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Polymerization of Sugars by Extrusion

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Abstract

Glucose syrup and lactose, mixed with citric acid as a polymerizing catalyst, was processed using twin screw extruder, in which 40 of L/D(length/diameter) ratio was designed to provide sufficient retention in extruder for polymerization of sugars. The polymerization yields of glucose syrup were 36.90%, 55.44% and 77.10% at 160, 180 and 200°C, respectively, while those of lactose were 26.45%, 38.16% and 45.86% at the same temperatures. Gel permeation chromatography exhibited that the higher molecular weight fractions were increased with extrusion temperature, which also led to increasing hydrodynamic intrinsic viscosity. Both gluco-oligosaccharides and lacto-oligosaccharides produced by extrusion of glucose syrup and lactose were stable for thermal treatments over a wide range of pH 3.0~11.0. In addition, α-amylase and amyloglucosidase treatment of gluco-oligosaccharides did not affect the solution viscosity, indicating the random linkages rather than α-1,4 linkages of glucose and thus the potential applications as a dietary fiber. In this research it was clearly observed that twin screw extrusion can be successfully utilized to produce gluco-oligosaccharides and lacto-oligosaccharides rapidly and continuously in conjunction with selective control of polymerized composition.

Key words: oligosaccharides, dietary fiber, sugars, extrusion

INTRODUCTION

It has been well documented that oligosaccharides confer a variety of functional and physiological properties in food and biological systems(1-4). Thus, oligosaccharides find their wide applications in various food products as prebiotics(5,6). Enzymatic biosynthesis is frequently employed to produce oligosaccharides such as isomalto-oligosaccharides, fructo-oligosaccharides, galacto-oligosaccharides(7,8). This enzymatic production of oligosaccharides possesses some problems such as long reaction time, enzyme inactivation, specific bioengineering control, difficulties in enzyme reuse, batch types of production, etc(9). In contrast, xylo-oligosaccharides, soy oligosaccharides and inulin-based fructo-oligosaccharides are produced by chemical hydrolysis of the raw materials(8). This chemical method also brings about manufacturing disadvantages such as corrosion of reactor, batch process, removal of chemicals, etc. Accordingly, the industrial demand to date has been proposed for economic and efficient manufacturing process.

Extruder is a multi-functional food processing equipment which can simultaneously perform many unit operations such as mixing, cutting, grinding, pressing, formulating, expansion, drying, sterilization, and cooling, etc (10, 11). It is noteworthy that the extrusion process accompanies high temperature, high pressure and high shear force. Thus, utilization of extruder as a reactor could provide many advantages from the viewpoint of economy and productivity(12). It has been well known that sugars can be polymerized in the presence of heat and acid(13). This reflects that the extrusion process may be potentially applied to produce sugar-based polymers in fast and continuous ways. This research aims at producing oligosaccharides with twin-screw extruder using glucose syrups and lactose as starting materials.

MATERIALS AND METHODS

Materials

Glucose syrup with the 60%(w/w) of total solid content was supplied from Sewon Co.(Korea). Lactose with a purity of 99.5% or more was obtained from Korcan International Resources, Inc.(Vancouver, Canada). Citric acid as a chemical catalyst was purchased from Sigma Chemical Co.(USA). The mixing ratio of glucose syrup to citric

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acid was 98:2(%, w/w), while that of lactose to citric acid 99:1(%, w/w).

Extrusion conditions

Extrusion was performed by corotating and intermeshing type twin-screw extruder(Bühler, Biex-DNDL 44, Switzerland) with a K-tron twin screw feeder. The extruder was designed with modular 176mm barrels and bored with two 44mm diameter holes, in which the barrel section was extended to the L/D(length/diameter) ratio of 40 to increase the retention time. There were four heating zones: the first zone was used for feeding and melting of material, and the temperature was maintained at 100°C by circulating mineral oil; the second zone for initiation of reaction, and the temperature at 130°C by circulating mineral oil; the third zone for propagation of reaction, and the temperature at 160, 180 & 200°C by using electric heater to bring about various glucose polymerization; the fourth zone for the termination of reaction, and the temperature at 130°C. The feed rate and screw speed were 65kg/hr and 180rpm, respectively.

