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Effect of pH of Dispersion on Some Physicochemical Properties of Regenerated Cashew Gum

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Cashew gum is the exudate obtained from the bark of the tree *Anacardium occidentale*. The gum has been modified by regenerating the native cashew gum from buffer solutions of different pH. The regenerated cashew gum was prepared by dispersing processed native cashew gum in buffer solution of different pH and recovered by precipitating with acetone. The physicochemical properties of the gums obtained were evaluated by determining their moisture sorption, swelling and thermal properties at similar temperature conditions. The isothermal moisture sorption and maximum swelling time increased with increase in the pH of buffer solutions used for dispersing the native cashew gum. The various DSC thermal transitions shown in the thermographs of the gums regenerated from distilled water were similar to those of the gums regenerated from buffer solutions of pH 7 and 2.5 but different from those regenerated from pH 10 buffer dispersion. Generally, samples of cashew gum regenerated from the dispersions of the different pHs showed characteristically different equilibrium moisture sorption, maximum swelling ratio and thermal properties.

Keywords: Regenerated cashew gum; Moisture uptake characteristics: Maximum swelling ratio; Thermal characteristics

Introduction

Gums are plant exudates and consist of heterogeneous complex mixtures of closely related polysaccharides, which produce viscous dispersions in hot or cold water (1). Cashew gum is the exudates obtained from the bark of the tree, *Anacardium occidentale*. It is a branched acidic heteropolysaccharide of low viscosity, comparable in many respects to gum Arabic (2, 3). The gum is a complex high molecular weight polysaccharide composed of 72-73% β-d-galactose, 11-14% α-d-glucose, 4.6-5 % arabinose, 3.2-4 % rhamnose and 4.7-6.3 glucuronic acid (3, 4).

Gums are versatile natural polymers employed in many industrial manufactures. About one billion pounds of gum is consumed in the United States of America each year (5). In Ghana about ten tones of gum is used annually (6). Generally, gums are obtained from numerous botanical sources, and *A. occidentale* has been identified as one of such sources (3). Cashew tree culture is very important to some countries such as Brazil, India, Mozambique, Tanzania and Kenya. In these countries, the average gum production per year could reach 120 kg/tree, thus, making cashew gum a potential industrial interest. In food and pharmaceutical processing soluble gums have been used to improve mouth feel and pourabilty. They are also used to modify the elasticity and freeze thaw stability of viscous food and drug products (7). Cashew gum has been employed as adhesive in book binding and envelope production, and as additives in chewing gum, canned food and jellies (3, 8). Cashew gum has been found to have some physicochemical and functional properties similar to gum Arabic, which has been used widely in both the food and pharmaceutical industries (9). The increasing cost of Gum Arabic has led to the assessment of other gums such as cashew gum as a potential substitute (3).

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The potential usefulness of cashew gum and the increasing attention as a result of its availability and high yield, there is a need for adequate characterization of the gum. Thus, the objective of this study is to evaluate some physicochemical properties of cashew gum obtained by regeneration from colloidal dispersions of native cashew gum in different pH solutions for use as a potential pharmaceutical excipient or food additive.

Materials and Methods

Materials

Cashew gum tears were collected from the bark of *Anacardium occidentale* in the surroundings of National Institute for Pharmaceutical Research and Development (NIPRD), Abuja, Nigeria. Sodium hydroxide, acetone, potassium thiocyanate, potassium chloride and calcium chloride (BDH, London), hydrochloric acid (Fisons, UK), sodium chloride and magnesium chloride (Sigma, Germany), potassium dihydrogen phosphate (May & Baker, England), buffer pH 2.5, 7 and 10 tablets (Fisher, USA).

