

Novel biocomposites based on wheat gluten and rubber wood sawdust

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ABSTRACT: Rubber wood sawdust (RWS) was used as a reinforcement for wheat gluten based bioplastics. The RWS content was varied from 0, 5, 10, 15–20 wt %. Effects of the RWS content on the morphology, water absorption, mechanical, thermal, and biodegradation properties of the wheat gluten based bioplastic were investigated. An addition of RWS caused an improvement of the tensile strength and water resistance of the wheat gluten based bioplastics. Scanning electron micrograph of the wheat gluten/RWS composites with a 10 wt % of RWS revealed a good dispersion and uniform embedding of the RWS within the wheat gluten matrix. Agglomeration of RWS was observed when the RWS loads were increased (15 and 20 wt %). The biodegradation process of the composites depended on the amount of RWS. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43705.

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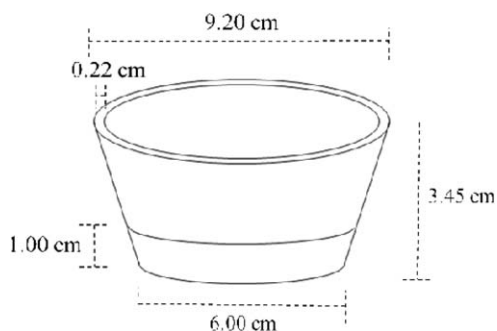
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INTRODUCTION

Wheat gluten (WG), soya, and zein are proteins derived from plants that are categorized as being renewable materials. WG has special properties compared to other plant proteins such as its unique viscoelastic properties. WG can be obtained from abundant sources at low cost as a by-product from wheat starch fabrications and the food processing industries. WG also allows for exceptional biodegradability and is composed of two major proteins, gliadin, and glutenin. These proteins can be converted to bioplastics via common thermoplastic processing such as extrusion and compression molding by mixing with plasticizers.^{1,2} During the process, the thiol (SH) groups of cysteine, in WG, forms disulfide bonds between other protein chains.^{3,4} These bonds influence the change of properties of WG based bioplastics.⁵ However, applications of WG based bioplastics are limited due to their poor water resistance, and their mechanical and thermal properties. An efficient method to improve the properties of WG based bioplastic is to make a composite with ligno-cellulosic materials. Lignin, a major component of the ligno-cellulosic material, is a complex phenolic polymer that can interact with proteins and lead to the formation of protein-polyphenol complexes.^{6–8} According to the literature, the properties of WG based bioplastics can be improved by using the ligno-cellulosic materials from coconut coir, jute, hemp, and wood fibers.^{8–10} Yang and Reddy⁹ found that the composites with 60% WG/40% jute showed higher flexural strength, tensile

strength, and modulus compared to those of a composite of polypropylene (PP) reinforced with jute fibers. Moreover, Kunanopparat *et al.*⁸ showed that an addition of 10% coconut coir fibers significantly reduced the water absorption of gluten-based materials from 75% to 66.5%. They also reported that variations of the lignin contents in the fibers, had no significant effect on the properties of the natural fiber/plasticized protein biocomposites.

Rubber wood sawdust (RWS) is a waste ligno-cellulosic material from the rubber wood furniture industries. It provides several advantages including low cost, environmentally safe, renewability, low density, and availability in large quantities. RWS has been used in many applications including as a raw material to provide activated carbon and bioethanol, and as a soil amendment material.^{11–13} Recently, several research groups have focused on preparations of wood-polymer composites. It has been reported that the tensile moduli and strengths of poly(lactic acid) composites increased with an increase of the RWS content.¹⁴ RWS improved the biodegradability of the composites with PP, however, the tensile strength of the composites decreased with an increase of the RWS content due to the low compatibility between RWS and the PP matrix.^{15,16} Ndlovu *et al.*¹⁷ reported that the compatibility between the polymer matrix and wood fibers is an important factor to maximize the performance of wood as a reinforcing filler.



Scheme 1. Dimensions of the sample prepared for a soil burial degradation test.

The aim of this work was to prepare compatible composites of WG and RWS. A possible application of this biocomposite is as a raw material to make biodegradable flower pots that can replace commercial non-degradable petroleum-based plastics. Effects of the RWS content on the morphology, water absorption, mechanical, thermal, and biodegradation properties of the composites were investigated.

