Extraction and Modification of Gum from Cashew Tree Exudates Using Wheat Starch and Glycerine

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Abstract

The objectives of this research were to extract cashew tree gum (CTG) from cashew tree exudates and to modify it into a new drying aid, which can act as a substitute for Arabic gum. The cost problem faced in the spray drying of fruit juices is expected to be solved with the use of modified CTG as a replacement of Arabic gum. The CTG was extracted and precipitated from its raw cashew exudates solution with the help of ethanol as antisolvent. Glycerine and wheat starch were the additives used in the modification of the gum. The good quality of modified CTG was obtained based on their close similarity to Arabic gum properties.

Keywords: CTG, Arabic gum, modification, starch, glycerine

Abstrak

Penelitian ini bertujuan untuk mengekstrak getah pohon mete dan memodifikasi sifatnya untuk dapat digunakan sebagai senyawa pembantu proses pengeringan menggantikan fungsi getah Arab. Dengan menggunakan getah mete termodifikasi dari penelitian ini, permasalahan biaya pada proses pengeringan jus buah dengan *spray dryer* dapat diatasi. Getah pohon mete dipungut dan diendapkan dari larutan hasil penyadapan dengan bantuan etanol sebagai *antisolvent*. Dalam penelitian ini gliserin dan pati gandum digunakan sebagai bahan tambahan untuk memodifikasi sifat getah. Hasil penelitian menunjukkan bahwa getah pohon mete termodifikasi yang dihasilkan memiliki kualitas yang baik dan kesamaan sifat dengan getah Arab.

Kata kunci : getah pohon mete, getah Arab, modifikasi, pati, gliserin

Introduction

Spray drying is a widely used technique to produce powders from liquid foods. However, drying of fruit juices into powder is difficult, especially because of the presence of low molecular weight sugars and acids, which have low glass transition temperature (Tg), being then very hygroscopic, because of their high molecular mobility above Tg (Jaya and Das, 2004). While under spray drying temperatures, they tend to stick to the walls of the drying chamber and can produce a paste-like structure instead of powder (Dolinksy *et al.*, 2000; Bhandari and Hartel, 2005). Some possible consequences are related to impaired product stability, decreased yields (because of stickiness on the drier chamber walls), and even operating problems to the spray drier (Bhandari *et al.*, 1997).

The sticky behaviour can be avoided by the addition of drying aids, which are high molecular weight carbohydrates, such as maltodextrins and Arabic gum, which decrease powder hygroscopicity and increase Tg (Bhandari and Hartel, 2005; Collares *et al.*, 2004; Silva *et al.*, 2006). Arabic gum has been reported to have higher Tg value than maltodextrin DE10 (MD10), and being very efficient in flavour retention (Collares *et al.*, 2004; Madene *et al.*, 2006; Galmarini *et al.*, 2008). Unfortunately, Arabic gum is expensive, which has motivated researchers to look for other materials to replace it (McNamee *et al.*, 1998). Cashew tree gum (CTG), a complex water soluble heteropoly-saccharide extracted from cashew tree (*Anacardium occidentale*), has been identified as a very promising Arabic gum replacement, due to its structural similarity (Paula *et al.*, 2002). The similarity of the thermal behaviour between CTG and Arabic gum has also been reported to suggest the possibility of replacing Arabic gum by CTG (Mothe and Rao, 2000). Such replacement, previously suggested by Owusu *et al*. (2005), could reduce costs and favour the cashew tree business, whose only high market value product is currently the cashew nut. Owusu *et al*. (2005) came out with that suggestion based on their

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findings that the viscosity characteristic of the CTG was very similar to Arabic gum, and this property was not significantly affected by pH, temperature and storage time. However, Owusu *et al*. (2005) did not carry out any modification to the CTG to improve its other drying properties.

CTG is a complex polysaccharide comprising 61% galactose, 14% arabinose, 7% rhamnose, 8% glucose, mannose 2%, xylose 2% and glucurine acid 6% (Anderson *et al*., 1974). Elementary analysis revealed the average water content 9.7%, total protein measured about 1.5%, total lipids 0.06%, fibres 3.24% and ash 0.5%, the total carbohydrate was 85%. Hydrolysis of CTG yields L-arabinose, L-rhamnose, D-galactose and glucuronic acid (Glicksman and Sand, 1973; Gyedu-Akoto *et al*., 2008). The variation in acid number is influenced not only by the source of the sample but also by its age. The sticky exudates from this tree darken and thicken rapidly on exposure to air. When applied as a varnish, it provides remarkable protection, as is unchanged by acids, alkalis, alcohols or heat up to 70°C.

