Physicochemical Properties and Rheological Behaviour of *Ficus glumosa* Gum in Aqueous Solution

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**Abstract:** The physicochemical properties, cationic composition and rheological behaviour of exudates from *Ficus glumosa* were investigated. The gum was found to be mild acidic, ionic and soluble in water but insoluble in organic solvents. The trend for the decreasing concentration of elements determined in the gum sample is Mg > Ca > Mn > Zn > Fe > Ni > Cu > Cd > Pb. Rheological properties of the gums have been adequately modeled using Huggins, Kraemer, Arrhenius, Tanglerpaibul and Rao theories. The results indicated that the viscosity of the gum increases with increasing pH and concentration but decreases with increase in temperature. Values of intrinsic viscosity obtained from Huggins and Kraemer plots were similar (11.197). The value of activation energy ($E_{vis}$) of the gum studied was found to be 1.915 kJ/mol. The low $E_{vis}$ values obtained suggests the existence of few inter and intra-interactions between the molecules of the gums within the investigated temperature. *Ficus glumosa* gum exudate hence possesses the potentials to be used as an additive in food and other industries.

**Keywords:** *Ficus glumosa*; gum; heavy metal; characterization; rheological modeling.

1. Introduction

Gums are considered to be pathological products formed following injury to the plant or owing to unfavorable conditions, such as drought, by a breakdown of cell walls (extra cellular formation; gummosis) [1]. They are complex carbohydrate derivatives of a polysaccharide nature, and either
soluble in water as in the case of gum arabic or form mucilages by the absorption of large amounts of water (gum tragacanth). Their principal use is in foodstuffs by nature of their ability to impart desired qualities to foods by influencing their viscosity, body and texture; most frequently in confectionery food, flavouring and soft drinks. They also have pharmaceutical and industrial applications as demulcents, adhesives in pill manufacture, lithography, paints, inks, corrosion inhibitors and emulsifying agents. These gums found wider application because of their physical, rheological and chemical properties (such properties include solubility, water sorption, swelling capacity, pH, effect of temperature, and viscosity among others) [2].

There is increasing in demands for gums globally because of its vast application, which causes the increase in prices of the existing gums in the local and international market. For the price to be stable and less expensive there is need to look for alternative or discoveries of more suitable natural gums which will be of the same quality or even surpass the existing ones. Ficus glumosa is an example of lesser known plant producing gum. The plant commonly called African rock fig tree in English and ‘kawuri’ in Hausa belongs to the Family, Moraceae. Ficus glumosa, a tall plant of about 24 meters in height and about 3 meter in diameter, occurs on rocky outcrops, where it splits rocks; along dry watercourses or in open country; frequently in valleys, where it reaches its greatest size [3]. The species also occurs in fringe forest in savannah areas, especially in swampy ground, and in swamp forest in coastal areas [4]. The bark also contains abundant sticky white latex which is used in Northern Nigeria like bird-lime to trap crickets [5]. The exudate is also chewed as chewing-gum and used for fastening arrowheads to their shaft.

Studies on the physicochemical and rheological properties of some gum exudates have been carried out. Gum exudates from Khaya senegalensis (Family Meliaceae) plants grown in northern Nigeria were investigated for its physicochemical properties such as pH, water sorption, swelling capacity and viscosities at different temperatures using standard methods by Mahmud et al. [6]. It was found that Khaya gum appeared to be colourless to reddish brown translucent tears. The 5 % w/v mucilage has pH 4.2 at 28 °C. The gum is slightly soluble in water and practically insoluble in organic solvents. Water sorption studies revealed that it absorbs water readily and is easily dehydrated in the presence of desiccants. A 5 % w/v mucilage concentration gave a viscosity value which was unaffected at temperature ranges (28 – 40 °C). The results indicated that the swelling ability of Khaya senegalensis gum may provide potentials for its use as a disintegrant in tablet formulation, as a hydrogel in modified release dosage forms and the rheological flow properties may also provide potentials for its use as suspending and emulsifying agents owing to its pseudo plastic and thixotropic flow patterns.
Mhinzi [7] analyzed gum samples from three selected *Albizia* species from Tanzania and determined their commercial potential by comparing their properties with those of *Albizia zygia* and *Acacia* gums. The properties of the gum exudates from *Albizia amara*, *Albizia pertesiana* and *Albizia harveyi* were found to be similar to those of *A. zygia* gum except that their aqueous solutions possess slightly lower viscosity and higher levels of tannin. The *Albizia* gums were much less soluble in water than Acacia gums; however, their methoxyl contents and acid equivalent weights (AEW) were similar to those of some Acacia gums.

