

## Miscibility Studies of Cashew Gum and Khaya Gum Exudates in Dilute Solution by Viscometry and FTIR Analysis.

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**Abstract:** The FTIR and coefficient of viscosity for Cashew/Khaya blends in deionized water were measured, the changes in specific viscosity of the blends with corresponding effect of temperature and ionic salts, i.e. KCl, KBr and AlCl<sub>3</sub> were modeled. The measured parameters were used to estimate other related physical quantities using Huggins, Tanglerpaibul and Rao, Frankel-eyring and Arrhenius-frankel models etc. these quantities includes the intrinsic viscosity ( $\eta$ ), conformation parameter ( $b_{law}$ ), standard Enthalpy and Energy change of blend flow ( $\Delta H$  and  $\Delta E$ ), Huggins parameter ( $K$ ), Interaction parameter ( $bm1$ ) were proposed by Higiroy et al., to identify the molecular conformation and the interaction arising in solution of gum blends. The peculiar deviation confirmed the structural changes in the solution of the blends, while the FTIR confirmed the formation of physical blends.

**Keywords:** Viscosity, polymer blends, Cashew gum (AO), Khaya gum (KS), molecular interaction, FTIR

### I. INTRODUCTION

Polymer blending provide a wide range of benefits which are of importance in aiding the engineering of new materials, some of this benefits includes Improved process-ability, product uniformity, scrap reduction, Quick formulation changes, Inherent recyclability of products, etc. (Rhooy et al., 1997; Stephen et al., 2000;). The miscibility of polymer blends depends on the balance of small enthalpic and non-configurational entropic effects and the Sensitivity of this balance to small variation of the macromolecular structure is illustrated in the series of papers on miscibility of model polyolefins Rabeony et al., 1998. The term gum is generally applied to a wide variety of colloidal substances that are similar in appearance and have peculiar characteristics (Columbia Encyclopedia, 2006). Ghani (1988) described gums as a group of non-crystalline polysaccharides which usually contain sugars such as mannose and galactose and their uronic acid derivatives, although in practical terms, gums are defined as molecular structures, tending to high molecular mass, usually with colloidal properties, which in an appropriate solvent produce gels or suspensions of high viscosity or solutions of low matter content that can absorb water at ten times their weight. (Umoren et al., 2006d).

Plant gums are obtained as an exudation from fruit, trunk or branches of the trees spontaneously or after mechanical injury of the plant by incision of the bark, the exudates become hard nodules or ribbons on dehydration to form a protective sheath against microorganism, an example of these gums includes cashew gum (*Anacardium occidentale*) and khaya gum (*Khaya senegalensis*) have been found to show promising properties for both industrial and pharmaceutical applications. *Khaya senegalensis* commonly called African mahogany in English, 'Homra' in Arabic, 'Dalehi' in Fulani, 'Madaci' in Hausa, 'ono' in Igbo and 'ogonowo' in Yoruba, belongs to the Family, *Meliaceae*, it is a tall plant of 15-30 meters in height and about 1 meter in diameter, which is easily recognized by its ever green crown, while its gum occur in long, thin glass-like translucent fragments. The gum which is dark brown, is known to contain highly branched polysaccharides consisting of D galactose, L-rhamnose, D-galacturonic acid and 4-O-methyl-D-glucuronic acid (Aspinall and Bhattacharjee, 1970). Khaya gum has been evaluated as a directly compressible matrix system for controlled release. The findings suggested that the gum could be useful in the formulation of sustained release tablets for up to 5 hrs and may provide a time independent release for longer periods when appropriately combined with HPMC (Oluwatoyin, 2006). Cashew tree (*Anacardium occidentale* L.) resin is synthesized in the epithelial cell lining pockets or canals and then secreted into these internal cavities. The gum is similar to gum arabic and may be used

as to a substitute for liquid glue for paper, in the pharmaceutical/cosmetic industry and as an agglutinant for capsules and pills Bovin (1998), De Paula *et al* (1998) and Amadeo *et al* (2003). The major cations of *A. occidentale* L. are  $K^+$ ,  $Na^+$ ,  $Ca^{+2}$  and  $Mg^{+2}$ . The crude *A. occidentale* gum, containing these cations tends to be naturally transformed into Na salt, after purification or dialysis against NaCl 0.15 M [De Paula *et al* (1998), Charlwood *et al* (1998), Carver (1997) and León de Pinto (1994)]. The cost of polymer or gum production is virtually fixed by the material and the compounding method and the economy depends on blend's morphology, tailored for a specific application, hence the objective of this study was to explore the effect of ionic environment on the interaction of the selected plant gums in dilute solution as well as other conditions: temperature, salt, acid etc. A sensitive rheometry technique was employed to capture this interaction. Different intrinsic-viscosity models and the elastic component of the gum blends was used to determine any conformational change or interaction occurring between the gums.

