



## **Intrinsic and Functional Properties of a Gelling Gum from *Dioclea reflexa*: A Potential Pharmaceutical Excipient**

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### **ABSTRACT**

**Aims:** *Dioclea reflexa* Hook F., is a woody vine widely distributed within tropical Africa and South America, in Nigeria flour prepared from the seeds is used as a soup thickener. The objectives of this study were to extract and modify the native gum from the seeds of *D. reflexa*, and evaluate their physicochemical and functional properties as a potential pharmaceutical excipient.

**Place and Duration of Study:** Department of Pharmaceutical Technology and Raw Materials Development, National Institute for Pharmaceutical Research and Development, Abuja, Nigeria. Between January 2009 and October 2010. And Department of Pharmaceutics, Faculty of Pharmaceutical Sciences, University of Nigeria, Nsukka, Nigeria. Between June 2010 and October 2011.

**Methodology:** Native *D. reflexa* gum (DR-gum) was extracted from the seeds of *D. reflexa* and modified by ionotropic gelation in calcium chloride solution. The gum's gel clarity and swelling in buffer solutions of different pH (4, 7, and 9.2), as well as the moisture sorption characteristics at different relative humidity (RH) were determined in relation to guar gum (G-gum). Also, the Fourier transform infrared (FT-IR) and Differential scanning calorimetry (DSC) analysis as well as the powders' flow properties were evaluated.

**Results:** DR-gum, XDR-gum and G-gum are typical hydrogels showing considerable responsiveness in swelling and gel clarity to changes in pH. The DSC thermographs of DR-gum and G-gum were similarly characterized by a glass transition and a cold crystallization transitions peaks as compared to the glass transition and melting transition

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peak of XDR-gum. The moisture sorption profile indicated that DR-gum and G-gum are moderately hygroscopic while XDR-gum is slightly hygroscopic. The FT-IR of the gums showed the basic differences in the functional groups of the respective polymer chain network. The bulk particles of the three gums showed comparative good flow.

**Conclusion:** The basic similarities and differences in the physicochemical and functional properties of DR-gum and XDR-gum, and G-gum indicate their potential as a pharmaceutical excipient.

*Keywords:* Guar gum; *Dioclea reflexa* gum; crosslinked *Dioclea reflexa* gum; physicochemical properties; functional properties.

## 1. INTRODUCTION

Polymers from natural sources have continued to gain popularity in pharmaceutical manufacture especially for drug delivery applications because of their diverse physicochemical and functional properties (Malafaya et al., 2007). In general the major attraction to this class of polymers in drug delivery applications includes their ready availability, low cost, biodegradability and biocompatibility as well as their functional versatility and modification potential (Jain et al., 2007; Malafaya et al., 2007; Shirwaikar et al., 2008; Beneke et al., 2009).

A large number of natural polymers that are used for drug delivery are non starch polysaccharides, many of which are hydrogels with high swelling ratios and capable of causing large viscosity increases in aqueous solutions even at small concentrations (Builders et al., 2010). These are among the properties that make them overtly dependable in several conventional and novel drug delivery systems (Boustra and Junginger, 1993; Rowe et al., 2003). Thus, natural biopolymers along with their modification products offer a wide range of properties and applications (Beneke et al., 2009).

Guar gum is a white to yellowish, nearly odorless, free-flowing gelling gum extracted from the seeds of *Cyamopsis tetragonoloba* (L.) Taub. It has extensively been investigated and used especially as binders, viscosity modifiers and suspending agents, also in novel drug delivery applications as matrix and particulate systems with controlled drug delivery properties (Goldstein et al., 1992; Rama Prasad et al., 1998).

The continuous need to develop new polymers with enhanced or new properties is to meet the increasing need for novel drug delivery technology especially to deliver challenging molecules. This is among the reasons for the evaluation of polymers from new sources such as those from *D. reflexa*. *D. reflexa* is a large woody vine commonly distributed within tropical Africa and South America. In Nigeria, the plant is cultivated and also grows wild. In Eastern Nigeria, it is cultivated as a cover crop and the seed is commonly used as a soup thickener (Burkill, 1995). The gelling potential and the folkloric use of the seed flour as a soup thickener make it a material of interest as a food and pharmaceutical excipient. In this study gum was extracted from the seeds of *D. reflexa* and modified by ionic gelation. The objective of this study therefore, was to evaluate some physicochemical and functional properties of the native and modified motif of the *D. reflexa* gum in relation to guar gum as a potential pharmaceutical excipient.

## 2. MATERIALS AND METHODS

### 2.1 Materials

*D. reflexa* seeds were obtained from a local market in Abuja Nigeria. Guar gum, calcium chloride and diethyl ether, acetone, sodium chloride; magnesium chloride were obtained from (Sigma-Aldrich, Germany), Potassium dihydrogen phosphate was obtained from May & Baker, UK. Sodium chloride, potassium thiocyanate, potassium chloride, Iodine, potassium iodide and calcium chloride were obtained from BDH, UK. Buffer tablets were purchased from Fluka Chimie, UK.

### 2.2 Extraction of *D. reflexa*

The method by Ross-Murphy et al., with slight modification was adopted for the extraction of the *D. reflexa* seed gum (Ross-Murphy et al., 2003; Builders et al., 2009a). The seeds were washed to remove any adhering dirt and cracked to remove the pericarp, before boiling for 3 h to make the seed coat tender and soft enough to remove. The hydrated tegmen obtained after removal of the seed coat was rinsed several times with distilled water and chopped into small multi-particulate granular pieces (>3 mm particle diameter) with a knife. The particles collected were boiled in ethanol for 1.30 h to denature proteins and inactivate enzymes. The granules were then treated with several portions of diethyl ether in a Soxhlet apparatus to remove lipids. The defatted granules were air dried (27°C) for 5 h to remove residual diethyl ether. A 0.1 kg quantity of the defatted granules was then soaked in 500 ml of distilled water for 18 h with continuous agitation using a shaker (Erweka, Germany). The viscous supernatant extracted was collected by filtration using a muslin cloth of 150 µm mesh size and centrifuged at 4500 rpm for 1 h to remove any particulate matter before precipitating with acetone. The precipitate was dried in a hot air oven at 40°C for 3 h and placed in a desiccator for 72 h. The dry powder was then transferred into an airtight container and stored at 27°C until used.

