

Influence of Starch on the Biodegradability of AGENACOMP®

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The compostable blend AGENACOMP®, which combines thermoplastic starch with other biopolymers, has shown potential for producing plastic bags with reduced environmental impact upon disposal, thanks to its good processability and ability to form thin films when extruded. In this study, we produced a blend of AGENACOMP® with additional incorporated starch and evaluated its properties using extrusion, injection, mechanical tests, optical microscopy, and FTIR analysis. Furthermore, we tested its biodegradability by placing samples in simulated soil for three months. Our findings revealed that the addition of starch not only accelerated degradation but also increased the tensile modulus by approximately 20%. This indicates that the modified blend exhibits improved mechanical properties while remaining environmentally friendly due to its biodegradability.

Keywords: Biopolymers. Thermoplastic Starch. AGENACOMP®. Plasticizer. Biodegradability.

In recent decades, the excessive use of polymers derived from non-renewable sources, such as polyethylene and polypropylene, has led to significant global environmental pollution, mainly due to the widespread use of plastic bags. Recognizing the necessity to continue producing these items while mitigating their environmental impact, it is imperative to explore modifications in their composition [1].

Biopolymers have emerged as promising alternatives to synthetic polymers derived from non-renewable sources. These materials, derived from biological sources, possess favorable characteristics such as biodegradability, biocompatibility, and low toxicity. The capacity to create polymeric blends using renewable resources has spurred considerable research and development in this field [2].

Among renewable sources, starch is a compelling biopolymer suitable for incorporation as a filler in polymeric blends. As an agricultural byproduct, starch is abundant, cost-effective, and contributes to biodegradability, thus reducing the environmental impact and cost of the final product. When

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combined with plasticizers, starch transforms into thermoplastic starch (TPS), a versatile and economical material with significant potential for film and packaging production applications. Numerous studies have highlighted the advantages of incorporating TPS into blends with polymers such as polybutylene adipate terephthalate and polylactic acid, showcasing improvements in mechanical strength. However, the intrinsic weak interfacial interaction between hydrophilic starch granules and hydrophobic polymers necessitates the addition of a compatibilizing agent like maleic anhydride. This agent has been demonstrated to enhance adhesion between the two phases, leading to more robust and functional polymeric blends [3,4].

AGENACOMP®, developed by AGRANA, is a compostable blend designed for extruding ultra-thin films. This blend combines TPS AMITROPLAST® with biopolymers and other undisclosed ingredients comprising over 50% renewable components. It is engineered to offer excellent processability in bag-manufacturing machinery, enabling the production of sub-10 µm films. Additionally, it holds certification according to the European EN 13432 standard, demonstrating its ability to degrade by 90% into CO₂, water, and minerals within 12 months under domestic composting conditions (~30°C) [5].

The current study aims to evaluate the biodegradability of AGENACOMP® with added starch after three months of exposure to simulated soil.

Materials and Methods

We utilized the following materials to prepare the samples: AGENACOMP® provided by the Austrian company AGRANA, cassava starch sourced from Podium Alimentos, and a maleic anhydride additive manufactured by Elekeiroz. The methodology of this study encompassed several stages: drying the raw materials, extrusion, and dehumidification to produce test specimens via injection molding, placing the specimens in soil prepared according to the ASTM G160 standard, and ultimately characterizing the samples.

After drying the AGENACOMP® and the cassava starch in an oven at 90°C for approximately 48 hours, the material underwent processing using a co-rotating twin-screw extruder, specifically the Imacom DRC 30:40 IF model, with a screw diameter of 30 mm and an L/D ratio of 40. The material was extruded using a temperature profile for the extruder: 80, 90, 95, 100, 110, 120, 130, 140, 150, 160, and 60°C. Additionally, the screw speed was set to 45 RPM.

Table 1 presents the compositions of the produced formulations in percentage. Both F0 and F0-S have identical compositions, as do F1 and F1-S. The "-S" designation indicates that the

samples from the respective formulations were placed in the simulated soil. Throughout this study, all results associated with formulations featuring this "-S" designation refer to test specimens after degradation.

We used a ROMI injection molding machine of the Primax model to obtain the test specimens, featuring a closing force capacity of 100 tons, a 50 mm diameter universal screw, and an L/D ratio of 20. Before injection, the material underwent dehumidification at 90°C using a PIOVAN dehumidifier, specifically the T501X model, for a minimum of 6 hours.