The results in this study aid us in improving on the quality or properties of this gums by carefully modeling their behaviours when salts are added to the gum blends as well its effect on the blends elastic component.

## II. MATERIALS:

Crude *Khaya senegalensis* (chewstick tree) gum was obtained as dried exudate from the parent tree grown at Kanya babba village in Bubura local Government Area of Jigawa State, the gum was collected around mid-November during the day time. The plant material had earlier been identified and authenticated and assigned a voucher number 872 in the herbarium Department of Biological Sciences of Ahmadu Bello University Zaria, while the crude *Anacardium occidentale* L gum was obtained as dried exudate from its parent tree grown in Ahmadu Bello university Zaria, close to the postgraduate school.

## III. PURIFICATION OF THE GUM:

The procedure adapted for the purification of the gum was that of Femi – Oyewo *et al.*, (2004) but with some modifications. The gums were dried in an oven (BS Size 3, Gallenkamp) at 40°C for 2hrs and their size reduced using a blender (Model. MJ-176 NR, Matsushita Electric Industrial Co., Ltd. Osaka, Japan). It was hydrated in double strength chloroform (Sigma-Aldrich, Germany) water for five days with intermittent stirring to ensure complete dissolution of the gum and then strained through a 75µm sieve to obtain particulate free slurry which was allowed to sediment. Thereafter, the gums were precipitated from the slurry using absolute ethanol (Sigma-Aldrich, Germany), filtered and defatted with dried flakes. The precipitate was dried in the oven at 40 for 48 hours. The dried flakes were then pulverized using a blender and finally stored in an air tight container.

### Preparation of Polymeric Blends:

Ternary solutions for the present system were prepared by mixing the calculated quantity of polymer solutions in different weight ratios up to the concentration of 1.0% (w/v). Dilutions to yield four lower concentrations were made by adding appropriate aliquots of solvent. To study the interaction between the gums, the following treatments were considered: *Anacardium occidentale* L (AO) 100%, *Khaya senegalensis* (KS) 100%, KS 80%- AO 20%, KS 60%- AO 40%, KS 50%-AO 50%, KS 40%-AO 60%, KS 20%-AO 80%.

### Effects of Temperature, Concentration And Salt Changes on Viscosities of Gums:

The Ostwald viscometer was used as described by Higiro *et al.*, 1 % w/v concentrations of each of the gums were prepared and their viscosities at temperature range (30-70) °C were determined. Another 1 % w/v concentrations of each of the gums were studied with different concentrations of KCl, AlCl<sub>3</sub>, KBr i.e. (0.2, 0.4, 0.6, 0.8 and 1.0M). Viscosity values of the blends and the pure gums at different concentrations of the salts as well as temperature were measured.

## IV. FTIR ANALYSIS:

FTIR analyses of the gums were carried out using (Scimadzu FTIR-8400S) Fourier transform infrared spectrophotometer. The sample was prepared using KBr and the analysis was done by scanning the sample through a wave number range of 400 to 4000cm<sup>-1</sup>.

### RHEOLOGICAL PROPERTIES:

The elastic and viscous components of each gum solution and of the blends were measured as a function of shear viscosity by using an Ostwald viscometer.

Rheological measurements were carried out at 20°C by using a temperature- controlled circulating water bath (Haake DC5, Gebr. Haake GmbH, Karlsruhe, Germany).

Microsoft Excel 2007 (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 ( $R^2$ ), to assess the best model.