Methods

Extraction of cashew gum

A 100 g quantity of dried cashew gum tears was placed in a 100 ml of distilled water (pH 7) maintained at 60^{o} C with continuous stirring using a magnetic bar stirrer (200 rpm) for 1 h. The resulting gum dispersion was then filtered while hot using a muslin cloth having a 150 µm mesh size to remove wood debris and other insoluble matter. The pH of the resulting gum dispersion was determined using a pH meter (Corning, Model 10 England). The polymer was precipitated with acetone according to the method of Builders *et al*., 2005 (10) and air-dried at an atmospheric laboratory temperature of 27 ^{o}C. The dried regenerated gum was pulverized using a porcelain mortar and pestle. The powdered gum was stored in a desiccant (21% RH) to remove residual moisture for 48 h and finally transferred into an airtight screw capped bottle until used. This procedure was repeated by replacing the distilled water with buffer solutions of pHs 2.5, 7 and 10 respectively. The buffer solutions were prepared by dissolving each buffer tablet in 100 ml of distilled water and the pH of the solution verified with the pH meter.

Moisture uptake characteristics

5 g quantities of the cashew gum samples were placed in Petri dishes and stored in a glass chamber containing activated desiccator at 27 ^{o}C for one week to remove any residual moisture from the materials. The profiles of the moisture uptake isotherm were determined by the gravimetric method (11). A 2 g sample of the dry gum was placed in an aluminum foil (8 x 6 x 2 cm) which was then put in a glass chamber with a gauze-holding tray. The glass chamber contained either distilled water or saturated solution of different salts to provide the required relative humidity (RH), (distilled water 100% RH, potassium chloride 84% RH, sodium chloride 75% RH, potassium thiocynate 47% RH and calcium chloride 31% RH at 25 ^{o}C). The powder was weighed at 12 h intervals until equilibrium was attained. The equilibrium moisture sorption (EMS) was determined using equation 1.

$$EMS = \frac{W_e}{W_d} \times 100\% \qquad \ldots. 1$$

Where W_e is the of moisture uptake at equilibrium and W_d is the dry weight of the material (12). The moisture uptake isotherm of percentage weight gain vs relative humidity was then prepared.

Swelling characteristics
A 300 mg of the dry cashew gum samples (W_d) were directly compressed into compacts using a single punch tabletting machine (THP Tablet Press, Shangha Tiaxiang & Chenta, Pharmaceutical Machinery Co. Ltd., China) at a compression force of 25 KN with an 8 mm flat-faced punch. The compacts were placed in a desiccator for 24 h to remove any moisture absorbed during the weighing and compaction processes. Each compact was placed on a mini glass plate (2 x 4 cm) of known weight contained in a Petri dish containing 60 ml of distilled water at 25 °C. At 5 min intervals the glass plates with the hydrated compacts were removed, dried by blotting with tissue paper and weighed (W_t). This process was continued until the compacts began to lose weight (W_{max}). The maximum swelling ratio (Q_{max}), was determined according to equation 2 (13).

$$Q_{max} = W_{max}/W_d \quad .... 2$$

Q_{max}, W_{max} and W_d are used as stated above.

Differential scanning calorimetric analysis
Differential scanning calorimetry (DSC) studies on the regenerated cashew gum were carried out on a DSC 204 F1 (Phoenix NETZSCH) machine equipped with a thermal analysis system. Indium (156.8 °C) was used as the internal standard. Samples of the dry gum powder approximately 2 mg were placed in an aluminum pan (25 µl) and covered with a perforated lid. Dry nitrogen was used as the purge gas (purge 20 mlmin^{-1}). The probes were heated from a start temperature of 25 to 500 °C at a rate of 10 °Cmin^{-1}. The relevant thermodynamic parameters were evaluated with the Proteus analysis software.

Result and Discussion

Moisture uptake profile
The moisture uptake profiles of the various samples of the cashew gum regenerated at different pH are shown in Fig. 1. The moisture uptake profiles of the cashew gum samples generated by precipitating the gum dispersion from distilled water and different pH buffer solutions with acetone generally show a hygroscopic characteristic. All the gums showed interaction with the moisture as indicated by the various degree of moisture uptake at the different RH (14, 15). The differences in the moisture uptake at each RH indicate the comparative variation in affinity of the different samples to water molecules. The moisture uptake profiles show the equilibrium amount of water taken up by the powdered gum samples as a function of steady state vapor pressure at a constant temperature (16). This parameter has been used to predict some physicochemical (12, 17) and functional (18) properties of polymers. Such information includes mechanism of water uptake by solid surfaces (19, 20), stability (21), comparative assessment of the amorphousity or crystallinity of polymers (10).

