



Corn Starch as a Substitute for Commercial Food Starch: FT-IR and Rheological Characterization

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Abstract Rheological and Fourier transformed infra red spectroscopy methods were used to characterized and compared starches extracted from corn with that of the commercial food starch, imported into Nigeria. The aim of the study was to source for possible sources of food starch from plant of Nigerian origin. Results obtained from rheological analysis indicated that both starches displayed similar trend in variation of relative viscosity with concentration. Values of their intrinsic viscosity obtained from Kraemer's plots (58.31 dl/g and 70.87 dl/g for the commercial (CS) and potato (PS) starches respectively) were relatively closer to each other and were within the range of values expected for food starch. Molecular conformation study, deduced from the power law plots reveals that the two starches have rod like structure. Calculated values of entropy of flow (ΔS_V) were -178.77 and -234.78 J/mol while ΔH_V were 14.77 and 16.38 J/g for CS and PS respectively while ΔH_V values were 14.77 and 16.38 J/g for CS and PS respectively. Therefore, the range of values obtained for the thermodynamic properties of the starches indicated that the attainment of transition state of flow by the two starches was achieved by bond breaking. Activation energy of flow for the two starches (12.15 and 13.78 J/g for CS and PS respectively) were also low and indicated the existent of few inter and intra-interactions between the polysaccharide chains. FT-IR spectra of the two starches gave convincing evidence that they have common absorption band at 994, 1078, 1151 and 1639 cm^{-1} . The ratio of the absorbance at these common wave numbers (*i.e.* 1639:1151, 1151: 1078 and 1078:994) indicated that there was no significant difference between the produced starch and the commercial food starch.

Keywords Corn Starch, Food Starch, FT-IR, Rheological

Introduction

Starch is next to cellulose as the most abundant carbohydrate. It is an important material for a wide variety of food and non-food applications, including thickeners, stabilizers, binding agents, fat substitutes, texturizers, fillers, and feedstock for biofuels. Although there are numerous source of plant sources through which starches can be extracted from, most developing countries are still importing food and non food starches for the servicing of the domestic and industrial needs for starch.

The major functional requirements for starch lie in their chemical composition and rheological properties [1-2]. Fourier transformed infra red spectroscopy provides analytical solution for establishing the functional groups as well as the finger print regions in a compound. Rheological properties of any polysaccharide, such as starch can be adequately investigated through viscosity measurements at various concentrations and at various temperatures [3-5]. In view of the above established facts, this study is aimed at extracting starch from corn seeds and to compare its FTIR and rheological properties with that of imported commercial food starch [6-7]. It is expected that if the locally produced starch can meet the properties that characterized the commercial food starch, then the local starch may be a good source of substitute for the imported ones.



Materials and Method

Maize seeds were purchased Ikot Ekpene central market, located in Akwa Ibom state, Nigeria. The seeds were sun dried, grinded and soak in water. Starch produced as the sediment from the solution that was allowed to stand over night, was obtained after decantation. The produced starch was dried to powdered form.

Viscosity Measurements

The intrinsic viscosity of the samples was determined in distilled water using a Cannon Ubbelohde capillary viscometer (Cannon Instruments, model I-71) which was immersed in a precision water bath maintained at the desired temperature.

FT-IR Analysis

FT-IR analysis of the starch was carried out using Scimadzu FTIR-8400S Fourier transform infra-red spectrophotometer. The sample was prepared in KBr and the analysis was carried out by scanning the sample through a wave number range of 400 to 4000 cm^{-1} [8].

Results and Discussions

Physical Properties

Both the produced and the commercial starch were whitish yellow in colour. The gelatinization temperature for the commercial food starch (48 °C) and that of the produced maize starch (50 °C) are relatively comparable.

FT-IR study

Figs. 1 and 2 show the FTIR spectra of the commercial food and corn respectively.