### 2.3 Crosslinking by Ionic Gelation

A 250 ml volume of a 0.5 %<sub>w/v</sub> dispersion of *D. reflexa* gum was prepared by allowing the powder to hydrate for 24 h. A 1 %<sub>w/v</sub> solution of calcium chloride was also prepared. A 200 ml volume of the *D. reflexa* gum dispersion was mixed with an amount of calcium chloride solution to obtain a solution containing 0.25 %<sub>w/v</sub> calcium chloride with continuous stirring at 100 rpm for 12 h after which an appropriate amount of acetone was added to produce an equal volume of calcium chloride and acetone (1:1) mix which was allowed to stand for another five minutes. The gelled polymer microparticles were then harvested by filtration using a filter paper (Whatman, USA) with the aid of a vacuum pump. The gelled particles were washed with more portions of acetone to harden and remove any residual water from the particles. The generated polymer material was dried in a hot air oven set at 40°C for 2 h and packed in an air tight screw capped container.

### 2.4 Gum Powder Particle Properties

The bulk and tapped densities of the powders were determined by measuring the volumes occupied by 50 g of the G-gum, DR-gum and XDR-gum powders using a 200 ml graduated measuring cylinder. The tapped volume corresponds to the stable final volume with unchanging particle arrangement when tapped with an automated tapping machine

(Stampfvolumeter, STAV 2003JEF, Germany). The bulk volume corresponds to the volume before tapping. These were used to evaluate the bulk and tapped densities (Well, 2003).

The compressibility indices of the various granules were determined with the data obtained for the bulk and tapped densities using equation (1) (Well, 2003; Builders et al., 2005).

$$\% \text{ Compressibility} = (\text{tapped density} - \text{bulk density} / \text{tapped density}) \times 100 \quad \dots \quad (1)$$

The angle of repose of the powdered gums were determined by measuring the internal angle between the surface of the heap of powders obtained when 50 g of each of the powders were allowed to flow through a glass funnel (orifice diameter 2 cm) and clamped 10 cm above a flat surface. The angle of repose was calculated using the equation (2) (Builders et al., 2005; Aulton, 1988).

$$\text{Angle of repose} = \tan \Theta = \text{Height of cone} / \text{Radius of cone} (r) \quad \dots \quad (2)$$

The packing characteristic of DR-gum, XD-gum and G-gum powder particles were determined using the Kawakita model (Paronen and Iikka, 1995). 50 g of a powdered gum was placed in a 200 ml measuring cylinder to determine the initial volume ( $V_0$ ) occupied by the powder, the volumes occupied after series of numbers of mechanical tapings ( $N$ ) were determined until total powder consolidation obtained. The compactibility of the gums was then evaluated by means of Kawakita's equation (3).

$$C = (V_0 - V) / V_0 = abP / 1 + bP \quad \dots \quad (3)$$

Where  $C$  is the degree of volume reduction,  $V_0$  initial volume reduction,  $V$  is volume of powder column under applied pressure and  $ab$  is constant characteristic to powder being compressed. When the volume reduction is described in terms of tapping, equation (3), can thus be rewritten thus: equation (4).

$$N/C = N/a + 1/ab \quad \dots \quad (4)$$

The intercept of the linear portion of the plot of  $N/C$  versus  $N$  gives a value representative of  $1/ab$  while the slope represents the reciprocal of the constant  $a$ . While  $a$  give an indication of the maximum of volume reduction available and characteristic for the powder also known as compressibility,  $b$  describes an inclination towards volume reduction (Paronen and Iikka, 1995).

## 2.5 pH of Gum Dispersion

The pH of 0.1 and 0.5  $w/v$ % dispersions of DR-gum, XDR-gum and G-gum were determined with a pH meter (Canon 126, England) (Builders et al., 2010).

## 2.6 Gel Clarity

The gel clarity of DR-gum and G-gum was assessed by measuring light transmission through their dispersions in different pH media. The transmittance of a 0.5 % dispersions of DR-gum and G-gum made in buffer solutions of pHs 2 to 10 respectively were measured at 580 nm using a UV-spectrophotometer (UV160A, Shimadzu Corporation, Japan) (Craig et

al.,1989). The effect of pH on gel clarity and sensitivity of the gels to change in pH were evaluated from the intercept and slope respectively of the transmittance versus pH curves.

## 2.7 Isothermal Swelling Characteristics

The powders of G-gum, DR-gum and XDR-gum were compressed into compacts each 300 mg ( $W_d$ ) using a compression machine (Shanghai Tiexiang and Chenta Pharmaceutical Machinery Co. Ltd.) set at a pressure of 22.5 KgF and fitted with an 8 mm flat faced punch and die. The presence of any residual moisture in the compacts was removed by desorption by storing under silica gel in a desiccating chamber for 24 h before the swelling assessments were made. The dry compacts were placed on tarred glass plates (2×4 cm). The plates were transferred into Petri dishes containing 60 ml of distilled water, 0.9 %<sup>w/v</sup> sodium chloride solution and buffer solutions of pH 4, 7, and 9.2 respectively maintained at 27°C. At 15 min intervals, the glass plates with the hydrated compacts were removed, dried by blotting with tissue paper and then weighed ( $W_t$ ). The weight-swelling ratio (Q) was determined using equation (5). When the hydrated compacts reached a constant weight the swelling ratio at this point is considered to be equilibrium swelling ratio ( $Q_e$ ) and was determined using equation (6) (Vervoort et al., 1998).

$$Q = W_t/W_d \quad \dots \dots \quad (5)$$

$$Q_e = W_e/W_d \quad \dots \dots \quad (6)$$

## 2.8 Moisture Sorption Characteristics

G-gum, DR-gum and XDR-gum powders were placed in Petri dishes and stored in a desiccator containing activated silica gel as the desiccant for one week at 25°C to remove residual moisture. The moisture sorption isotherms were determined by the gravimetric method (Lin and Chen, 2005; Builders et al., 2009a). 1 g of G-gum, DR-gum and XDR-gum were each placed in an aluminum foil and put in a sealed glass chamber with a gauze holding tray containing water or saturated solution of different salts to provide the required relative humidity (RH) (water 100%, potassium chloride 84%, sodium chloride 75%, potassium thiocyanate 47% and calcium chloride 31%). The powders were then weighed at 12 h intervals until equilibrium was attained. The percentage equilibrium moisture uptake was determined using equation (7).

$$\text{Moisture uptake} = M_e/M_d \times 100\% \quad \dots \dots \quad (7)$$

Where  $M_e$  is the amount of moisture absorbed at equilibrium and  $M_d$  is the dry weight of the material (Lin and Chen, 2005). The moisture sorption profile of percentage weight gain versus RH was then determined.