EXPERIMENTAL

Materials

WG was purchased from Zhangjiaguan Longxiang Co., Ltd. WG was dried at 105 °C for 24 h in an oven and was kept in a desiccator before use. RWS was kindly supplied by a local furniture factory. RWS was ground by a mortar grinder, FRITSTSCH (Germany). After grinding, it was filtered through a 250 μm sieve and was dried in a hot air oven until a constant weight was achieved. RWS was kept in a desiccator prior to use. The glycerol was purchased from Ajax Finechem.

Preparation of Composites

WG, glycerol (30 wt % of dry WG basis) and RWS (0, 5, 10, 15, and 20 wt % of dry WG basis) were premixed in polyethylene bags. Then, the mixtures were further mixed in a two-roll mill at room temperature for 2 min. Sample sheets (13 cm \times 13 cm \times 1.5 mm) were prepared by using a compression molding machine at 130 °C for 10 min with a pressure of 250 kg/cm² applied to the molds.

Characterization of the Composites

The samples were stored in a controlled humidity chamber for 7 days. The humidity in the chamber was measured by a thermo-hygrometer and recorded each day to find the average humidity inside the chamber and this was $66 \pm 2\%$ RH. Tensile tests (ASTM: D412-06ae2) were conducted with a universal testing machine (Instron model 3365) at a 100 N load cell and a crosshead speed of 100 mm/min. The tensile testing was conducted at a room temperature of $25 \pm 3^\circ\text{C}$ and the room humidity of $55 \pm 2\%$ RH as measured by a thermo-hygrometer. Ten specimens were tested for each sample.

A scanning electron microscope (SEM-Quanta 400) was used to study the fracture surface and morphology of the samples. The composites were immersed in liquid nitrogen before fracturing. All specimens were mounted on the stubs with double-side sticky tape. The samples were coated with a thin layer of evaporated gold.

The thermal decomposition temperatures of the samples were obtained using a thermogravimetric analyzer (TGA), PerkinElmer[®] TGA 7. The TGA was operated at a heating rate of 10 °C/min from 50 to 600 °C in a nitrogen atmosphere.

Water Absorption Measurement

Square samples (1.5 cm \times 1.5 cm \times 1.5 mm) were stored at $66 \pm 2\%$ RH for 7 and 30 days before testing, and were dried overnight in an oven at 105 °C. These samples were weighed immediately after removing from the oven. Water absorption was calculated as shown in eq. (1):

$$\text{Water absorption (\%)} = [(w_1 - w_2)/w_2] \times 100 \quad (1)$$

where w_1 is the weight of the sample before drying and w_2 is the weight of the sample after drying. All measurements were performed in triplicate.

Soil Burial Degradation Test

The WG/RWS composites with 10 and 20 wt % of RWS were used as representatives of low and high compositions of RWS in the composites, respectively. The samples were cup shaped (top diameter = 9.20 cm, bottom diameter = 6.00 cm, depth = 3.45 cm, side-wall thickness = 0.22 cm, and bottom thickness = 1.00 cm) as shown in Scheme 1. This sample preparation technique was previously reported by Schettini *et al.*¹⁸ In order to obtain similar dimensions and thickness of the samples, equal amounts of each composite system was added into the mold. The mold was then pressed with a pressure of 100 kg/cm². The sample cups were buried in natural soil for 15 and 30 days and the weight loss of the sample was measured. A sample of neat wheat gluten in a similar shape was used as a control experiment.

The average environmental temperature ($28 \pm 0.5^\circ\text{C}$) and the RH of natural soil ($95.5 \pm 0.7\%$) was measured by burying a thermo-hygrometer under the soil in the same area of the test for a specific time. After 15 and 30 days, the samples were collected, washed with distilled water several times, and dried in the oven at 105 °C for 24 h. The weight loss of the sample was calculated using eq. (2):

$$\text{Weight loss (\%)} = [(S_1 - S_2)/S_1] \times 100 \quad (2)$$

where S_1 was initial weight and S_2 was final weight (after drying).