The uptake of water molecules by polysaccharide is related to the interaction between the unbound hydroxyl groups of the various sugar moieties and water molecules. The free hydroxyl groups of the polysaccharide interact with water molecules via hydrogen bonding (11). The differences in the moisture uptake by the different samples show the differences in the free hydroxyl groups available within the polymer chain network for interaction with water molecules. Generally, the moisture uptake for the regenerated cashew gum samples increased as the pH of the dispersion medium increased (pH 10> pH7 = distilled water> pH2.5). In acidic medium, the hydroxyl group on the polymer chain network interacts with the protons from the acid thereby reducing the amount of free hydroxyl group. Based on the IUPAC classification, different types of moisture sorption isotherm are observed (Fig. 1). Cashew gum samples generated from pH 10 and pH 7 dispersions show type 2 uptake. This type of moisture uptake is associated with monolayer-multilayer sorption on a nonporous or macroporous powdered surface (15). Gums generated from distilled water and pH 2.5 dispersions show a near type 3 moisture uptake isotherm. Their profiles show a characteristic low moisture uptake at low RH and a strong increase in uptake at high RH. In type 3, the moisture uptake occurs according to a multilayer mechanism through out the range of RH. In all, the difference in the type of moisture uptake profile is due to the orientation of the polymer chains at the different levels of acidity resulting in a difference in the number of free hydroxyl groups available for interaction with water molecules.

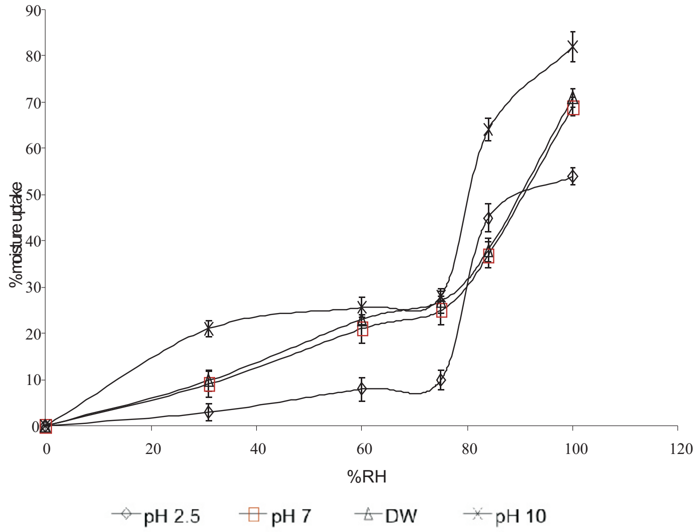

Figure 1: Moisture sorption profile of the cashew gum samples

Polymers are characterized by two component domains, amorphous and crystalline. The domain that dominates determines the overall characteristics of the polymer. Moisture sorption profile has been reported to be the most sensitive technique for assessing variation in the amorphous and crystalline content of polymers (22). For similar polymeric materials the moisture uptake profile for the amorphous form exhibits a higher shift when compared to the more ordered crystalline form (22, 23). Regeneration of polymers dispersed in media with different pH may result in change in their molecular orientation thus resulting in polymers with different properties. The change in the molecular orientation of the native cashew gum is responsible for the differences in the moisture uptake characteristic of the various regenerated samples. Fig. 1 shows that the cashew gum regenerated from buffer of pH 10 took up the highest amount of moisture at all the RH assessed.