Rheological properties of Xanthan and locust beans gums have been studied by Higiro *et al.* [8] and the gums were found to obey Huggins and power law models, and from the rheological modeling of the gums, the conformation of the gums were established.

The aim of this work therefore is, to establish some of the physicochemical and rheological properties of *Ficus glumosa* gum, hence providing the information about the nutritional values, the metal composition and the functional properties of the gum.

2. Materials and Methods

2.1. Collection of Samples

Crude FG gum was obtained as dried exudates from their parent trees grown at Adepe – Otukpa in Ogbadibo LGA of Benue State, Nigeria. The plant material had earlier been identified and authenticated in the herbarium Department of Biological Sciences of Ahmadu Bello University Zaria. The gum were collected from the plant species by tapping during the mid of August and in the day time.

2.2. Purification of the Gum

The crude sample of *Ficus glumosa* gum consists of mixture of large and small modules admixed with bark and organic debris. These were hand sorted to remove fragments of bark and other visible impurities, and then the gum particles were spread out in the sun to dry for one to two weeks.

The crude gum was dissolved in cold distilled water, and the solution was strained through muslin, and then centrifuged, depositing a small quantity of dense gel. The straw colored supernatant liquor was separated and acidified to pH 2 with dilute hydrochloric acid. Ethanol was then added until 80 percent. The gum that precipitated out was removed by centrifugation at 2000 r/min, washed with alcohol followed by ether, and finally dried in a desiccator. The dried flakes were pulverized using a blender and stored in an air tight container.

2.3. Physicochemical Analysis
In order to characterize the gums, it was subjected to the following physicochemical tests.

2.3.1. Determination of percentage yield of the purified gum

The dried, precipitated and purified gum obtained from the crude dried exudate was weighed, and the percentage yield was expressed in percentage using the weight of the crude gum, as the denominator.

2.3.2. Determination of solubility

The solubility of the gum was determined in cold and hot distilled water, acetone, chloroform and ethanol. A 1.0 g sample of the gum was added to 50 mL of each of the above mentioned solvents and left overnight. A 25 mL of the clear supernatants were taken in small pre-weighted evaporating dishes and heated to dryness over a digital thermostatic water bath. The weights of the residue with reference to the volume of the solutions were determined using a digital top loading balance (Model XP-3000) and expressed as the percentage solubility of the gums in the solvents [9].

2.4. Determination of Concentration of Metals

Concentrations of Zn, Mg, Ca, Mn, Fe, Ni, Cu, Cd and Pb were determined using Perkin Elmer atomic absorption spectrophotometer. Calibration curve for each metal was prepared, and the concentration of the metal was estimated by extrapolation.

2.5. Determination of Nitrogen and Protein Content

Crude protein content of the gum was determined using the Kjeldahl method with the nitrogen content being multiplied by a factor of 6.25 [10].

2.6. Determination of pH

The sample powder was thoroughly mixed and 1 g was dissolved in 100 mL of hot distilled water. The mixture was allowed to stand for 5 min at room temperature before the pH and temperature was recorded using a pre-calibrated pH meter (Oaklon pH meter, Model 1100).

2.7. Viscosity Measurements

The apparent viscosity of the mucilage was measured using a digital Brookfield DV I prime viscometer.

