



Biocomposites of wheat gluten and sawdust: effect of matrix composition on structure and mechanical properties

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Abstract

A recent interest in green polymeric materials for general application has been growing. The public's demand for environmentally products has also motivated the development of green composites. Two of the most interesting biodegradable materials in this field are wheat gluten and sawdust. Wheat gluten (WG) is an abundant inexpensive natural protein derived from wheat. It is insoluble in water and has good viscoelasticity and biodegradability. Sawdust is a by-product of cutting, grinding, and drilling wood. In this work, the biocomposites of WG and sawdust were prepared by thermo-molding at 130°C under an applied force of 60 tons for 10 min. Without plasticizer, WG-based materials can be quite brittle. Glycerol (Gly) was, therefore, used to improve flexibility of the biocomposites in this work. The effect matrix composition at different ratios of WG:Gly (i.e. 6:4, 7:3 and 8:2, respectively) on structure and mechanical properties of the biocomposites was studied. It was found that the bulk density of the biocomposites with different matrix compositions was similar, ~1.26-1.31 g/cm³. The flexural tests indicated that the matrix composition of the biocomposites greatly affected their mechanical performances. The biocomposite with matrix composition of 6:4 presented the lowest strength and modulus but having good flexibility. With increasing WG content in the matrix composition, a large increase in strength and stiffness of the biocomposites were gained. However, the composites were more brittle. SEM results also suggested that too high content of Gly can lead to a poor interfacial interaction between the matrix phase and sawdust reinforcing particles.

Keywords: biocomposites, wheat gluten, sawdust, scanning electron microscopy, mechanical properties

Introduction

At present, the accumulation of the plastic waste has become an important environmental concern. Biodegradable polymers have created an increasing interest because of their potential to solve this problem and this has led to further interest on “ecocomposites” or “green composites” (Kaewtatip et al. 2013). This type of composites is considered environmental friendly since the polymer matrix is biodegradable and come from renewable sources. Therefore, polymer-based ecocomposites have been focused and their market is continuously growing (Mantia and Morreale 2011). The composites is generally known as a combined system of a polymer and one (or more) solid fillers such as glass fiber, synthetic filler, and natural fibers which allows several advantages in the end composite products (Moigne et al. 2011). The fillers play an important role in improving the properties of the

polymer-based. Currently, the biodegradable fillers were of considerable interest. Among the fillers used, natural fiber (pineapple leaves, husk, sawdust, coconut coir, etc.) is a very promising class of reinforcing agents. As compared with classical glass fibers: natural fibers are lower in density, coming from renewable resources and much less abrasive which is important in view of processing (Moigne et al. 2011). For the natural filler, sawdust, the waste from cutting of wood or otherwise is considered as a cheap and locally available resource. Recently, Kunanopparat and co-workers (2008a and b) reported the addition of wood in plasticized wheat gluten improved the composite overall mechanical properties, but decreased its elongation at break.

Numerous protein sources (soy, cottonseed, and wheat) have been proposed for the preparation of biodegradable materials. Among candidate proteins, wheat gluten (WG) has been widely studied due to its viscoelastic properties, low cost, and biodegradability (Payne and Corfield 1979). WG is unique among other plant proteins in its ability to form a cohesive blend with viscoelastic properties once plasticized. It is able to form network upon thermosetting, so that it can be processed into films and plastics conveniently through thermoplastic molding (Cuq et al. 2000). During molding, WG proteins are cross-linked together (Jansens et al. 2011). Plasticizers like glycerol are frequently used to reduce the brittleness of WG-based materials (Pommet et al. 2005). Addition of glycerol increased the failure strain at the expense of modulus and strength of materials (Gallstedt et al. 2004). It has been also reported that, at high content of plasticizer, the material tends to be rubbery at room temperature (Lagrain et al. 2010). In this present work, the objectives were to prepare WG-based biocomposites reinforced with sawdust in various matrix compositions. Glycerol (Gly) was used as a plasticizer in this biocomposite systems. The effect of different ratios of WG:Gly (i.e. 6:4, 7:3, and 8:2, respectively) in the matrix phase on morphologies and properties of the biocomposites was investigated by scanning electron microscopy (SEM), bulk density analysis, and mechanical test (UTM).

