

Effect of Acetylation on Physicochemical Characteristics of Cashew Exudate Gum (*Anacardium occidentale*). A Potential Excipient

O. Adeyanju^{1,*}, U. C. Nwanta¹, Y. Shuaibu², Y. Hussaini³ and A. I. Adejoh¹

¹ Department of Chemistry, University of Jos, Jos, Nigeria.

² Department of General Studies, College of Administrative and Business Studies, Potiskum, Nigeria

³ Department of Science Laboratory Technology, Federal College of Forestry, Jos, Nigeria.

Received: 5 Jan. 2016, Revised: 12 Feb. 2016, Accepted: 15 Feb. 2016.

Published online: 1 Sep. 2016.

Abstract: The modification discussed include the acetylation of cashew gum with acetic anhydride in the presence of sodium hydroxide. The resulting product was characterized by FTIR spectroscopy. Physicochemical characteristics such as solubility, viscosity and swelling index of the native cashew gum and acetylated cashew gum were also determined. The results showed that the acetylated gum had higher values of solubility, viscosity and swelling index as 113.40% at 80°C, 53.4cs and 49.54% respectively while the native gum had solubility viscosity and swelling index as 50.10% at 80°C, 20.20cs and 10.94% respectively. Chemical modification via acetylation increased the solubility, viscosity and swelling index of cashew gum. The experimental work provides enough evidence to exploit this natural biopolymer in food, textile and pharmaceutical industry, especially as an efficient alternative approach for the oral delivery of hydrophilic macromolecules.

Keywords: Cashew gum, Chemical modification, acetyl group, drug delivery.

1 Introduction

Anacardium occidentale Linn gum is a natural polysaccharide extracted from the bark of Cashew tree. It is basically composed of a straight chain of D – mannose units, united by $\beta(1-3)$ glycoside linkages and bearing a single D-galactose unit on approximately every alternate mannose joined to it by an $\alpha(1\rightarrow6)$ glycoside linkage [2,14]. Due to excellent properties of gums such as solubility, viscosity, thickening, binding, stabilizing and emulsifying, they are utilized in several multibillion-dollar industries such as adhesive, cosmetic, confectionaries, paint, paper, pharmaceutical and most importantly Food [3, 24-25]. Even if gums and its derivatives are well known for a wide range of applications, like other polysaccharides, there are evidences of some drawbacks, such as uncontrolled rate of hydration, pH-dependency, solubility, thermal decomposition, low shear stress resistance, high retrogradation and syneresis [1,4].

Chemical modification provides an efficient route not only for removing such drawbacks but also for improving physicochemical properties such as solubility, viscosity and swelling index and to introduce new properties for different applications. A number of modifications via chemical

treatment can be effected resulting in products suitable for specific purposes in the food and pharmaceutical industries [5].

According to [2] chemical modification of *anacardium occidentale* gum by oxidation increases the uronic acid content of the gum from 3.7% to 38% which further increases solubility and water holding capacity. Also according [6] oxidation of gum generally increases their hydrophilicity and solution clarity which make them more soluble in aqueous system. Chemical modification through acetylation generally increases the emulsifying capacity which further increases swelling index and solubility [7]. Nowadays, the development of new products in gum based industries are searching for gums with different or better physicochemical and functional properties such as viscosity, solubility, low retrogradation and syneresis tendency. In recent years, substantial progress have been made in obtaining polysaccharides from non-conventional botanical sources and studying their functional and physicochemical properties [8-11].

The acetylated gum is produced by the esterification of native gum with acetyl groups. The functional properties of the gum acetate will depend on the number of acetyl group incorporated to the glucose unit of gum molecules [12 -14].

Acetylation was selected as a chemical means of attaching pendant acetic anhydride groups due to its technical simplicity, low cost of chemical reagents and wide range applications to produce acetylated gum. The result of this research is likely to highlight the effect of acetylation on the physicochemical properties of cashew gum in order to amplify the possibilities of the gum applications in food and pharmaceuticals as an emulsifier, effective binder and suspending agent in drug formulation.

The objective of this research is to prepare and characterize an acetylated *Anacardium occidentale* gum in order to improve on its physicochemical characteristics and amplify the possibilities of the gum applications.

2 Materials and Methods

Anacardium occidentale gum was collected by tapping from owena forestry Ondo - State, Nigeria. Superficial incision was made at the bark of the tree and the bark was later stripped off. After five weeks, gum was manually collected. The gum samples were dried at room temperature, cleaned, milled with Kenwood blender [UK], sieved through a mesh-size 250 microns to obtain fine – size particles, kept in labeled plastic container and stored in the refrigerator for subsequent analysis.