The intrinsic viscosity of the gum samples was determined in distilled water. The gum solutions were prepared by dispersing 50 mg of each gum sample (db, dry basis) separately in 100 mL of the distilled water at room temperature and mixed using a magnetic stirring overnight. The solution
(2 mL) was transferred into a Cannon Ubbelohde capillary viscometer (Cannon Instruments, Model I-71) which was immersed in a precision water bath to maintain the temperature at 25.0 ± 0.1 °C after equilibration for 10 min, and the flow time was determined between the two etched marks. Serial dilution was performed in situ, and three readings were taken for each dilution and the average was obtained. The relative viscosity (η_{rel}) was calculated using the equation 1 below:

\[
\eta_{\text{rel}} = \frac{T - T_0}{T_0}
\]

where T is the flow time of gum solution in seconds, T_0 is the flow time of solvent (water) in seconds.

Microsoft Excel 2010 (Microsoft Corporation, Seattle, WA) was used to plot viscosities against concentrations, as well as to obtain linear regression lines with the corresponding equations and correlation coefficients (R^2) in order to assess the best model.

3. Results and Discussions

3.1. Physicochemical Parameters of Ficus glumosa Gum

Table 1 presents physicochemical parameters of Ficus glumosa gum. The color of crude Ficus glumosa gum is pale yellow. After purification, the yield of gum obtained was 68 % w/w. The purified gum had bland taste and is odorless. The measured pH of the gum is 4.3, indicating that the gum is mild acidic. This compared favorably with that of gum Arabic which is reported to be between 4.0 and 4.8 [11]. The solubilities of Ficus glumosa in cold water and hot water are 10.20 % and 11.10 %, respectively, indicating that the solubility of the gum is temperature dependent. Since solubility is expected to increase with increase in temperature, the solubility of the gum in hot water is higher than the corresponding solubility in cold water. On the other hand, the samples were not soluble in acetone and chloroform but sparingly soluble in ethanol. These indicate that the studied gum is ionic in character, unlike the covalent counterpart that is soluble in organic solvents [12]. The sparingly solubility of the gum observed in ethanol is due to the fact that it can ionize to produce hydroxyl ion (OH^-) and the value of its dielectric constant is higher than those of acetone and chloroform. Consequently ethanol has some polar character over acetone and chloroform which are characterized by low values of dielectric constant.

The nitrogen content of Ficus glumosa gum was found to be 0.41 % which is higher than karaya (0.20%) [13], but lower than those of kondagogu gum (1.0%) [13] and acacia gum (0.44%) [14]. Protein content of Ficus glumosa gum was found to be 2.56%. This indicates a possibility of its usage as a supplement to other protein sources in the food.
Table 1. Physicochemical parameters of *Ficus glumosa* gum

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Ficus glumosa gum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Pale – yellow</td>
</tr>
<tr>
<td>Odor</td>
<td>Honey</td>
</tr>
<tr>
<td>Taste</td>
<td>Bland</td>
</tr>
<tr>
<td>pH</td>
<td>4.3</td>
</tr>
<tr>
<td>Percentage yield (% w/w)</td>
<td>68%</td>
</tr>
<tr>
<td>Solubility (% w/v)</td>
<td></td>
</tr>
<tr>
<td>Cold water</td>
<td>10.20</td>
</tr>
<tr>
<td>Hot water</td>
<td>11.10</td>
</tr>
<tr>
<td>Acetone</td>
<td>0.0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.0</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.4</td>
</tr>
<tr>
<td>Nitrogen (%)</td>
<td>0.41</td>
</tr>
<tr>
<td>Protein (%)</td>
<td>2.56</td>
</tr>
</tbody>
</table>

3.2. Cationic Composition of *Ficus glumosa* Gum

Table 2 presents concentration of elements identified in the gum sample. Cationic composition of *Ficus glumosa* gum exudate demonstrated that calcium and magnesium are the main metals present among the metals determined. These major metals are also present in *A. senegal* gum [15]. The high level of the magnesium and calcium shows that the exudates could provide an alternative source of magnesium and calcium in diets. Magnesium is required in large quantities by the body for the activation of enzymes involved in protein synthesis. Possible outcomes of deficiency are growth failure, behavioral disturbances, weakness and spasms [16].