Methodology

Materials

Sawdust was supplied from Chiang Sean district, Chiang Rai, Thailand. It was sieved into the range of desired particle sizes of 500-2500 μm . Wheat gluten powder was purchased from Zhangjiagang Hengfeng Starch Products Co. Ltd., China. Glycerol was supplied by Unionscience Co. Ltd., Chiang Mai, Thailand.

Preparation of the biocomposites

The biocomposites were prepared by mixing WG, Gly, and sawdust together by hand for 10 min. The ratio of the matrix (WG and Gly) phase to the discontinuous phase (sawdust) was fixed at 50/50wt%. For the matrix phase of the biocomposites, the ratio of WG to Gly was varied at 6:4, 7:3, and 8:2, respectively. After mixing, the mixture was placed in the metal mold with cavity size of 13 cm \times 17 cm \times 0.3 cm and compressed at 130°C in a hot press machine (Scientific LP-S-80, Labtech engineering company Ltd.). A force of 60 tons was

directly applied to the sample in the mold for 10 min. Then, the specimen was cooled for 5 min at a cooling rate of 10°C/min.

Bulk density analysis

The density of the biocomposites was determined by their volumes and masses. The sample overall dimensions were measured using a digital vernier caliper. Three measurements were made of each dimension. The mass of specimen was measured after conditioning the specimen in 50% relative humidity over a saturated salt solution of $\text{Mg}(\text{NO}_3)_2$ at least 40 hrs. The density was calculated by following equation;

$$\text{Density (g / cm}^3\text{)} = \frac{\text{Mass (g)}}{\text{Volume (cm}^3\text{)}}$$

Mechanical Test

Flexural tests (3-point bending) were performed on Universal Testing Machine (UTM, Instron tensile tester, model 4201), according to ASTM D6109. The biocomposite specimens were cut into a rectangle shape with dimension of approximately 2.0 cm × 8.2 cm and preconditioned at 50% relative humidity over a saturated salt solution of $\text{Mg}(\text{NO}_3)_2$ at least 40 hrs. All tests were performed at room temperature. Flexural strength is equal to the maximum stress in the outer fibers at the maximum load, load of rupture, or when the strain reaches 3%, whichever occurs first. Modulus was calculated based on slope of initial linear portion of load-displacement curves. All flexural properties were evaluated from at least five duplicates and reported as averages values with $\pm\text{SD}$.

Scanning Electron Microscopy (SEM)

Fractured surface morphology of the biocomposites after the flexural test were observed by a scanning electron microscope (LEO/1450 VP), using a voltage of 10 kV. Each biocomposite samples were deposited on carbon tape mounted on an aluminum stub and then gold-coated to make the samples conductive.

Results and Discussion

Bulk density of the biocomposites

Table 1 shows the bulk density of the biocomposites with different matrix compositions. The highest density was found in the biocomposite with the matrix ratio of 7:3. From the fact that WG (1.39 g/cm³) has higher density than Gly (1.26 g/cm³) (Mantia and Morreale 2011), it was initially expected that the biocomposite with the matrix (WG:Gly) ratio of 8:2 would have the highest density. However, during mixing the ingredients to prepare the biocomposites, it was noticed that with low amount of Gly, the homogeneous mixing of WG and Gly with sawdust particles was difficult to achieve. This inhomogeneity in the mixture possibly led to in the resulting composite with high porosity after thermo-molding and thus presenting the lowest density opposing to the initial expectation.