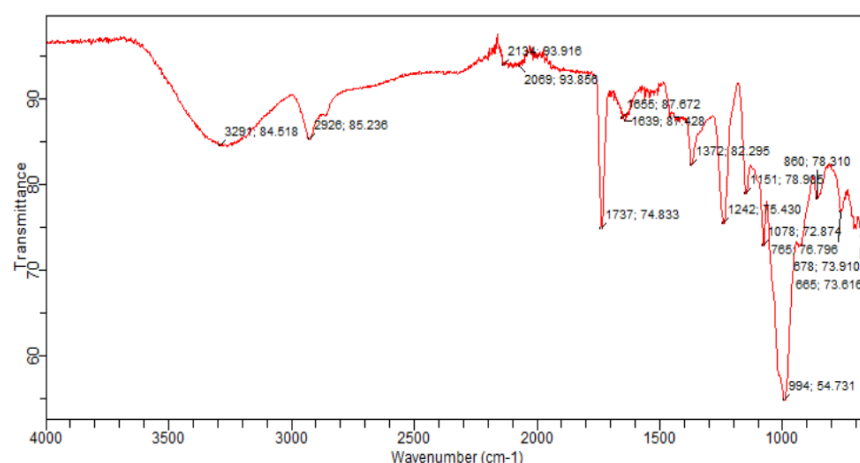


Figure 1: FT-IR of commercial starch

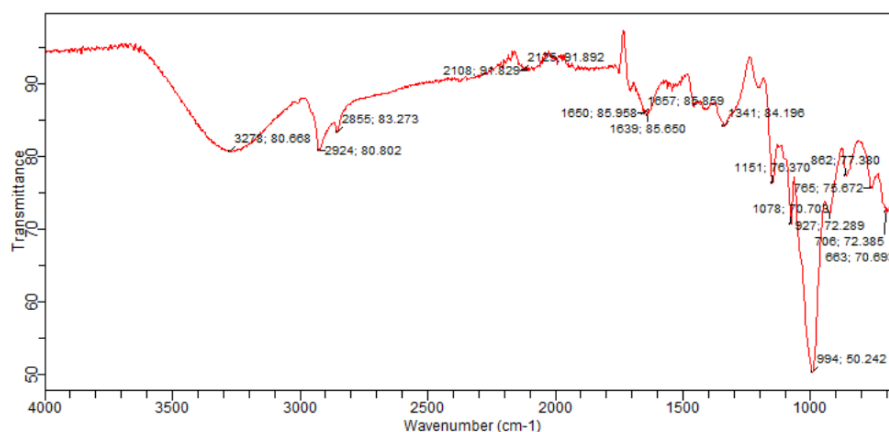


Figure 2: FT-IR of maize starch



In the FTIR spectrum of the commercial starch, 15 peaks were found while 16 peaks were identified in the spectrum of the starch produced from corn seed. Peaks obtained from both spectra as well as assignments to the respective peaks are presented in Table 1. The results presented in Table 1 shows % transmittance corresponding to the respective wave length of absorption. According to Beer-Lambert law, absorption is related to concentration (C in mole), path length (d in cm) and molar absorptivity (ϵ in $\text{Lmol}^{-1}\text{cm}^{-1}$) according to the following equation [8],

$$A = \epsilon dC \quad 1$$

If the incident radiation entering the sample cell is given by I_0 and the amount transmitted is I_t . The transmittance of the solution is defined as the fraction of the incident radiation that is transmitted (equation 2),

$$T = \frac{I_t}{I_0} \quad 2$$

On the other hand, percentage transmittance is given by equation 3 while equation 4 gives the amount of light that is absorbed (I_a):

$$T = \frac{I_t}{I_0} \times \frac{100}{1} \quad 3$$

$$I_a = I_0 - I_t \quad 4$$

From the logarithm of equation 4 equation 5 is obtained,

$$\log I_a = \log I_0 - \log I_t = \log \left(\frac{I_0}{I_t} \right) \quad 5$$

The left hand side of equation 5 correspond to absorbance (I_a). Therefore, the relationship between absorbance and transmittance is given according to equation 6,

$$A = \log \left(\frac{1}{T} \right) \quad 6$$

Since %transmittance is equal to transmittance x 100, equation 6 can also be written as

$$A = \log \left(\frac{100}{\%T} \right) = 2 - \log \left(\frac{1}{T} \right) \quad 7$$

Using equation 7, values of absorbance corresponding to various wave numbers were calculated and are presented in Table 2 and the plots developed from these values is presented in Fig.3.

The spectra for both starches were taken within the wavelength of 4000 to 500 cm^{-1} . From the spectra, it is evident that the starches have common absorption band at 994, 1078, 1151 and 1639 cm^{-1} . The ratio of the absorbance at these common wave numbers (*i.e.* 1639:1151, 1151: 1078 and 1078:994) are presented in Table 3. The results obtained indicated that there is no significant difference between the produced starch and the commercial starch.

