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Biodegradation of chemically modified wheat gluten-based natural polymer materials

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ABSTRACT

Biodegradation of a series of chemically modified thermally processed wheat gluten (WG)-based natural polymers were examined according to Australian Standard (AS ISO 14855). Most of these materials reached 93–100% biodegradation within 22 days of composting, and the growth of fungi and significant phase deformation were observed during the process. Chemical crosslinking did slow down the rate or reduce the degree of the biodegradation with different behaviours for different modified systems. The segments containing structures derived from the reactions with additives such as tannin or epoxidised soybean oil remained in the degradation residues while the glycidoxypropyl trimethoxysilane agent produced ~20% un-degraded residues containing silicon-crosslinking structures. The biodegradation rate of each component of the materials was also different with the protein and starch components degraded fast but lipid degraded relatively slowly.

1. Introduction

Natural polymers derived from agricultural products (such as starch, proteins, cellulose and plant oils) are the major resource for developing renewable and biodegradable polymer materials to supplant petrochemicals in many industrial applications due to increased environmental concern and diminishing petrochemical resources [1–4]. The application of these natural polymer-based materials in packaging industries can significantly reduce the plastic waste in the environment due to their biodegradable nature. The biodegradation property in conjunction with biocompatibility also plays a key role when using the materials in medical applications. However, natural polymers usually suffer from performance disadvantages in certain aspects as compared to petro-derived materials. The major challenge in the material research is to develop suitable modification methodologies to improve the properties of natural polymers.

One example is the development of wheat proteins (WP) or wheat gluten (WG)-based natural polymer materials. As one of the cheapest plant proteins derived from the second largest cereal crop wheat (after maize), WP or WG have excellent properties in viscoelastic performance, tensile strength and gas-barrier performance. However, thermal processing the materials requires a large amount of plasticizers (such as water and glycerol) to interrupt the strong self-association among protein segments through intra-/inter-molecular interactions and to increase the mobility of the protein chains, therefore improving the flexibility and the extensibility of the materials [5–13]. However, the plasticization also results in high moisture sensitivity and low strength of the materials, thus improvement of the mechanical strength especially under wet or humid condition becomes a challenge task. Formation of crosslinked networks through chemical modification has usually used to build up additional covalent linkages within the protein matrix to enhance the mechanical strength and water (or humidity) resistance [14–16]. It has been demonstrated in our recent publications that grafting/crosslinking polymer segments onto the protein matrix is an efficient way to achieve effective structure–property modifications [17–21]. Formation of enhanced WG crosslinked networks with silane additives significantly improved the mechanical properties of the materials especially under high humidity conditions [17]. Grafting mobile polymer segments onto WP or WG matrix and conducting crosslinking simultaneously under controlled conditions provides a pathway to modify the material flexibility without using plasticizers while maintaining or even enhancing the mechanical properties [18–20]. New functional groups can also be introduced into the materials thereby supplying new functional properties or reactivity for further material modifications [18–21]. Hydrophobicity of the materials could also be

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enhanced by introducing epoxidised soybean oil into WG matrix through the polymer grafting approach [21].

It is desirable that these chemical modifications do not significantly change the biodegradable nature of the WP or WG materials. On the other hand, controlling the biodegradation process (variation of the rate or the degree of degradation) is necessary in many applications, thus the effect of chemical modifications on the material biodegradation behaviour is also an interesting subject for both academic research and material application. To the best of our knowledge, there was no report published on the relationship between biodegradability and the chemical modification of wheat proteins-based materials.

Natural polymers containing hydrolysable linkages (such as starch, cellulose and proteins) are generally susceptible to biodegradation by the hydrolytic enzymes produced by microorganisms. However, such nature could be modified when the materials experienced different processing conditions with different additives involved [22,23]. It was reported that thermally processed glycerol plasticized WG-based plastics were fully degraded within 36 days in aerobic fermentation and 50 days in farmland soil with no toxic products generated during the biodegradation [24]. In the present study, the biodegradation behaviour of a series of chemically modified thermally processed WG materials were studied under compost conditions following Australian Standard (AS ISO 14855). All of the chemical modifications were conducted on the same raw WG sample, which makes it possible to compare the behaviours among these different modified WG systems and then to investigate the chemical modification effect on material biodegradation. Scanning electron microscopy (SEM) was used to examine the microbial growth and morphology changes while high-resolution solid-state NMR technique was used to study the change in chemical structures and the biodegradation behaviour of different components in these complicated multi-component/multi-phase materials.

