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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.

Samples were collected from bioreactors (2–3 g each time, such weight change was taken into the calculation program of biodegradation) during the initial 2 weeks of composting. These samples were washed by ethanol immediately and dried at room temperature for one week in a funnel cabinet (without heating and vacuum) before SEM and NMR analysis. Sampling after 2 weeks was difficult as the samples either disappeared or became too small in size and quantity to separate from the compost. The original carbon content in these modified WG samples were measured at Chemical & Micro Analytical Services Pty. Ltd. (Belmount, Victoria, Australia).

2.4. SEM and high-resolution solid-state NMR

The SEM images of samples collected during the biodegradation process were examined by Philips FEI XL-30 SFEG microscopy. The samples were mounted onto SEM stages with double-sided conductive tape and then sputter coated with gold to 20 nm in thickness under argon atmosphere. The electron beam with an accelerating voltage of 3–5 kV was used to produce high definition images.

High-resolution solid-state NMR experiments were conducted at room temperature using a Varian NMR300 System at resonance frequencies of 75 MHz for ^{13}C and 300 MHz for ^{1}H. ^{13}C NMR spectra were observed under either cross-polarization, magic angle spinning and high power dipolar decoupling (CP/MAS/DD) conditions, or using a single 90° pulse excitation (SPE) method under MAS and DD conditions. The 90° pulse was 5.5 μs for ^{1}H and ^{13}C channels while the spinning rate of MAS was set at a value around 8 kHz. A contact time of 1.0 ms was used for measuring CP/MAS spectra while the repetition time was 2 s for both CP/MAS and SPE/MAS measurements. The chemical shift of ^{13}C MAS spectra was determined by taking the carbonyl carbon of solid glycine (176.3 ppm) as an external reference standard.

