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Reduction of gelatinization temperatures of starch blend suspensions with supercritical CO_2 treatment

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ABSTRACT

Modification of starch blend properties by contact with supercritical carbon dioxide ($scCO_2$) was studied. Potato starch (PS), sweet potato starch (SPS), and cassava starch (CS) were blended with wheat starch (WS) at 15, 25, 50, 75 and 85% (w/w) ratios. For WS, the maximum decrease in gelatinization temperature (T_P) was 13 °C. The WS–PS and WS–CS blends exhibited a decrease in T_P of 13 to 17 °C. Reduction in T_P by treatment was 10 to 18 °C for all blend ratios. Conditions for lowering the starch blend T_P were determined to be a minimum contact time of 1 h with $scCO_2$ at 60 °C and 20 MPa. Swelling of starch granules that leads to the lowering of T_P involves both kinetic and physicochemical factors. Gelatinization of wheat starch blends with $scCO_2$ pressure treatment provides a versatile and non-thermal method for modifying the properties of ingredients used in food processing applications.

1. Introduction

Starch is a carbohydrate that consists of numerous glucose units joined by glycosidic bonds that are insoluble in water at room temperature [1]. Starch is widely used in the food industry for conditioning of dough in bread manufacturing, for thickening of soups and sauces and for stabilizing ice cream [2–5]. To improve its versatility, starch can be blended from different origins to improve the rheological behavior, pasting, gelatinizing and textural properties of the mixtures [6,7]. The modification of the properties of starch, not only through blends, but by thermal, mechanical or chemical treatment is very important in many applications [3].

Gelatinization of starch is one of the most important properties that is used for making starch edible and for making its structure accessible via swelling [8]. In the process of gelatinization, irreversible changes occur in the starch granule structure that significantly influences its properties and reactivity [9]. Differential scanning calorimetry (DSC) is the most widely accepted used technique for determination of the degree of starch gelatinization [9,10].

Supercritical carbon dioxide ($scCO_2$) has some important advantages when used as a method for starch modification. CO_2 is inexpensive, non-flammable, and is generally recognized as being safe in food products. Although $scCO_2$ treatment requires pressure containment devices, it can be viewed as an efficient processing step, since it can eliminate chemical or thermal treatments and modify the properties of starch without concerns associated with chemical residues in the product or chemical waste streams.

Muljana et al. [11] reviewed research that reported on the gelatinization of starch under high hydrostatic pressure and noted few works have studied the effect of pressurized gases on starch gelatinization. Francisco and Sivik [12] studied the gelatinization of potato, cassava, and wheat starches in $scCO_2$ and those authors aimed to develop starch gelatinization with high pressure treatment up to 30 MPa. Comin et al. [13] provide an example in which flax oil is impregnated into pre-gelatinized corn starch with supercritical CO_2 ($scCO_2$). Muljana et al. [14] reported on $scCO_2$ induced gelatinization of potato starch and potato starch derivatives. All of those studies applied both temperature and pressure simultaneously and demonstrated that the starch gelatinization temperature could be lowered by treatment with $scCO_2$. Nevertheless, the reduction in starch gelatinization temperature by the

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application of $scCO_2$ is still insufficient for many applications in the food industry. One method to lower the gelatinization temperature further is to use of starch blends for which one type of starch is affected more by $scCO_2$ than the other.

High pressure food processing offers many methods for modifying physicochemical, rheological, nutritional, sensory quality and shelf life of products without the use of thermal treatment [12,15]. In this study, we aimed to study the gelatinization that can be obtained with $scCO_2$ for starch blend mixtures. The use of wheat starch blends is a distinctive point about this study since the use of starch blends expands the versatility of the supercritical technique. Samples are contacted with $scCO_2$ and then the results are analyzed with DSC.

2. Materials and methods

2.1. Materials

Commercial milled hard-wheat flour from the Japanese cultivar, Kitanokaori, was obtained from Ebetsu Flour Milling Co., Ltd., Ebetsu, Hokkaido, Japan. Wheat starch (WS) was isolated from wheat flour according to Noda et al. [16]. Potato starch (PS) (*Solanum tuberosum* L.) was obtained from Toukouren, Urahoro, Hokkaido, Japan. Sweet potato starch (SPS) (*Ipomoea batatas*) was obtained from the Haraigawa Starch Factory, Kimotsuki Agricultural Cooperative Association, Kanoya, Kagoshima, Japan. Cassava starch (CS) isolated from cassava tubers (*Manihot esculenta*) of Thailand origin was obtained from Nippon Starch Chemical Co., Ltd., Osaka, Japan.

2.2. Preparation of blended samples

The PS, SPS, and CS were blended individually with WS at the ratios of WS:PS, WS:SPS, WS:CS at 15:85, 25:75, 50:50, 75:25, 85:15, 0:100 (control PS/SPS/CS), and 100:0 (control WS) on weight basis (w/w). The blended samples were mixed for a prolonged period of time (30 min), to confirm the homogeneity of mixing.