Swelling characteristics

The swelling profiles of the compacts prepared with the different cashew gum samples generated from solutions of different pH are presented in Fig. 2. Native cashew gum has similar solubility characteristics as gum Arabic. The maximum swelling ratio (MSR) increased, with increase in the pH of the medium. The affinity for water molecules shown by the swelling of the various regenerate samples were similar to that obtained for moisture uptake. The lower MSR obtained for samples obtained by regeneration from dispersions in buffers of lower pH may indicate a relative lower solubility of native cashew gum in media of similar pH. The increased swelling at higher pH corresponds to increased solubility, due to the presence of large numbers of deprotonated labile functional groups (OH and COOH) of the sugar moieties that constitute the polysaccharide chain

(26). The differences in the MSR for the various regenerated cashew gum samples show that they all have different degrees of protonation. The large number of deprotonated groups in the polysaccharide chains network results in increased free volume that resulted in the uptake of large volume of water molecules. However, because of the limited degree of cross-linking in the polymer chain network, there is increased repulsion between functional groups that interact with water molecules. Similarly, at low pH values charge suppression will result in a lower degree of conformation of the polymer chains. This is because the acidic components exist in the free acid form. Generally, for polymers with similar properties as the pH value is raised from the acidic pH towards alkaline, the functional groups induce electrostatic repulsion that tends to keep the molecules in an extended form, thus increasing water uptake (27).

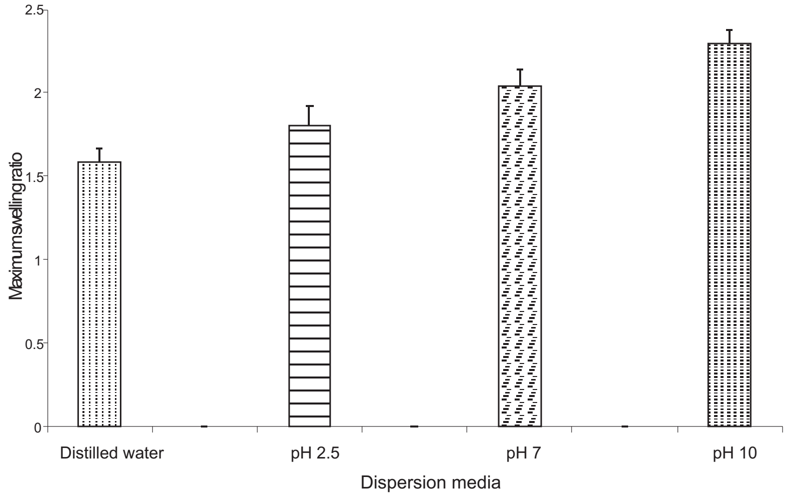

Figure 2: Maximum swelling ratio of regenerated cashew gum in different media

The limited cross-linking in the cashew gum polymer chain network is also responsible for the high solubility and poor gelling property of the gum. Compression of the powdered gum into solid compacts will increase their dispersion retardation thus preventing the gum from quickly swelling to infinity (24)**.** The compaction process introduces some interparticulate interactive bonds between the powder particles. This is also enhanced by the interactions between the numerous functional groups contained in the polysaccharide chains network, which results in the formation of temporary three-dimensional structure that diminish solubility (25).