**V. DETERMINATION OF INTRINSIC VISCOSITY:**

The intrinsic viscosity  $[\eta]$  is a measure of the hydrodynamic volume occupied by a macromolecule, which is closely related to the size and conformation of the macromolecular chains in a particular solvent (Lai and Chiang, 2002). The intrinsic viscosity  $[\eta]$  is determined experimentally from measurements of the viscosity of very low concentration (C) solutions. Denoting solution and solvent viscosity as, respectively,  $\eta_{\text{solution}}$  and  $\eta_{\text{solvent}}$ ,

$[\eta]$  is defined by the following relationships:

Relative viscosity:  $\eta_{rel} = \frac{\eta_{\text{solution}}}{\eta_{\text{solvent}}}$  ..... (1)

Specific viscosity:  $\eta_{sp} = \eta_{rel} - 1$  ..... (2)

Intrinsic viscosity:  $[\eta] = \lim_{C \rightarrow 0} \frac{\eta_{sp}}{C}$  ..... (3)

The intrinsic viscosity can be obtained by measuring specific viscosities at different concentrations at the same shear-rate, and extrapolating the course of specific viscosity to infinite dilution (Heitmann and Mersmann, 1995). The intrinsic viscosity  $[\eta]$  is, therefore, obtained by extrapolating data to zero concentration by using a linear regression, which will be called the graphic double-extrapolation procedure (GDEP) in this study. McMillan (1974) showed that

$\frac{\eta_{sp}}{C}$  also called reduced viscosity, could be written in the form of a Huggins equation (Huggins, 1942)

$$\frac{\eta_{sp}}{C} = [\eta] + K^l [\eta]^2 C \text{ ..... (4)}$$

where  $k^l$  is the Huggins constant. The determination of the intrinsic viscosity is, therefore, the extrapolation of reduced viscosity to the value at zero solute concentration. The extrapolations are usually done in very dilute regimes ( $C \ll C^*$ ) with relative viscosity values between 1.2 and 2.0, the corresponding specific viscosities being between 0.2 and 1.0 (Da Silva and Rao, 1992).  $C^*$  is defined as the overlap concentration, the transition from the dilute to the semi-dilute region which mark the onset of polymer entanglement (Launay, Cuvelier, and Martinez- Reyes, 1997). In the present work, gum solutions were therefore diluted to be within the described range. In addition, McMillan (1974) reported that the intrinsic viscosity could be obtained from the Kraemer equation (Kraemer, 1938) by extrapolation to zero concentration (C)

$$\frac{\ln \eta_{rel}}{C} = [\eta] + k^{ll} [\eta]^2 C \text{ ..... 5}$$

where  $k^{ll}$  is the Kraemer constant. For very dilute solutions, however, Eq. (5) can be shortened by retaining only the first-order term, and  $[\eta]$  can be determined from the slope of a plot of  $C$  against  $\ln \eta_{rel}$  (Sornsrivichai, 1986).

McMillan (1974) showed that methods of determination of the intrinsic viscosity that were based on slopes of plots had higher correlation coefficients and lower standard errors, compared with those based on intercepts of plots.

On the basis of such findings, Tanglertpaibul and Rao (1987) used the following equations to obtain the intrinsic viscosity of tomato serum:

$$\eta_{rel} = 1 + [\eta]C \text{ .....(6)}$$

The intrinsic viscosity  $[\eta]$  is the slope obtained by plotting  $\eta_{rel}$  vs. C

$$\eta_{rel} = e^{[\eta]C} \text{ .....(7)}$$

The intrinsic viscosity  $[\eta]$  is the slope obtained by plotting  $\ln \eta_{rel}$  vs. C

$$\eta_{rel} = \frac{1}{1 - [\eta]C} \text{ .....(8)}$$

The intrinsic viscosity is the slope obtained by plotting  $1 - \frac{1}{\eta_{rel}}$  vs. C.

The intrinsic viscosity  $[\eta]$  was estimated based on the slope of  $\eta_{sp}$  vs. C for polyelectrolytes, as suggested by Chou and Kokini (1987); this is similar to the method discussed in Eq. (6). Chou and Kokini (1987) reported that when there is essentially no molecular interaction, as in dilute solutions, the second term of the Huggins equation (Eq. (4)) is negligible, and a plot of  $\eta_{sp}$  against concentration is linear. In this study, the intrinsic viscosity in the dilute domain was estimated on the basis of Eqs. (3), (6), (7), and (8), and the four methods were statistically compared for a better fit.