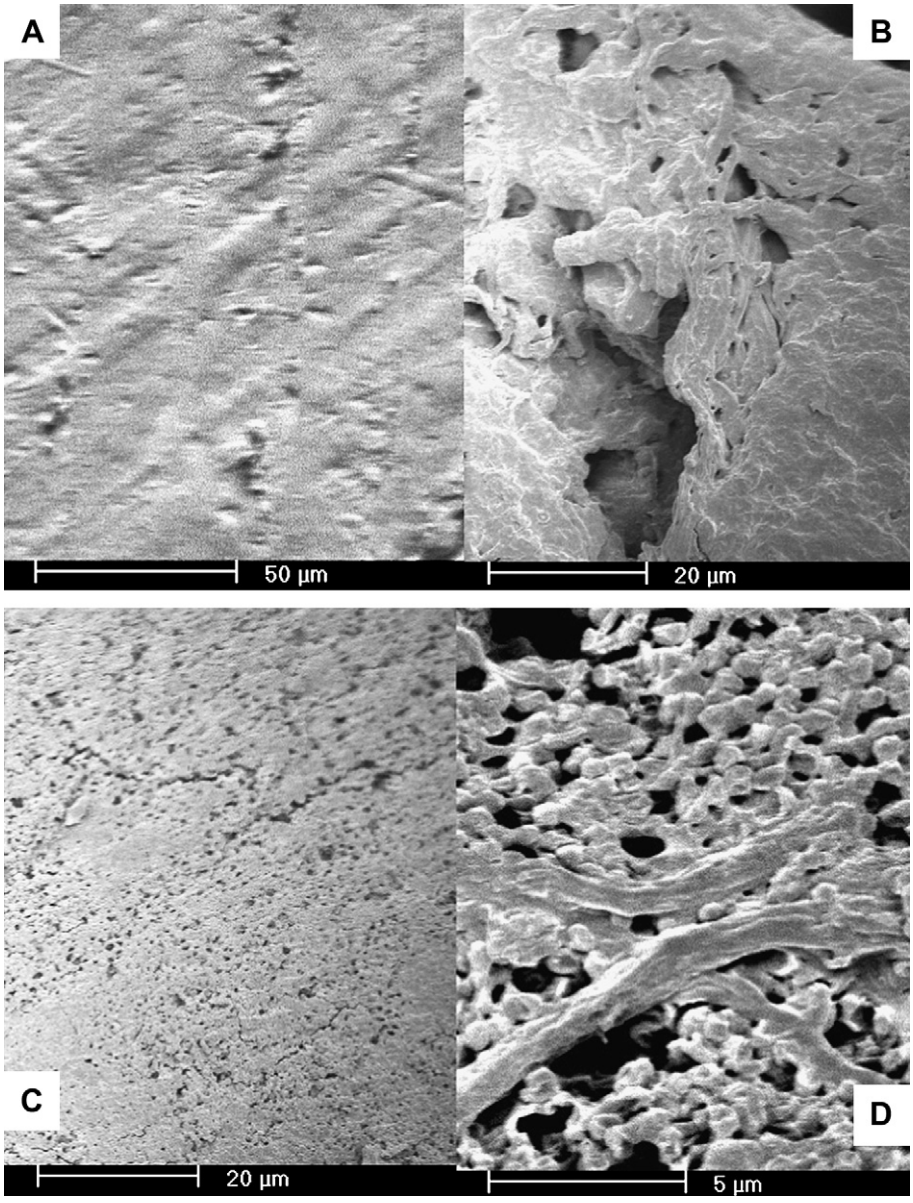

Fig. 1. SEM images of the WG-0 sample before the biodegradation test (A) and after composting for 7 (B), and 10 days (C, D).

3. Results and discussion

All of the chemically modified WG samples appeared as yellow or brown (WG-AFTR only due to tannin additives) translucent sheets with smooth outer surface before incubation in compost. After 2–3 days composting, most of these samples turned dark brown to black in colour. Fig. 1 shows the SEM images of WG-0 before and after 7 or 10 days of biodegradation in the compost. Phase deformation was observed after 7 days in conjunction with the formation of mycelium networks spread across the sample surface. After 10 days, the sample disintegrated into small pieces and phase deformation occurred more significantly.

Similar results were obtained for WG-SiA and WG-ESO as shown in Fig. 2. Growth of fungi and the formation of mycelium networks under the surface of WG-AFTR materials was clearly observed after composting for 7 days (Fig. 3A and B), and material phase deformation occurred simultaneously. After 14 days, mycelium networks as the predominate feature were observed for the WG-AFTR sample (Fig. 3C and D).

The biodegradation behaviours of these modified WG materials are shown in Fig. 4 in comparison with the result of reference cellulose, while Table 2 summarizes some key data of these biodegradation results. Among all tested samples, thermally processed glycerol-plasticized WG (WG-0) degraded faster than all of other samples and reached 100% biodegradation within 12 days of composting. The result of full biodegradation is consistent with that reported in literature [24], but the biodegradation rate was faster since a higher composting temperature (58 °C) was used in this study. Chemically modified WG-AF sample also achieved 100% biodegradation within 19 days, but the initial degradation rate (slope of the curve of biodegradation vs. time within initial 5 days) was 5.6% per day, just half of that of WG-0 (12.1% per day). When tannin additive was involved in the WG-AF crosslinked networks (WG-AFTR), a degradation of 95% was achieved for the sample within a similar period of time, and the biodegradation became insignificant after 18 days of composting. The WG-ESO sample displayed a fast initial degradation rate (only slightly lower than that of WG-0) and also reached 93% degradation in 15 days with

