

PREPARATION AND PROPERTIES OF WHEAT GLUTEN/RICE PROTEIN COMPOSITES PLASTICIZED WITH GLYCEROL^{*}

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Abstract Environment friendly thermosetting composites were prepared by blending wheat gluten (WG) and rice protein (RP) at different weight ratios with glycerol as plasticizer followed by compression molding the mixture at 120°C to crosslink the proteins. Reducing agent of sodium bisulfate and sodium sulfite and crosslinking agent formaldehyde were used to adjust the properties of the composites. Morphology, moisture absorption and tensile properties were evaluated. The results showed that formaldehyde could increase tensile strength of the composites without significant influence on Young's modulus and elongation at break. On the other hand, reducing agents could improve tensile strength and extensibility simultaneously, which was much marked at WG/RP ratios from 7/3 to 3/7.

Keywords: Wheat gluten; Rice protein; Composites; Mechanical properties.

INTRODUCTION

Nowadays, more attention is paid to biodegradable package films and plastics made from renewable agricultural resources^[1]. Proteins, lipids and polysaccharides have been used as biopolymer sources for many years^[2, 3]. The biodegradability of protein-based biomaterials is among the rates of fast-degrading polymers^[4]. The bioplastics and package films based on proteins extracted from various renewable plant such as soy^[5, 6], corn^[7, 8], cottonseed^[9] and wheat^[2, 10, 11] show the advantage because of their abundant resources, low cost, good biodegradability and suitable properties for usage as films and plastics.

Wheat gluten (WG) contains more than 75% proteins with 40%–50% viscous gliadins and 35%–45% elastic glutenins^[12]. WG has been widely used to prepare package films and bioplastics^[13]. WG is able to form network upon thermosetting so that plasticized WG can be processed into films and plastics conveniently through thermal molding^[14–16]. Several factors including plasticizer content, molding temperature and crosslinking type might influence moisture absorption, mechanical and dynamic mechanical properties of the final products^[1]. Additionally, reducing agents have been used to tailor the flow viscosity of the plasticized dough and the mechanical properties of the thermally molded bioplastics^[17].

Rice protein (RP) extraction contains about 70% proteins with more than 56% glutenins and less than 14% gliadins. Due to the high content of glutenins, the RP extraction could not be well plasticized using common plasticizers, which makes it difficult to prepare thermoset articles with appropriate strength and toughness. RP

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has been combined with functional polysaccharides to develop edible films using casting method^[18]. Edible films with RP to pullulan ratio of 1:1 have a good balance of tensile strength and water vapor permeability, which is not achievable for films with either component alone. Very little work has been focused on RP-based bioplastics. Thermoset RP sheet shows a complex modulus higher than that of LDPE and similar to that of HDPE^[19]. In addition, the water absorption values of RP are much lower than those of WG.

The aim of the present work was to develop WG/RP composites that may be used as biodegradable package materials. A combination of two types of proteins is expected to improve the processibility of RP using the thermal molding method and to reduce the moisture sensitivity of WG bioplastics. Reducing agents (sodium bisulfate and sodium sulfite) and crosslinking agent (formaldehyde) are used to enhance the interaction between the WG and RP molecules and to improve the final properties of the crosslinked protein network^[1]. Influence of plasticizer content is also discussed.

EXPERIMENTAL

Materials

WG powders with a protein content $\geq 75\%$ and an ash content $\leq 0.95\%$ were supplied by Shanghai Wangwei Food Co. Ltd., China. RP powders with a protein content about 70% were supplied by Shanghai Wangwei Food Co. Ltd., China. Formaldehyde, sodium sulfite, sodium bisulfite and glycerol were of analytical grade and were used without further purification.

Sample Preparation

Formaldehyde, sodium bisulfite or sodium sulfite was dissolved in deionized water to form a 10 wt% aqueous solution. Ten grams of WG/RP (10/0, 9/1, 7/3, 5/5, 3/7, 1/9, 0/10 in mass) mixture were hand-mixed with 5 g glycerol and 2 g solution of formaldehyde, sodium bisulfite or sodium sulfite in a mortar. The resultant dough was mixed on a three-rolling mixer at room temperature. The material was cold-pressed into dumbbell shape with a thickness of 1 mm and a width of 6 mm in a multicavity mold at 10 MPa for 3 min, followed by thermal molding at 120°C and 10 MPa for 10 min. Ten grams of proteins powders were directly mixed with glycerol and molded at the same condition, the samples being denoted as control A series. Before testing, the samples were allowed to rest for 48 h at room temperature.