RESULTS AND DISCUSSION

Figure 1(a) shows the SEM micrograph of RWS. The surface of the RWS was rough. The appearance of the untreated natural fiber surface was in agreement with other studies.^{19,20} The SEM micrographs of the fracture surface of the neat WG based bioplastic, as shown in Figure 1(b), appeared to have a smooth surface. In contrast the SEM micrographs of the fractured surface of the WG/RWS composites with a low amount of RWS (5 wt % and 10 wt %), shown in Figure 1(c,d), respectively, revealed a good dispersion and uniform embedding of the RWS in the WG matrix. This behavior was expected because the lignin in the structure of the RWS formed a strong interaction with proteins. Kunanopparat *et al.*¹⁰ reported that lignin acted as an interfacial compatibilizer between the WG matrix and fibers, leading to an improvement of the fiber/WG matrix

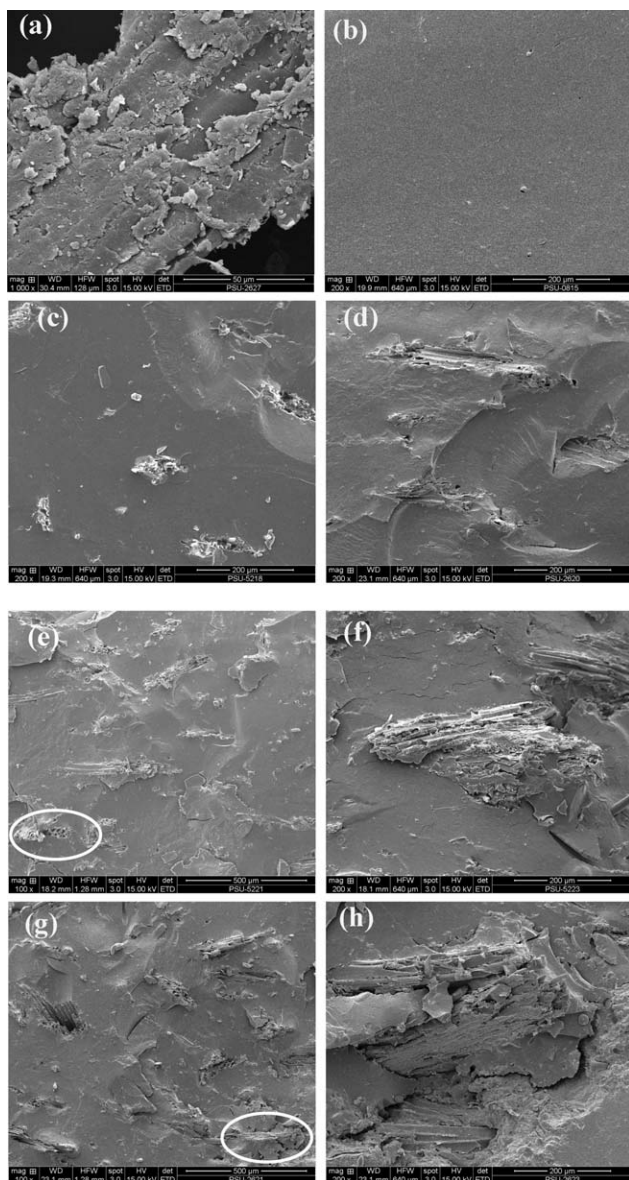


Figure 1. SEM micrographs of the surface of RWS (a), fracture surface of a neat WG based bioplastic (b), WG/RWS composites with 5 wt % (c), 10 wt % (d), 15 wt % (100 \times) (e), (200 \times) (f), and 20 wt % of RWS (100 \times) (g), (200 \times) (h).

chemical adhesion. However, the SEM micrographs of the fractured surface of the WG/RWS composites at higher RWS contents (15 and 20 wt %) [Figure 1(e–h)] revealed agglomerations of RWS in the WG matrix (marked with circles) probably due to an increase of interfiller contact as a filler (RWS) content increased.²¹ These results were similar to those of Yuan *et al.*²² who studied the structures and properties of biodegradable WG/attapulgite nanocomposite sheets. In their work, attapulgite agglomerations increased with an increase of the attapulgite powder content in the composites.

The mechanical properties of the WG based bioplastic and the WG/RWS composites are presented in Figure 2. The tensile strength of the neat WG based bioplastic was 3.40 MPa. The results showed that an incorporation of RWS strongly enhanced

the tensile strength of the WG based bioplastics. The maximum tensile strength was obtained when the RWS load was 10 wt % (5.42 MPa). This value was 59% higher than the tensile strength of the neat WG based bioplastic due to the stronger adhesion between the WG matrix and RWS as well as an improvement of a stress transfer from the matrix to the fiber leading to an increase of the tensile strength of the composites. Kunanopparat *et al.*⁸ also reported that the lignin introduced an important effect on the mechanical properties of the biocomposites as it was located on the surface of the fibers, and thus showed an amorphous structure, and performed reactively with the WG matrix. However, a higher content of RWS (15 and 20 wt %) decreased the tensile strength from 5.27 MPa to 3.73 MPa, respectively. This behavior was due to an influence of the agglomeration of RWS in the WG matrix that corresponded well with the SEM micrographs (Figure 1). However, the tensile