Table 1: Peaks of FTIR absorption, % transmittance and functional group assignments for commercial starch and starch produced from maize seed

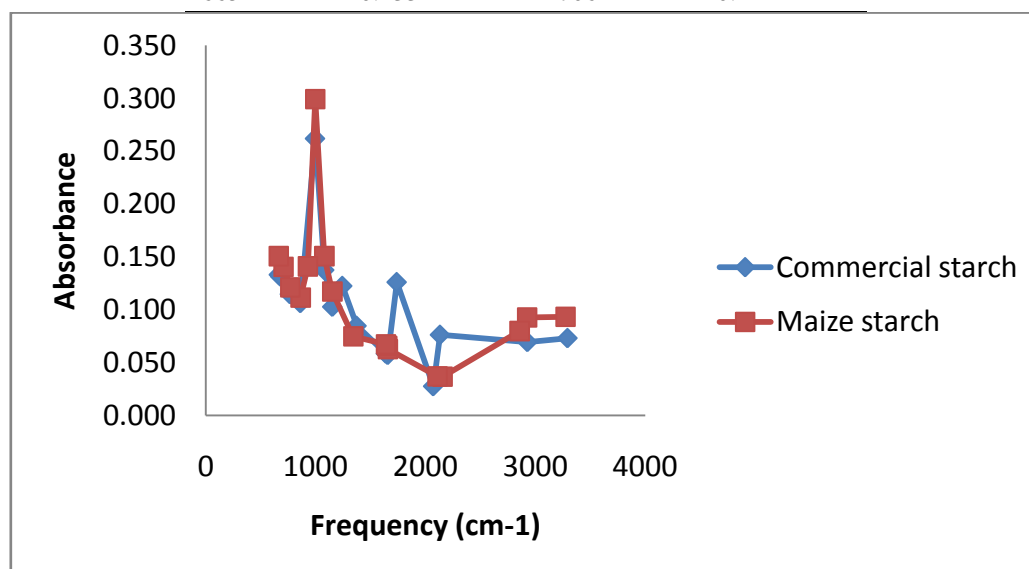
Commercial starch		Maize starch		Functional group/assignment
Peak (cm^{-1})	% Transmittance	Peak (cm^{-1})	% Transmittance	
3291	84.518	3273	80.668	OH stretch due to hydroxyl
2926	85.236	2924	80.802	C-H stretch
		2855	83.223	Triple bond in alkyne
		2155	91.892	Triple bond in alkyne
2131	83.916	2108	91.829	Triple bond in alkyne
2069	93.856			
1737	74.823			C=O stretching vibration
1655	87.672	1657	86.559	C=O stretching
		1650	85.958	C=O stretch
1639	87.428	1639	85.650	C=O stretch due to Carbonyl group
1372	82.295	1341	84.196	C-H stretch in alkane
1242	75.450			CH ₂ OH stretching
1151	78.945	1151	76.370	C-O-C asymmetrical Stretching



1078	72.874	1078	70.700	C-O-H stretching in carboxylic acid
994	54.731	994	50.242	C-O-H stretch
		927	72.289	C-O stretching
860	78.310	862	77.380	C-O stretching
765	76.796	768	75.672	CH ₂ ring breasing
		706	72.355	Aromatic C-H bending
678	73.910			Aromatic C-H bending
665	73.616	663	70.693	C-OH out of plane bending

Table 2: FT-IR absorbance of the commercial and the produced starches at various wave numbers

Commercial Starch		Maize Starch	
Peak (cm ⁻¹)	% Absorbance	Peak (cm ⁻¹)	Absorbance
3291	0.073	3273	0.093
2926	0.069	2924	0.093
2131	0.076	2855	0.080
2069	0.028	2155	0.037
1737	0.126	2108	0.037
1655	0.057	1657	0.063
1639	0.058	1650	0.066
1372	0.085	1639	0.067
1242	0.122	1341	0.075
1151	0.103	1151	0.117
1078	0.137	1078	0.151
994	0.262	994	0.299
860	0.106	927	0.141
765	0.115	862	0.111
678	0.131	768	0.121
665	0.133	706	0.141

*Figure 3: Variation of absorbance with frequency for commercial and maize starches*

In the FT-IR spectrum of both starch, maximum and minimum absorption were obtained at 994 cm⁻¹ (Table 2) respectively. Absorption spectrum at 994 cm⁻¹ is typical for most starch including potato, cassava and other plant starch. Van Soest *et al.* (1999) ascribed absorption band at 994 cm⁻¹ to C-O-H. Sun (2009) also pointed out that IR absorption within the wave number range of 994 to 998 cm⁻¹ (the so called anomeric region) by starch provides evidence to distinguish sugar [9].