2.3. Thermal properties of starch blends

Differential scanning calorimetry (DSC) analyses were performed with a DSC 6100 (Seiko Instruments, Tokyo) according to a previous procedure reported by Noda et al. [17]. Approximately 10 mg on dry basis of control WS, PS, SPS and CS and their blends of WS–PS, WS–SPS and WS–CS was weighed in a silver pan and distilled water (about 70 wt%) was then added to make a suspension of 30% (dry weight basis, w/w). Distilled water was used as a reference. Scans were heated at a rate of 2 °C/min from 25 to 130 °C. The gelatinization peak temperature (T_P) was deduced from the data scans as described by Zaidul et al. [18]. DSC was studied for the control and blend samples of both without $scCO_2$ induced and with $scCO_2$ induced samples. The DSC measurements were performed in triplicate. The averages were computed to assess the variations for the control and blend starches.

2.4. Supercritical carbon dioxide treatment

The experimental set-up used for supercritical fluid treatment of the samples has been previously described in previous work [19]. A pump unit (SCF-GET, JASCO) was used to deliver CO_2 at the given temperature (60 °C) and given pressure (20 MPa) to a 170 cm^3 vessel, which had an outside diameter of 25.5 cm and inner diameter of 10.2 cm. A pressure gauge was connected to the vessel. The vessel was heated with a mantle heater and its temperature was controlled and measured with thermocouples (K type). In the vessel, samples were placed into 3.0 cm measurement pans that were anchored within the lower part of the vessel to prevent movement. Temperature was measured at the CO_2 inlet just before the vessel and in the wall of the extraction vessel to within ±0.05 °C. Pressure fluctuations were less than 0.5 MPa during the treatment time. Experimental uncertainty of the measured pressures was ±0.1 MPa.

The control WS, PS, SPS and CS and each ratio (15 to 85% WS) of the blends of WS–PS, WS–SPS and WS–CS were mixed with water to obtain starch-water slurries containing 30% starch and 70% water (w/w). Then, 1 g of control and blended starch slurry were placed into measurement pans and covered to prevent evaporation of water. These were then placed into the vessel and acclimated for 1 h at atmospheric conditions without introducing $scCO_2$ into the vessel. Subsequently, the vessel was pressurized up to 20 MPa with CO_2 that was at a temperature of 60 °C. The pressurization was complete within 5 min and samples were held at the conditions for 1 h hold time. After treatment, the vessel was depressurized and the samples were analyzed with optical and thermal methods.

2.5. Visual analyses of samples

All samples were prepared by dispersing starch citrate in excess water on a microscope slide. The treated starch samples were observed with an optical light microscope (Olympus SZX ZB12, Tokyo), under 50× magnification and images were captured with a CCD camera (Olympus CS230, Tokyo). Images were taken of the 30% starch slurry of control starches and their blends with and without $scCO_2$ treatment.

3. Results

3.1. Reduction of gelatinization temperature

Table 1 shows the gelatinization peak temperature (T_P) of the control WS, PS, SPS and CS with and without $scCO_2$ treatment. For all starches, the gelatinization peak temperatures were found to be lower for $scCO_2$ treated starches than those that were untreated (Table 1). Comparing the values of T_P for the starch samples for cases of either with or without $scCO_2$ treatment, the highest gelatinization peak temperature was for SPS and the lowest gelatinization peak temperature was for WS. The largest change in T_P caused by $scCO_2$ treatment was found for WS, which showed a decrease in T_P of 13.8 °C. Literature values of the gelatinization peak temperatures have been reported in the literature of 67.1 °C for PS, 77.6 °C for SPS, 69.7 °C for CS, and 62.6 °C for WS [18]. The values of T_P reported in this work are in accord with literature values and have the same relative order. For the starch blends, WS–PS, WS–SPS and WS–CS, the first gelatinization peak temperature (T_{p1}) was assigned to WS (Table 2) and the second gelatinization peak temperature (T_{p2}) was assigned to PS, SPS and CS (Table 3).

In Table 2, for WS–SPS blends, the first gelatinization temperature decreased about 16 °C with $scCO_2$ treatment for each blend ratio. Similar trends were observed for WS–PS and WS–CS, in which the decrease in T_{p1} was about 12 and 15 °C, respectively (Table 2).

Table 1
Gelatinization peak temperature for control wheat starch (WS), potato starch (PS), sweet potato starch (SPS), and cassava starch (CS) with and without $scCO_2$ treatment.

Starch	Gelatinization peak (°C)	
	Without $scCO_2$ treatment	With $scCO_2$ treatment
WS	58.8 ± 0.5	45.0 ± 0.4
PS	68.3 ± 0.1	65.0 ± 0.6
SPS	78.6 ± 0.3	75.0 ± 0.5
CS	70.5 ± 0.8	57.5 ± 1.0

Values are means ± SD of triplicate.