2.1 Purification of gum sample.

Dried crude gum [10g] was stirred in cold distilled water [250ml] for 2 – 3 hours at room temperature. The supernatant was obtained by centrifugation. The supernatant was made up to 500ml and treated with ethanol [1.4v/v] in order to precipitate the carbohydrate. The material was washed again with ethanol followed by distilled water and freeze-dried.

2.2 Preparation of acetylated gum

Acetylated gum was obtained using the method reported by [13]. In brief, gum (10g) was dispersed in 50cm³ of distilled water and then constantly stirred for 30 minutes. The slurry was adjusted to pH 8.0 with 3% NaOH. Acetic anhydride (1.2g) was then added to the slurry. After the addition of the acetic anhydride, the reaction was allowed to proceed for another five minutes. The pH of the slurry was adjusted to 4.5 with 0.5MHCl and filtered through whatman No 1 filter paper. The residue obtained was washed four times with distilled water to remove completely some acids that may be present in the product and finally air dried at room temperature.

2.3 Solubility

The solubility of gum was determined according to a standard method reported by [15]. Gum sample (10g) was suspended in 40ml of distilled water. It was heated to the

desired temperature (60⁰c, 70⁰c or 80⁰c) for 30 minutes with continuous shaking. The mixture were centrifuged at 1,000rpm for 15 minutes. An aliquot of supernatant (5ml) was evaporated at 130⁰c and weighed. The percentage solubility of the gum was the ratio in mass (g) of the dried supernatant to the initial mass (g) of the dry gum expressed in percent.

2.4 Swelling and gel fraction studies

Swelling and gel fraction studies were carried out according to a standard method reported by [16] Samples weighing 0.01g of gum were placed in small dishes that were carefully inserted into glass flasks. Total volume of 60mL distilled water was slowly poured into each glass flasks. The samples were allowed to soak for 2 hours at room temperature, after which the excess solution was carefully removed and the gelled sample remaining in the gelled bottle were weighed. The gelled samples were lyophilized for three days and then weighed again. The swelling ratio and percentage of gel fraction were calculated. Using Equations (1) and (2)

$$\text{Swelling ratio} = W_{\text{water}}/W_{\text{gel}} \dots\dots\dots(1)$$

$$\text{Percentage fraction} = W_{\text{gel}}/W_{\text{solid}} \times 100\dots(2)$$

W_{water} = weight of the sample after 2 hours soaking

W_{gel} = weight of the sample after lyophilization

W_{solid} = initial weight of the sample.

2.5 Viscosity

Apparent viscosity of gum was determined using a Brookfield Viscometer (Model RVF, Stoughton, MA). The gum slurry (5%) was placed in a boiling bath for 15 minutes and then cooled to 22⁰c. cold paste viscosity was determined using spindle at 25⁰c.

2.6 Fourier Transform Infra Red (FTIR) Spectroscopy.

FTIR spectra were obtained on a FTIR spectrometer [Shumadzu 8400s] using a KBr disc. The equipment was operated with a resolution of 4cm⁻¹ and the scanning range from 4000 to 400cm⁻¹

3 Statistical Analysis

The data obtained from the study were analyzed using the Statistical Analysis System (SAS) software and the means were separated by T-Test.

4 Results and Discussion

The viscosity value for the acetylated gum (53.40 ± 0.28 cs) (Table1) was higher than the native gum

Table1: Physicochemical characteristics of acetylated and native *anacardium occidentale* gum

	Solubility (%)		Swelling ratio (%)	Viscosity (M.Pa.S)	Gel fraction (%)
Native gum	60 ⁰ c	5.90 ± 0.01	10.9 ± 0.2	20.20 ± 0.28	56 ± 2.60
	70 ⁰ c	33.1 ± 0.03			
	80 ⁰ c	50.1 ± 0.01			
Acetylated gum	60 ⁰ c	66.7 ± 4.05	49.5 ± 0.1	53.4 ± 0.28	22 ± 1.16
	70 ⁰ c	110.8 ± 7.14			
	80 ⁰ c	113.4 ± 9.20			

(20.20 ± 0.28cs). This higher value of viscosity could be explained by the increase in the swelling power and solubility of the chemically modified gum. According to [17]. Acetylation of gum generally increases the emulsifying capacity which further increases the viscosity and water holding capacity. During the acetylation process, the gum-gum interactions in the granules are weakened by the introduction of acetyl groups, this makes the gum to be more attracted towards water molecules[18-20, 26]. Also the swelling index and

solubility of acetylated gum were higher than the native gum (Table1).Hovers and susilki.[21] reported that the introduction of acetyl groups during the acetylation process reduces the bond strength between gum.