The trend for the decreasing concentration of other elements determined in the gum sample is Mn > Zn > Fe > Ni > Cu > Cd > Pb. The body requires in a minute quantity of Mn for the activation of various enzymes. Nutritionally, Co^{2+} can function as a replacement in-vitro for other divalent cations in human [17]. Fe is needed in trace amount by the body as it is a constituent of hemoglobin and enzymes involved in energy metabolism in iron transport [18]. The concentration of lead detected in the gum was found to be within the permissible range of 2 ppm for substances used as food additives [19].

Table 2. Cationic composition of *Ficus glumosa* gum

<table>
<thead>
<tr>
<th>Element</th>
<th>Ficus glumosa gum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg (% w/w)</td>
<td>1.28</td>
</tr>
<tr>
<td>Ca (% w/w)</td>
<td>0.60</td>
</tr>
<tr>
<td>Mn (ppm)</td>
<td>105.53</td>
</tr>
<tr>
<td>Zn (ppm)</td>
<td>18.27</td>
</tr>
<tr>
<td>Fe (ppm)</td>
<td>14.57</td>
</tr>
<tr>
<td>Ni (ppm)</td>
<td>10.12</td>
</tr>
<tr>
<td>Cu (ppm)</td>
<td>7.32</td>
</tr>
<tr>
<td>Cd (ppm)</td>
<td>1.69</td>
</tr>
<tr>
<td>Pb (ppm)</td>
<td>1.20</td>
</tr>
</tbody>
</table>
3.3. Rheological Study

Rheological measurements provide useful behavioural and predictive information for various products in addition to knowledge of the effects of processing, formulation changes, and aging phenomena [20]. Rheology deals with those properties of materials that determine their response to mechanical force. For solids, rheological studies involve elasticity and plasticity. For fluids, on the other hand, this involves viscosity measurements, viscosity being a measure of the internal friction of a fluid. Anderson and Dea [21] stated that viscosity is one of the most important analytical and commercial parameters in polymers because it is affected by the size and shape of macro-molecules.

Fig. 1 shows plots for the variation of viscosity with concentration of *Ficus glumosa* (FG) gum. From Fig. 1, it is evident that the viscosity of FG gum tends to increase with increase in concentration. Jefferies *et al.* [22] and Ashton *et al.* [23] have reported respectively that the viscosity of gum *ghatti* and *albizia* gums increases with increasing proportion of dispersible gel. This rheological behaviour is also exhibited by gum exudate studied. The high viscosity experience at higher concentrations may be due to increase in the strength of molecules-molecules interaction and the corresponding reduction in molecule-solvent interaction.

![Figure 1](image_url)

**Figure 1.** Variation of viscosity with concentration of *Ficus glumosa* gums.

Fig. 2 presents plots for the variation of viscosities of the gums with pH. It can be seen from the figure that the viscosity of the gum tends to increase with increase in pH, indicating that the emulsifying properties of the gum is pH dependent [24].
In Fig. 2, plot for the variation of viscosity with pH for *Ficus glumosa* gum is presented. In order to verify the onset of degradation or conformational transitions during heating, the viscosity of the gums was again measured as cooling proceeded. The tests did not indicate any difference between the two set of data, suggesting that there was no degradation or conformational transition when the gums were heated [2]. Fig. 3 revealed that the viscosity of the gum decreases with increasing temperature. This trend occurs because the increased kinetic motion at higher temperatures promotes the breaking of intermolecular bonds between adjacent layers.

In Fig. 3, plot for the variation of viscosity with temperature for the studied gum is presented.
From the viscosity results, the activation energy of viscous flow, $E_{vis}$, of the gum exudate was determined using the Arrhenius equation given by equation 2:

$$[\eta] = Ae^{-E_{vis}/RT}$$

where $T$ is temperature, $A$ is the Arrhenius coefficient and $R$ is the universal gas constant. A plot of log $[\eta]$ against $1/T$ was made. The results obtained indicated a linear ($R^2 = 0.9959$) relationship between log $(\eta)$ and $1/T$. The slope of the plot (Fig. 4) is equal to $-E_{vis}/2.303R$ from which $E_{vis}$ was evaluated. The value of $E_{vis}$ of the gum studied was found to be 1.915 kJ/mol. The calculated activation energy of flow is relatively low when compared with data obtained for some plant gums such as Arabic gum (15 kJ/mol) [25] and Albizia lebbeck gum (15.9 kJ/mol) [2]. The low $E_{vis}$ values obtained suggests the existence of few inter and intra-interactions between the molecules of the gums within the investigated temperature.