## 2.9 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) studies were carried out on a differential scanning calorimeter (DSC 204 F1, Phoenix NETZSCH, Germany) equipped with a thermal analysis system. Indium (156.8°C) was used as the internal standard. Samples of approximately 10 mg of powdered G-gum, DR-gum and XDR-gum were placed in an aluminum pan (25 µl) and covered with a perforated lid, respectively. Dry nitrogen was used as the purge gas

(purge 20 ml min<sup>-1</sup>). The probes were heated from a start temperature of 25°C to 500°C at a rate of 10°C min<sup>-1</sup>. The glass transition ( $T_g$ ), melting point ( $T_m$ ), and cold crystallization ( $T_c$ ) temperatures were evaluated with the Proteus analysis software (Builders et al., 2009b).

## 2.10 Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were acquired on a NICOLET IR 100 (Thermo Electro Corporation, USA). Spectra over a range of 4000-400 cm<sup>-1</sup>, with threshold of 1.303, sensitivity of 50 and resolution of 2 cm<sup>-1</sup> range were recorded on KBr tablets (1 mg of the powder samples per 400 mg of KBr). Spectra scans for G-gum, DR-gum and XDR-gum were determined (Builders et al., 2010).

## 3. RESULTS AND DISCUSSION

### 3.1 Extraction and Crosslinking of *D. reflexa* Gum

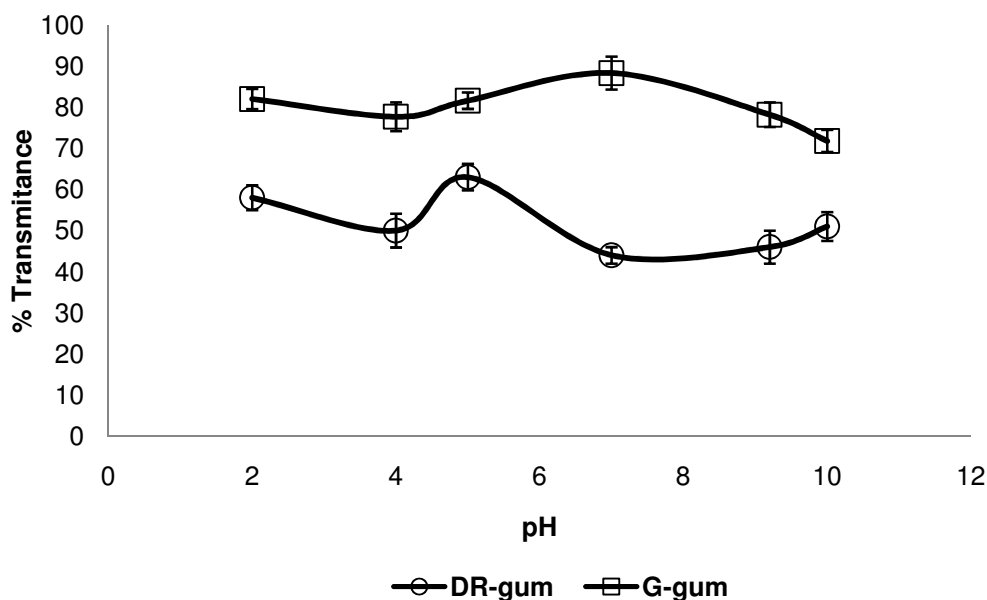
The gum extracted from the seeds of *D. reflexa* when pulverized and passed through a 250 µm mesh sieve was an off-white powder and a yield of 15 %<sup>w/w</sup> of the whole seed. The economic and folkloric importance of the seed of *D. reflexa* as used in Nigeria is attributed to the gelling polysaccharide contained in the seed that impact viscosity increase.

Many new polymers with innovative functional properties are continuously been produced from natural polymers by manipulation of their chain structure. Treatment of DR-gum with calcium chloride formed a water insoluble coacervate resulting from ionic gelation induced by the calcium chloride solution (Patil et al., 2010). The ionotropic gelation has been proposed to be due to the binding of the calcium ions to the free carbonyl groups on each repeat unit of the polymer chain network resulting in the formation of a three dimensional lattice of an ionically crosslinked moiety. A proposed gelling mechanism involves the formation of double-helical calcium ion junction-zones within the polymer chain network, followed by the aggregation of the double-helical structure to form three-dimensional networks stabilized by the electrostatic interactions between the calcium ions and the carbonyl groups (Chandrasekaran and Radha, 1996). This is characteristic of the interaction between the divalent cations and an anionic polymer (Patil et al., 2010).

### 3.2 Gel Clarity

One of the essential attribute that defines the functional applications of gelling polymers is their gel clarity, the highly clear gels being more favored for use in many foods and drugs (Bixler, 1994). The clarity characteristics of G-gum and DR-gum gels are presented in Fig.1, as an average transmittance versus pH curve. Both gums showed a pH responsive gel clarity profile. The effect of pH on the clarity of the colloidal dispersion of these two natural hydrogels could be due to the neutralization of acidic and basic functional groups in the polymer chains (Laua and Tanga, 2001). There was a decrease in the clarity of the gums dispersion at the extremes of pH (Fig. 1). This phenomena has been attributed to the over neutralization of the acidic and basic functional groups resulting in the reversion of the polymer dispersion to large aggregates thus diminishing the passage of light through the dispersion (Fig. 1). The profiles of the gel clarity of DR-gum and G-gum dispersions as assessed from acidity through neutral to basic show maximum clarity at pH 7 and pH 5 respectively. The intercept and slope of the % transmittance versus pH curves were 60.03

and 1.3 for DR-gum and, 84.47 and 0.733 for G-gum respectively. The higher intercept obtained for G-gum correlates to higher gel clarity than DR-gum. The higher value of the slope obtained for DR-gum indicates a higher sensitivity of the gel clarity to pH changes. The lower gel clarity shown by DR-gum is essentially due to the relative lower solubility and the formation of larger aggregates in its aqueous dispersions that reduced the transmittance of light through its dispersion. The differences can be related to higher molecular weight and degree of crosslinking in the DR-gum polymer chain network as compared to G-gum due to variation in the botanical source (Bixler, 1994).



**Fig. 1. Effect of pH on the gel clarity of *D. reflexa* gum and Guar gums**

### 3.3 Gum Powder Particle Properties

The particle properties of DR-gum, XDR-gum and G-gum are presented in Table 1. The particle properties of pharmaceutical excipient are critical especially when they are to be considered in direct compression applications. This is because important processes such as mixing, flow and compression are dependent on particle properties (Paronen and Ikka, 1994).