DSC thermal analysis

The DSC thermographs and thermal analysis of the regenerated cashew gum are shown in Fig. 3 and Table 1 respectively. The thermographs of the different cashew gum samples indicate that all the samples are characterized by a glass temperature, a cold crystallization and melting peaks. The thermograph of native cashew gum as generated from distilled water is a semi-crystalline polymer consisting of an amorphous and a crystalline region. The amorphous and crystalline domains are characterized by the presence of a glass transition (Tg), melting and cold crystallization peaks. The glass transition temperature is a second order transition and is characterized by neither heat transfer nor change in heat capacity. Below the glass transition temperature, molecules in the different samples of cashew gum are immobile thus, the gum is in characteristic glassy state whereas at temperature above the glass transition the gum is in a rubbery state and the molecules are in continuous motion (29). Polymer melting is a first order transition that is characteristic of only the crystalline domain of the polymer. Below the melting temperature, the chains of the polysaccharide are in an ordered arrangement and above the melting temperature, the molecular chains of the cashew gum polymer become disordered. Cold crystallization is a dominant feature in semi-crystalline polymers. The crystallization peak is an exothermic peak occurring at temperature higher than the Tg but lower than the melting peak. The cashew gum samples regenerated from distilled water and buffer solutions of pH 7 and 2.5 showed similar thermograph. However, the thermograph of that regenerated from pH 10 buffer solutions showed only one distinct characteristic domain (Curve 3D and Table 1), the amorphous as characterized by the Tg. The cold crystallization and melting peaks present in the thermograph were too weak to be detected by the Proteus analysis. The thermograph of cashew gum regenerated from pH 10 solution indicates that beyond the glass transition temperature, polymer degradation commenced at 184.2 °C and ended at 295.8 °C. The cashew gum generated from dispersion of buffer pH 7 show four distinct characteristic peaks. Two endothermic and two exothermic peaks. The first peak which represents the Tg is followed by a mild exothermic peak representing cold crystallization, then an endothermic peak which represents the melting of the crystallized material. Another exothermic peak representing crystallization followed the melting peak. The thermograph of cashew gum regenerated from dispersions of pH 2.5 buffer solutions is characterized by five peaks. The first endothermic peak represents the glass transition temperature followed by a cold crystallization exothermic peak which flowed into the melting of the crystallized polymer. A more prominent cold crystallization exothermic peak with its onset at 323.4 °C and end at 334.3 °C was followed by a mild melting endothermic peak. The values of the various endothermic and exothermic peaks obtained by the various peaks are presented in Fig 3 and Table 1. These show that by regenerating the native cashew gum from different pH media samples with different thermal characteristics are produced.

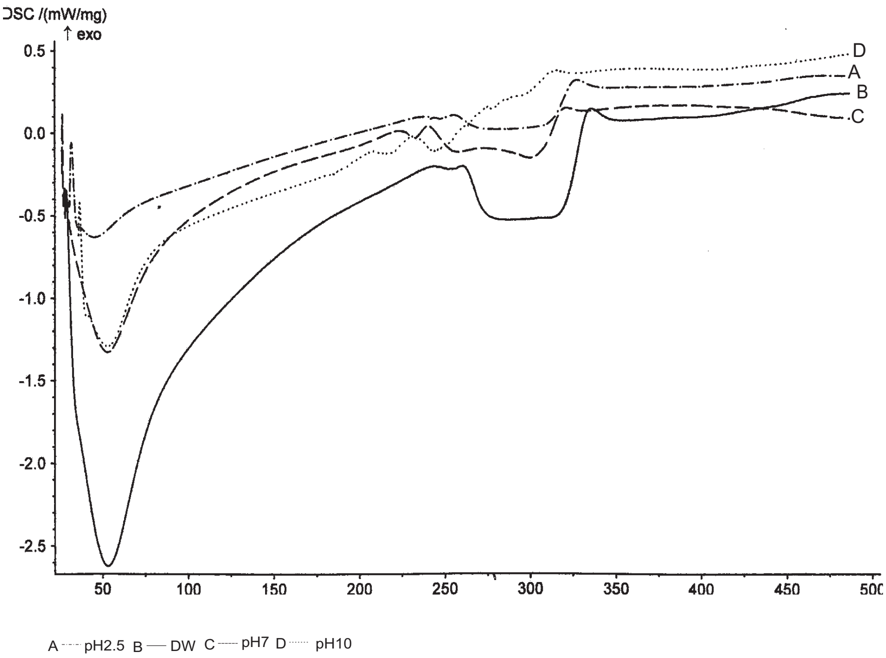

Figure 3: The thermal characteristic of cashew gum generated from different pH media

Table 1: Thermal properties of cashew gum regenerated from different pH media

Parameters	Distilled water	pH 2.5		pH 7		pH 10
T_g (°C)	44.2	50.2		41.4		46.2
ΔH J/(gK)	0.191	0.053		0.654		13.801
T_m (°C)	Peak 1	Peak 1	Peak 2	Peak 1		Peak
Onset	246.1	251.1	323.4	234.4		-
Peak	262.9	251.8	319.4	245.4		-
End	279.6	269.1	334.3	247.4		-
Crystallization	Peak 1	Peak 1	Peak 2	Peak 1	Peak 2	Peak
T_{cr} Onset (°C)	279.6	248.6	308.8	234.7	303.8	-
Peak (°C)	317.6	251.8	319.4	240.1	309.9	-
T_{cr} End (°C)	333.8	251.1	334.3	247.4	317.3	-