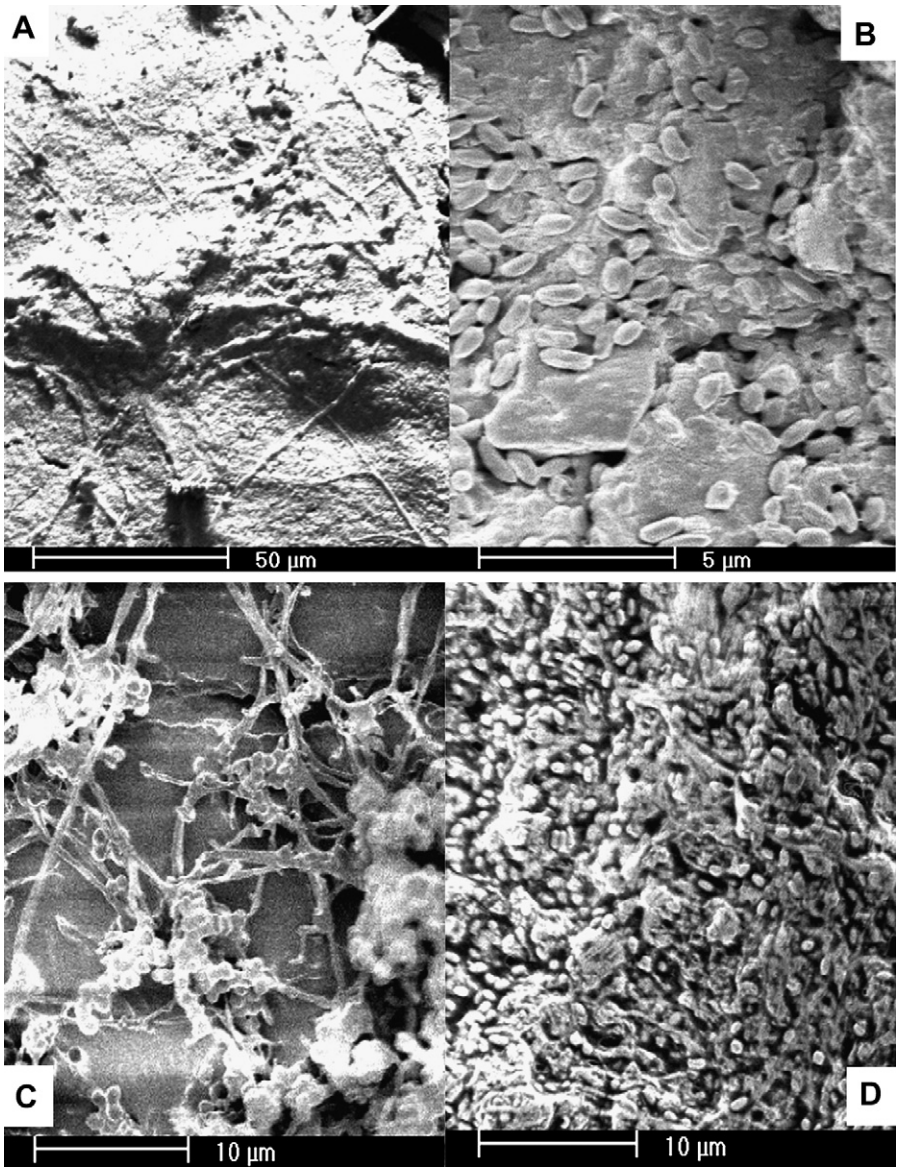

Fig. 2. SEM images of the WG-SiA sample after composting for 7 (A), 14 (B) days, and those of the WG-ESO sample after composting for 3 (C) and 10 (D) days.

