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Plasticization of Wheat Starch-Gluten Mixture under an Elevated Temperature

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Wheat starch-gluten mixture was converted into a bioplastics like material (bioplastics) under processing at an elevated temperature. The density of the bioplastics was 1.24-1.26 g/cm^3 depending on the ratio of starch to gluten. The color difference of the bioplastics was altered with the starch-gluten ratio. Endothermic peak by differential scanning calorimetry was considerably decreased with the increase of the ratio of gluten to starch. It was revealed that the physical characteristics of the bioplastics were dependent on the starch-gluten ratio and that wheat starch and gluten interacts at their interface with the increase of the glass-transition temperature.

INTRODUCTION

Wheat starch is normally composed of highly branched amylopectin molecules, the partially crystalline component, and essentially linear amylose molecules that are apparently amorphous in the starch granule (Zeleznak and Hoseney, 1987). It has also been described that wheat gluten is an amorphous random polymer which has basically no long-range order (Hoseney ***et al., 1966).*** These natural biopolymers can be melted under an elevated temperature with the proper moisture content. Bioplastics can be prepared by cooling molten biopolymers. Characteristics of the bioplastics prepared by the procedure (melt to cool) can perform important roles in the development of new food processing technologies. One of such examples is the extrusion processing of food materials (Davidson ***et al.,*** 1984; Lawton ***et al.,*** 1985). Physical properties of the bioplastics processed from wheat starch and gluten could provide an important information in studying such a processing technology. However, a few fundamental study on the physical properties have been reported to date. The paper by Khoda and Komiya (1971) dealt with the characteristics of cereal-plastics processed from wheat flour and rice grain. More recently, Lim and Fujio (1988) and Fujio and Lim (1989) reported the characteristics of bioplastics prepared from wheat starch and wheat gluten under air-tight compressed conditions.

This paper deals on the characteristics of the bioplastics prepared from wheat starch-gluten mixture and the interaction between wheat starch and gluten during the processing.

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MATERIALS AND METHODS

Raw materials and sample preparation

Wheat starch and wheat gluten (reagent grade, Ishizu Pharmaceutical Co. Ltd.) were mixed in a mixer (National Electric Co., Ltd., Cook Master, MK-6000) to give ratio of starch to gluten of 4:0, 3:1, 2:2, 1:3, and 0:4. Moisture contents of the wheat starch-gluten mixture were adjusted to 13% (w/w) and 23% by adding a calculated amount of ice powder at -20°C to the mixture as described in the previous report (Fujio *et al.*, 1988). Distilled and deionized water were used throughout all experiments.

Heat-processing conditoins

Koka Flow Tester (Shimadzu Seisakusho Co. Ltd., Model 61323) was used for heat -treatment of the mixture under stress pressure by plunger. The outline of the flow tester, details of the plunger loaded on cylindrical heating cell, and experimental procedures used for this study have been described in the previous report by Fujio *et al.* (1988). By the similar procedures, the mixtures were heat-processed at 80°C and 160°C under the pressure of 200 Kg/cm^2.

Measurement of color difference (4E)

The changes in color differences of the bioplastics prepared under the various conditions were measured with a chroma meter (Minoruta Camera Co., Ltd., CR-100) using the true daylight. A standard white tile was used as a reference for determining the change "E" in color difference. The processed bioplastics were placed on the standard white tile and the surface color of the bioplastics was measured by the chroma meter equipped with a circumferential sensor. The difference in color was determined as the color difference by the built-in memory of the instruments.

Measurement of density

The bioplastics from the flow tester, after being heated and subsequently cooled, showed a circular cylindrical shape with 11.3 mm in diameter (1.0 cm^2 in cross sectional area). Therefore the densities of the bioplastics sample were determined by simply measuring the length and the weight of the sample.

Measurement of cold-water solubility

Five hundred mg of the ground bioplastics sample was dispersed in 30 ml of deionized water and the resultant suspension was stirred for 1 h at the room temperature (ca. 25°C). The same procedure was repeated one more time in order to thoroughly extract water soluble fraction from the ground sample. The suspension was then centrifuged at 9,500Xg for 30 min in order to separate the supernatant solution from the water insoluble residue. The supernatant liquid and the water insoluble residue were separately dried out in an oven at 105°C to determine the weight of water soluble and insoluble fraction. The amount of soluble fraction was expressed as the percentage toward the initial sample weight.

Differential scanning calorimetry (DSC)

Ground bioplastics sample was heated in a differential scanning calorimeter

(Seiko DSC-100, Seiko Electric Co., Ltd.) in order to determine the thermal transition. The ground sample prepared from each bioplastics was precisely weighed in a silver anti-leak pan. Moisture content of the sample in a silver pan was adjusted to about 70% (by adding desired amount of distilled water) and about 4% (dry basis). After weighing the pan with the sample, the pan was covered with a silver lid using pan-press. Seal of the lid was intact at 200°C applied during the integrity test. Another pan containing the same weight of water was used as a reference in the case of the samples of 70% moisture content, while an empty pan was used as a reference for the samples of 4% moisture content. Calibration of DSC was carried out by measuring the melt enthalpy and the glass-transition point was carried out under the heating rate at 5°C per min. The enthalpy was determined based on the area of endothermic peak and the glass-transition point was determined by finding the mid-point of the transition in the heat capacity.