T_g Glass transition temperature
T_m Melting temperature
T_{cr} Temperature of crystallization ΔH J/(gK)

The thermographs were characterized with the first derivative curves analysis of the Proteus software. The advantage of the first derivative curve analysis is in the determination of the temperature characteristic of individual segments of the thermograph. The first derivative curve gives the expansion coefficient of the material when the thermal evaluation is done at constant heating or cooling.

Thermal methods using DSC have been widely used for the characterization of polymers; this method measures the total heat flow into and out of a material as a function of temperature and/or time (28). Generally, polymers display melting and glass transition endotherms as major features (10). The DSC analysis was used to investigate the differences in the thermal properties of cashew gum samples regenerated from dispersions of the native cashew gum in different pH media since melting and glass transitions are characteristic parameters, which are strongly dependent on processing conditions (29).

Conclusion

Cashew gum with different physicochemical and thermal properties were prepared by dispersing native cashew gum in buffer solutions of different pH and regenerated by precipitating with acetone. Generally, the different cashew gum samples showed characteristic variations in the moisture uptake, swelling, and thermal properties. The moisture uptake characteristic and the maximum swelling ratio of the regenerated gum increased as the pH of the dispersion media increased. The cashew gum regenerated from buffer solution of pH 10 showed the highest moisture uptake and maximum swelling ratio. The thermal transitions for the cashew gum samples regenerated from distilled water and buffer solutions of pH 2.5 and 7 were similar but distinctly different from that obtained by regenerating from buffer solution of pH10.

References

1. D., Grosch, W. and Schieberle, P., (2004). Food Chemistry, 3rd Edition, Springer, Berlin, pp. 309-314.
2. Owusu, J., Oldham, J. H., Oduro, I., Ellis, W. O. and Barimah, J., (2005). Viscosity studies of cashew gum. Trop. Sci. 45: 86-89.
3. Gyedu-Akoto, E., Oduro, I., Amoah, F. M., Oldham, J. H., Ellis, W. O., Opoku-Ameyaw, Asante, F. and Bediako, S., (2008). Quality estimation of cashew gum in the production of chocolate pebblesBelitz H.. Afric. J. of Food Science. 2, 016-020.