The intrinsic viscosity of the gum samples was determined in distilled water. The gum solutions were

prepared by dispersing 10 mg of each of the gum sample (db, dry basis) separately in 100 ml of the distilled water at room temperature and mixing with magnetic stirring overnight. 2 ml of solution was transferred into an Ostwald viscometer which was immersed in a precision water bath to maintain the temperature at 25.0±0.1 °C and after equilibration for 10 minutes, 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 averaged. The relative viscosity ( $\eta_{rel}$ ) would be calculated using the equation

$$\eta_{rel} = \frac{t - t_0}{t_0}$$

Where  $t$  is the flow time of gum solution in seconds,  $t_0$  is the flow time of solvent (water) in seconds.

## VI. DETERMINATION OF THE MOLECULAR CONFORMATION AND POLYMER INTERACTION:

The power-law equation

$$\eta_{sp} = aC^b \dots\dots\dots 9$$

Was used to estimate the exponent  $b$  from the slope of a double logarithmic plot of  $\eta_{sp}$  against concentration, and provides an indication of the conformation of polysaccharides (Lai, Tung, and Lin, 2000). To determine the gums interaction, the verified theory (Chee, 1990; Sun, Wang, and Feng, 1992), based on the classical Huggins equation expressing the specific viscosity ( $\eta_{sp}$ ) of a polymer as a function of polymer concentration  $C$ , was used

$$\frac{\eta_{sp}}{C} = [\eta] + bC \dots\dots\dots 10$$

and

$$b = K[\eta]^2 \dots\dots\dots 11$$

Where  $[\eta]$  is the intrinsic viscosity, and  $b$  and  $K$  are Huggins parameters. Chou and Kokini (1987) reported that for dilute solutions, the term  $bC$  from Eq. (11) is negligible, and the plot of the specific viscosity against the concentration gives a straight line. The term  $b$  was approximated from the small intercept value of the plot of specific viscosity against the concentration (Higiro, Herald, and Alavi, 2006).

According to this theory, the following equation applies to a ternary polymer–polymer–solvent dilute solution, in which there is no aggregation between molecules

$$\alpha = b_m - (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 \dots\dots\dots 12$$

Where  $b_m$ ,  $b_1$ , and  $b_2$  are the Huggins coefficients for blend, polymer 1, and polymer 2, respectively.  $W_i$  is the weight fraction of polymer  $i$  in the polymer blend ( $i = 1$  or  $2$ ). The equation may be used to provide qualitative information on polymer–polymer interaction: two polymers are attractive in solution when  $\alpha \geq 0$ , whereas they are repulsive when  $\alpha < 0$  (Wang, Sun, and Wang, 2001).

Three types of interaction contribute to the value of  $b_m$  for a ternary polymer–polymer–solvent interaction (Cragg and Bigelow, 1955)

1. Long-range hydrodynamic interaction of pairs of single molecules:

$$b_{m1} = b_1W_1^2 + b_2W_2^2 + 2\sqrt{b_1b_2}W_1W_2 \\ = (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 \dots\dots\dots 13$$

Where  $b_i$  is the Huggins parameter  $b$  for component  $i$  ( $i = 1$  or  $2$ ).  $W_i$  is the weight fraction of polymer  $i$  in the blend.

2. The formation of double molecules. This assumes actual contact:

$$b_{m2} = K^l([\eta]_1 - [\eta]_2) \dots\dots\dots 14$$

Where  $[\eta]_1$  and  $[\eta]_2$  are intrinsic viscosities of double- and single-molecule species, respectively, and  $K^l$  is a constant. In the absence of aggregation between molecules and at sufficiently low concentrations ( $C \ll C^*$ ), this term is neglected.

3. Intermolecular attraction or repulsion:

$$b_{m3} = \alpha \dots\dots\dots 15$$

Where  $\alpha \geq 0$  means attraction, whereas  $\alpha < 0$  means repulsion.

Therefore,

$$b_m = b_{m1} + b_{m2} + b_{m3} \approx b_{m1} + b_{m3} \dots\dots\dots 16$$

$$b_m = (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 + \alpha \dots\dots\dots 17$$

$$\alpha = b_m - (\sqrt{b_1}W_1 + \sqrt{b_2}W_2)^2 \dots\dots\dots 18$$

By measuring  $b_m$  from the Huggins equation for polymer– polymer–solvent solution,  $a$  was calculated and the interaction was characterized.