Table 3: Ratio of absorbance at common wave numbers in the commercial and in the produced maize starches

Ratio	Commercial starch	Maize starch
1639	1.1075	1.1215
1151	1.0833	1.0802
1078	1.3315	1.4072
994		

Literature abound that suggest that absorption between 300 and 1300 cm^{-1} falls into finger print region for starch and that absorption between 750 to 800 cm^{-1} indicate that the presence of β configuration as distinct from α configuration. In the commercial and coen starches, there are IR absorption at 765 cm^{-1} due to pyrrole, indicating that the configuration of both starches is β . The bands at 927 cm^{-1} in corn starch fall within the range (930 to 900 cm^{-1}) expected for D-glucopyranosyl ring vibrational modes [10]. Both starches also displayed similar absorption band at 765 cm^{-1} which is within the range ($766 \pm 10 \text{ cm}^{-1}$) for vibrations in D-glucopyranosyl ring stretching. Absorption bands at 1078 cm^{-1} were also found in both starches, which can also be attributed to C-O-H stretching [1]. Both starches also exhibited intense spectrum at 1151 cm^{-1} , which can be ascribed to C-O-C antisymmetric stretch (Ferreira *et al.*, 2009). Peaks at 1639 cm^{-1} in both spectra are attributed to the presence of carbonyl (C=O) functional group in carbonyl compound (likely carboxylic acid) [7]. Closeness in wave numbers of absorption at 665 and 663 cm^{-1} in the commercial and in the produced starch was also observed. This vibration is due to C-OH out of plane bending. C-H stretching at 1372 and 1341 cm^{-1} as well as C=O stretching at 1655 and 1657 cm^{-1} were present in the spectra of the commercial and the produced starches respectively. Other absorbance bands that were common to the commercial and the produced starch were OH stretch, which occurred at 3291 and 3273 cm^{-1} as well as C-H stretch at 2926 and 2924 cm^{-1} respectively. The C-O stretching at 860 and 862 cm^{-1} for the commercial and the produced starch are assigned to the coupling of C-O and O-S vibrations of D-galactose-4-sulphate, respectively.

Absorption bands that were unique to the produced starch were C-O stretching vibration of the 3,6-anhydro bridge CH_2OH stretch at 1242 cm^{-1} , alkyne triple bond stretches at 2855 and 2155 cm^{-1} . On the other hand, those that were unique to the commercial starch were C-H bending at 678 cm^{-1} and C=O stretch at 1737 cm^{-1} . In Fig. 3, plots showing the variation of absorbance with wave number are presented. From the plot, it can be seen that both starched exhibited maximum absorption at closely similar wave number and also show similarity or closeness at other wave numbers. This shows that the produce starch has some compatibility factors with the commercial starch.

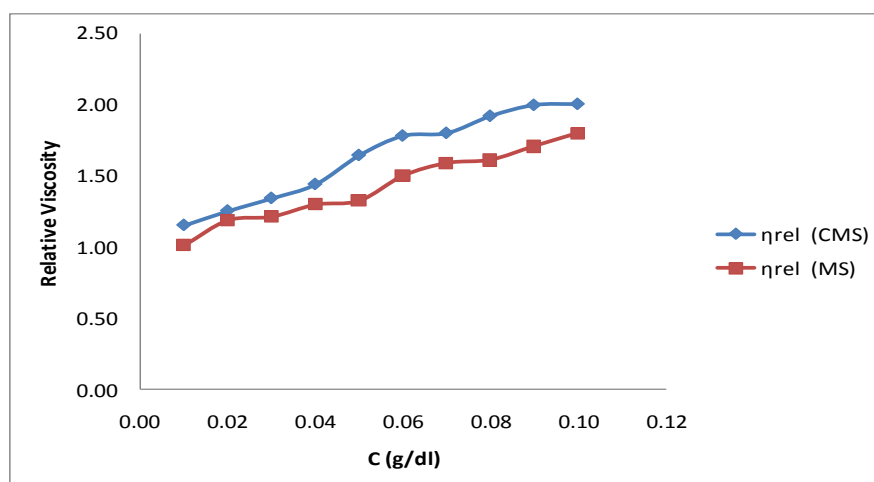


Figure 4: Variation of relative viscosity of commercial (CMS) and maize (MS) starches with concentration