The bulk and tapped densities of DR-gum, XDR-gum and G-gum are presented in Table 1. Though bulk and tapped densities are not intrinsic properties attention to these parameters are important because they are dependent on interparticulate interaction which can be used to predict the flow property of powders. The tapped and bulk densities of the crosslinked motif of *D. reflexa* gum were lower than those of DR-gum and G-gum (Table 1).

**Table 1. Some physicochemical properties of *D. reflexa* gum, Crosslinked *D. reflexa* gum and Guar gum**

Parameter	<i>D. reflexa</i> gum	Crosslinked <i>D. reflexa</i> gum	Guar gum
pH	7.5±0.1	6.7±0.1	6.8±0.1
Bulk density (g/ml)	0.5637±0.05	0.1739±0.06	0.4743±0.06
Tapped density (g/ml)	0.7059±0.01	0.2251±0.05	0.5455±0.05
Compressibility index (%)	20.14±0.2	22.75±0.5	13.05±0.7
Angle of repose (°)	25.36±0.1	27.3±0.06	19.24±0.05
Kawakita constants			
a	24.096	22.12	14.77
b	0.189	0.122	0.658

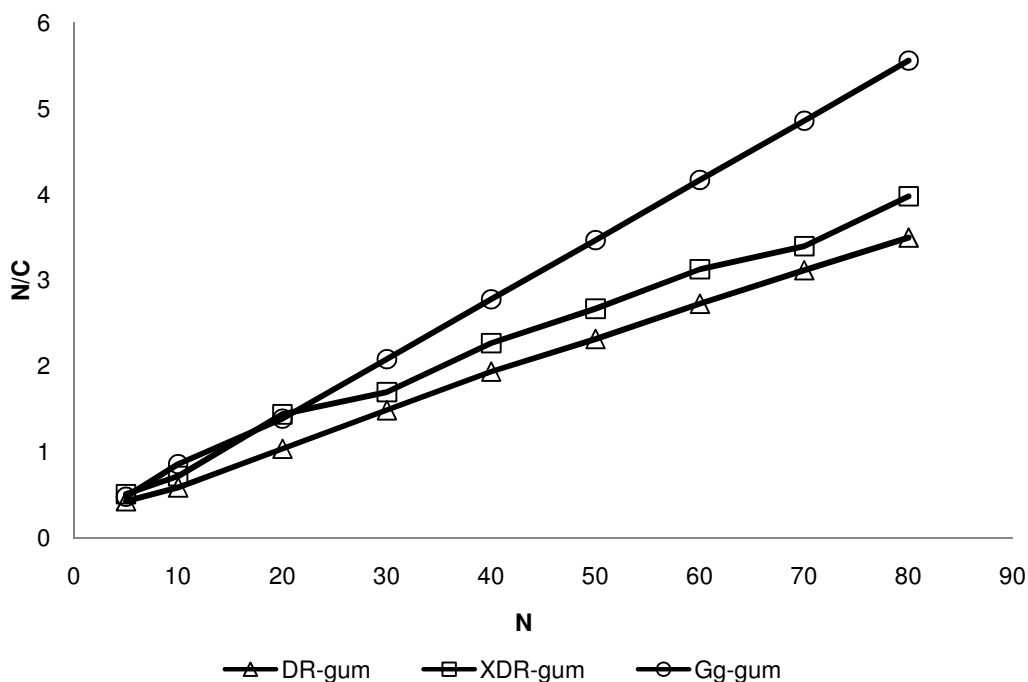
This is due the comparative higher bulk volume per unit weight due to their relative fluffy nature. The flow-ability of the gum powders as estimated with the Carr's compressibility index was evaluated using the bulk and tapped densities. Generally when assessing with the Carr's compressibility indices, values below 15% represent good flow and 15% to 25% is fair while values above 25% is indicative of poor flow (Well, 2003). Thus, the powdered gums all showed acceptable flow. A comparison of the flow qualities of DR-gum, XDR-gum and G-gum powders show that the powders of G-gum had very good flow while DR-gum and XDR-gum had good flow characteristics (Table 1). When the flow characteristics of the gums were estimated by their angle of repose, results show that the flow qualities of the powders as determined by their angle of repose correlated with their respective Carr's compressibility indices. Generally the flow of the powders as assessed by their angle of repose is based on the cohesion between the powder particles with value of less than 25° indicative of very-good flow whereas values equal and greater than 25° and less than 50° is good and equal and greater than 50° represent poor flow.

The compressibility of the powders was estimated by assessing with the Kawakita model. The plot of N/C versus N produced a linear curve (Fig. 2). The constants a and b representing the maximum powder volume reduction and the inclination towards volume reduction respectively are presented in Table 1. The potential volume reduction of the DR-gum was higher than that of G-gum however inclination towards volume reduction was higher for G-gum. The volume reduction and the inclination of the powder towards volume reduction were generally higher for the unmodified gum as compared to the crosslinked motif. DR-gum thus, has a higher compactibility potential when compared to XDR-gum and G-gum (Donini et al., 2003).

### 3.4 pH of Gum Dispersions

The pH of the polymer dispersion relates to the presence of ionizable groups that could protonate when dispersed in water to form hydrogen ions (Builders et al., 2009a). The pH of a 0.5 %<sup>w/v</sup> dispersion of DR-gum in distilled water at 27°C was 7.5 ± 0.2 while that of XDR-gum and G-gum were 6.7 ± 0.1 and 6.8 ± 0.1 respectively. The difference in the pH of the polymer dispersion reflects the differences in the intrinsic characteristics of the polymers.