### Statistical Analyses

A two-way factorial design was used to generate the best-fitting intrinsic viscosity model. For each gum blend as well as for the effects of these three salts (KCl, KBr and  $AlCl_3$ ) at the concentration ( $10g/dm^3$  or  $1g/dl$ ) were compared for the intrinsic viscosity, the elastic component, the molecular conformation coefficient  $b$ , the miscibility coefficient  $a$ , and the Huggins coefficient  $K$ , in a factorial design. In each instance, the analysis of variance and means comparison were conducted by the general linear models procedure (Proc GLM), with Statistical Package for social science (version 16.0). Comparisons among treatments were analyzed by using Duncan and Tukey significant test, with a significance level at  $P < 0.05$

## VII. RESULTS AND DISCUSSION:

In order to successfully study the trend in the specific viscosity as a result of addition of inorganic salt, a uniform concentration of the gums were maintained at ( $1.0 g/dl$ ) while that of the salts chosen were varied from ( $0.20-1.00 g/dl$ ). The AO-KS blends viscosity decreased when KCl and KBr were added with an exception of 80:20 and 60:40, which increased as the concentration of the salts were added. The blends of AO:KS increased in specific viscosity when  $AlCl_3$  was added (fig 3), whereby a pronounced increase was noticed for 40:60 and 50:50 blends when the concentration added increases between  $0.4 - 0.6 g/dl$ , while a continuous smooth decrease was noticed for 80:20 and 60:40 blends. Due to impracticability in the obtaining a good regression model for the AO:KS blends when these salts are added it would be difficult to generate an intrinsic viscosity at these conditions, Lai *et al.* (2000) reported similar results when determining the intrinsic viscosity of hsian-tsao leaf gum in different salt solutions. Lapasin and Pricl (1995) reported that non-ionic polysaccharides (i.e., LBG) exhibited linear plots of lower slope, whereas ionic polysaccharides (i.e., xanthan) displayed a sharp increase in slope, possibly due to expanded coil dimensions and electrostatic repulsion between chain segments, dependence upon concentration was observed, with the appearance of a maximum, becoming more pronounced and shifting to the left. Without salt addition, the specific viscosity of the gums increased steadily with dilution, and very rapidly at high dilution. Our results showed an increase of specific viscosity/concentration for 95% of all the blends when  $AlCl_3$  was added and decreased for the other salts used except AO:KS (80:20 and 60:40) in some salt concentrations.

As shown in fig 1, 2 and 3, the hydrodynamic behavior of *Khaya senegalensis* and *Anacardium occidentale* blends was strongly affected by ion types and ion concentrations. Within each gum blend, trivalent ions from  $AlCl_3$  showed a more pronounced effect on the specific viscosity, compared with monovalent ions from KCl and KBr. The increase in ionic strength of the three salts from 0.2 to 1 caused a significant increase in specific viscosity for all gum blends. The specific viscosity increased by more than 30% of the value obtained with the pure gums and their blends when only  $1g/dl$  salt was added to the gum blends.

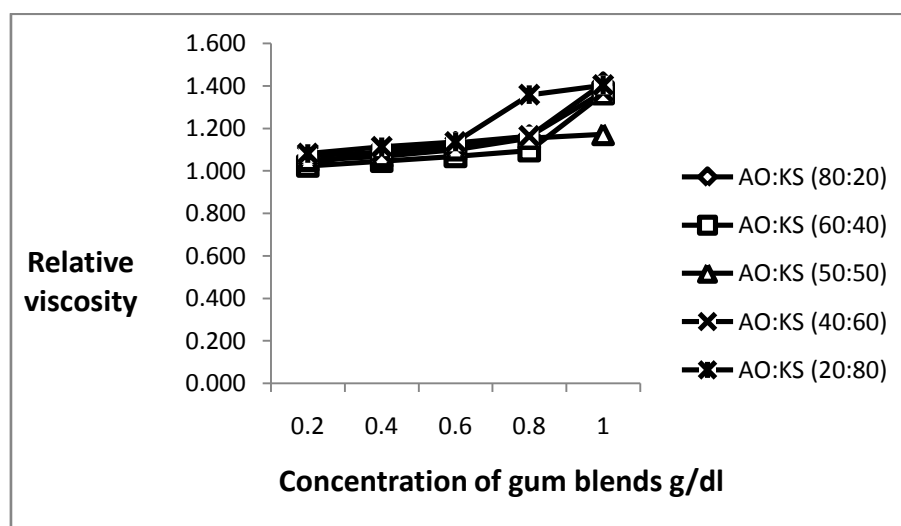


Fig 1: Variation of relative viscosity of the blend AO:KS with concentration of the blends at room temperature