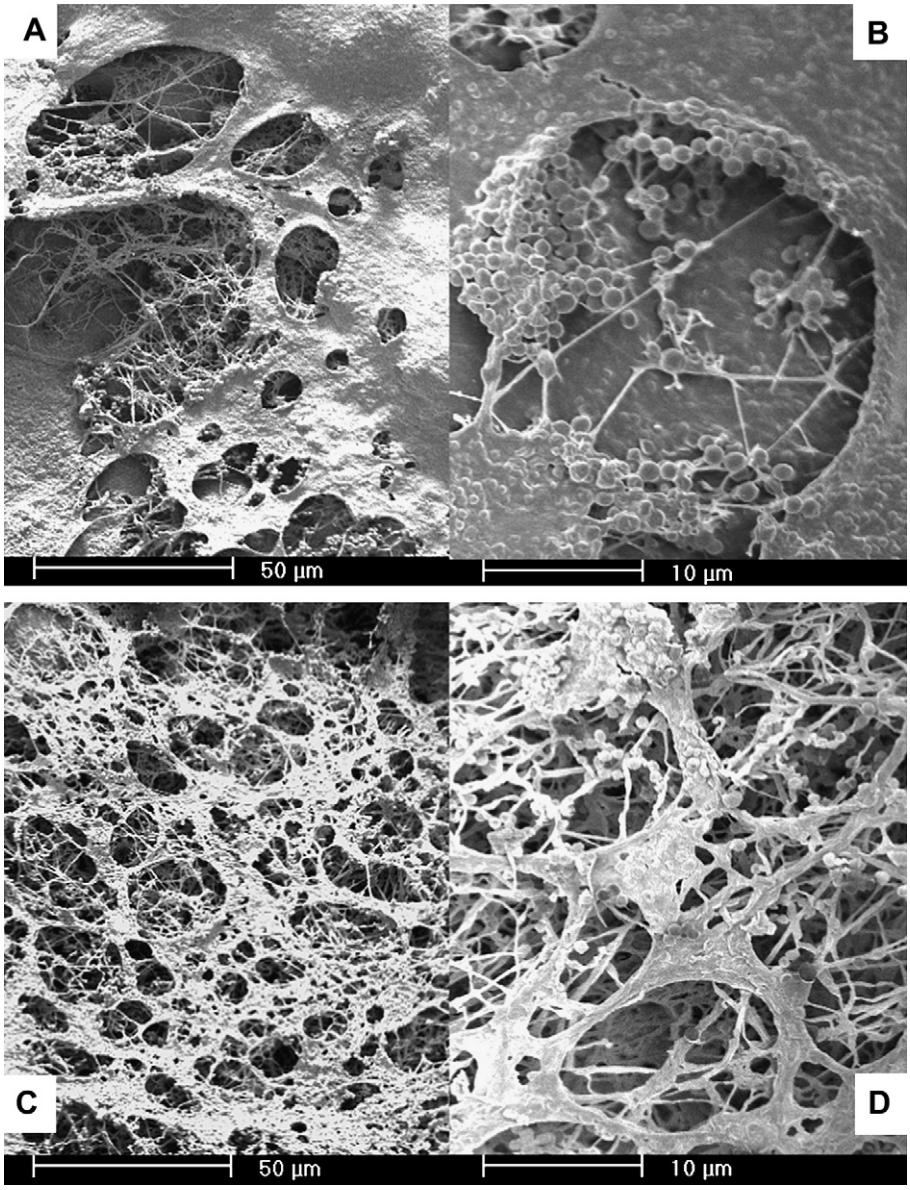

Fig. 3. SEM images of the WG-AFTR sample after composting for 7 days (A, B) and 14 days (C, D).

no significant degradation thereafter. On the other hand, the WG-SiA sample only reached 78% degradation within the same period of time, although the initial biodegradation rate was only slightly slower than those of WG-0 and WG-ESO. The biodegradation behaviour of reference cellulose was consistent with the results obtained under similar conditions as a control for the test.

High-resolution solid-state NMR is a powerful technique to study the changes in chemical structure for non-soluble systems such as crosslinked polymer materials in the solid state. It has also been used in study of the biodegradation of plant materials [27,28]. The high-resolution nature, although difficult to achieve quantitative observation easily, makes it possible to study the behaviour of each component in multi-component/multi-phase systems. Fig. 5 shows the ^{13}C CP/MAS and SPE/MAS spectra of the WG-0 residue sample after composting. The CP/MAS method is sensitive to rigid materials when strong dipolar interactions in the system efficiently enhance the polarization transfer from protons to nearby carbons thus enhancing the intensities of carbon resonances. The SPE/MAS method is sensitive to mobile components when a repetition time is as short as 2 s. The rigid components in WG-0 before biodegradation detected by the CP/MAS method were assigned to proteins with the C=O at 174 ppm, the C-α, C-β and C-γ resonances at 54, 30–15 ppm, while the minor resonances at 157, 138, 129 and 116 ppm were due to Arg, Tyr and Phe segments in the proteins. The resonances of residual starch in WG were also detected in the CP/MAS spectra at 103, 83 and 74 ppm (C-1, C-4 and C-2,3,5 of starch) while the C-6 (at 64 ppm) could overlap with the signals of proteins in the similar area. On the other hand, the major components observed via SPE/MAS method for WG-0 before biodegradation were the plasticizer glycerol (at 74 and 64 ppm) and lipid (mainly the narrow resonances at 15–35 ppm) plus a small amount of plasticized proteins and starch. Bearing in mind that only 5 wt% of lipid existed in WG raw material but their intensity was strong in the SPE/MAS spectra, this indicates only a small proportion of proteins and starch existing in the WG-0 mobile phase. It is noticed that