Morphology Observation

The samples were broken in the tensile test at room temperature. Morphology of the break surface was observed with a scanning electron microscope (JSM-5510LV Low Vacuum SEM, JEOL, Japan) at 20 kV after being coated with gold.

Moisture Absorption

The specimens were preconditioned in a desiccator containing allochroic silica gel powders for a week at room temperature. After drying, the specimens were transferred into desiccators and allowed to reach moisture equilibrium with saturated solutions of sodium bromide and sodium chloride giving relative humidities of 52% and 75%, respectively, at room temperature for a week. Moisture absorption was evaluated on a dry basis and was reported as the average of three replicates at each relative humidity condition.

Tensile Tests

Tensile test was performed on a universal testing machine (CMT-4204, Shenzhen SANS Test Machine Co. Ltd., China) with an extension rate of 10 mm/min at 45% relative humidity at 25°C. Tensile strength, elongation at break and Young's modulus were evaluated from at least five duplicates for each product.

Statistical Analysis

Statistical analysis of the results for tensile strength, elongation at break, Young's modulus and moisture absorption were performed using OriginPro 7.50 software (OriginLab co., Northampton, MA, USA).

RESULTS AND DISCUSSION

Morphology

Figure 1 shows SEM micrographs taken at the break surface of the 33 wt% glycerol plasticized control A composites with different WG/RP ratios. The fracture surfaces are rather coarse and fluctuant, displaying some characteristics of tough fracture with delamination and corrugation. Spherulite-like domains with a size less than 10 μm are observed, whose number and size increase with increasing RP content of the samples. Probably, the RP particles are less plasticized than the WG ones.

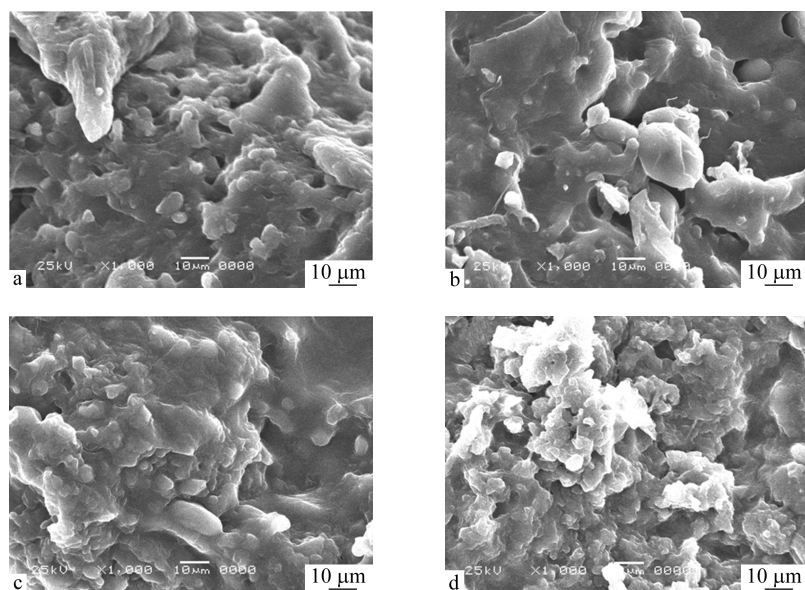


Fig. 1 SEM micrographs taken at the break surface of the 33 wt% glycerol plasticized control A composites with WG/RP ratios of 10/0 (a), 9/1 (b), 5/5 (c) and 3/7 (d), respectively

Influence of Crosslinking Agent

Figure 2 shows stress-strain curves of the 33 wt% glycerol plasticized control A composites. Young's modulus increases and elongation at break decreases with decreasing WG/RP ratio. The plasticized WG sheet is somewhat tough and exhibits large extensibility. On the other hand, the plasticized RP sheet is very brittle and breaks at very low strains.