RESULTS AND DISCUSSION

Change in density

Figure 1 shows the changes in density of bioplastics prepared from wheat starch -gluten mixtures as a function of starch to gluten ratio. The density of the bioplastics prepared from gluten only was about 1.24-1.26 g/cm^3. As the starch content increased, the density of the bioplastics linearly increased in all treatment conditions except in the case of the condition of 80°C and 13% moisture content. At the condition of 80°C and 13% moisture content, starch cannot be melted while gluten is completely plasticized, as reported in previous paper (Lim and Fujio, 1988). As a result, the bioplastics prepared from wheat starch only at this condition has a porous appearance, allowing loosely arranged heterogeneous structure. When the gluten is added to starch, however, the plasticized gluten at this condition penetrates into the porous starch and fills up the pore of bioplastics, resulting in the increase of density. This fact indicates that the bioplastics prepared from wheat starch-gluten mixture have more dependency on the starch-gluten ratio.

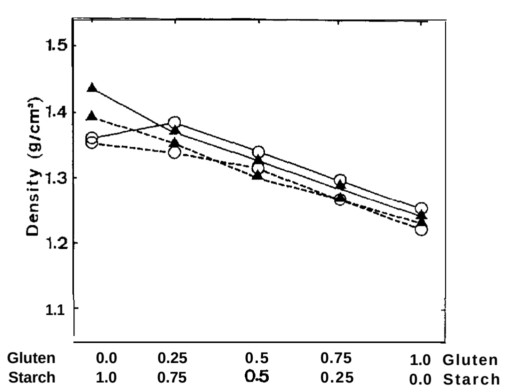

Fig. 1. Changes in density of bioplastics prepared from starch and gluten mixture. —, 13% moisture; ---, 23% moisture; O, 80°C; ▲ 160°C.

Change in color difference

Figure 2 shows the change of the color difference of bioplastics processed at 80” C and 160°C with starch-gluten ratio. The color difference value for process temperature at 160°C was maintained at a 4E value of around 50, independent of the starch-gluten ratio and moisture content. However, in the case of process temperature of 80” C, the 4E value was increased with an increase of starch-gluten ratio and was converged at a 4E value of 50. It is speculated from these findings that bioplastics prepared from completely plasticized wheat starch and/or gluten give almost same color difference value, and gluten is more easily plasticized than starch at low heating temperature. Therefore, the color difference value of bioplastics from the starch-gluten mixture at low heating temperature is mainly dependent on the starch-gluten ratio. This result also suggests that the color difference value can be used-to estimate the level of plasticization of wheat starch and/or gluten.

DSC thermogram behaviour of bioplastics

Figure 3 shows the DSC thermograms of the bioplastics processed from wheat starch-gluten mixtures at 80°C and 13% moisture content. Generally, in the case of a semicrystalline material, the crystallinity is dispersed in a homogeneous amorphous matrix. Furthermore, as the polymer chains are accommodated in the crystallites, the remaining disordered segments are under tension and thus do not possess the typical characteristics of a bulk amorphous phase (Biliaderis et *al.*,1986). Thus changes in heat capacity at glass-transition temperature become less conspicuous and more difficult to detect at higher moisture content. Therefore, in Fig. 3A it was measured at about 4% moisture in order to detect the change in heat capacity in DSC thermogram. In Fig. 3A, the curve for’starch only shows two endothermic peaks at 61°C and 101°C. Endothermic enthalpies of these two peaks are 4.0 cal/g and 0.5 cal/

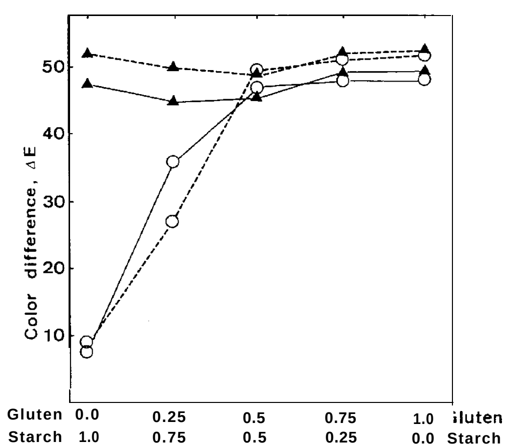

Fig. 2. Changes color difference of bioplastics prepared from starch and gluten mixtures.
—, 13% moisture; ---, 23% moisture; 0, 80°C; A 160°C.

g respectively, which is almost same with the two peaks for the natural wheat starch (Lim and Fujio, 1988). Endothermic peak significantly decreased with the increase of gluten content, and was too small to detect for gluten only. The DSC patterns (not shown) for bioplastics processed at other treating conditions were similar to the curves shown in Fig. 3.