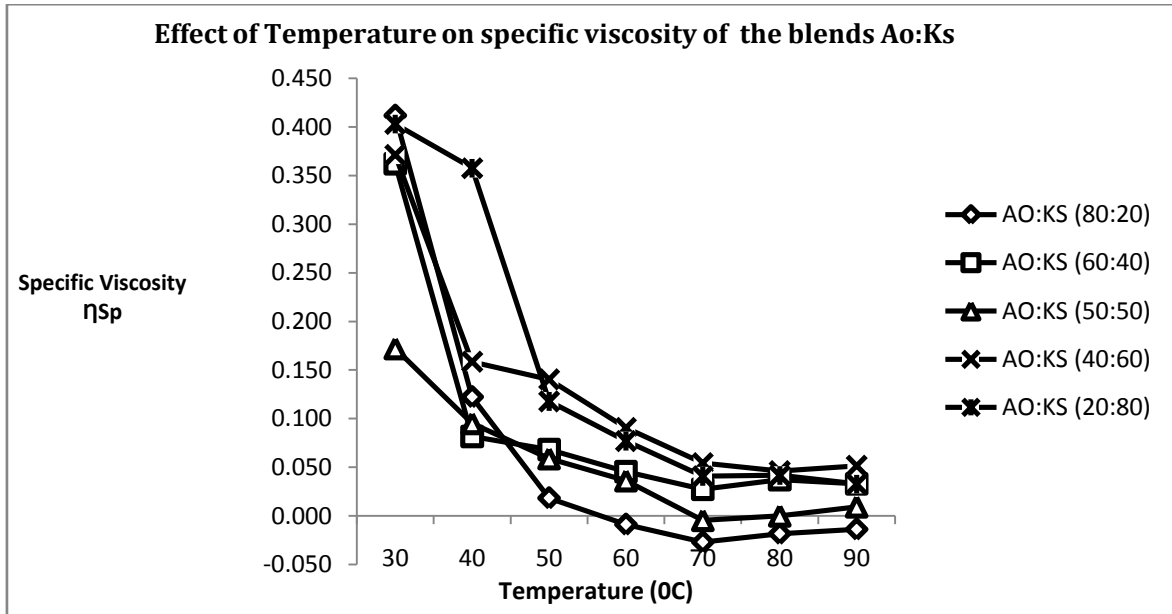


Fig. 2: Variation of specific viscosity of the blend Ao:Ks with temperature

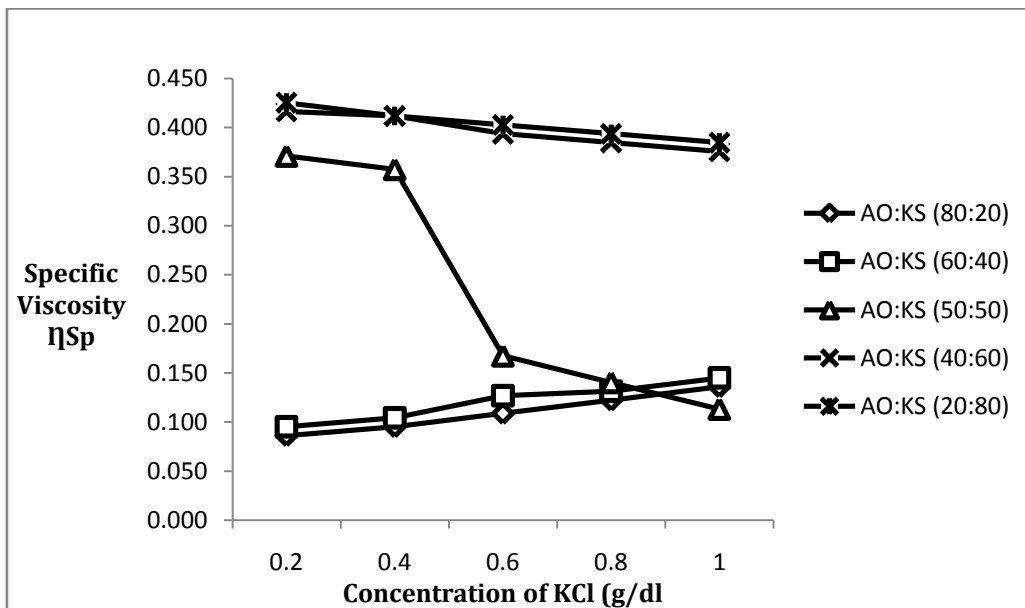