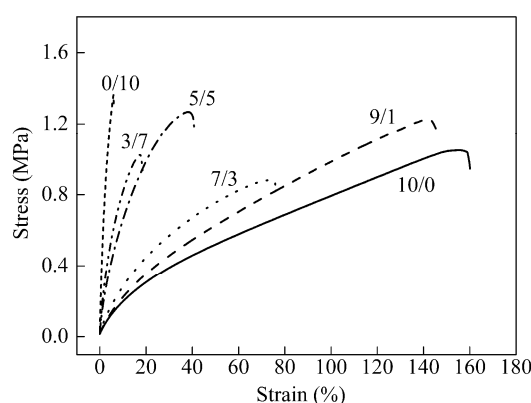


Fig. 2 Stress-strain curves of the 33 wt% glycerol plasticized control A composites with different WG/RP ratios as indicated

Figure 3 shows elongation at break, tensile strength and Young's modulus as a function of WG/RP ratio. Young's modulus decreases significantly with increasing WG/RP ratio ($p < 0.05$) and there is no significant ($p > 0.05$) difference between Young's modulus of the samples of the control A and the formaldehyde-containing series. Formaldehyde has broad reaction specificity to proteins and is able to crosslink the amine group of lysine as well as the side chains of cysteine, tyrosine, histidine, tryptophan and arginine, thus promoting the formation of intra- and intermolecular covalent bonds^[20]. Tensile strength of the control A series fluctuates around 1 MPa, being approximately independent of WG/RP ratio ($p > 0.05$). Addition of formaldehyde introduces significant increase in tensile strength ($p > 0.05$) and this effect is very marked at WG/RP ratios from 7/3 to 3/7. Elongation at break increases substantially with increasing WG/RP ratio for both the control A and the formaldehyde crosslinked series ($p < 0.05$). When WG/RP ratio is less than 7/3, addition of formaldehyde causes a slight increase ($p > 0.05$) in elongation at break, which is consistent with the previous observation in WG plastics^[1]. On the other hand, addition of formaldehyde causes a decrease in elongation at break for higher WG/RP ratio samples ($p < 0.05$).