The preparation of 20 kg of simulated soil adhered to ASTM G160 standard guidelines, involving an equal mixture of animal manure, beach sand (passed through a 40-mesh sieve), and soil. The specimens were subsequently placed in a composter for three months, after which they were removed, washed, and subjected to optical microscopy using Zeiss Axio equipment. Sample characterization was conducted utilizing the Thermo Scientific Nicolet iS10 FTIR spectrometer.

We conducted tensile tests to evaluate the mechanical properties of the various blends using an EMIC testing machine, specifically the DL 2000 model, per ISO 527 standard procedures, without using an extensometer. A 9 kN load cell was employed, and the testing speed was 50 mm/min. The properties evaluated included tensile strength, elongation at break, and tensile modulus.

Table 1. Composition of the blends produced via an extrusion process, in percentage.

	AGENACOMP®	Starch	Maleic anhydride
F0	100	-	-
F1	60	37	3
F0-S	100	-	-
F1-S	60	37	3

Results and Discussion

To evaluate whether the material properties were compromised after exposure to the simulated soil conditions, we proposed that the "-S" formulations also be subjected to mechanical testing. However, only F0-S was suitable for the tests, as the F1-S samples significantly deteriorated, with a substantial mass loss. Figure 1 exhibits the appearance of the test specimens from F0-S and F1-S after the period spent in the composter and subsequent tensile testing in the case of F0-S.

After conducting the tensile tests, the tensile strength, elongation at break, and tensile modulus values were recorded for the formulations F0, F1, and F0-S. Figure 2 displays the graphs plotted with this data.

The inclusion of starch in AGENACOMP® notably decreased the material's flexibility, with the F1 formulation exhibiting an elongation at a break five times smaller than that of F0 and a tensile strength value approximately 10% lower than the control formulation (refer to Figure 2b and Figure 2a). This indicates a heightened stiffness, as reflected in the tensile modulus (refer to Figure 2c), attributed to the additional load introduced by starch. Starch's molecular structure reinforces polymeric matrices through hydrogen bonding between the polysaccharide

chains and the biopolymer, increasing stiffness and mechanical strength. Additionally, three-dimensional networks form within the material's matrix, contributing to the rise in tensile modulus. The F0-S formulation displayed even lower tensile strength and elongation at break values. While the tensile modulus exhibited an overall average increase, there was significant variation in its values, indicating varying degrees and types of degradation among the test specimens. These outcomes are attributed to exposing the polymeric matrix to a humid environment. During this exposure, the hydrogen bonds between polymeric chains dissociate due to competition for interaction with water molecules, leading to material deformation and reduced stiffness [6,7].

The FTIR test plays a crucial role in the analysis and characterization of polymeric blends. Interacting with infrared light provides detailed insight into the chemical bonds in the sample under study and the presence or absence of additives, impurities, or chemical modifications [8]. Figure 3 shows the samples' FTIR spectra.

From the FTIR, it is possible to evaluate the index of terminal carboxylic groups (IGCT) because, during the degradation of polyesters by the action of microorganisms, the ester bonds break, resulting in a reduction in the molecular weight of the sample, indicated by the increase in the number of IGCT [8].

Figure 1. Test specimens after degradation and tensile testing (left: F0-S; right: F1-S).