Polymerization yield

Sugar extrudates were characterized in terms of raw sugars, oligosaccharide(OS) and dietary fiber(DF), which represent different degrees of polymerization in the increasing order. Five grams of extrudates were dissolved in 20ml of water for 30min, and 180ml of isopropanol was added to precipitate the polymeric materials. After placing for 4hr at room temperature, the mixtures were centrifuged at 5,000×g for 15min, and the precipitate was dried and weighed as DF. Some sugars are not polymerized during extrusion and exist as the original sugars. Those unreacted sugars were measured by HPLC using Waters carbohydrate column. Finally, OS, whose polymerization degree is between sugars and DF, was calculated by weight difference(i.e., OS=total sample weight-sugar-DF). The yield was demonstrated as a percent ratio for the initial sample weight.

Molecular weight

Gel permeation chromatography(GPC) was used to measure the molecular weight. 0.2%(w/w) sample solution was filtered through 0.45μm filter paper, and 100μl solution was then injected to HPLC(Waters LC Module I/M410 RI detector/Millennium 2010) equipped with Waters Ultrahydrogel 120 and 250 columns. 0.1 M $NaNO_3$ was used as a mobile phase, and its flow rate was 0.8ml/min. Pullulans(MW=50000, 23000, 12200, 5800) and lactose(MW=342) were employed as standard materials.

Intrinsic viscosity

The extrudates were dissolved in water for 1hr and filtered through 0.45μm Millipore filter. The viscosity of solutions was measured by Cannon-Fenske capillary viscometer(size 50; Cannon Instrument Co., State College, PA, USA) at 25°C. Prior to measurements, the solution was placed for 30min at 25°C waterbath for temperature equilibrium.

Specific viscosity(η_{sp}) and intrinsic viscosity([η]) were determined as follows:

$$\eta_{sp}=(\eta-\eta_s)/\eta_s \text{ and } [\eta]=\lim_{C\to 0} \eta_{sp}/C$$

where η is the solution viscosity, η_s is the solvent viscosity, and C is the solution concentration.

Thermal and pH stability

Five grams of extrudates were dissolved in 100ml at pH 3.0, 7.0 and 11.0, which were then heated at 100°C for 1hr. The viscosity was measured by Cannon-Fenske capillary viscometer(size 50; Cannon Instrument Co., State College, PA, USA) at 30°C. Stability was expressed as a percent ratio to the viscosity of untreated samples.

Enzymatic stability

α-Amylase(Sigma Chemical Co.; A 3306) and amyloglucosidase(Sigma Chemical Co.; A 9913) were used to test the enzymatic stability of gluco-oligosaccharide. Five percent(w/w) gluco-oligosaccharide solutions, mixed with 100μl of original enzyme solution, were incubated in a 30°C shaking waterbath for 5hr, and the viscosity was measured by Cannon-Fenske capillary viscometer(size 50; Cannon Instrument Co., State College, PA, USA). Stability was expressed as a percent ratio to the viscosity of untreated samples.

RESULTS AND DISCUSSION

Polymerization of glucose syrup

Table 1 shows the polymerization yield of glucose by twin screw extrusion using glucose syrup as a starting material. It can be seen that the polymerization of glucose greatly depends on the extrusion temperature. At 180°C, the polymerization yield, i.e. the sum of dietary fiber(DF)

Table 1. Characteristics of glucose syrup extrudates (GSE)

	Samples[1]		
	GSE-1	GSE-2	GSE-3
Yield(% w/w)[2]			
DF	0.72	2.74	21.08
OS	36.18	52.70	56.02
Glucose	63.10	44.56	22.90
Mw[3]	273	371	540
$[\eta]$[4] (ml/g)	2.24	2.26	2.28
A_{450}[5]	0.04	0.10	0.22

[1]Extrusion temperature : GSE-1, 180°C; GSE-2, 200°C; GSE-3, 220°C
[2]DF, dietary fibers; OS, oligosaccharides
[3]Weight average molecular weight, [4]Intrinsic viscosity
[5]Absorbance at 450nm of 5% solution

and oligosaccharides(OS), was 36.90%, while 55.44% and 77.10% at 200°C and 220°C, respectively. Hwang et al.(9) reported that, when glucose powder was employed as a starting material, the polymerization yield was 43.87%, 75.01% and 93.70% at 160°C, 180°C and 200°C, respectively. This indicates that the polymerization yield of glucose syrup is much lower than that of glucose at the same polymerization temperature. This may be attributed to the difference in the moisture content between glucose syrup and glucose powder. It is well known that sugars are polymerized under anhydrous and acidic conditions (13-15). Extrusion accompanying high temperature provides the more anhydrous environment to glucose powder than glucose syrup containing the higher initial moisture content. Despite somewhat lower polymerization yield, it is noteworthy from the commercial viewpoint that glucose syrup can be significantly polymerized by extrusion, since glucose syrup is much less expensive than glucose.