2. Experimental section

2.1. Chemically modified WG materials

Vital WG was kindly supplied by Manildra Group Australia as a raw WG food-grade product and used in all of the chemical modifications and thermal processing. It contained 80% proteins, 15% residual starch, 4% lipid, and around 1% fibres and other impurities on dry basis. The moisture content was 11–12 wt% as received. The chemically modified thermally processed WG samples were prepared following the methods as described in previous publications [13,17,20,21] and are summarized in Table 1. The additives namely glycerol, epoxidised soybean oil (ESO), acetone–formaldehyde resin (AF) and glycidoxypropyl trimethoxysilane (SiA) were obtained from Sigma–Aldrich, Cognis (as EDENOL D81), National Starch & Chemical Company (as ULTRA-GUARD™), and Dow Corning Company respectively. The Colatan tannin resin (TR) was produced by hydrolysis of Argentine Quebracho extract and was kindly supplied by Manildra Group Australia. These additives were mixed with raw WG powder according to the formulations listed in Table 1 in a high-speed mixer for 2–3 min at a speed of 3000 rpm. The pH of the additives was adjusted by either acetic acid or NaOH solution. The mixed samples were left overnight and then compression moulded at an optimum temperature of 130 °C for 5 min under a pressure of 12 ton. The sample size was 145 mm × 145 mm with a thickness of 1.0 ± 0.1 mm. All of the thermally processed samples were conditioned under relative humidity (RH) of 50–52% for 2 weeks before any testing. The moisture content in these samples after conditioning was measured as the weight loss after drying at 105 °C for 5–6 h.

Table 1
Chemically modified thermally processed WG samples.

Samples	Chemical modification agents and conditions	Moisture content (wt%)[a]	Ref.
WG-0	pH = 4, 18 wt% of glycerol	11.2	13
WG-ESO	pH = 11, 20 wt% of ESO	10.9	21
WG-AF	Natural pH (~6), 10.5 wt% of AF resin	11.1	20
WG-AFTR	Natural pH (~6), 8.5 wt% of AF resin, 2.1 wt% of tannin resin	10.0	20
WG-SiA	Natural pH (~6), 4 wt% of SiA, 16 wt% of glycerol	12.2	17

[a] The values were measured by drying the samples at 105 °C for 5–6 h after conditioning at 22 °C, RH = 50–52% for 2 weeks.

2.2. Compost characterization

Compost used for biodegradation testing was collected from Natural Recovery System (Victoria, Australia). The compost consisted of food-processing waste, supermarket produce waste, sawdust and shavings, grass clippings, tree pruning and waste paper fibre. The compost was sieved through a screen (8 mm) and large inert materials such as glass, stones or pieces of scrap metal were manually removed. Water was added into the compost mixture prior to the test to ensure the moisture content within the range of 48–50%, which was measured by drying the compost samples at 105 °C for 3 days until the constant compost weight. The pH of the compost was measured by mixing compost with deionised water at a weight ratio of 1:5.

Compost analysis was conducted at MGT Environmental Pty Ltd (Oakleigh, Victoria, Australia) as: pH 8.2, dry weight 49 wt% (Method 102 – ANZECC), volatile solids (mass loss after incineration in a muffle furnace at 550 °C) 54 wt% on dry basis (APHA 2540E) and C/N ratio of 22/1 (APHA 5310B – Total organic carbon; APHA 4500 – total nitrogen).

2.3. Respirometric unit

The biodegradability of the WG samples was examined according to Australian Standard AS ISO 14855 using an in-house built respirometer unit as described previously [25,26]. The 3 L glass jars (as bioreactors) were filled with 2.5 kg of compost and 100 g sample initially in triplicate for three different mixtures: blank (compost only), positive reference (compost + cellulose) and test samples (compost + test samples). All bioreactors were placed in a water-bath maintained at 58 ± 2 °C. The moisture content of the compost was maintained between 48–50% with supplementary water (pH of 7.8–8.5) to ensure a favourable condition for growing compost microorganisms involved in the process. Aerobic conditions were maintained by supplying an uninterrupted humidified air stream to the bioreactors and shaking the contents in the bioreactors twice a week to ensure uniform distribution of the air throughout the compost. The CO_2 produced in each bioreactor was measured by an infrared CO_2 analyzer (Servomex) during the testing period. The theoretical and actual amount of CO_2 produced by the testing samples and reference materials during the biodegradation process, as well as the degradation rates (taken from an average of three reactors for each sample, error bar of 3–5%) were calculated following the method as described in AS ISO 14855. The reference sample of microcrystalline cellulose particles with a particle diameter of ~20 μm (according to AS ISO 14855) was obtained from Sigma–Aldrich and used as received.