Mechanical properties of the biocomposites

The mechanical properties, i.e. modulus, strength and elongation at break values of the biocomposites with different matrix compositions are shown Table 1. From the results, it is evident that the matrix composition (ratio of WG:Gly) strongly affect the mechanical properties of the biocomposites. Figure 1 also clearly presents that the biocomposite with matrix composition of 6:4 had the lowest flexural strength and modulus of elasticity. However, this material showed good flexibility instead. For the biocomposite with matrix composition of 7:3, with increasing WG fraction in the matrix, the flexural strength and modulus of the material increased. Additionally, this biocomposite was still not broken at strain of 3%. After adjusting the matrix composition to 8:2, the considerable increase in strength and stiffness of the material was apparent. But this biocomposite exhibited much low degree of flexibility and failed at the average strain of 1.96%.

Stress-strain curves of the biocomposites with different matrix compositions are illustrated in Figure 2. It is well known that glycerol is a plasticizer that can help improving flexibility of materials. Therefore, the biocomposite with the largest fraction of Gly (the matrix composition of 6:4) exhibited the highest flexibility. This is because Gly molecules can insert in between WG protein molecules and thus lessen molecular interaction of WG proteins. With lower molecular interaction, the material can extend more under an applied force and also become weaker and less stiff. The same effects have been previously reported in the works of Kunanopparat and co-workers (2008a and b). A great reduction in modulus of the composites of WG reinforcement with natural fibers was shown when glycerol content increased.

Table 1 Bulk density and mechanical properties of the sawdust reinforced WG-based biocomposites (50wt%)

Wheat gluten : Glycerol	Bulk Density (g/cm ³)			Strain at break (%)
	Composites	Strength (MPa)	Modulus (MPa)	
6:4	1.285±0.010	9.02±0.21	867.30±45.84	*
7:3	1.312±0.068	12.48±0.23	1182.80±54.38	*
8:2	1.262±0.020	23.87±1.08	2402.60±89.24	1.96±0.15

* The specimens did not break before 3% strain.

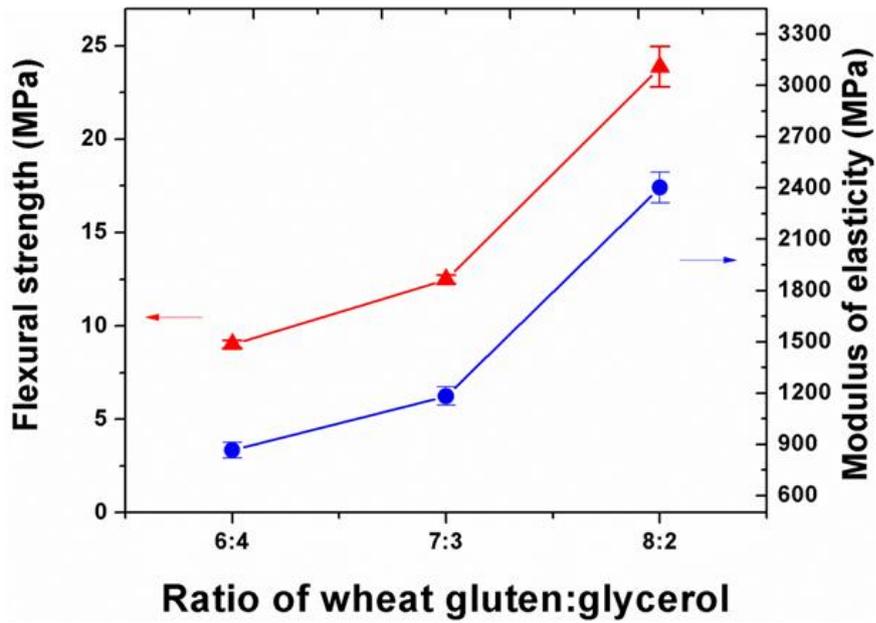


Figure 1: Flexural strength and modulus of elasticity of the sawdust reinforced WG-based biocomposites (50wt%) in various matrix compositions.