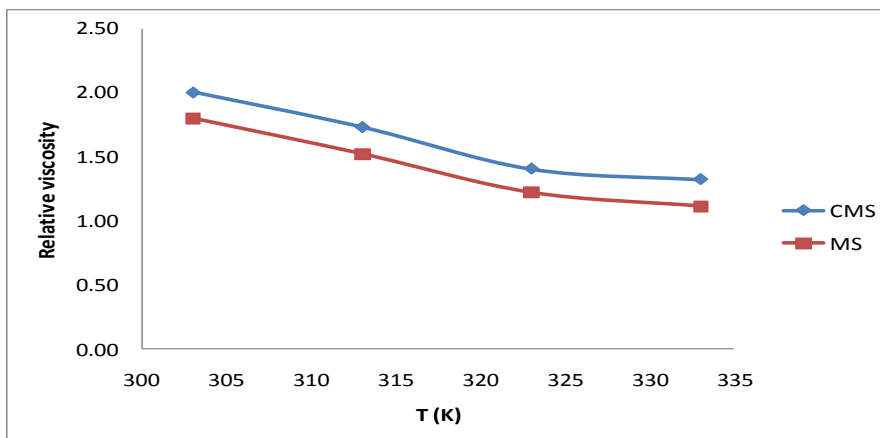


Figure 5: Variation of relative viscosity of CMS and MS with temperature

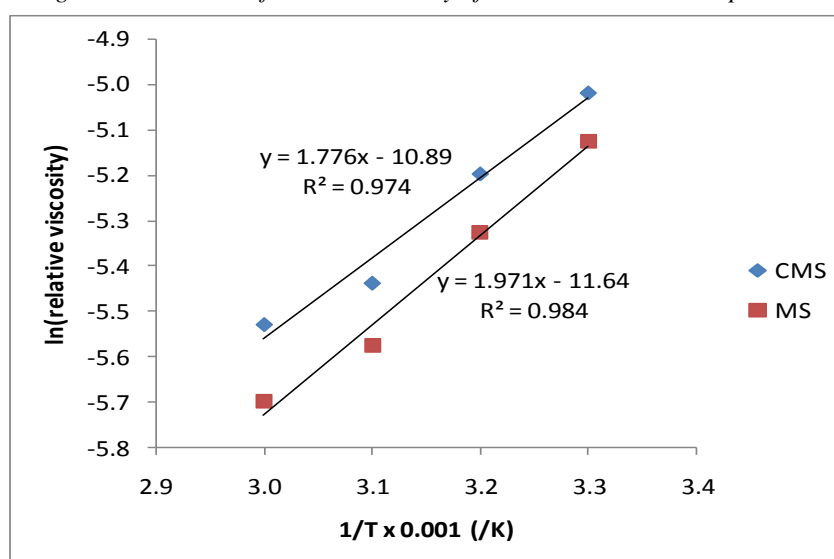


Figure 6: Arrhenius plot for the CMS and MS

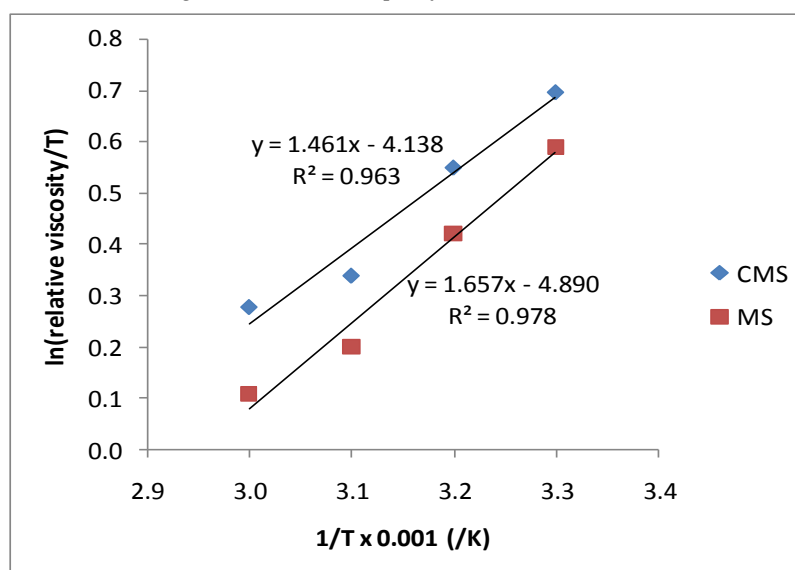


Figure 7: Transition state plot for the CMS and MS

Rheological Study

Rheology is the study of the flow of polymers or macromolecules. Starch is a polysaccharide and as such their properties and application is strongly influence by their rheological parameters. The rheology of the commercial (CMS) and that of the produced corn starch (MS) was study through viscosity measurements (*i.e.* their flow behaviour). Fig. 4 shows the variation of viscosity of CMS and MS with concentration. It is evident from the results that the relative viscosity of both starches increases with increase in concentration. It is significant to state that the pattern and trend of variation of relative viscosity of the two starches with concentrations are closely similar indicating that both starches have common rheological properties.