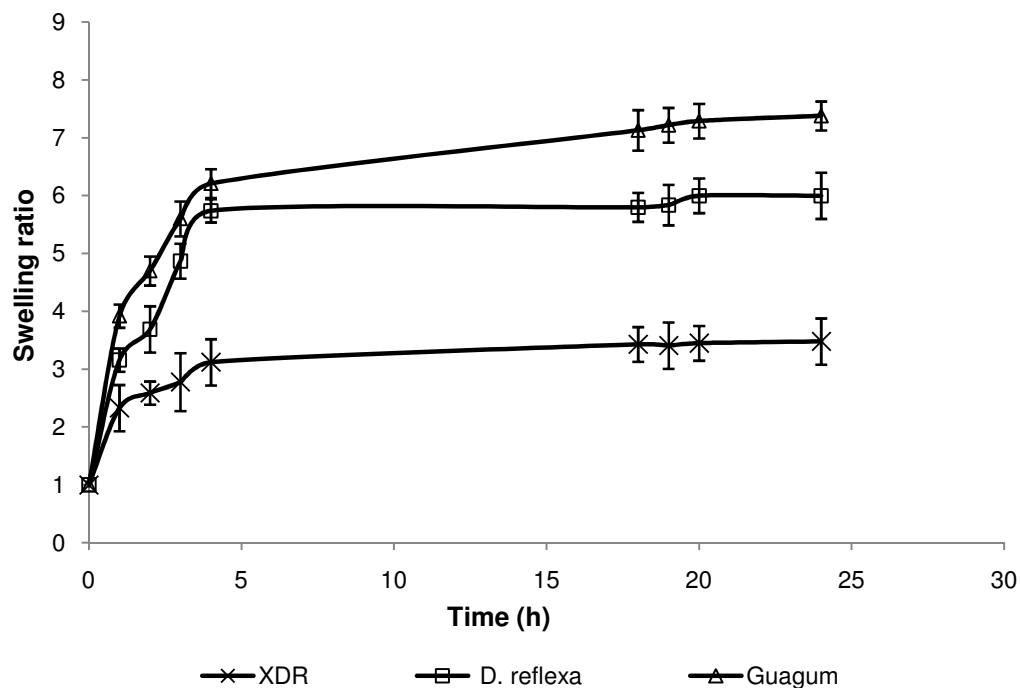




**Fig. 2. Effect of pH on the gel clarity of *D. reflexa* gum and Guar gums**

### 3.5 Isothermal Swelling Characteristics

A general assessment of the interaction between G-gum, DR-gum and XDR-gum with water as presented in Fig. 3, show that these polymers are hydrogels. This is due to the ability of their compacts to absorb and hold several times their weight of water while maintaining a stable physical structure. The interaction of XDR-gum with water was also similar to that of DR-gum. The formation of a stable gel by the polymers in the aqueous media indicates the presence of crosslinks, entanglements or crystalline region within the polymer network (Gustafsson et al., 1999). Water transport in and out of hydrogels and the dynamics of dimensional response when they are exposed to aqueous media of different pH are important in assessing and predicting their suitability as food additive or excipients for pharmaceuticals. The swollen state of hydrogels is a consequence of the balance between cohesive and hydration forces on the polymer chains network. The hydrophilic polymers swell when water molecules interact with the polar groups mainly -OH and -COOH, on the polymer backbone or side chains (Rodriguez et al., 2005). Indeed a fundamental relationship exists between polymer type and swelling in different solvents as shown by the varying degrees of swelling of different polymers in different solvents (Pourjavadi and Mahdavinia, 2006).



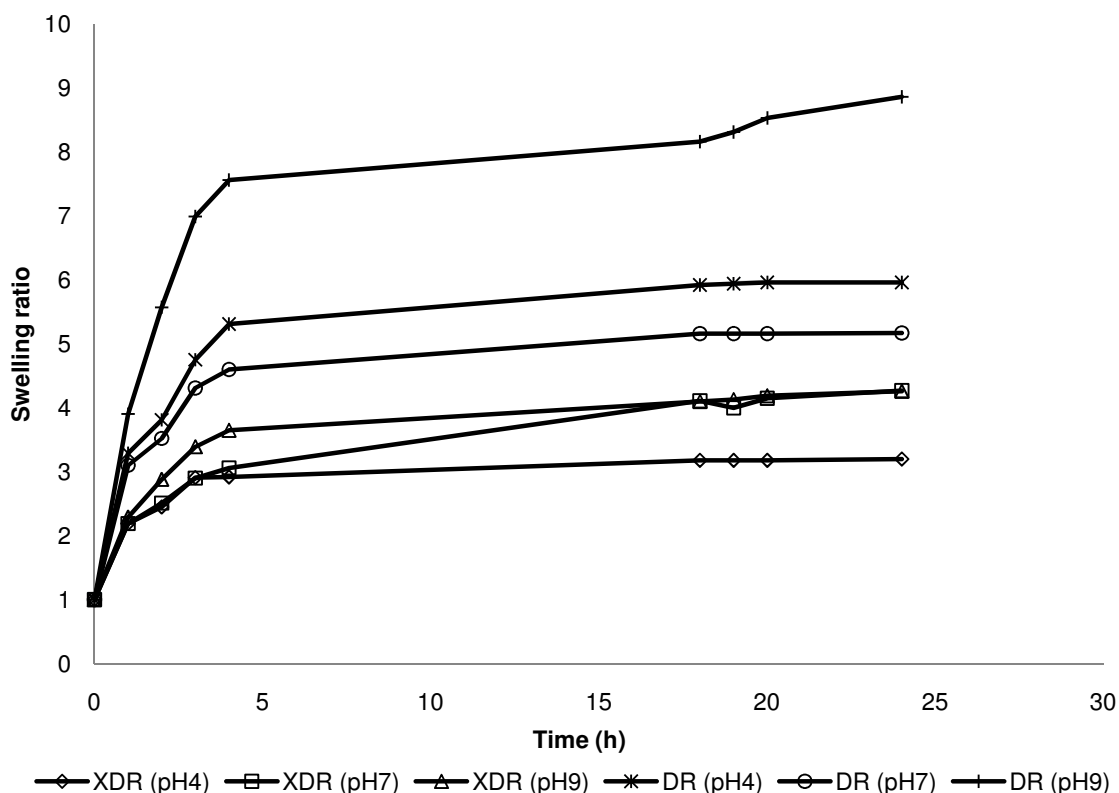
**Fig. 3. The swelling profile of *D. reflexa* gum, crosslinked *D. reflexa* gum and guar gum in water**

XDR-gum=crosslinked *D. reflexa* gum: DR-gum= *D. reflexa* gum

Fig. 4 shows the swelling profile of DR-gum and XDR-gum in buffer solutions of different pHs. DR-Gum and XDR-Gum are pH sensitive as shown by the marked differences in their swelling in solutions of different pHs. The swelling of DR-gum, XDR-gum increased with increasing pH. The swelling responsiveness of DR-gum and XDR-gum shows that they are anionic polymers as their equilibrium swelling capacities increased as the pH of the solution increased (Schmidt et al., 2009). Thus, indicating that the pendant functional groups of their chain network are predominantly carboxylic acid. At higher pH values, the polyelectrolyte chains on the polymer network will have a large osmotic pressure that favors swelling. The degree of ionization in a particular pH medium is responsible for the extent of chain repulsion that results in change in free volume required for water uptake (Builders et al., 2009a). The swelling of DR-gum and XDR-gum in different pH media can be represented thus: pH 9>pH 7>pH 4. XDR-gum generally had a lower swelling ratio in all the different buffer solutions (Fig. 4). This is because the crosslinking results in the reduction of the number of free hydroxyl and carboxyl groups exposed for interaction with water molecules and a tendency towards crystalline perfection.