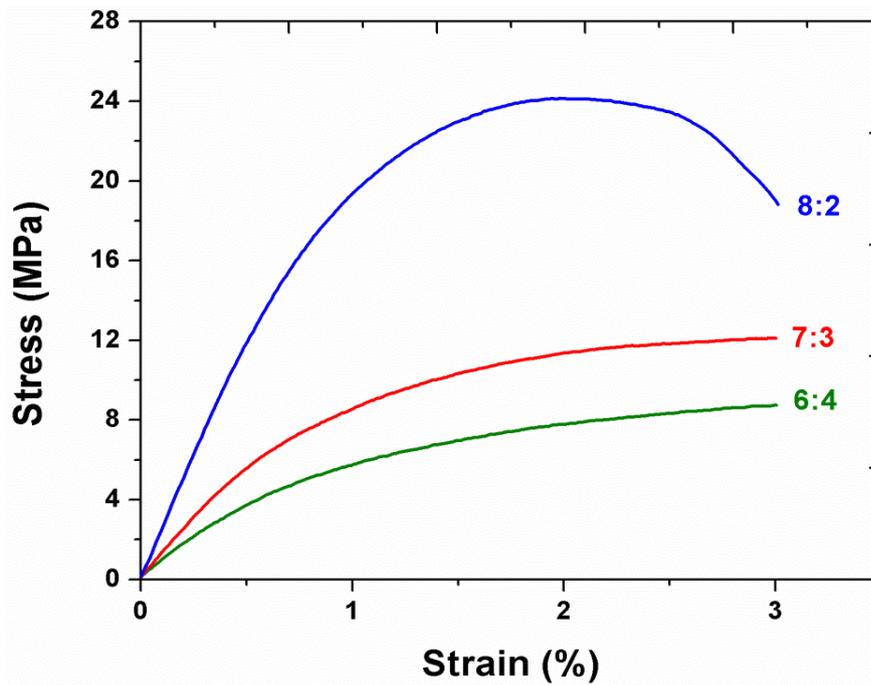


Figure 2: Stress-strain relationships of the sawdust reinforced WG-based biocomposites (50wt%) in various matrix compositions (ratio of WG: Gly).



Fractured surface morphology of the biocomposites

From SEM results, it was suggested that glycerol can also lead to a poor interfacial interaction between the matrix and sawdust particles. Figure 3a and b show the fracture surface of the composite with the matrix composition of 6:4. There are several deep and large holes appear on the fracture cross-sections which are possibly caused by sawdust particles pull-out from the matrix phase. When adjusting the matrix composition to 7:3, lower content of Gly in the composite system leads to the rougher fracture surface, revealing that sawdust particles are pull-out and partially debonded from the matrix (Figure 3c and d). Nevertheless, deep holes from sawdust particle pull-out are not clearly observed which suggests to a better interface between sawdust and matrix in this composite. With further decreasing Gly fraction in the matrix to the ratio of 8:2, the fracture surfaces of the composites are shown to be more even from the concurrent failure of sawdust particles together with the matrix (Figure 3e and f). This indicated that a good interfacial adhesion was achieved in this composite. Still, this sample was failed at the lowest strain in a brittle manner.