![Figure 4. Arrhenius molecular kinetic plots of Ficus glumosa gum.](image)

In order to study the effect of centrifugal forces on the viscosity of the gum, the viscosity of the gum were measured at various speeds of rotation. Fig. 5 shows the plot of viscosity versus the rotation speed of a centrifuge containing similar concentration of the gum. From Fig. 5, it can be seen that the viscosity of the gum tend to decrease with increasing speed of rotation until a critical value is reached after which the viscosity increases with increase in speed of rotation. Several explanations may be ascribed to the observed behaviour of the gum. One of such explanations is the increase in the extent of shaking as a result of increasing speed of rotation. Gundlah and Kapur [26] found that the viscosity
behaviour of polystyrene fractions in benzene and methyl ethyl ketone is markedly dependent on the extent of shaking of the solutions and concluded that the anomalous viscosity behaviour of polymers at high dilutions results from configurational changes of the macromolecules. Therefore, alteration in the composition of the various gums as a result of rotation may be responsible for the observed changes in viscosity of the gums with rotation speed of the centrifuge.

**Figure 5.** Variation of viscosity with rotation speed of *Ficus glumosa* gum.

Intrinsic viscosity, $\eta_\text{rel}$, represents the volume occupied by the unit mass of the polymer molecule. It is not actually a viscosity. This parameter is generally measured in order to obtain information about the molecular weight and conformation of a polymer [27, 28]. Intrinsic viscosity is determined experimentally by measurements of the viscosity of solutions of very low concentrations ($c < c^\ast$). Denoting solution and solvent viscosity as, $\eta$ and $\eta_s$, respectively, it is defined formally by the following standard relationships:

Relative viscosity: $\eta_\text{rel} = \eta / \eta_s$  

Specific viscosity: $\eta_\text{sp} = (\eta - \eta_s) / \eta_s = \eta_\text{rel} - 1$  

Intrinsic viscosity: $[\eta] = \lim_{c \to 0} \frac{\eta_\text{sp}}{C}$

The intrinsic viscosity $[\eta]$ was determined using Huggins, Kraemer Tanglertpaibul and Rao plots as proposed by [8]. The Huggins equation is given as equation 6 below:

$$\frac{\eta_\text{sp}}{c} = [\eta] + K'[\eta]^2 C$$
It can be deduced from equation 6 that a plot of $\eta_{\text{red}}$ versus C should be linear with slope equal to $[\eta]^2$ and intercept equal to $[\eta]$.

Fig. 6 shows Huggins plot for the gum exudate. Values of Huggins constant deduced from the plot are presented in Table 3. Based on experimental observations, the physical meaning of the dimensionless Huggins coefficient $k$ can be summarized as follows [29]: (1) A polymer exhibits a higher value of $k$ in a poor solvent than in a good solvent, i.e., when the polymer–polymer interactions become favourable over polymer–solvent interactions. (2) It has a value of 0.5–0.7 in a theta solvent. (3) The $k$ is very sensitive to the formation of molecular aggregates.

The value of $k$ obtained for the studied sample is 0.955. Therefore the degree of polymer-polymer interaction in FG gum is low.