Molecular weight of extrudates is also presented in Table 1 in conjunction with intrinsic viscosity. The results show that increasing the polymerization yield with extrusion temperature led to the higher molecular weight and, correspondingly, higher intrinsic viscosity. Intrinsic viscosity reflects the hydrodynamic volume occupied by a material, depending on the molecular size and shape(16, 17). Generally, it is proportional to the molecular size, and thus increased intrinsic viscosity in Table 1 can be attributable to the increased molecular weight. Table 1 also shows that browning reaction underwent more severely with increasing extrusion temperature.

Fig. 1 shows the enzymatic and thermal stability of

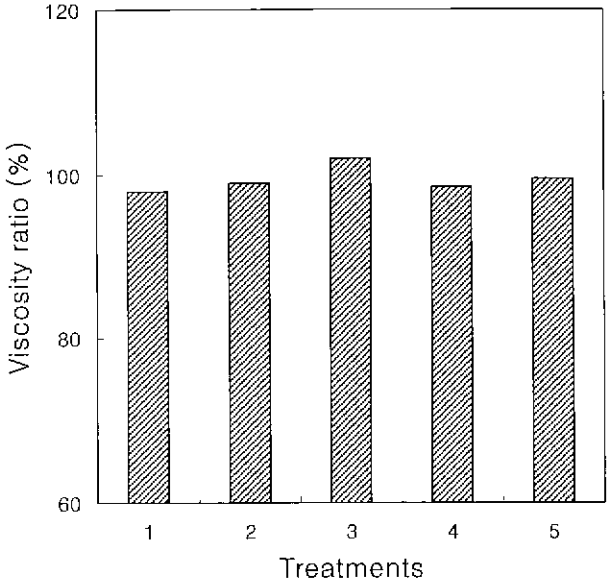

Fig. 1. Effect of enzyme treatments and heating at various pH on the ratio of initial 5% solution viscosity of glucose syrup extrudates to viscosity after treatments.
1, α-amylase; 2, amyloglucosidase; 3, heating(100°C, pH 3.0); 4, heating(100°C, pH 7.0); 5, heating(100°C, pH 11.0)

glucose syrup extrudates. The treatments of α-amylase and amyloglucosidase, which can cleave α-(1,4) linkage of glucose, did not affect the viscosity of 5% sample solutions. This indicates that the glucose polymers are not connected by α-(1,4) linkages, otherwise the enzymatic treatment can significantly decrease the viscosity. This is consistent with the report that the commercial polydextrose, produced by thermal treatment of glucose in the presence of citric acid as a catalyst, consists of random glucose linkages(18). Thus, the glucose syrup extrudates can impart various nutritional benefits in food systems as dietary fiber materials(19,20). Fig. 1 also demonstrates the high thermal stability of glucose syrup extrudates at various pH ranges. Since a majority of food processing accompanies the thermal treatments at various pH values, it is expected that the glucose extrudates, exhibiting good thermal and pH stability, can find the wide range of applications in food industry.

Polymerization of lactose

The polymerizing characteristics of lactose by extrusion are demonstrated in Table 2 in terms of yield, molecular weight, intrinsic viscosity and color. The results show that the polymerization of lactose is also greatly dependent on the extrusion temperature. The polymerized yield,

i.e. the sum of dietary fiber(DF) and oligosaccharides(OS), of lactose was 26.45% at 180°C, which is significantly lower than 36.90% of glucose syrup shown in Table 1 and 75.01% of glucose powder of Hwang et al.'s report(9) at the same temperature. This lower polymerization yield may be ascribed to the disaccharide structure of lactose, consisting of glucose and galactose, and thus to be less effective to the polymerization mechanism. This is consistent with the report that sucrose, disaccharide of glucose and fructose, conferred much lower polymerization yield than glucose(21). The polymerization yield of lactose was 38.16% and 45.86% at 200°C and 220°C, respectively. Thus, it can be concluded that lactose is much less polymerized than glucose by extrusion at the same temperature.