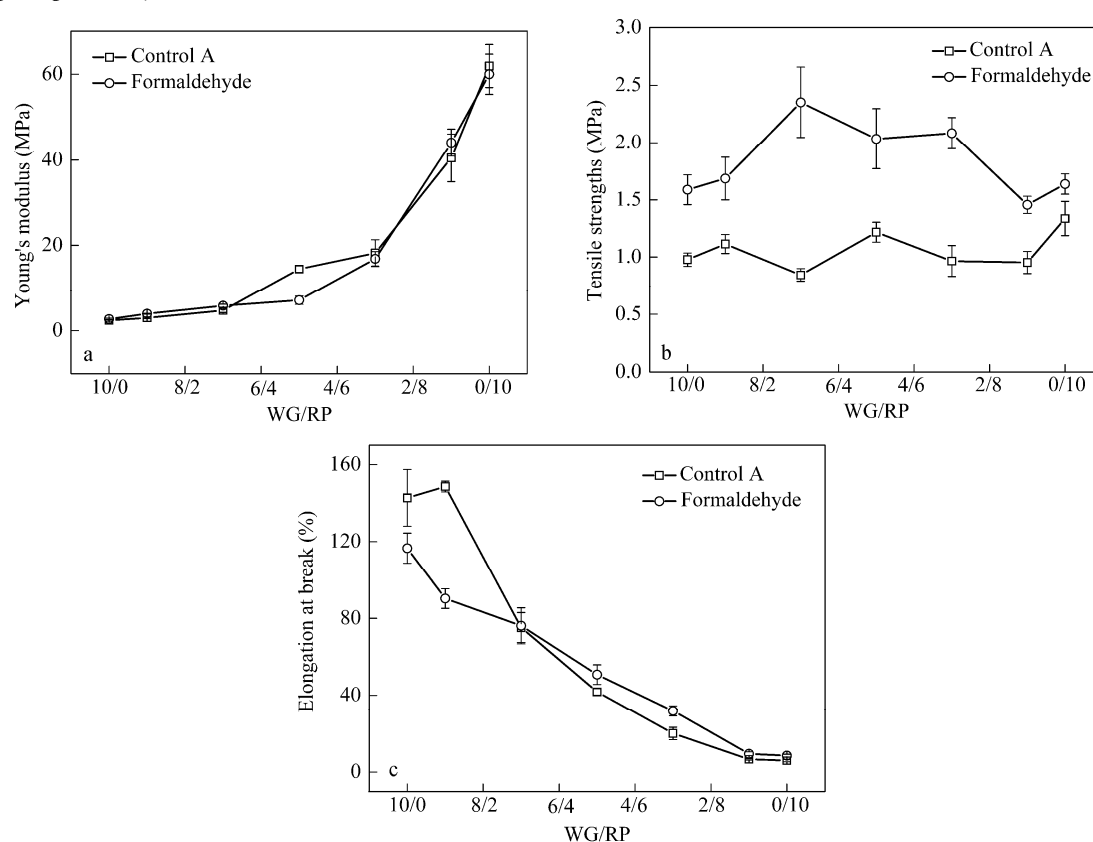


Fig. 3 Effect of WG/RP ratio on Young's modulus (a), tensile strength (b) and elongation at break (c) for the 33 wt% glycerol plasticized composites

Figure 4 shows moisture absorption of the 33 wt% glycerol plasticized WG/RP composite plastics as a function of WG/RP ratio. Moisture absorption strongly depends on the relative humidity, the values at a relative humidity of 75% are almost double of those at a relative humidity of 52%. Moisture absorption increase markedly ($p < 0.05$) as WG/RP ratio increases. In comparison with the Control A series, incorporation of formaldehyde causes a slight decrease in moisture absorption at both relative humidities.

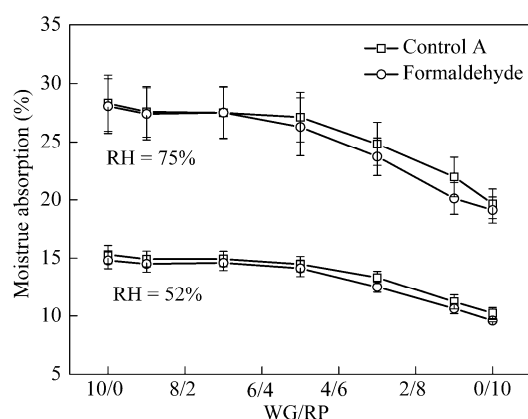


Fig. 4 Effect of WG/RP ratio on moisture absorption for the 33 wt% glycerol plasticized composites

Influence of Reducing Agent

Figure 5 shows the effect of reducing agents on mechanical properties of the composites containing 23 wt% and 33 wt% glycerol, respectively. At the 23 wt% glycerol level, Young's modulus of the Control A composites is almost independent of WG/RP ratio ($p > 0.05$) while tensile strength and elongation at break increases ($p < 0.05$) with increasing WG/RP ratio. The mechanical properties at the low glycerol level might be related to the lower plasticization effect of RC. Incorporation of sodium bisulfite or sodium sulfite leads to similar variations in