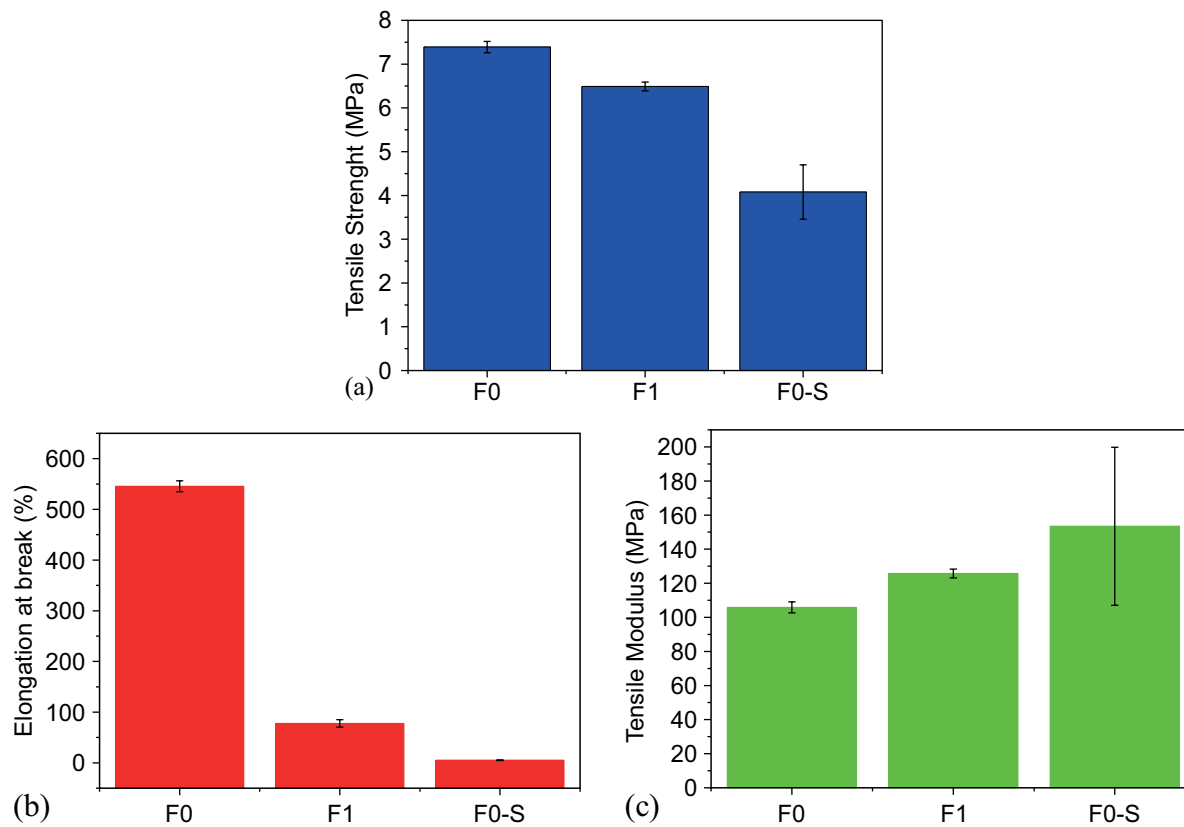
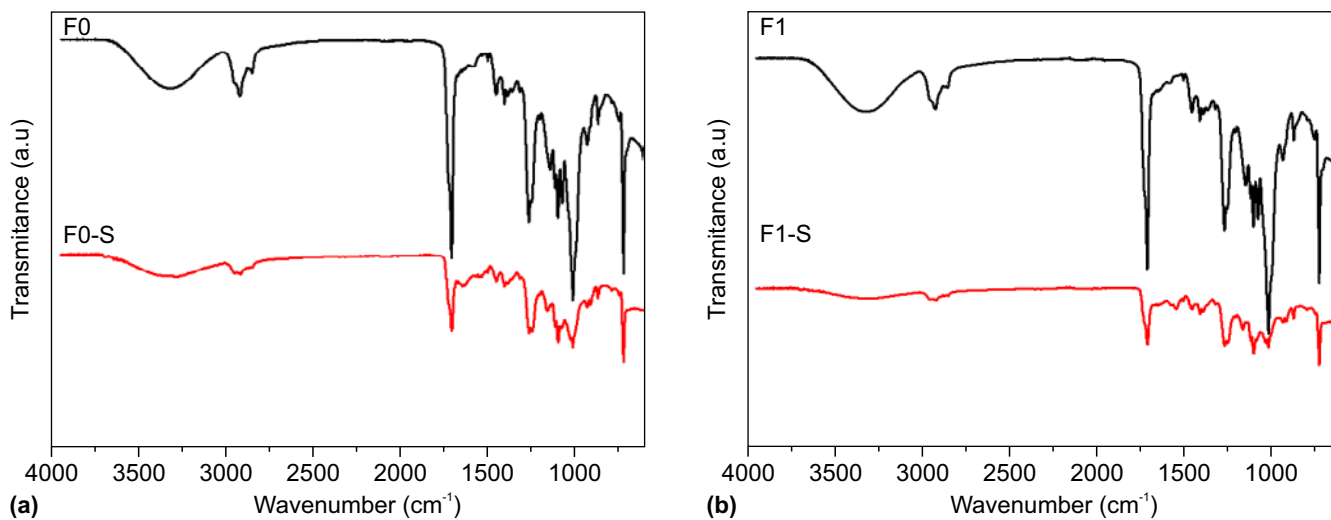
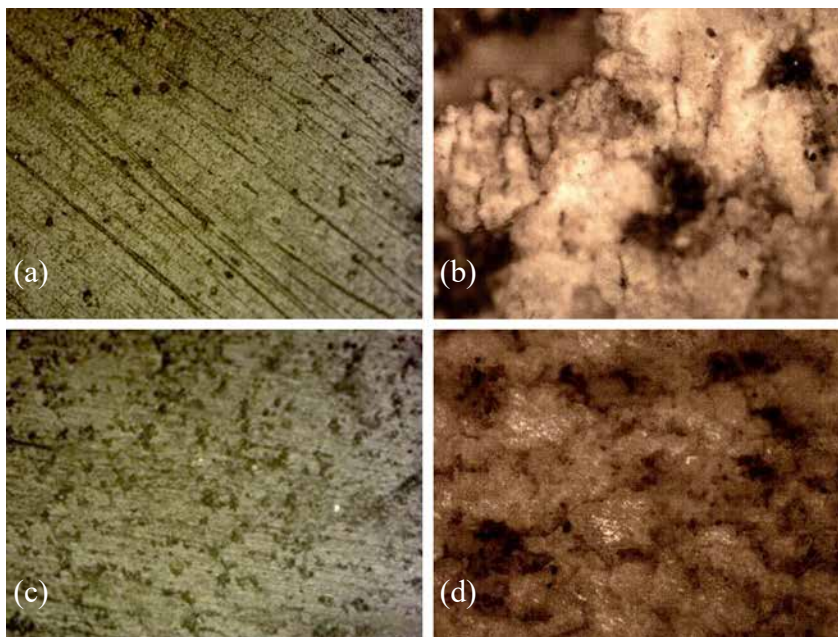
Figure 2. Values of (a) tensile strength, (b) elongation at break, and (c) tensile modulus.**Figure 3.** FTIR (a) F0 and F0-S; (b) F1 and F1-S.