![Figure 6. Variation of reduced viscosity with concentration (Huggins plot) for *Ficus glumosa* gum.](image)

| Table 3. Huggins and Kraemer parameters for *Ficus glumosa* gum |
|-----------------|-----------------|-----------------|---------|---------|
|                 | slope           | $[\eta]$        | $[\eta]^2$ | K       | $R^2$   |
| Huggins         | 114.32          | 11.197          | 120.734    | 0.955   | 0.9874  |
| Kraemer         | 8.300           | 11.397          | 136.306    | 0.059   | 0.9544  |

The intrinsic viscosity was also analyzed using the Kraemer equation, which is given by equation 7 below [8]:

$$\ln (\eta_{\text{rel}}/C) = [\eta]+ k'[\eta]^2C$$

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where \( k' \) is the Kraemer constant. From equation 7, a plot of \( \ln(\eta_{rel}/C) \) versus \( C \) should be a straight line with intercept and slope equal to \( [\eta] \) and \( k' \) respectively. Fig. 7 shows Kraemer plots for the studied gum. Values of Kraemer parameters deduced from the plot are recorded in Table 3. From the results obtained, \( k' \) values obtained from Kraemer plot are comparable to \( k' \) values obtained from Huggins plot. However, value of \( [\eta] \) deduced from Huggins plots are relatively higher than those obtained from Kraemer plot.

Tanglertpaibul and Rao [30] obtained three equations that can also be used in the determination of the intrinsic viscosity of a polymer. These are equations 8, 9 and 10.

\[
\eta_{rel} = 1 + [\eta]C \\
\eta_{rel} = \exp([\eta]C) \\
\eta_{rel} = 1/(1-[\eta]C)
\]

Figure 7. Variation of \( \ln(\eta_{rel}/C) \) with concentration (Kraemer plot) of *Ficus glumosa* (FG) gum
From equation 8, $[\eta]$ is the slope obtained by plotting $\eta_{rel}$ versus C. Also, the implication of equation 9 is that $[\eta]$ is the slope obtained from the plot of $\ln \eta_{rel}$ versus C and from equation 10, $[\eta]$ is a slope obtained by plotting $(1- 1/\eta_{rel})$ versus C. Tanglertpaibul and Rao plots for the studied gum (from equations 8 to 10) are presented in Figs. 8 to 10, respectively. Values of Tanglertpaibul and Rao parameters deduced from the plots are presented in Table 4. The excellent correlation between the values of $[\eta]$ computed from the various methods used in evaluating intrinsic viscosity indicates the consistency of the methods for the study of intrinsic viscosity of the system.

Table 4. Tanglertpaibul and Rao parameters for *Ficus glumosa* (FG) gum

<table>
<thead>
<tr>
<th>Gum</th>
<th>Eq. 8 $[\eta]$</th>
<th>$R^2$</th>
<th>Eq. 9 $[\eta]$</th>
<th>$R^2$</th>
<th>Eq. 10 $[\eta]$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>FG</td>
<td>24.40</td>
<td>0.9928</td>
<td>5.6254</td>
<td>0.9967</td>
<td>7.3244</td>
<td>0.9756</td>
</tr>
</tbody>
</table>

**Figure 8.** Variation of $\eta_{rel}$ with concentration of *Ficus glumosa* gum

**Figure 9.** Variation of $\log(\eta_{rel})$ with concentration of *Ficus glumosa* gum.
Figure 10. Variation of \((1-1/\eta_{rel})\) with concentration of *Ficus glumosa* gum.

4. Conclusions

From the results obtained, the following conclusions are drawn: (1) *Ficus glumosa* gum occurs as pale yellow, translucent tears. The gum mucilage has a bland taste, and is odourless, and mild acidic with a pH of 4.3 at 303 K. It is soluble in water, sparingly soluble in ethanol and practically insoluble in acetone and chloroform. (2) The mineral elements compositions of the gum are within the range specified by WHO and FAO, hence *Ficus glumosa* gum exudate can be used as an additive in food and other industries. (3) *Ficus glumosa* gum is a macromolecule whose viscosity depends on temperature, concentration, speed of rotation and pH. (4) The rheological properties of the gum can be adequately modeled using the Arrhenius model, Huggins model, Kraemer model, Tanglertpaibul and Rao models. The excellent correlation between the values of \([\eta]\) computed from the various methods used in evaluating intrinsic viscosity indicates the consistency of the methods for the study of intrinsic viscosity of the system.

References