4. Cunha P.L. R., Maciel, J. S., Sierakowski, M. S., de Paula, R.C.M. and Feitosa J. P. A., (2007). Oxidation of cashew tree gum exudate polysaccharide with TEMPO reagent. J. Braz. Chem. Soc. 18 (1): 85-92.
5. FAO (2002). Int. trade on non-wood forest products: An overview – Plant gums, FAO Corporate Document repository.
6. Frimpong-Mensah, K., (2000). Characterization of gums from local acacia species for food and pharmaceutical uses. J. Ghana Science Ass. 21: 1-79.
7. Hydrocolloids/Gums.Learning Food Resource. Htt://food.oregonstate.edu/learn/gum.html
8. De Paula, R.C.M., Heatley, F. and Budd, P. M. (1998). Characterization of *Anacardium occidentale* exudates polysaccharide, *Pol. International* 45, 27-35.
9. Azeez, O. S. (2005). Production of gum from cashew tree latex. Leonard Electro. J. Practic. and Technol. Htm
10. Builders, P. F, Kunle, O. O., and Adikwu, M. U., (2008). Preparation and characterization of mucinated agarose: A mucin–agarose physical crosslink Int. J. Pharmaceutics 356, 174-180.
11. Beristain, H. G. (1995). Overview of physical characterization methodology. In physical characterization of pharmaceutical solids, Beristtain H. G. ed., New York; Marcel Dekker Inc. p. 1-35.
12. Lin, Y. C., and Chen, X., (2005). Moisture sorption-desorption-resorption characteristics and its effect on the mechanical behaviour of the epoxy system. Polymer 46(25): 11994-12003.
13. Ritger, P. L. and Peppas, N. A. (1987). A simple equation for desorption of solute release II Fickian and anomalous release from swellable devices. J. Controll. Rel. 5, 37.
14. Callahan, J. C. Cleary, G. W. Elefant, M. Kaplan, G. Kensler, T. and Nash, R. A., (1982). Equilibrium moisture content of pharmaceutical excipients. Drug Dev. Ind. Pharmacy. 8, 355-369.
15. Okubayashi, S., Griesser, U.I., Bechtold, T., (2004). A kinetic study of moisture sorption and desorption on lyocell fibers. Carbohydrate Polymer 58, 293–299.
16. Pe´rez-Alonso, C. Beristain, C. I., Lobato-Calleros, C.M.E. and Rodrı´guez-Huezo, Vernon-Carter E. J., (2006). Thermodynamic analysis of the sorption isotherms of pure and blended carbohydrate polymers. J. Food Engin. 77, 753–760.
17. Bravo-Osuna, I., Ferrero, C., Jimenez-Castellanos, M.R., (2005). Water sorption–desorption behavior of methyl methacrylate-starch copolymers: effect of hydrophobic graft and drying method. Eur. J. Pharm. Biopharm. 59, 537–548.
18. Trung, T.S., Thein-Han, W. W., Qui, T.N., Ng, C., Stevens, W., (2005). Functional characteristics of shrimp chitosan and its membranes as affected by the degree of deacetylation. Bioresour. Technol. 97, 659–663.
19. Roos, Y., (1995). In: Phase transitions in foods. Academic Press, San Diego, USA. p. 151-235.
20. Bell, L. and Labuza T. P., (2000). Moisture sorption: practical aspects of isotherm measurement and use, 2nd Ed. St. Paul, MN: American Association of Cereal Chemists.
21. Swaminathan, V. and Kildsig, D. O., (2001). An examination of the moisture sorption characteristics of commercial magnesium stearate. AAPS Pharm. Sci. Tech. 2(4) article 28. Moisture sorption.htm.
22. Mackin, L., Zanon, R., Park, M. J., Foster, H.O. and Demonte, M., (2002). Quantification of low levels (<10%) of amorphous content in micronised active batches using dynamic vapours sorption and isothermal microcalormertry. Int. J. Pharmaceutics 231, 227–236.
23. Burnett, D. J., Theilmann, F., Sokoloski, T., and Brum, J., (2006). Investigation of the moisture-induced crystallization kinetics of spray-dried lactose. Int. J. Pharmaceutics. 313, 23–28.

24. Sumathi, S. and. Alok R. R. (2002). Release behaviour of drugs from tamarind seed polysaccharide tablets. J. Pharm. Pharmaceutical Science 5(1):12-18.
25. Mazza, G. and Biliaderis, C. G. (1989). Functional properties of flax seed mucilage, J. of Food Science 54, pp. 1302–1305.
26. Fedeniuk, R.W. and Biliaderis, C. G. (1994). Composition and Physicochemical Properties of Linseed (*Linum usitatissimum* L.) Mucilage. J. Agric. Food Chem., 42, 240-247 - pubs.acs.org.
27. Launay, B., Doublier J. L. and Cuvelier, G. (1986). Flow properties of aqueous solutions and dispersions of polysaccharides. In: Functional properties of food macromolecules. Mitchell, J. R. and Ledward, D. A.(Eds.), Elsevier Applied Science Publishers, New York. pp. 12-19.
28. Campbell, D. Pethrick, R. A. P., and White, J. R. (2007). Polymer Characterization: Physical techniques. 2nd Ed. United Kingdom: Stanley Thornes (Publishers) Ltd. Cervera. pp. 362-399.
29. Macrogalleria Directory, Copyright, (2005). Polymer science learning centre. Department of Polymer science. The University of Southern Mississippi.