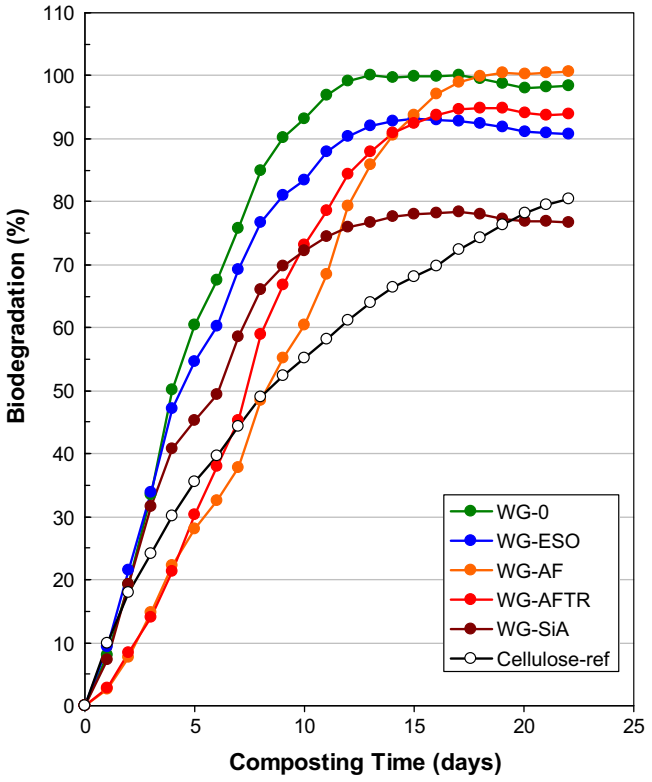

Fig. 4. Biodegradation process of the modified WG materials detected as conversion to CO_2 (error bar of 3–5%).

glycerol signals were also detected in the CP/MAS spectra, indicating its strong interactions with protein and starch components.

After 3 days of biodegradation, the intensity of glycerol signals in the WG-0 disappeared from both SPE/MAS and CP/MAS spectra, while the changes of relative intensities of other components were minimal. It seems glycerol was either the first component being biodegraded or more likely was extracted from the sample under the wet condition in the bioreactors. However, it should have biodegraded during the composting period due to 100% degradation was achieved for WG-0 and the carbon contribution from glycerol was also taken into account in the overall material biodegradation (converting to CO_2). The relative intensity of starch in the CP/MAS spectrum became stronger (comparing the resonance at 74 ppm to the C=O peak at 174 ppm) after 10 days, while those at 20–35 ppm (corresponding to lipid signals) were also increased. The SPE/MAS spectrum of WG-0 after 10 days of composting remained similar to that after 3 days, and lipid signals remained towards the end of biodegradation. SEM images have shown the growth of fungi and the formation of mycelium networks during the biodegradation process. The signals of the fungi and products of metabolic activity could overlap with those of WG due to similar proteinaceous/carbohydrate structures. To distinguish the degradation behaviour of the WG components and the formation of the mycelium networks is difficult as it is impossible to separate the fungal component and the biodegraded residues of WG-0. An external reference is also difficult to choose before knowing the fungi structures. However, the signals derived from WG-0 components should be dominant at initial degradation stage while the formation of mycelium networks might become observable only after a certain period of composting or until the late stage of the biodegradation. Nevertheless, as residual starch was only 15% while proteins were 80% in the original WG, the higher relative intensity of starch observed after longer composting time suggests that some proportion of residual starch degraded at a slightly slower rate than that of proteins. Lipid had the slowest rate in the biodegradation, and this should be due to the presence of aliphatic double bonds in the fatty acid segments (at ~130 ppm in SPE spectra) in lipid which restricted the bioavailability [29]. The hydrophobic nature of the lipid could also contribute to its slow biodegradation and resulted in lipid partitioned in the residues [29].

Table 2
Initial degradation rates and maximum degree of degradation achieved for the WG samples

Samples	Initial rate[a] (%/day)	Max. degradation reached (%)	Days to reach max. degradation
WG-0	12.1 ± 0.4	100 ± 3	12 ± 1
WG-ESO	10.9 ± 0.5	93 ± 4	15 ± 1
WG-AF	5.6 ± 0.2	100 ± 4	19 ± 1
WG-AFTR	6.1 ± 0.3	95 ± 4	18 ± 1
WG-SiA	9.1 ± 0.4	78 ± 5	17 ± 1

[a] Slope of curve biodegradation vs. time within initial 5 days.

The ^{13}C CP/MAS and SPE/MAS NMR spectra of the WG-ESO residues after composting are shown in Fig. 6, where the relative intensity of starch also became stronger in the biodegraded residues after 14 days of composting as compared to the C=O intensity (at 174 ppm) of proteins. ESO and lipid components remained unchanged in the SPE/MAS spectra during the biodegradation up to 10 days but the linewidth became broader after 14 days possibly due to their small amount and intimate interactions with other biodegradation products in the residues. Note that the epoxy structure (marked as * peaks in Fig. 6) of ESO remained stable during the biodegradation.

The situation of WG-AF and WG-AFTR samples displayed a similar behaviour to each other thus only the ^{13}C NMR spectra of WG-AFTR are shown in Fig. 7. The spectra were similar to those of WG-0 except no glycerol was present in the system. The intensity of tannin additives was weak and overlapping with those of proteins thus its behaviour was difficult to be observed.