In order to provide better information about CTG as a potential substitute for Arabic gum and maltodextrins as drying aids, this research was conducted. The objectives of this research were to extract CTG from cashew tree exudates and to modify it into a new drying aid.The first part of this study deals with the precipitation of CTG using ethanol as antisolvent. Then, in the second part, modification of CTG with starch and glycerine were carried out in order to determine the best additives composition.

Materials and Methods

Dried raw cashew tree exudates were collected from local cashew plantation nearby Diponegoro University Campus. Ethanol, sodium hydroxide, wheat starch and glycerine of analytical grade with minimum purity of 98% were purchased from Sigma-Aldrich-Singapore Pte. Ltd. Whereas, distilled water was supplied by the reverse osmosis unit available in the Department of Chemical Engineering, Faculty of Engineering, Diponegoro University.

The dried raw cashew tree exudates were purified as a sodium salt using the method previously described (de Paula *et al*., 2001; Torquato *et al*., 2004). Cashew tree exudates gum (10 g) sample was collected and was dried at 45°C to reduce the moisture content. The dried sample was ground to pass through 2.5 mm size mesh sieve. The gum was isolated, that is the separation of the polysaccharides present in the raw gum, and this was done by stirring the gum sample in 250 mL distilled water for 6-8 hours at room temperature. The solution pH was adjusted to approximately 7.0 by adding diluted NaOH. The sample was centrifuged to remove the impurities and was concentrated by heating to a temperature of 100°C. The residue was washed with water and the washings were added to the separated supernatant. The procedure was repeated four more times. Finally, the supernatant was made up to 500 mL and treated with ethanol in order to precipitate all the carbohydrates. The precipitated material was washed again with distilled water, freeze-dried and ground with mortar to obtain fine powder. The ratio of ethanol to crude CTG weight was studied here.

The CTG was then modified by the use of additives and the properties of gum were measured, i.e gum viscosity, pH, density and glass transition temperature. The viscosity was measured by the use of A programmable Brookfield rheometer (Brookfield Engineering Laboratories, Vertriebs GmbH, Model DV-111, Lorch, Germany), pH measured by the use of pH meter (Hanna Instruments, Model HI 98129, Singapore) and density measured by the use of capillary tube pycnometer of 10 ml capacity; the solution weight were recorded in analytical balance with 0.0001 g precision (Mettler-Toledo GmbH, Model AL54, Greifensee, Switzerland). The glass transition temperatures of the modified CTG samples were determined by differential scanning calorimetry (DSC) (DSC-7, Perkin-Elmer, Norwalk, CT). Various concentrations of starch and glycerine were prepared and were used in the modification and the optimum condition that gave the best modified CTG was noted.

Result and Discussions

In this work, the effects of ethanol content on the extraction of gum from cashew tree exudates and the composition of additives on the modification of cashew gum extract into a new drying aid were investigated. The results of this study are as follows:

Extraction of CTG

Extraction of cashew gum from raw cashew tree exudates was conducted at 30°C. The effect of ethanol composition used as antisolvent on the extract yield can be seen in Figure 1. Gum extract was nearly unextractable from raw cashew exudates when the ethanol content in the cashew exudates-water solution was very low (below 30%, v/v). Almost all of the gum can be extracted when ethanol was added into cashew exudates-water solution at 30%, v/v composition. However, further addition of ethanol did not increase the extraction yield significantly. Therefore, from economical and technical point of views, the addition of ethanol into cashew exudates-water solution at 30%, v/v may be considered as the optimum condition to extract CTG from its raw exudates.

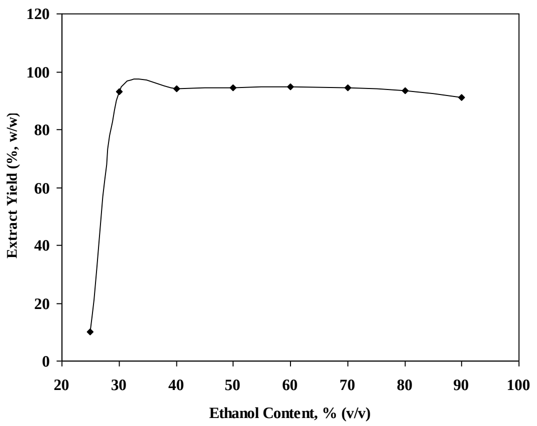

Figure 1. Effect of ethanol content on the cashew gum extraction yield

CTG analysis and modification

The results in Table 1 show that the pH and viscosity of natural cashew exudates were 4.70 and 4.79 Ns/m^2, respectively. These values fall within the natural pH of Arabic gum with range of 3.9 - 4.9 (Anderson and Wieping, 1990). These findings support the previous report that there was a structural similarity between cashew gum and Arabic gum (Paula *et al*., 2002).