Fig. 5 shows the effect of sodium chloride on the swelling of DR-gum and XDR-gum compacts. The crosslinked motif of *D. reflexa* gum showed a higher equilibrium swelling in sodium chloride solution than in water. The phenomenon is related to the tendency of the sodium ions to diffuse into the internal structures of the polymer network and forming sodium carboxylate groups with free carboxyl groups. The sodium carboxylate groups generate osmotic pressure that increases the ingress of water molecules. The entry of the water molecules is the same for both the modified (crosslinked) and the native moieties. However,

because of the tight junctions in the crosslinked motif which creates higher mechanical resistance that slows the excessive ingress of water molecules that leads to the hydrated polymer becoming tender and disintegrating. The lower swelling ratio obtained for the native *D. reflexa* gum is due mainly to loss of polymer due to disintegration.

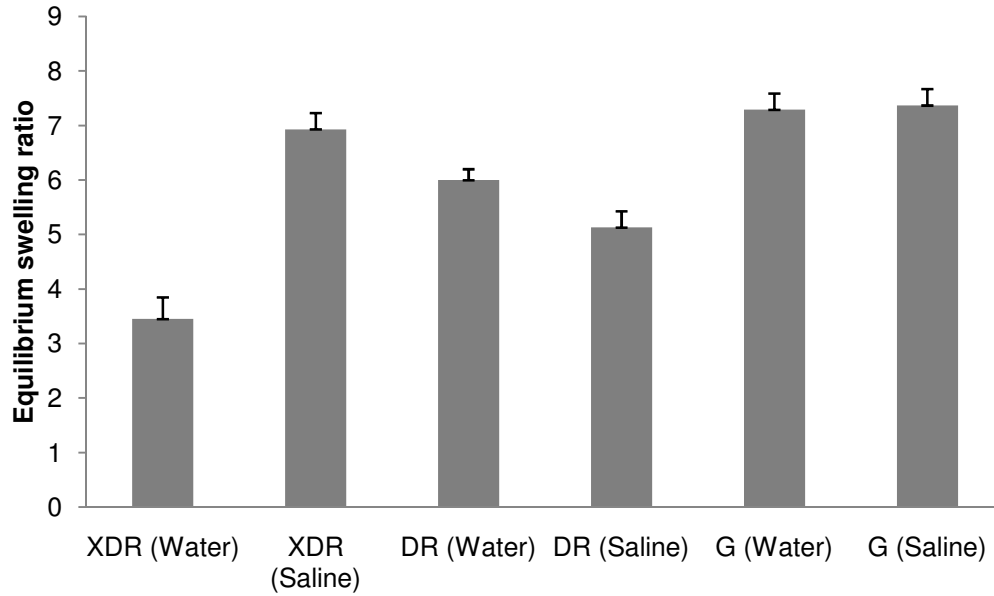


**Fig. 4. The swelling profile of DR-gum and XDR-gum in buffer solution of pH 4, 7 and 9.2**

*XDR-gum=crosslinked D. reflexa gum: DR-gum= D. reflexa gum*

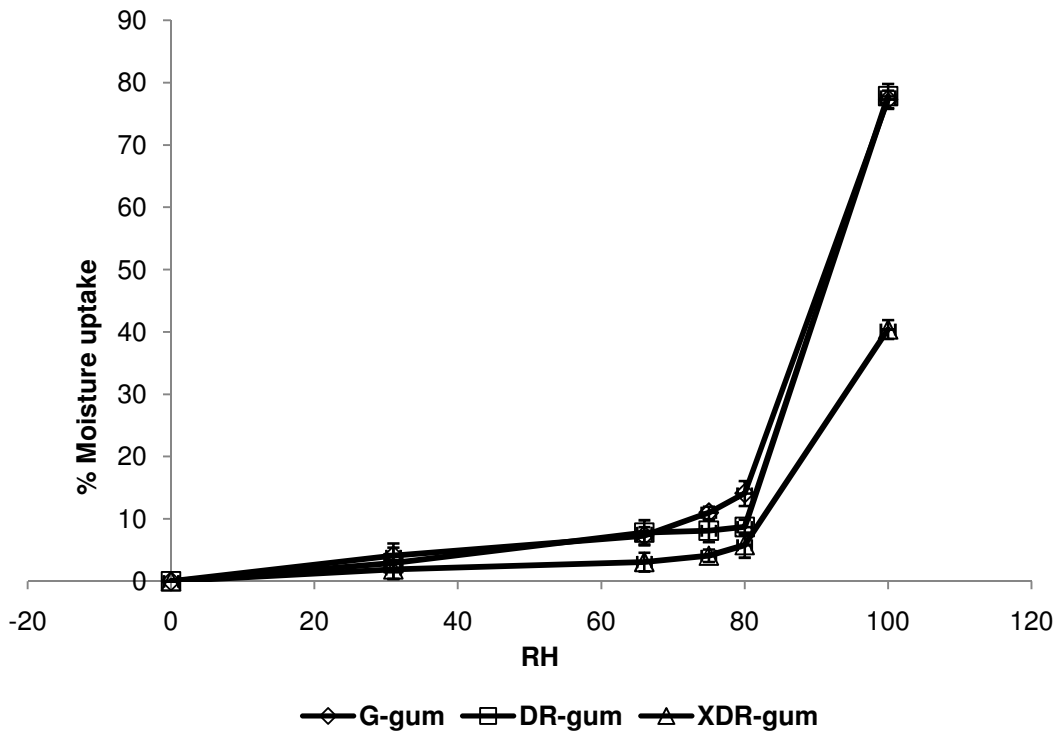
### 3.6 Moisture Sorption Characteristics

The moisture sorption profiles of G-gum, DR-gum and XDR-gum are presented in Fig. 6. Polymeric materials generally interact with moisture by adsorption and/or absorption when exposed to a humid atmosphere. The assessment of the interaction of polymers especially those intended to be used as excipients becomes imperative as this affects some important physicochemical and functional properties of these materials and the basic stability of active pharmaceutical ingredients (API) and food when they are employed in drug formulation as excipients or as additives in food.



