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Compostable properties of antimicrobial bioplastics based on cinnamaldehyde cross-linked gliadins

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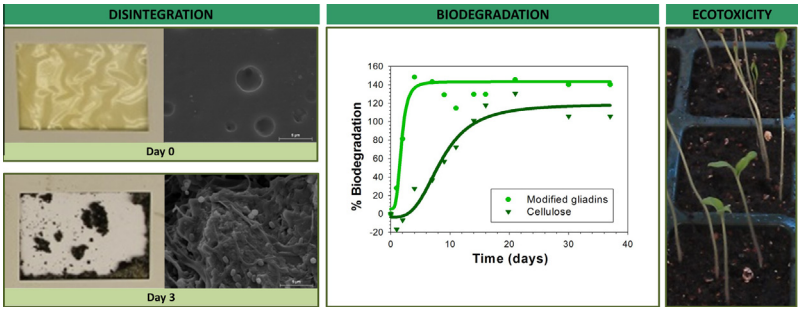
HIGHLIGHTS

- Compostable properties of antimicrobial cross-linked protein films were evaluated.
- Cross-linked gliadin films completely disintegrated in 4 days in compost.
- Biodegradation of films was complete but affected by cross-linking degree.
- No ecotoxic effects were observed in tomato seeds using the resulting compost.

GRAPHICAL ABSTRACT



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ABSTRACT

The disintegration, biodegradation and ecotoxicity of cross-linked wheat gliadin films with antimicrobial properties were assessed under controlled composting conditions. Gliadins were chemically modified with different percentages of cinnamaldehyde (1.5%, 3% and 5%) increasing their cross-linking degree and imparting antimicrobial activity. After the films were subjected to simulated conditions of use in a food packaging application, they were composted. The most cross-linked gliadin film showed a very fast disintegration profile. It completely disintegrated into fine visually indistinguishable residues after 4 days of being inserted in compost medium. Scanning electron microscopy revealed the rapid microbial colonization of the films' surface. Biodegradation was assessed by measuring the amount of carbon dioxide produced in a static system specifically designed for this study. The cross-linking degree of the proteinaceous matrices modified their biodegradation rate without impairing their complete biodegradation. The presence of residual cinnamaldehyde in the films, which can exert antimicrobial activity, did not hamper their biodegradation neither caused ecotoxicity on tomato seeds germination and plant growth.

1. Introduction

In the last decades there has been an increasing interest in the development of renewable materials with biodegradable properties in an attempt to contribute to the sustainable development and to reduce the environmental impact associated with non-biodegradable petroleum-based plastics [1]. Many unsubstantiated claims to biodegradability were made in the past as a consequence of the lack of well-identified environmental requirements, and thus the inexistence of well-established testing methods [2]. However, nowadays diverse standardization organizations have standard test methodologies, where specific disposal pathways, specific time frames and passing criteria are indicated in order to evaluate the suitability of a packaging material for its organic recovery [2]. These standards tests require high amounts of

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packaging materials to be tested (around 15 kg) and costly facilities to conduct the assays, thus only final materials with the aim of being certified and placed on the market are usually evaluated. For novel materials developed at laboratory scale and produced in lower quantities some preliminary tests need to be developed to serve as a reference to choose or discard among them.

Composting is the aerobic treatment of the biodegradable parts of packaging waste, which produces stabilized organic residues, under controlled conditions and using microorganisms (94/62/EC). Although recycling could be energetically more favorable than composting in some cases it may not be practical because of excessive sorting and cleaning requirements [3]. Moreover, the use of compost reduces chemical inputs, suppresses crop diseases, replenishes organic carbon, increases water and nutrient retention, and improves soil productivity [4].

It is important to note that all compostable plastics are biodegradable, but not all biodegradable plastics are compostable. According to ISO 17088 a compostable plastic is a plastic that undergoes degradation by biological processes during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visible distinguishable or toxic residues. Therefore, the evaluation of compostability includes three phases: disintegration, biodegradation and ecotoxicity.

Materials based on proteins from plants (wheat gluten, corn zein, and soy protein) and animals (gelatin, keratin, casein, and whey) are renewable and inherently biodegradable [5]. Among them, gluten proteins present remarkable advantages since they are highly available, have low cost, and can be obtained as by-product from the wheat starch industry, which is steadily rising as starch is used for bioethanol production, and in the manufacturing of other bioplastics such as thermoplastic starch (TPS) and poly (lactic acid) (PLA). However, gluten proteins have poor mechanical and water resistant properties making their modification essential to obtain suitable materials for diverse applications. Their improvement can also lead to changes in their compostability, since their disintegration could be hampered or their biodegradation could be incomplete.