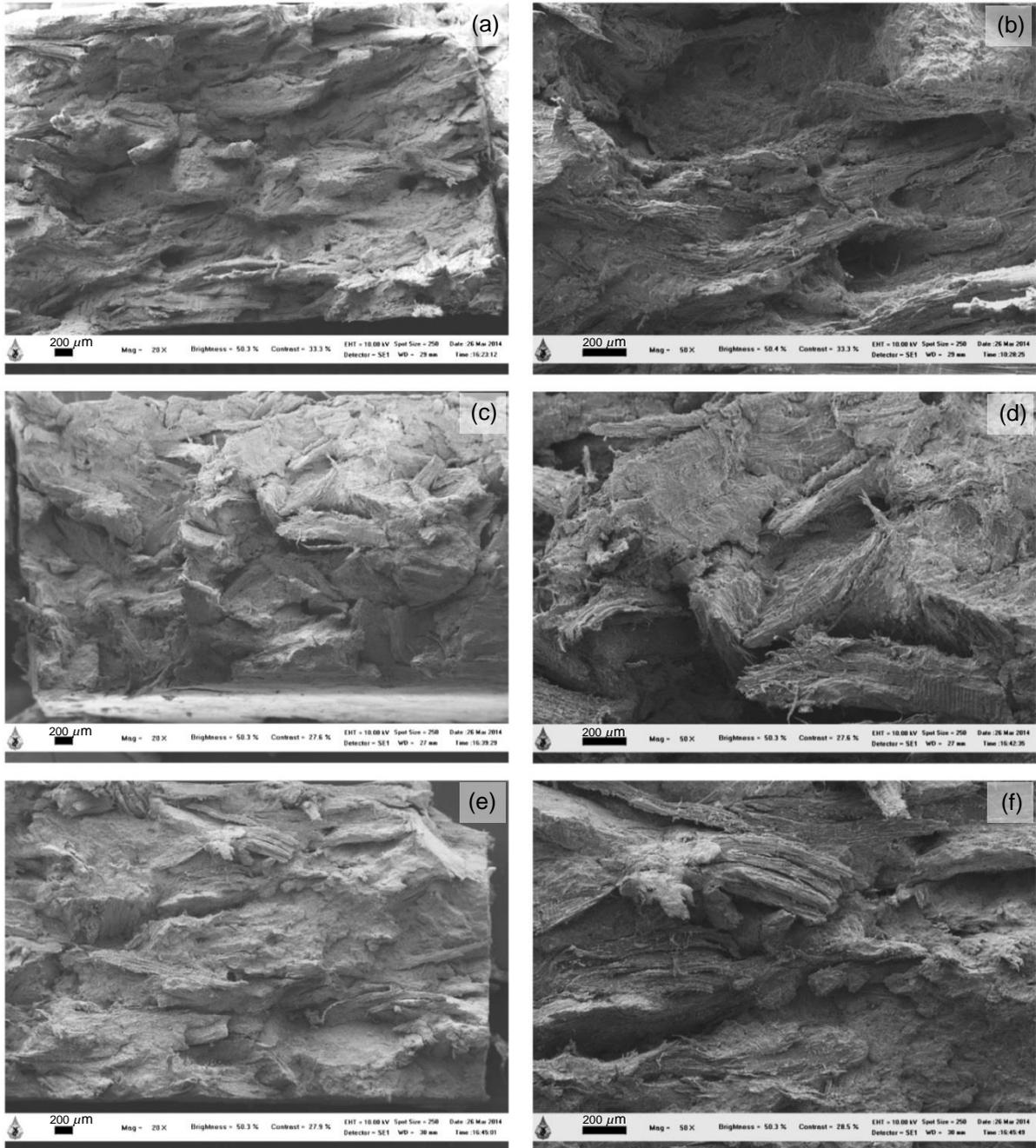


Figure 3: SEM micrographs of fracture surface of biocomposites in various compositions of WG:Gly at 6:4 (a-b), 7:3 (c-d), and 8:2 (e-f).

Conclusion

The biocomposites from sawdust in various matrix compositions of WG:Gly were prepared by thermo-molding technique. The bulk density of the biocomposites with different matrix compositions was similar in range of 1.26-1.31 g/cm³. The highest density was not found in the biocomposite with the matrix ratio of 8:2 as expected but 7:3. Low fraction of added Gly was observed to cause an inhomogeneous mixing during the biocomposite preparation which perhaps leads to high porosity in the material, hence, lower the density. From flexural test

results, it was indicated that the matrix composition of the biocomposites considerably affect their mechanical properties. The biocomposite with matrix composition of 6:4 displayed the lowest flexural strength and modulus but possessing good flexibility. This is because Gly molecules lessen the molecular interaction between WG proteins. In the biocomposite with matrix composition of 7:3, the flexural strength and modulus increased and it still was not broken at 3% extension. With the matrix composition of 8:2, a considerable increase in strength and stiffness of the biocomposites were exhibited. However, this sample was failed in a brittle manner. In addition, SEM results also revealed that high content of Gly lead to a poor interfacial interaction between the matrix phase and sawdust reinforcing particles.

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