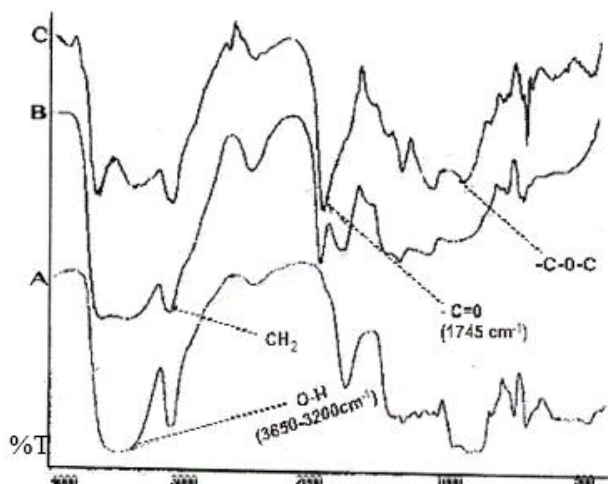


Fig 1: FTIR of native(A), purified(B) and acetylated(C) cashew gum

This facilitates the access of water to amorphous areas, enhancing the water holding capacity of the gum matrix and developing a more organized structure, leading to a higher resistance to deformation and achieving a higher peak viscosity. The solubility of modified and unmodified gum profoundly increased with

increase temperature (Table 1). This is due to introduction of acetyl groups. The increased solubility of acetylated gum may be due to the presence of (CH₃C=O) groups which allow formation of more hydrogen bonds [22-23]. The polysaccharide unit of glucose with hydroxyl group [OH] as the major functional groups appear in the region [3650 to 3200cm⁻¹] and disappeared when the gum was acetylated, there was introduction of acetic groups and the spectra now processed peaks around [1750cm⁻¹ to 1735cm⁻¹] attributed to C=O stretching, indicating the presence of the acetyl group. This peak was seen to decrease and in the case of purified gum the peak was not resolved from that of the C=O group. The peak at 3300-3400cm⁻¹ caused by OH stretching was also seen to decrease with an increase in acetyl content. Thus, the FTIR spectrum confirms the acetylation of Cashew gum.

5 Conclusion

The study confirms that acetylation may improve physicochemical properties of *Crude Anacardium occidentale* gum. This was demonstrated by FTIR spectroscopy. This may increase its efficacy in applications.

References

- [1] O. Adeyanju. and S. F. Akomolafe(2013). Extraction and physicochemical characterization of a New polysaccharide obtained from *Daniella oliveri (Rolfe) Hutch and Dalz(LEGUMINOSAE)* Proceeding of the 36th Annual International Conference of Chemical Society of Nigeria, Minna, Nigeria. 2:513-520.
- [2] D. S. Raquet, L.L., Jacira, and R.S., Cellio(2002) Cashew – tree (*Anacardium occidentale. L*) exudates gum: a novel bioligand and tool in *Biotechnology application. Biochemistry* 35: 45 – 53
- [3] G, O. Philip and P. A., William(2001). Tree Exudates Gum. National and Vasetile food Additives and ingredient *Food IngridAnals* 23:26
- [4] O. Adeyanju, M. E. Emefiene, and M. I. Ewaleifor(2013a). Chemical Modification of *Anacardium occidentale. L.* exudate gum. A new Tablet binder and emulsifier. Proceeding of the 36th Annual International Conference of Chemical Society of Nigeria, Minna, Nigeria 2:391-394.