The WG-SiA material only reached 78% biodegradation during the same composting period as seen in Fig. 4 and Table 2. The ^{13}C NMR spectra of their degradation residues (shown in Fig. 8) display a similar behaviour to that of WG-0. ^{29}Si MAS NMR spectrum of the WG-SiA residue obtained after composting for 14 days is shown in Fig. 9. The major ^{29}Si resonances were detected at −60 and −69 ppm, corresponding to the T^2 ($Si(OR)_2(OH)_2$) and T^3 ($Si(OR)_3(OH)$) structures [17]. This result indicates that these silicon-containing crosslinking structures in the WG-SiA networks remained in the residues. Keeping in mind that only 4% of SiA was used in the material, it resulted in ~20% of the material as residues after 22 days of composting. It was difficult to collect those undegraded samples for NMR examination due to their small amount/size or the difficulty in separating them from the compost materials after composting over 14 days.

These results demonstrate that different chemical modifications displayed different effects on the material biodegradation due to different crosslinking structures in the networks. The modification of WG matrix using AF additives (WG-AF system) resulted in formation of C–O bonds as the predominant aliphatic linkages between WG matrix and AF chains and the reactions mainly occurred at the free ε-amino groups of the proteins. The hydroxyl groups in residual starch could also take part in the crosslinking reaction with linkages between starch chains. Such crosslinking did slow down the biodegradation process similar to other crosslinked protein materials reported previously [30,31]. However, the whole WG-AF material still achieved 100%

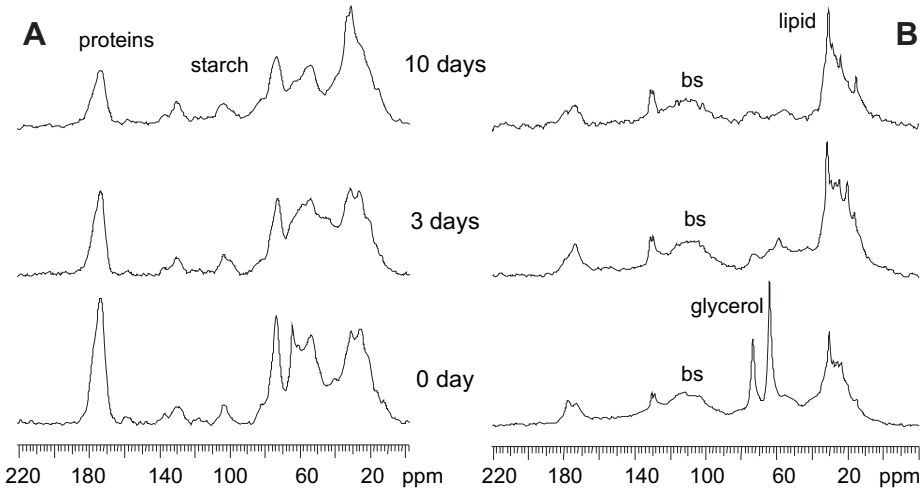

Fig. 5. ^{13}C CP/MAS (A) and SPE/MAS (B) NMR spectra of the WG-0 sample after biodegradation up to 10 days. bs: background signals from the spinner.

biodegradation, possibly due to the low crosslink density with long aliphatic crosslinking AF segments (biodegradable as well) within the WG matrix.

The addition of tannin resins did not change the biodegradation rate, but the involvement of the aromatic structure derived from tannin did result in ~5% of residues in the WG-AFTR sample after composting for 22 days. Besides taking part in reactions with AF resins, the phenolic reactive sites in tannin could also directly react with ε-amino groups of the proteins (e.g. lysine or arginine units) to form C-N covalent linkages between the phenolic rings of tannin and WG matrix [32–40]. It is known that phenolic compounds were relatively difficult to undergo biodegradation and maintaining a low phenol concentration was essential for achieving some level of degradation [41,42], thus, the crosslinked segments involving tannin structures could be very slow to be biodegraded. Considering the error of the testing shown in Table 2, this small proportion (5%) of residues is not significant.

All major components used in the WG-ESO sample were derived from natural renewable agriculture resources; however, there was also a small amount of un-degraded residues obtained after composting for 15 days. It was reported that the ESO component in ESO/polymer systems was biodegradable with a slow mineralization process [43]. Note that the initial biodegradation rate of WG-ESO was almost as fast as that of WG-0, reflecting the low crosslink density in the materials [21]. Since 20% of ESO was applied in the WG-ESO system and all of them were taken into account in the overall material biodegradation (converting to CO_2) but only 7% residues retained after 22 days of composting. Taking into consideration the testing error, it can be concluded that the majority of the ESO segments in WG-ESO material did biodegrade.