Fig. 5 shows plots for the variation of the relative viscosity of CMS and MS with temperature. From the figure, it can be seen that both starches show similar trend in their respond to viscosity changes with temperature indicating that MS can withstand heat changes in a manner that is similar to CMS. In rheology, effect of temperature on viscosity changes can be adequately studied by estimating thermodynamic parameters of flow (*i.e.* the activation energy, entropy and enthalpy of flow). Consequently, the effect of temperature on the viscous flow of the starches was studied using the Arrhenius-Frenkel-Eyring equation (equation 8) [11].

$$\eta = A \exp\left(\frac{E_F}{RT}\right) \quad 8$$

where A is the pre-exponential factor, E_F is the activation energy of flow, R is the universal gas constant and T is the absolute temperature in Kelvin. From the logarithm of both sides of equation 8, equation 9 is obtained,

$$\ln(\eta) = \ln A + \frac{E_F}{RT} \quad 9$$

Equation 9 reveals that a plot of $\ln(\eta)$ versus $1/T$ should be linear with a slope and intercept equal to E_F/R and $\ln(\eta)$ respectively. Fig. 6 shows the Arrhenius-Frenkel-Eyring plots for the commercial starch and that of the corn starch. The plot reveals high degree of linearity ($R^2 = 0.9706$) while calculated value of E_F was 14.71 J/mol. This value is within the range of values reported for some polysaccharides including *Albezia lebbeck* gum by de Paula *et al.* (1995) and gum Arabic (15 kJ/mol: *Varfolomeeva et al.*, 1980). Generally, low activation energy of flow indicates few inter and intra-interactions between polysaccharide chains in the concentration range investigated while higher values of E_F indicate that the polymer is less sensitive to change in temperature [12-13]. Hence there are few inter and intra molecular interactions in the starches.

Thermodynamic parameters for the starches were estimated using the Frenkel-Eyring Transition state equation [8]

$$\ln\left(\frac{\eta}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_V}{R} - \frac{\Delta H_V}{RT} \quad 10$$

where ΔS_V and ΔH_V are changes in entropy and enthalpy of flow respectively. From equation 10, a plot of $\ln(\eta/T)$ versus $1/T$ is expected to be linear with slope and intercept equal to $\frac{\Delta H_V}{R}$ and $\left(\ln A - \frac{\Delta S_V}{R}\right)$ respectively. Fig. 7 shows the Transition state plot for the CMS and MS. From the plot, it can be seen that there is a high degree of linearity ($R^2 = 0.9706$) while calculated values of ΔS_V and ΔH_V are -280.77 and 14.71 J/mol. Since changes in the value of enthalpy and entropy of flow are positive and negative respectively, it can be concluded that the attainment of transition state of viscous flow by the starches is accompanied by bond breaking. Also, a negative value of entropy change is associated with uncoiling orientation of the polymer molecules and the system becomes more ordered in the course of flow [14].

Conclusions

The aim of this study was to produce starch from corn seeds (obtained locally), with the view of meeting or replacing the demand of commercial food starch that is normally imported into Nigeria. From the results and findings of the study, the following conclusions were drawn.

- i. corn starch has functional group similar to those in the commercial starch
- ii. The wave number of maximum absorption (*i.e.* 994 cm^{-1}) is the same for corn and commercial starches. The absorbance at this wave number is also similar. However, at other wave numbers, the absorbance values for the commercial starch seems to be higher than those found in maize starch, indicating that the concentrations of the active species are higher in commercial starch than in maize starch.



- iii. The ratio of absorbance between some wave numbers of absorption by maize and commercial starches approximate each other indicating that there is no much distinction between maize starch and the commercial starch.
- iv. The rheology of corn and that of the commercial starches has similar trend based on the variation of relative viscosity with concentration. However the commercial starch seems to exhibit higher values of relative viscosity compare to corn starch.

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