Fig. 3: Variation of specific viscosity of Ao:Ks gum blends with concentration of KCl

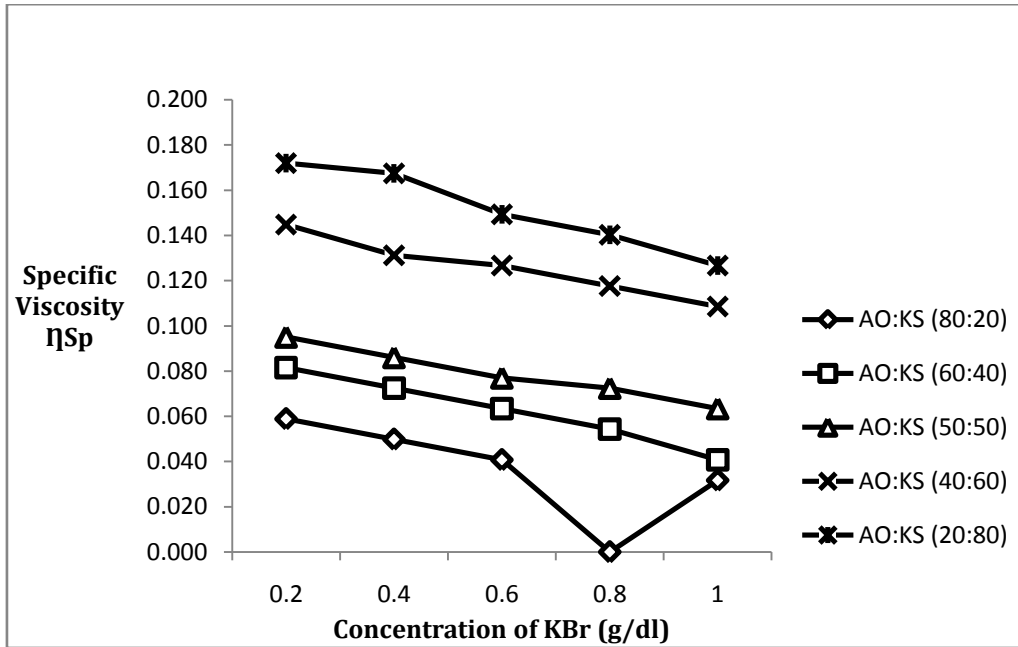


Fig. 4: Variation of specific viscosity of the blend AO:KS with concentration of KBr