Table 1. pH, Density and Viscosity of CTG and Arabic Gum

Parameters	CTG	Gum Arabic
pH	4.70	3.9 - 4.9
Density, g/mL	1.05	1.042
Viscosity, Ns/m^2	4.79	4.87
Tg, °C	68	62

In Table 2, when wheat starch was added to the gum extract, the pH of the gum dropped slightly in the range of 4.51 - 4.69 as compared to the original gum extract. On the other hand, the viscosity increased to the range of 4.67 - 9.63 Ns/m^2. Starch thus acts as a binding agent since it increases the thickness of the gum when added to the gum solution. It can also be seen that the measured densities remain more or less constant and fall a little below that of the original gum solution. Whereas, the Tg values increased when the percentage of the wheat starch added to the CTG was increased. This is because the Tg of the wheat starch (143°C), is far higher than the CTG (de Graaf *et al*., 2003). From molecular point of view, the increase in Tg with the addition of wheat starch is mainly attributed to interfacial interactions through hydrogen bonding, van der Walls forces, and electrostatic forces between the carbohydrate polymer matrix of the CTG and wheat starch (Awad *et al*., 2011).

Table 2. Effect of starch addition to physical properties of CTG

No. Sample	Starch	pH	Density	Viscosity	Tg
1	3%	4.51	1.03	4.67	68.2
2	5%	4.54	1.03	5.02	68.7
3	7%	4.56	1.03	7.38	69.1
4	10%	4.69	1.03	9.63	69.9

It is reported in Table 3, that when glycerine was added to the gum solution, the pH of the gum solution dropped in the range of 4.22 - 4.52. The viscosity of the gum rose to its highest value between the ranges of 5.23 - 10.18 Ns/m^2. With the addition of glycerine, the gum became more slippery, which suggest that glycerine aids easy spread of the gum. This property is supported with the fact that the density of the gum rose to within 1.06-1.09 g/mL. Whereas, the Tg values decreased when the percentage of the glycerine added to the CTG was increased. This is because the Tg of the glycerine (-85^{o}C), is far below the Tg of CTG (de Graaf *et al*., 2003).

Table 3. Effect of glycerine addition to physical properties of CTG

No. Sample	Glycerine	pH	Density	Viscosity	Tg
5	3%	4.22	1.06	5.23	65.2
6	5%	4.40	1.06	6.70	60.6
7	7%	4.45	1.08	8.46	57.5
8	10%	4.52	1.09	10.18	55.1

Table 4 reports the combinations of additives used to modify the CTG. In this table, the pH range of the gum is 4.18 - 5.27 and the viscosities of the gum were in the range of 4.55 - 6.81 Ns/m^2. The best samples were found to be those of sample number 9 and 10, which their pH, viscosity and Tg of 4.18, 4.55 Ns/m^2 and 62.2^{o}C, and 4.50, 4.65 Ns/m^2 and 62.6^{o}C, respectively. This conclusion is based on the fact that the pH of these samples fall within the range of pH of gum Arabic i.e. 3.9 - 4.9 (Anderson and Wieping, 1990), and they also have satisfactory viscosities and Tg. In general, it was shown in the entire results that the increase in pH of the CTG lead to an increase in its viscosity, and the higher the quantity of the additive, the higher the pH and the higher the viscosity of the modified CTG. The pH of the CTG must be in such range so that the material to be dried will be highly soluble in water. While the viscosity and density of the modified CTG as a drying aid cannot be too high because it may reduce the flow ability of the solution and finally also will disturb the nozzle to spray the solution to be dried into the drying chamber. However, the Tg of the CTG should be high enough to enable the formation of coating film on the dried solid from the solution during heating and drying.

Tabel 4. Effect of combination of starch and glycerine addition to physical properties of CTG

No. Sampel	starch, glycerine	pH	Density	Viscosity	Tg
9	3%, 5%	4.18	1.05	4.55	62.2
10	5%, 5%	4.50	1.06	4.65	62.6
11	7%, 5%	4.79	1.07	5.50	63.6
12	10%, 5%	5.27	1.08	6.81	65.2

Conclusions

CTG can be produced from cashew tree exudates using ethanol as antisolvent and the use of additives improves substantially, the quality of the CTG. The good quality of modified CTG was obtained with viscosity, pH and Tg of 4.55 Ns/m^2, 4.18 and 62.2^oC, with the following composition of additives: starch 3% and 5 ml glycerine, and with viscosity, pH and Tg of 4.65 Ns/m^2, 4.5 and 62.6^oC with the following composition of additives: 5% starch and 5 ml glycerine.

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