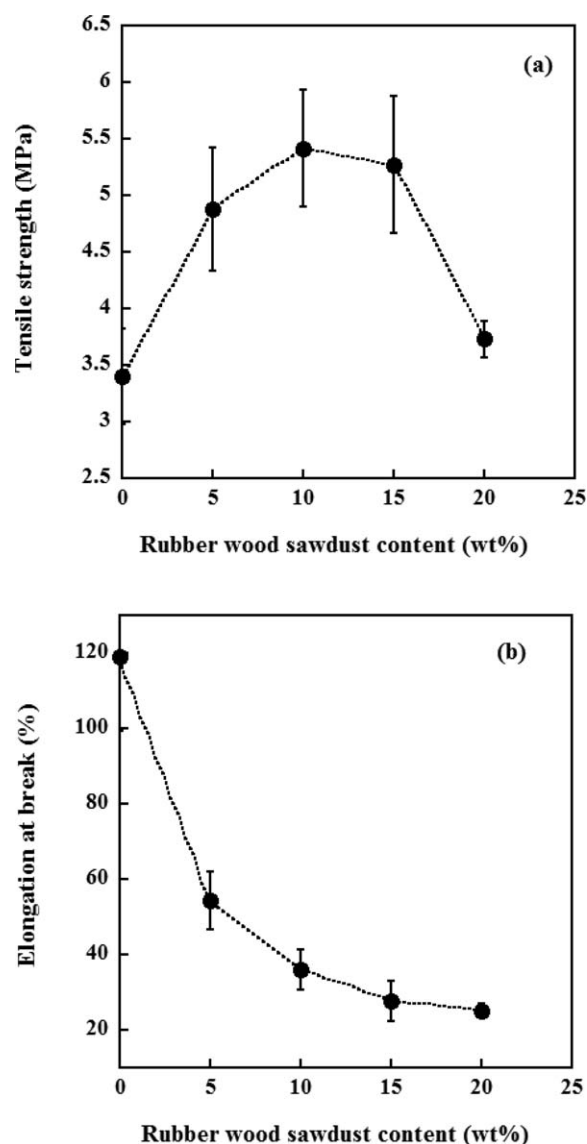


Figure 2. Tensile strength (a) and elongation at break (b) of the neat WG based bioplastic and WG/RWS composites.

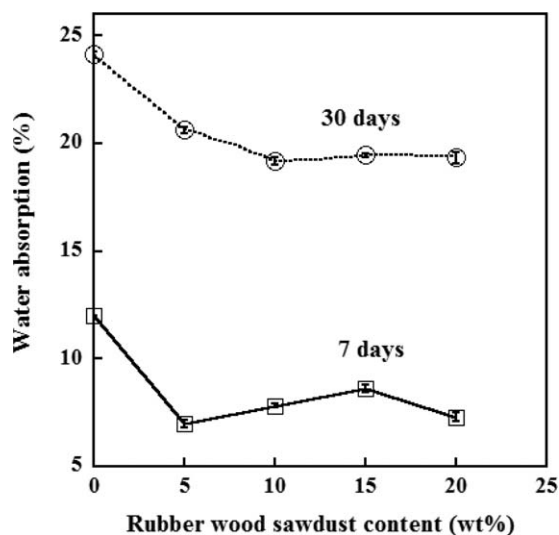


Figure 3. Water absorption (%) of the neat WG based bioplastic and the WG/RWS composites during storage at $66 \pm 2\%$ RH for 7 and 30 days.

strengths of the WG/RWS composites were still higher than that of the neat WG based bioplastic.