**Fig. 5. Effect of sodium chloride on the equilibrium swelling ratio of native *D. reflexa* gum, *D. reflexa* gum and guar gum**

*XDR =crosslinked D. reflexa gum; DR = D. reflexa gum; G=guar gum.*



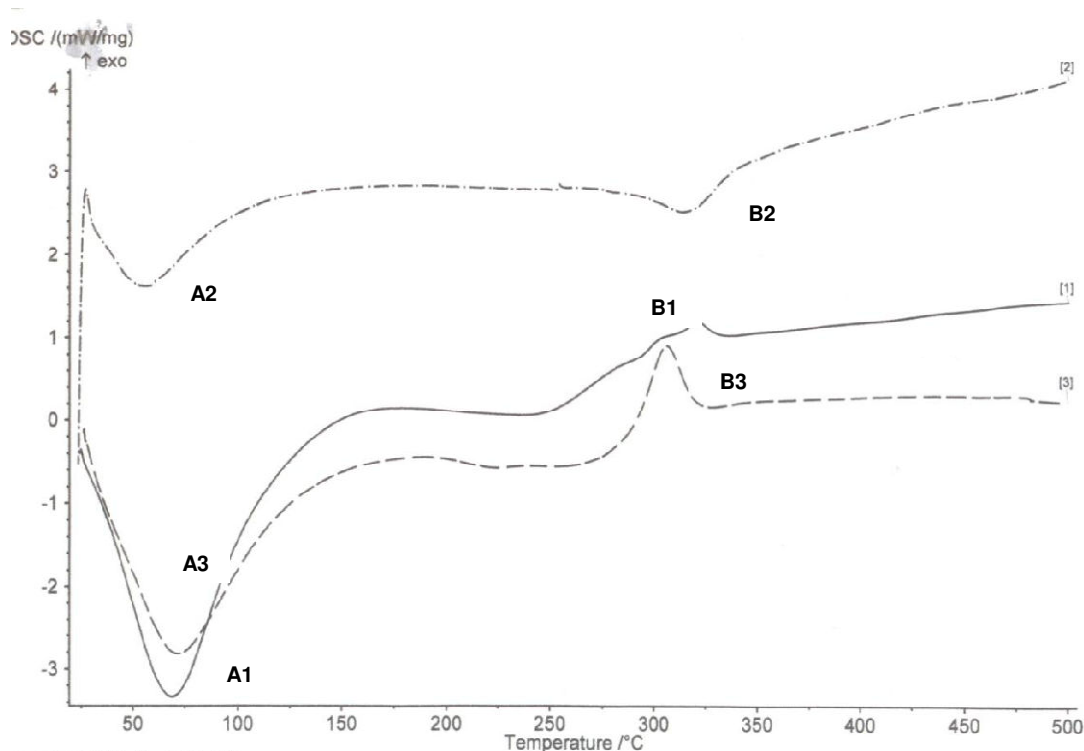
**Fig. 6. Moisture sorption profile of *D. reflexa* gum, crosslinked *D. reflexa* gum and guar gum**

The empirical data of the moisture sorption at various relative humidity obtained for DR-gum, XDR-gum and G-gum (Fig. 6), coincide with the classification of Callahan et al. (Callahan et al., 1982). The moisture sorption profiles show that while G-gum and DR-gum are moderately hygroscopic as their moisture uptake increase were greater than 5% after storage at below 60% RH, and less than 50% at 80% RH. XDR-gum showed slightly hygroscopic characteristics as the moisture uptake between 80% RH and 100% RH was less than 40 %.

Moisture sorption has been reported to be one of the most sensitive techniques for assessing variation in the amorphous or crystalline content of polymers (Manek et al., 2005) as well as predicting some physicochemical and functional properties of polymers (Craig et al., 1989; Bravo-Osuna et al., 2004). This is because the moisture uptake is predominantly due to the interaction of the water molecules with the amorphous part of the polymer network. Moisture is taken up by the polymer powder bed as a result of the water molecules interacting with the polar groups of the polymer chains. In the amorphous part of the polymer network, there is a larger surface area available for interaction due to the numerous chain entanglements (Bravo-Osuna et al., 2004). G-gum and DR-gum have similar isothermic moisture uptake profiles (Fig. 6). It has been reported that for similar polymeric materials the moisture uptake profile for the amorphous form exhibits a higher shift when compared to the more ordered crystalline form (Beery and Ladisch, 2001; Franklin and Wang, 2002) The similarities in the moisture sorption profile of G-gum and DR-gum indicate similarity in their polymer chain arrangement, thus possessing comparable amorphous domain. The reduction in the dynamic moisture sorption capacity of XDR-gum is attributed to the decrease in the free volume available for moisture-polymer interaction due to the ordered arrangement of the polymer chain network (Builders et al., 2010). This indicates a possible conversion of DR-gum to a more crystalline motif. Thus, the numbers of free -OH and -COOH groups available for interaction with water molecules are reduced due to ionic induced crosslinking within the XDR-gum. Apart from the polymorphic nature of polymers, other factors could affect their moisture uptake. These include physical properties like particle size, surface area, porosity and surface versus bulk sorption.

### **3.7 Differential Scanning Calorimetry (DSC)**

When polymers are exposed to heat at different temperatures they show behaviors that are characteristic and related to their crystalline and amorphous composition. The DSC technique is essentially useful in characterizing polymers based on their thermal transitions (Campbell et al., 2007). The DSC thermographs and the thermal characteristics of G-gum, DR-gum and XDR-gum are presented in Fig. 7 and Table 2 respectively.



**Fig. 7. DSC thermograph of DR-gum, XDR-gum and G-gum**

Line 1=Guar gum (G-gum); Line 2=crosslinked *D. reflexa* (XDR-gum); Line 3= *D. reflexa* gum (DR-gum)

The thermographs of G-gum, DR-gum and XDR-gum (Fig. 7), are characterized by two prominent transition peaks. DR-gum and G-gum have similar transitions, being characterized by a first peak (A1 and B1), which are second order transition endotherms, corresponding to the glass transition. The second peaks (A2 and B2) are exothermic peaks that correspond to the polymer's cold crystallization. Cold crystallization is an exothermic transition that is characteristic of the pseudo-amorphous domain of the polymer chain network. The results of the thermograph indicate that the DR-gum and G-gum presents predominantly in its pseudo-amorphous form. Further heating of the polymer after the glass transition resulted in the rearrangement of the pseudo-amorphous chain conformation to a more ordered conformation before decomposition. Thus, these polymers have no distinct melting peak. The thermograph of XDR-gum also consists of two endothermic peaks, an initial C1 that corresponds to the glass transition ( $T_g$ ) and a second (C2) which is a first order transition endotherm corresponding to the polymer melting.

