6. In all cases, deterioration is evident as the test progresses, suggesting that the use of ZnO as an additive in starch formulations is unlikely to affect their soil degradation. Hashem et al., (2023), reported soil degradation of composite films made of hydroxypropyl starch, polyvinyl alcohol and zinc oxide nanoparticles and observed biodegradation percentages of 85% to hydroxypropyl starch film and between 70% to 80 % to the composite's films.

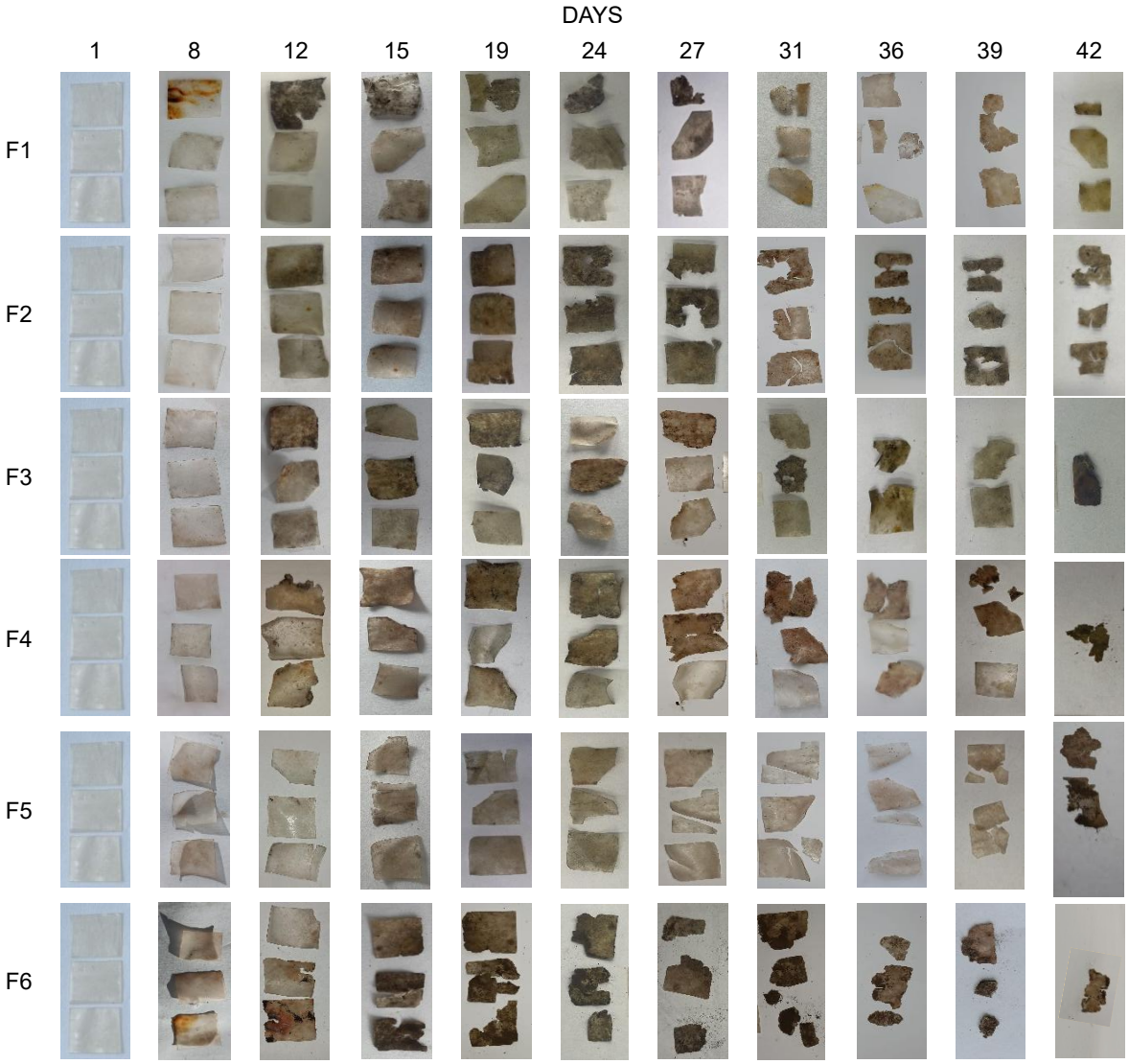

Figure 4. Monitoring of the degradation of the samples from formulations F1, F2, F3, F4, F5, and F6 in compost over 42 days.

4. Conclusions

Gelatinized starch films composed with zinc oxide nanoparticles were obtained, which appeared uniform and translucent to the naked eye. However, SEM images revealed aggregates that increased in size as the zinc oxide concentration in the formulation increased. For formulations F3 and F4, phase separation between the polymer matrix and the additive was evident, while formulations like F6 showed partial adherence between the phases. The tensile strength results showed that formulations F3 and F4 exhibited the highest elongations. The

infrared spectra showed the characteristic signals of starch. However, in the spectra of formulations F3 and F4, a slight shift of the OH stretching peak was observed compared to the same peak in the other formulations, which could indicate a change in the interaction between the polymer matrix and the ZnO. As for the degradative behavior, deterioration was observed in all formulations over the course of the test, which may suggest that the presence of the additive does not significantly affect their soil degradation behavior under the temperature and humidity conditions of the test. Finally, F3 is the best formulations because of its combination of elongation and tensile strength.

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