An addition of RWS resulted in a significant decrease of the elongation at break [Figure 2(b)]. The reason was that the flexibility of the polymer decreased due to a strong adhesion between the WG matrix and RWS. This behavior was usually observed when the WG-based materials were reinforced.²³ A similar trend was obtained in the green biocomposites from the WG and hydroxyethyl cellulose. It was reported that the elongation at break decreased with an increase of the hydroxyethyl cellulose contents due to the strong interactions, hydrogen bonding, and other physical forces, with the WG matrix.²⁴

The effect of RWS on the water absorption of the WG based bioplastic, was performed at $66 \pm 2\%$ RH for 7 and 30 days, and results are shown in Figure 3. The water absorption of the neat WG based bioplastics was about 12% and 24% after storage for 7 and 30 days, respectively. It was clearly observed that an addition of RWS significantly decreased the water sensitivity of the WG composites probably due to (1) its hydrophobic characteristics and the three dimensional network of lignin^{23,25} and (2) a strong adhesion between the RWS and the WG matrix.^{3,26} This behavior correlated with the results of Chevillard *et al.*²⁶ that there was a good interaction between the fillers and protein chains that reduced interactions between the composite and water molecules leading to a restriction on water penetration. However, after the same storage time, the amount of RWS showed only a slight impact on the reduced water absorption by the WG based bioplastics.

Figure 4 revealed the weight losses of the WG based bioplastics and the WG/RWS composites containing a 10 and 20 wt % of RWS after burial in the soil for 15 and 30 days. During the initial period, (after burial in soil for 15 days), the weight losses of the neat WG based bioplastic and the WG/RWS composites with 10 and 20 wt % of RWS were 18.53, 22.69, and 23.93%, respectively. These losses were due to the loss of the glycerol used as a plasticizer in all samples, as confirmed by the

derivative thermogravimetric (DTG) curves (Figure 5). The leaching of glycerol from the protein-based biocomposites was reported as a result of the drainage of the soil water during the soil burial test. Moreover, the study of the biodegradation of the biocomposites by Mohanty *et al.*²⁷ showed that the small molecule (glycerol) was easily digested by micro-organisms. Figure 5(d) showed the DTG curve of the RWS presenting two peaks. The first peak had a shoulder around $310\text{--}340^\circ\text{C}$ that was attributed to the decomposition of hemicellulose and the pectin, and other small molecules in RWS.^{11,17,28} The second peak was a major peak at $340\text{--}380^\circ\text{C}$ that correlated to the decomposition of cellulose that was the main component of RWS.¹¹ These results agreed with the results of Wei *et al.*²⁸ in which lignin and natural wax in the ligno-cellulosic materials degraded at $250\text{--}600^\circ\text{C}$. The DTG curves of the neat WG based bioplastic and the WG/RWS composites with 10 and 20 wt % of RWS before and after burial in soil for 15 days are presented in Figure 5. The DTG curves of the samples before burial in soil showed two peaks. The first, a small peak at $218\text{--}277^\circ\text{C}$, was assigned to glycerol removal.^{19,29} These results are in agreement with those reported by Gomez-Martinez *et al.*²⁹ for the thermal degradation of WG and gluten/glycerol based bioplastics. They showed that a higher glycerol/gluten ratio led to a stronger peak signal. The second peak that appeared at approximately $280\text{--}385^\circ\text{C}$ was due to the decomposition of WG and cellulose in the RWS.^{11,30,31} However, it was difficult to observe an actual peak position because of an overlap between the WG and cellulose in the RWS. It was of interest that, the DTG curves for all samples after burial in soil for 15 days no longer showed a small shoulder at $218\text{--}277^\circ\text{C}$ but exhibited a single decomposition peak for WG and cellulose in the RWS. These results confirmed that the weight loss during the initial period of soil burial of the WG based bioplastic and the WG/RWS composites was due to the loss of glycerol.

After burial in soil for 30 days (Figure 4), the weight loss of the WG/RWS composite with 10 wt % of RWS, i.e., a low

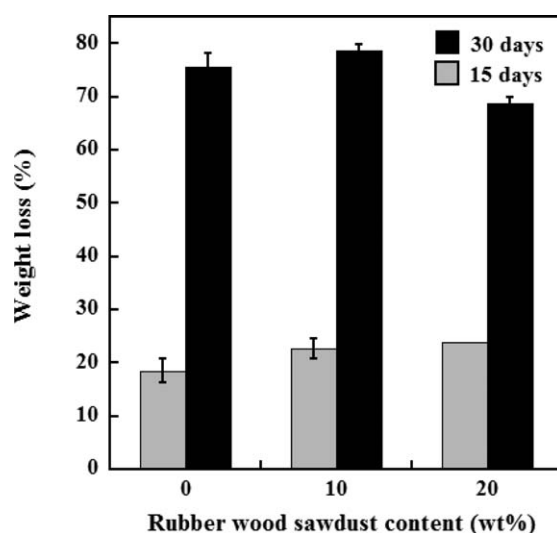


Figure 4. Weight loss of the neat WG based bioplastic and the WG/RWS composites with 10 wt % and 20 wt % of RWS after burial in soil for 15 and 30 days.