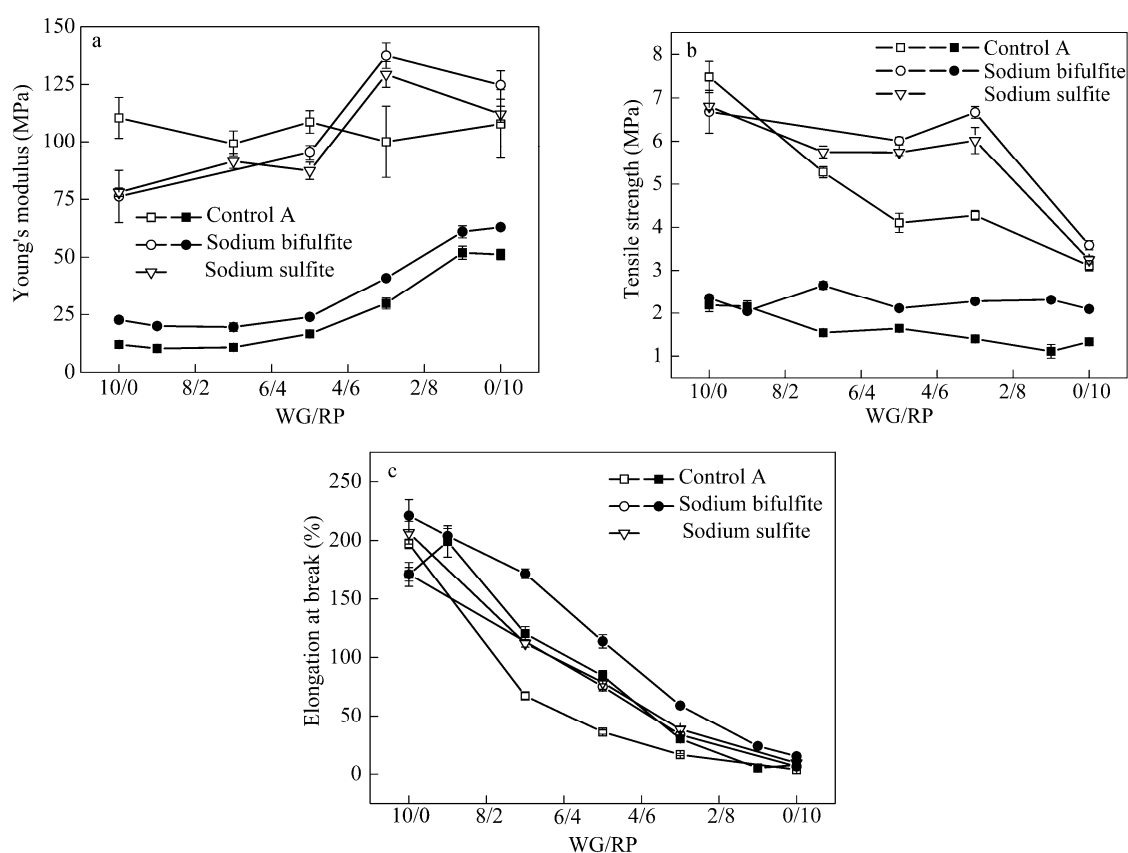


Fig. 5 Effect of WG/RP ratio on Young's modulus (a), tensile strength (b) and elongation at break (c) for the 23 wt% (hollow symbols) and 33 wt% (filled symbols) glycerol plasticized composites

mechanical properties while influence of sodium bisulfate on elasticity and strength is more marked than sodium bisulfite. The reducing agents cause Young's modulus to increase at WG/RP ratio below 5/5 and the inverse is true at high WG/RP ratios. The reducing agents lead to simultaneous decreases in tensile strength and elongation at break at WG/RP ratios from 7/3 to 3/7. At the 33 wt% glycerol level, addition of sodium bisulfate results in simultaneous improvement in Young's modulus, tensile strength and elongation at break over the Control A composites. Similarly, Sun, *et al.* found that L-cysteine additive can improve extensibility, strength and stiffness of thermo-molded WG plastics^[1].

A small number of cysteine residues on protein macromolecular chains are involved in both inter- and intra-molecular disulfide bonding, which plays an important role in the formation of protein network^[21, 22]. Reducing agents could cleave disulphide bonds to thiol groups^[23, 24] and facilitate the viscous flow of the plasticized proteins while they do not hinder the crosslinking reaction through thiol-disulfide interchange^[14, 15] during thermo-molding at high temperatures. The released thiol groups as a result of chemical reduction are converted into inter-chain disulfide bonds through the thiol-disulfide interchange reaction, allowing both WG and RP participation in the network formation during the thermo-molding^[17].

CONCLUSIONS

The mechanical properties of WG/RP composites are highly dependent on WG/RP ratio and glycerol plasticizer content. At a given glycerol level, decreasing WG/RP ratio leads to reductions in extensibility and moisture absorption greatly. Formaldehyde crosslinking could improve tensile strength greatly, which is much significant at WG/RP ratios from 7/3 to 3/7. Reducing agents could improve tensile strength and elongation at break simultaneously at the same WG/RP ratio.

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