- [5] D. Le Cert., F. Frinei and G. Muller (1990). solution properties of gum exudates from *sterculi aurens* (*karaya Gum*). *Carbohydrate polymer* 13(4): 375 – 386.
- [6] D. Risica. L., Barbetta, C., Vischetti and M., Dentini(2010). chemical modification of gum *karaya polymer* 51:1972
- [7] S.,Pal.(2009). Analytical studies and characterization of a new binder and emulcifier. *J. Appl. Polym. Sci* III:2630
- [8] J.Y.Zhao(1994). Isolation and characterization of gum from *amaranth* flour, *cereal chemistry* 71: 392 – 393.
- [9] R., Hoover (2001). Composition, Molecules Structure and Physicochemical Properties of tuber and root starches, a review. *Carbohydrate Polymers* 45: 253 – 267.
- [10] A. N. Hernandez, Cr., Mendez Montealvo, M. Cr., Velazquez, and L. A., Bello –perez (2004). Isolation and Partial Characterization of *Mexican Oxalis tuberosa* starch. *Starch/starke* 56:357 – 363.
- [11] M. C. Nunez – Santiago, L.A., Bello – Perez, and M. G., Lope (2004). Swelling – Solubility Characterization, granule size distribution and rheological behavior of banana (*Musa paradisiacal*) Starch. *Carbohydrate Polymers* 56: 65 – 75.
- [12] D. Betancur – Ancona, L, Y., Chel – Guerrero, and Z. E., Canizarez – Hernandez (1997). Acetylation and Characterization of *Canava liaensiformis starch*. *Journal of Agriculture and Food Chemistry*. 45,378 – 382
- [13] M. O. Henry (2007). Effect of chemical Modification on starch of some Legume flours. *Pakistan Journal of Nutrition* 6(2): 167 – 171.
- [14] G. Dodi, D., Hritcu and M. I. Popa (2011). *Carboxymethylation of guar gum: synthesis and characterization*. *Cellulose Chemistry and Technology* 45; 171 – 176.
- [15] P.H., Yiv, S. L, Loh, A., Rajan., S. C., Wong and C. F. J., Bong (2008). Physicochemical Properties of Sago Starch Modified by Acid Treatment in *Alcohol*. *American Journal of Applied Sciences* 5(4) : 307 – 311.
- [16] Y, Onuki. H, Hoshi. M, Okabe. M., Fujiyama and M., Takeya (2008). solution properties of *gum exudates* as drug release agent in pharmaceutical *Int. J. Pharm*349:47
- [17] E. A., Samia., E. M., Babitar and A., Karamalla, (2009). Analytical studies on Gum exudates of *anogeissus leiocarpus*. *Pakistan Nutrition* 8(6): 782 – 786
- [18] P.,Taggart, (2004). Starch as an ingredient: Manufacture and applications of starch in Food : Structure, function and applications, (A.C. Eliasson, ed.). CRC press LLC, New York.
- [19] K. O., Adebowale, A.T., Adeyiniyi, and B., IromidayoOlu – Owolabi, (2006). Functional, Physicochemical and retrogradation properties of sword bean (*Canavalia gladiate*) acetylated and oxidized starches. *Carbohydrate Polymers* 65:93 – 101.
- [20] R.A., Cronzalez – Soto, R., Mora – Escobedo, and I. T.,Hernandez – Sanchez, Bello – perez, L.A (2007). Extension of banana starch. Characterization of the exudates. *Journal of Science, Food and Agriculture* 87 : 348 – 356.
- [21] R.Y., Hoover, F., Susulski, (1985). A Comparative Study of the effect of acetylation on Starches of *Phaseolus Vulgaris* biotype. *Starch/Starke* 12 : 397 – 404.
- [22] D, Risica., M., Dentini. and V., Crescenzi. (2005). isolation and characterization of *guar gum polymer* 46:12247.
- [23] D. A., Silva Feitosi, J.P,A, Macial J.S Paula H.C. and de Paula RCM (2006). characterisization of crosslinked *cashew gum derivatives*. *Carbohydrate polymer* 66(1): 16 – 26
- [24] O, Adeyanju. L., Lajide. and T.G., Abayomi (2013b). Nutritional assessment of *Antiaris africana* exudates Gum: A new emulsifier in food processing. *The Journal of Phytochemistry*.Photon 114:196-200.
- [25] O, Adeyanju, and L., Lajide. (2012). physicochemical and Binding properties of oxidized *Anacardium occidentale*.L exudates gum in paracetamol Tablet formulations.*African journal of Natural sciences* 15:53-57.
- [26] J., Singh, L., Kaur, and N., Singh, (2004a). Effect of acetylation on some properties of corn and potato starches. *Starch /Starke* 56:586 – 601
- [27] Y, Brummer., W., Cui and Q., Wang (2003). Extraction, purification and physicochemical characterization of *fenugreek gum*. *Food Hydrocolloid*, 7(3), 229 – 236.
- [28] B., Janaki and R, B., Sashidharv (1998). Physicochemical analysis of gum kondagogy. *A potential food additives food chem*. 61 (1-2): 231 – 236.
- [29] M. W., Rutenberg, (1984). Starch derivatives: Production and Uses: *Starch Chemistry and Technology* 80:243 – 248.
- [30] N., Singh, D., Chawla and J., Singh. (2004b). Influence of acetic anhydride on physicochemical, morphological and thermal properties of corn and potato starch. *Food Chemistry* 86: 601 -608.