Table 1 summarizes enthalpies of endothermic peaks within the limit of the process conditions of bioplastics. As it is clear in Table 1, the integrated enthalpies for the samples drastically decreased with the increase of the process temperature, moisture and gluten content. From this result, it can be concluded that the higher the process temperature and the moisture, the greater is the degree of randomness in starch molecule arrangement in the resultant bioplastics. On the other hand, the endothermic peaks could be interpreted as showing the thermal behaviour of straight starch, since DSC thermograms for straight gluten showed that the enthalpies of the transitions that could be assigned to the straight gluten were less than 0.1 Cal/g-gluten (Hoseney et ***al.,*** 1986; Eliasson, 1983; Eliasson and Hegg, 19800).

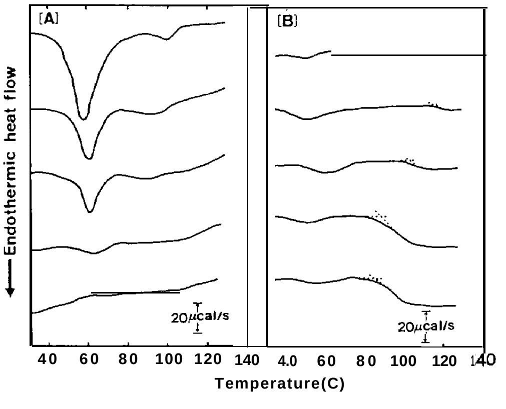

Fig. 3. DSC thermograms of bioplastics prepared from starch and gluten mixture. Heat process conditions were 13% moisture, 80°C and 200 kg/cm^2. A and B were measured at ca. 70% and 4% moisture, respectively. The ratios of starch to gluten are 4:0, 3:1, 2:2, 1:3 and 0:4 (top to bottom).

Table 1. Enthalpies of endothermic peaks (cal/g)* at about 61°C of bioplastics prepared from starch and gluten mixtures.

Treating condition		Starch : Gluten				
Temp.	Moisture	4 : 0	3 : 1	2 : 2	1 : 3	0 : 4
80°C	13%	4.2	1.7	1.3	0.4	
	23%	2.0	1.5	0.8	0.3	
160°C	13%	1.4	1.1	0.9	0.4	
	23%	0.5	0.5	6.8	0.4	—

*; measured at ca.70% H_2O
—; not detected

Table 2 shows the change in the glass-transition temperature (Tg, changes in heat capacity as shown in Fig. 3B) measured by DSC at about 4% moisture. The wheat gluten used in this study showed only a change in heat capacity at 80-90°C, and showed in endothermic peak when the moisture content was about 4% (Lim and Fujio, 1988). The glass-transition temperature remarkably increased with the increase of starch content at all treatment conditions. From these results, it is speculated that the presence of unmelted starch crystallites suppresses the change in specific heat at Tg, and increases the Tg by interaction at the interface between the amorphous parts of gluten and the crystalline regions of starch. It can be also thought that the interaction between the molten starch and gluten, such as physical cross-links, added the rigidity to the amorphous region and restricted the segmental motion of gluten molecules.

Changes in cold-water solubility

Figure 4 shows the changes in cold-water solubility of bioplastics prepared from wheat starch-gluten mixtures at various process conditions. The water solubility of bioplastics prepared at 80°C temperature was around 5%, independent from the starch -gluten ratios. This value also corresponded with that of untreated starch and/or

Table 2. Glass transition temperatures (°C)* of bioplastics prepared from starch and gluten mixtures.

Treating condition		Starch : Gluten				
Temp.	Moisture	4 : 0	3 : 1	2 : 2	1 : 3	0 : 4
80°C	13%		115.2	99.6	91.9	90.1
	23%		101.8	101.9	97.1	82.9
160°C	13%		100.9	83.9	80.4	78.1
	23%		109.1	96.7	85.5	82.1

*; measured at ca.4% H_2O
—; not detected

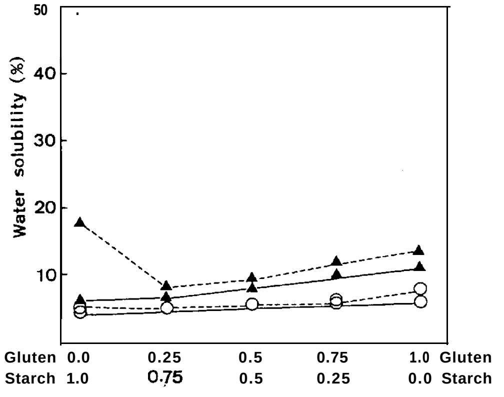

Fig. 4. Cold water solubility of bioplastics prepared from starch and gluten mixtures. —, 13% moisture; ---, 23% moisture; O, 80°C; ▲ 160°C.

gluten mixtures. At 160°C and 23% moisture, at which condition the starch was completely melted, starch showed a higher water solubility at 18%. The water solubility, however, drastically decreased to about 8% when gluten was added. From the observation in Fig. 4, it can be concluded that the molten starch interacts with the plasticized gluten at interface during plasticization process as mentioned above and become insoluble in cold water.

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