**Table 2. Thermal properties of G-gum, DR-gum and XDR-gum**

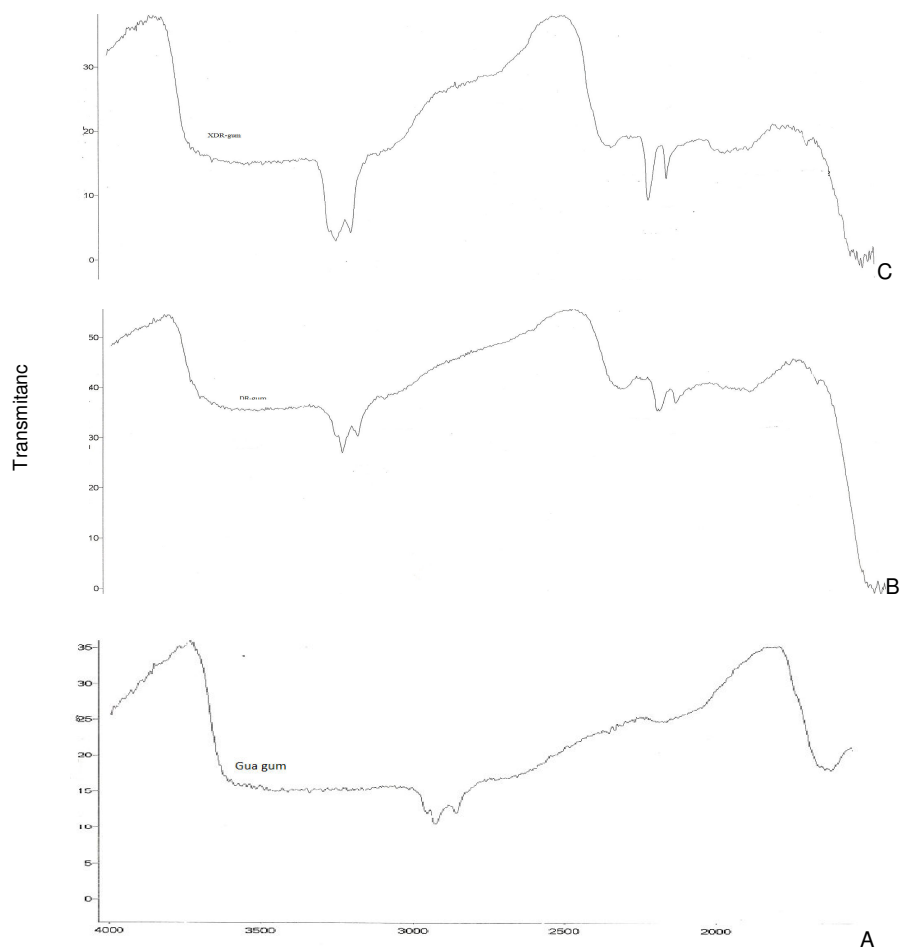
Parameter	G-gum	DR-gum	XDR-gum
$T_g$ (°C)	85	76.4	59.8
$\Delta H$ J/(gK)	9.56	9.384	38.919
$T_m$ (°C)			
Onset	-	-	293.7
Peak	-	-	313.0
End	-	-	333.9
$T_{cr}$			
Onset	302.3	311.1	-
Peak	321.2	323.0	-
End	344.8	349.8	-

$T_g$  =Glass transition temperature;  $T_m$ =Melting temperature;  $T_{cr}$ =Crystallization temperature

Analysis of the thermographs indicates that the  $T_g$  of the DR-gum was higher than that of the crosslinked motif. Although crosslinking is known to increase  $T_g$  by reducing chain mobility, the lower  $T_g$  of the XDR-gum may be attributed to higher degree of branching due to higher number of chain ends and greater free volume (Manley et al., 1989; Toufeili et al., 2002). The higher  $T_g$  of G-gum compared with that of DR-gum could be attributed to any or a combination of factors that are related to polysaccharide composition or monomer arrangement. These include rigid polymer backbone, higher chain length, larger number of free hydroxyl groups and side chains, and higher degree of crosslinking (Wunderlich, 1990). Short down.

### 3.8 Fourier Transform Infrared Spectroscopy (FT-IR)

The IR-spectra of DR-gum and G-gum are presented in Fig. 8. The IR-spectrum of a given compound is always unique and characteristic. Thus, IR spectroscopy is a quick and relatively cheap technique for identifying compounds (Sherman, 1997). The IR-spectra of DR-gum and G-gum are determined as finger prints to identify the basic differences in DR-gum, XDR-gum and G-gum. The IR-spectrum of DR-gum, XDR-gum and G-gum were characteristic and different (Fig. 8). A comparison of the native polymer (DR-gum) and the crosslinked motif (XDR-gum) show that there were a series of electronic shifts and the formation of new bond types and functional groups in the saturated, unsaturated and finger print regions of their spectra. The strong absorption at  $3436.54\text{ cm}^{-1}$  due to OH groups was absent in XDR-gum, there was also a shift at  $1022\text{ cm}^{-1}$  to  $1116\text{ cm}^{-1}$  of a new bending in the C-O bond of the carboxylic group in the glycans in this *D. reflexa* gelling polysaccharide. The poor resonance at  $3436.54\text{ cm}^{-1}$  due to the absence of a prominent hydroxyl (OH) peak in the spectra of the XDR-gum could be related to the absence free hydroxyl groups which is collaborated by the diminished swelling and moisture sorption comparative to DR-gum.



**Fig. 8. FT-IR spectra of Guar gum, *D. reflexa* gum and crosslinked *D.reflexa* gum**  
A= Guar gum; B= *D. reflexa* gum; C= crosslinked *D. reflexa* gum

#### 4. CONCLUSION

A gelling gum was extracted from the seeds of *D. reflexa* and modified by ionic gelation using calcium chloride solution. The compacts of the native and modified *D. reflexa* gum formed stable hydrogels in aqueous media, showing differential and marked pH sensitive swelling. Similar to guar gum, the native gum showed marked pH sensitive gel clarity. Generally, the swelling and moisture sorption as well as the thermal and FT-IR spectral properties of the native *D. reflexa* gum and its modified motif showed characteristics that relate to similarities and differences that correspond to the properties of guar gum as a pharmaceutical excipient.



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## COMPETING INTERESTS

Authors have declared that no competing interests exist.

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