Several authors have studied the biodegradation properties of diverse wheat gluten-based materials [6–8] in different environments such as soil, water, and compost; however, no reports have been found about their compostability.

In this study, the monomeric fraction of wheat gluten, gliadins, was treated with cinnamaldehyde to produce improved protein-based bioplastics. Cinnamaldehyde involved in the chemical cross-linking of the gliadins enhances the functional properties of the resulting films, especially their mechanical and water resistance [9–11], whereas free cinnamaldehyde which eventually do not undergoes covalent bonding between proteins imparts active antimicrobial properties to the films [11]. Therefore, its incorporation can alter the inherent biodegradation properties of naturally-occurring not-modified materials.

The aim of the present work was to explore the disintegration, biodegradation and ecotoxicity at laboratory scale of the active antimicrobial wheat protein-based bioplastics after its use. To the best of our knowledge, this is the first report that deals with the compostable properties of active antimicrobial bioplastics that can be used in food packaging applications.

2. Materials and methods

2.1. Reagents

Crude wheat gluten (⩾80% protein), trans-cinnamaldehyde 99%, glycerol, ethanol, hydrochloric acid, and microcrystalline cellulose with a particle diameter of around 20 μm, all laboratory grade, were supplied by Sigma (Madrid, Spain).

Compost was obtained from a municipal urban solid waste treatment plant where aerobic composting was produced (Tetma, Guadassuar, Spain). The compost selected was between two and four-months old. Initial physico-chemical characteristics were supplied by the manufacturer.

A mixture of peat with siliceous sand, both obtained from Viveros Alegre (Chiva, Spain), was employed as reference substrate in the determination of ecotoxic effects to higher plants. Tomato (*Solanum lycopersicum*) seeds from Vilmorin S.A. (La Ménitré, France) with a seedling emergence of 97%, evaluated with the reference substrate, were purchased at Leroy Merlin (Aldaia, Spain).

2.2. Preparation and characterization of antimicrobial cross-linked gliadin films

Antimicrobial films were produced from wheat proteins according to the method described by Balaguer, Gomez-Estaca, Gavara and Hernandez-Munoz [9]. Basically, a solution rich in gliadins was extracted from wheat gluten and different percentages of the cross-linker, namely 1.5% (G1.5C_pH2), 3% (G3C_pH2), and 5% (G5C_pH2) (g cinnamaldehyde/100 g protein) were incorporated into the solution. Glycerol was added as a plasticizer at 25% (g/100 g protein). The film-forming solution containing the plasticizer and different amounts of the cross-linker was adjusted at pH 2 with HCl and stirred for 30 min. Films were produced by casting and subsequent evaporation of the solvent at 37 °C for 24 h. A gliadin film produced at the native pH of the gliadin film-forming solution (pH 6) and without cinnamaldehyde addition was employed as the control (G_pH6). The mean film thickness was 100 ± 12 μm measured using a micrometer (Mitutoyo, Kanagawa, Japan), and calculated from measurements taken at ten different locations on each film sample. The grammage of the films was 0.015 ± 0.002 g/cm^2 measured at 50% RH (relative humidity) and 23 °C. Actual concentration of cinnamaldehyde after the production of the films was evaluated in a previous work by solvent extraction followed by gas chromatography determination [12]. Remaining cinnamaldehyde was present in concentrations lower than 1% [12]; therefore, biodegradation of this constituent was not necessary to be tested separately.

In previous studies it was shown that cinnamaldehyde release is triggered by the presence of ambient moisture [12]. Low relative humidity conditions enable the retention of cinnamaldehyde in the gliadin matrix, and high or medium relative humidity conditions trigger its release. Therefore, in order to simulate their potential use as antimicrobial food packaging materials, gliadin films were conditioned during one week at 75% RH and 23 °C (common conditions that can be achieved inside a packaged foodstuff of medium a_w) to trigger the release of cinnamaldehyde, and to achieve a remaining level after their use in accordance to their application. After the use simulation step, films were conditioned at 0% RH and 23 °C with P_2O_5 until achieving a constant weight, reporting all data in dry basis.

The carbon content of the film samples was measured with an elemental analyzer EA1108 CE Instruments (Thermo Fisher Scientific, Madrid, Spain).

2.3. Compost conditioning and characterization

The compost was sieved discarding fragments ⩾0.5 cm and large inert objects such as glass, stones, and metal pieces were manually removed to obtain a homogeneous material. The total dry solids content was determined by drying the compost at 105 °C until a constant weight was achieved (Eq. (1)). The total