Figure 4. Optical microscopy at 10x magnification of the test specimens. (a) F0; (b) F0-S; (c) F1; (d) F1-S.



Quantification was calculated using Equation (1).

$$IGCT = \frac{\text{absorption at } 3290 \text{ cm}^{-1}}{\text{absorption at } 2970 \text{ cm}^{-1}} \quad (1)$$

From the IGCT calculations, values of 15.7 and 10.3% were found for F0 and F0-S samples, respectively. As for F1 and F1-S samples, the results were 5.8 and 9.4%, correspondingly. These findings enabled the identification that only the sample containing more starch contributed to biodegradation, attributed to the IGCT increase. This result corroborates the results of the tensile test and morphology. We used an optical microscopy to assess the extent of degradation of the materials produced (Figure 4).

Optical microscopy plays a crucial role in analyzing the morphology of degraded test specimens, offering a comprehensive visualization of the materials' characteristics and structural changes [9]. Microbial degradation follows a process wherein functional groups form within the polymeric matrix, increasing its hydrophilicity and enhancing microorganism adhesion. This initiates reactions that break the polymeric chains, reducing their molecular weight and rendering the material

more accessible to these organisms. In the case of polymeric blends containing starch, biodegradation occurs in three stages. Microorganisms target the surface starch chains, leading to minor erosion, fissure development, and mass reduction. Subsequently, deeper microbial infiltration and moisture trigger more extensive material degradation. In the final stage, if starch persists in the structure, degradation can accelerate up to six times due to increased surface area [9, 10]. As depicted in Figure 4, evidence indicates that the structures underwent the action of microorganisms in the simulated soil. The presence of starch in the formulation expedited degradation, as evidenced by the fissures (dark spots). These cracks enlarge with prolonged incubation time due to ongoing microbial activity.

Conclusion

The analyses provide compelling evidence that incorporating thermoplastic starch into AGENACOMP® accelerates the material's degradation. A substantial portion of the mass of the test specimens from F1-S was lost after

exposure to the simulated soil for approximately three months, as confirmed by optical microscopy and FTIR images. Additionally, the tensile test revealed reinforcement by the molecular structure of the added starch to the polymeric matrix, leading to increased stiffness and mechanical strength of the material containing the added starch. Specifically, the tensile modulus results demonstrated an approximate 20% increase.

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