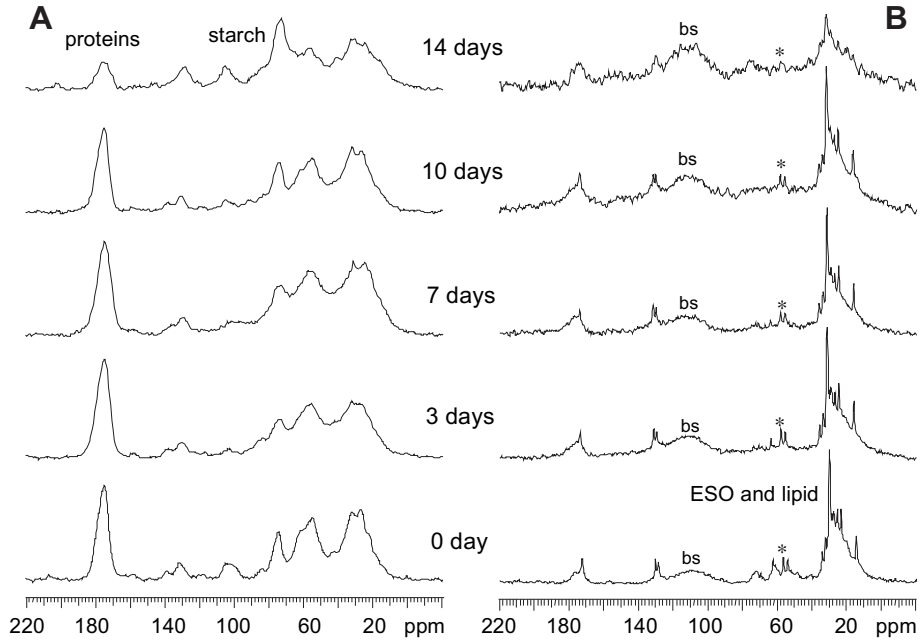

Fig. 6. ^{13}C CP/MAS (A) and SPE/MAS (B) NMR spectra of the WG-ESO sample after biodegradation up to 14 days. * peaks: epoxy groups in ESO. bs: background signal from the spinner.

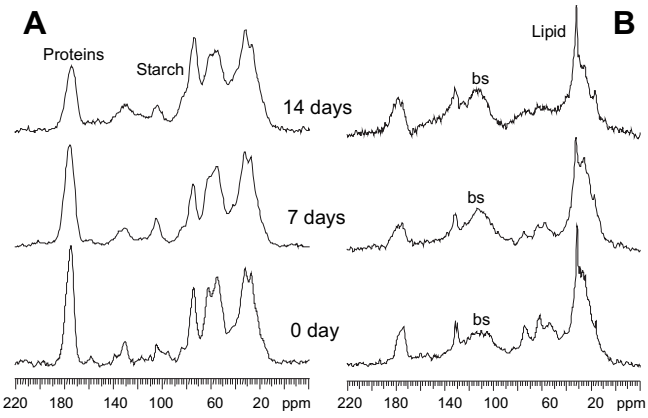

Fig. 7. ^{13}C CP/MAS (A) and SPE/MAS (B) NMR spectra of the WG-AFTR sample after biodegradation up to 14 days. bs: background signal from the spinner.

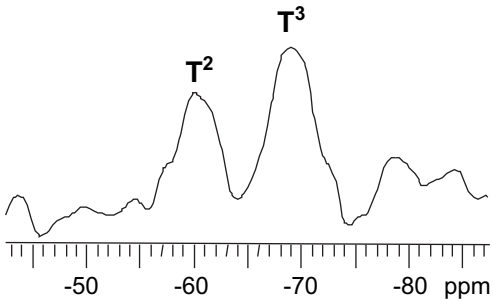

Fig. 9. ^{29}Si MAS NMR spectra of the WG-SiA sample after biodegradation for 14 days.

The significant impact to the material biodegradation was observed in the WG-SiA material which generated nearly 20% degradation residues although only 4% of SiA was applied to WG. The Si-containing structure seemed to play an incompatible role in the process and its hydrophobic nature should also have a negative effect in biodegradation, resulting in most WG segments directly linked to the Si-containing structures being very slow to biodegrade.