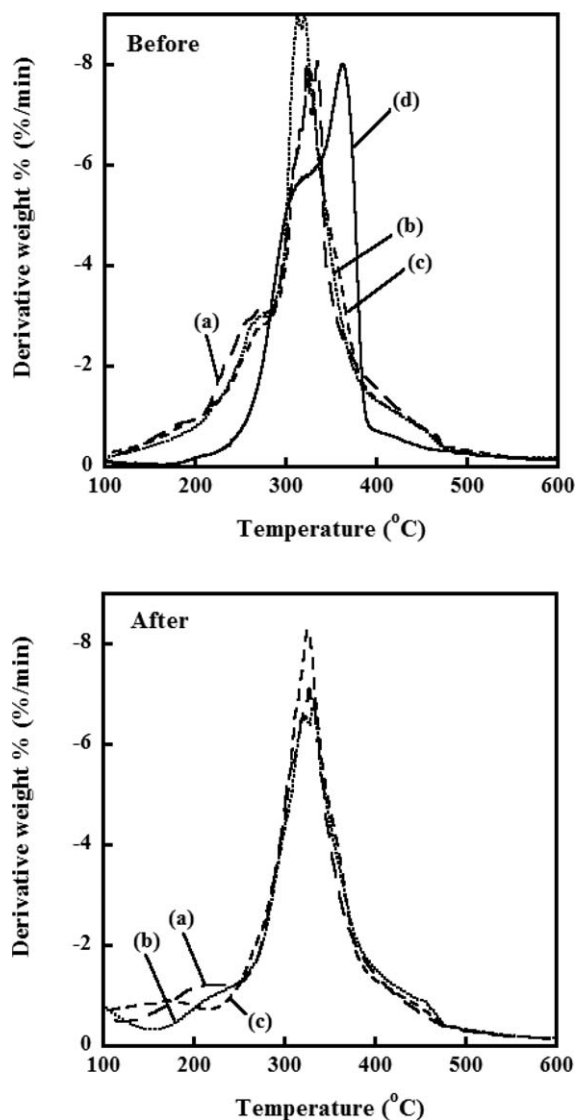


Figure 5. DTG curves of the samples before and after burial in soil for 15 days; neat WG based bioplastic (a), WG/RWS composites with 10 wt % (b), 20 wt % of RWS (c), and RWS (d).

composition of cellulose, was comparable to the control experiment (0 wt % RWS) (78.52% and 75.65%, respectively). Whereas, the WG/RWS composite with 20 wt % of RWS, i.e., a high composition of cellulose, showed a decrease in weight loss (68.63%) due to the lower degradation rate, a higher resistance to microbial attack, and a better restriction to the hydrolytic enzymes of the RWS fibers compared to the wheat gluten.³² As a result, the composite with a higher amount of RWS showed a lower weight loss after the biodegradation process. Similar findings were explained by Corradini³¹ in that the starch/gluten/glycerol composite without and with 10 wt % of coconut fiber showed a similar degradation rate whereas an addition of a higher coconut fiber content (30 wt %) caused a decrease of the degradation rate. They reported that the lignocellulosic fibers improved the resistance to microbial attack and inhibited the availability of hydrolytic enzymes to the starch/gluten/glycerol

matrix. This indicated that the amount of RWS did affect the biodegradation of the biocomposites.

CONCLUSIONS

The rubber wood sawdust effectively improved the tensile strength and water resistance of the wheat gluten based bioplastics. The maximum tensile strength (5.42 MPa) was obtained when the RWS content was 10 wt %. An addition of RWS of only 5 wt % significantly decreased the water sensitivity of the WG based bioplastics. During the first period of soil burial (15 days), the change of weight loss resulted from the loss of glycerol throughout the process of biodegradation. Later (after burial in the soil for 30 days), the biodegradation rate of the WG/RWS composites containing 20 wt % of RWS was slower than that of the WG based bioplastics because of the lignocellulosic fibers that retarded the biodegradation process. The WG/RWS bioplastic in this work can be degraded within 15 days of soil burial. This property leads to a possible application as a biodegradable flower pot to replace commercial non-degradation petroleum-based plastics.

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