Table 2. Characteristics of lactose extrudates(LE)

	Samples[1]		
	LE-1	LE-2	LE-3
Yield (% w/w)[2]			
DF	7.77	23.21	35.43
OS	18.68	14.95	10.43
Lactose	73.55	61.84	54.14
Mw[3]	302	559	735
$[\eta]$[4] (ml/g)	2.46	2.82	2.98
A_{450}[5]	0.92	1.38	1.63

[1]Extrusion temperature : LE-1, 180°C; LE-2, 200°C; LE-3, 220°C
[2]DF, dietary fibers; OS, oligosaccharides
[3]Weight average molecular weight, [4]Intrinsic viscosity
[5]Absorbance at 450nm of 5% solution

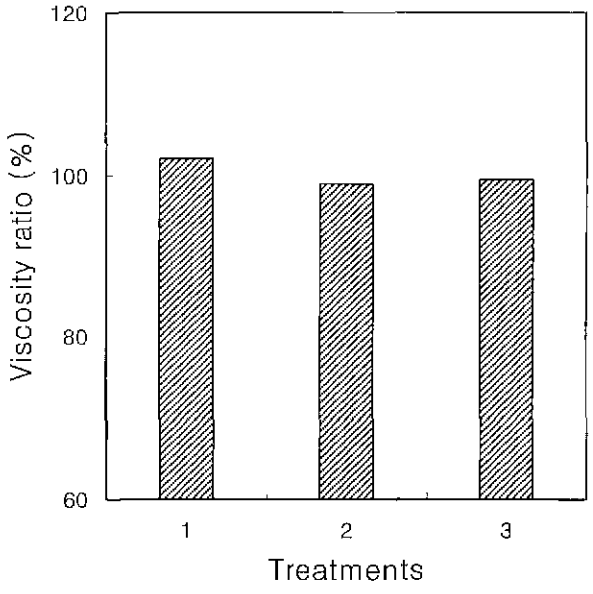

Fig. 2. Effect of heating at various pH on the ratio of initial 5% viscosity of lactose extrudates to viscosity after treatments.
1, heating(100°C, pH 3.0); 2, heating(100°C, pH 7.0); 3, heating(100°C, pH 11.0)

It is apparent that both molecular weight and intrinsic viscosity of lactose extrudates were increased with the polymerization yield(Table 2). Intrinsic viscosities of gluco-oligosaccharide and lacto-oligosaccharides produced by extrusion were relatively low, which may be ascribed to the branch-on-branch structure of chemically polymerized sugars(16). Table 2 also demonstrates that the extruded lactose possessed much more browned color than glucose extrudates. The similar results were also reported for chemically synthesized sucrose(i.e. disaccharide of glucose and fructose) polymers(21). Despite somewhat lower polymerization yield of lactose by extrusion as shown in Table 2, it is anticipated that the extrusion process can replace the conventional enzymatic method to produce galacto-oligosaccharides due to its economical potential.

The thermal stability of lactose extrudates were presented in Fig. 2 at various pH ranges. It can be seen that the viscosity remains nearly unchanged during thermal treatments under acidic and alkaline conditions. Similar to glucose extrudates, the lactose extrudates can be also widely utilized in various food processes including severe thermal processing.

CONCLUSIONS

This research clearly shows that twin screw extrusion reactor can be used as a potential tool to bring about the polymeric synthesis of gluco-oligosaccharides and lacto-oligosaccharides using glucose syrup and lactose. Since extrusion process provides advantages such as fast reaction, continuous process and flexible manipulation of composition, it is highly expected that a variety of sugar based oligosaccharides can be economically produced by the extrusion process. Presently, a variety of functional sugar materials are produced by chemical, enzymatic or chemo-enzymatic methods(22-24). It is suggested that the extrusion process attempted in this research is called to be a chemo-mechanical method, since the polymerization degree and composition can be mechanically controlled by the operating conditions in the presence of citric acid as a chemical catalyst.

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