The residual starch in WG seemed to biodegrade slightly slower than the proteins in these WG materials especially after modifications. The hydroxyl groups in starch can take part in most of the chemical crosslinking reactions occurring in the WG matrix when using all of these mentioned additives. Thermal crosslinking could also occur to starch during the thermal processing. As each glucosyl unit of starch contains 3 hydroxyl groups, the starch component might experience a more significant crosslinking effect as compared to protein matrix, and these crosslinked starch segments could be biodegraded at a slower rate as reported in other starch-based materials [44–46].

The other important issue in material biodegradation is whether the degradation products generated during the biodegradation are toxic to fauna and flora. The toxicity of the products derived from degradation is also a key concern for biomaterials in medical applications. For thermally processed WG materials, no toxic products were generated during the biodegradation process [24]. Thermally processed starch and vegetable oils-based resins including ESO have been studied previously with results showing no toxic substance was produced in biodegradation process [29,47]. However, when WG was chemical modified by the additives mentioned in this work (Table 1), various new chemically structures were formed in the grafting segments and crosslinking linkages in the networks since a large number of different reactive groups in proteins and starch could take part in the reactions. These structures could produce a number of intermediates during the biodegradation process or stable products remaining in the biodegradation residues. The toxicity examination in conjunction with the study of microbial structure and population during the biodegradation process should provide further mechanism information of the effect of these chemical modifications on the biodegradation behaviour of the WG-based natural polymer materials.

4. Conclusion

The biodegradation study of a series of chemically modified thermally processed WG materials indicates that most of the materials were still biodegradable but the rate and the degree of degradation could be varied due to formation of different network structures by different chemical modifications. Thermally processed plasticized WG was 100% biodegradable. Most of the chemically modified WG materials reached 93–100% biodegradation within 22

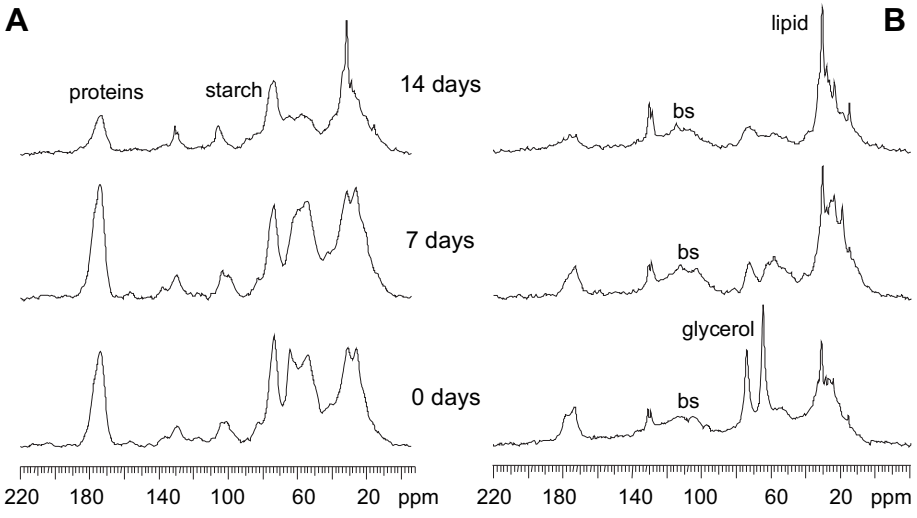

Fig. 8. ^{13}C CP/MAS (A) and SPE/MAS (B) NMR spectra of the WG-SiA sample after biodegradation up to 14 days. bs: background signal from the spinner.

days of composting. The WG-AF sample reached 100% biodegradation, but the degradation rate was slower. The tannin additive generated a small amount of residues for the WG-AFTR material after the composting while the WG-ESO sample displayed a similar behaviour. Nearly 20% of residues containing silicon-crosslinking structures were obtained in the WG-SiA material after the same period of composting. Some proportion of the residual starch degraded slightly slower than proteins especially in the modified WG materials, while the lipid experienced the slowest biodegradation in the materials. The study also demonstrated that SEM and high-resolution solid-state NMR are powerful tools to examine the growth of fungi, formation of mycelium networks, phase deformation and biodegradation behaviour of each component in a multi-component/multi-phase system. The toxicity of the biodegradation and microbial structure and population produced during the process should be further studied to provide additional mechanism information of the chemical modification effect on the biodegradation behaviour of these WG-based natural polymer materials.

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