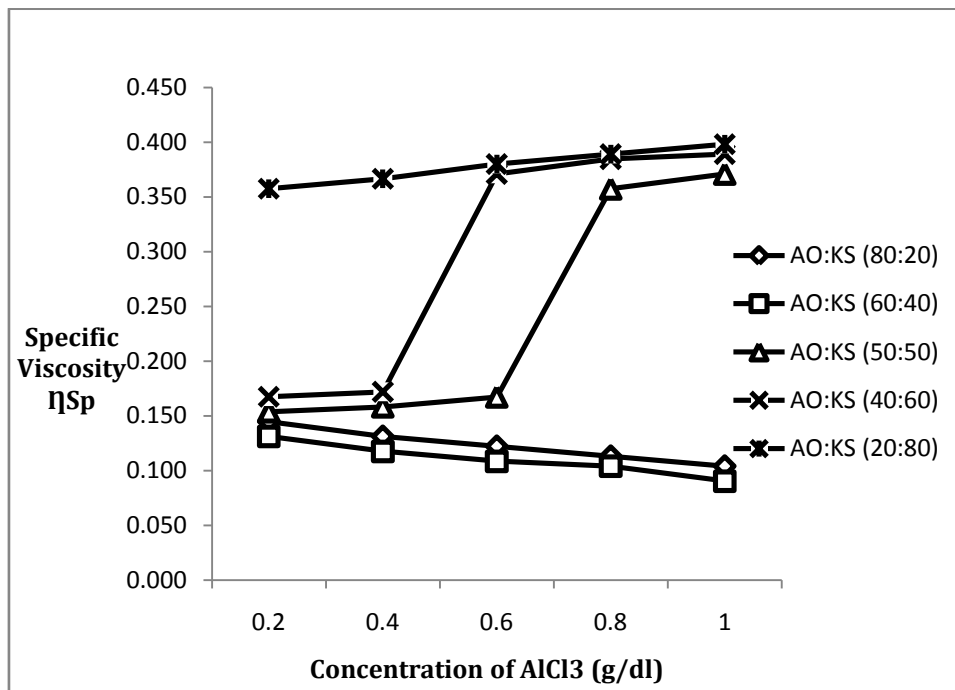
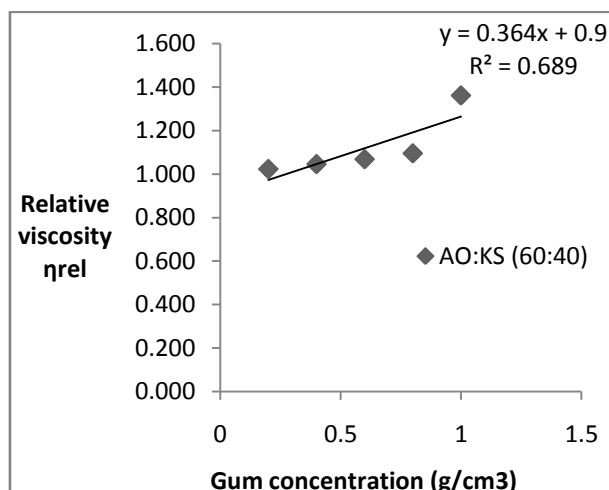
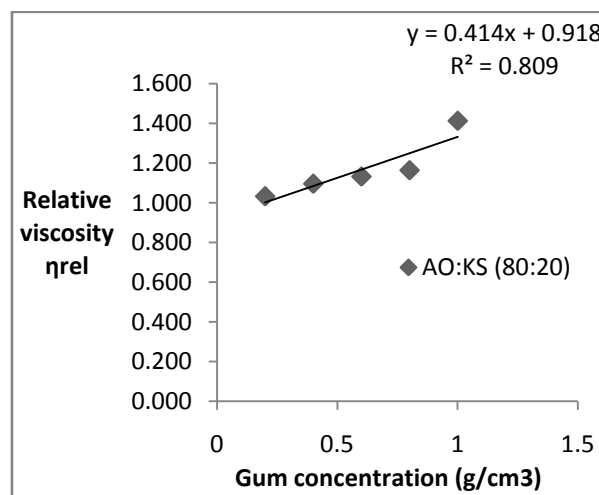


Fig. 5: Variation of specific viscosity of the blend AO:KS with increasing concentration of AlCl<sub>3</sub>

### VIII. INTRINSIC VISCOSITY:

The intrinsic viscosity determined for all the pure gums and their blends had an increase in relative viscosity which was observed as the concentration increases (Table 1), but a more pronounced increase in relative viscosity was evident for concentrations more than 0.4 g/dl. The GDEP therefore failed to generate the intrinsic viscosity for the pure gums and their blends since the datas generated did not fit with the linear regression model. The Huggins and Kraemer plots did not provided a better fit and, therefore, Tanglertpaibul and Rao plot was used, it was found to have the best fit (Chou and Kokini, 1987; Tanglertpaibul and Rao, 1987), this was done to determine the intrinsic viscosity by plotting  $\eta_{rel}$  vs. C. Straight-line relationships with large linear regression coefficients were obtained for all the gums. McMillan (1974) reported that methods of determination of intrinsic viscosity based on slopes of plots had larger correlation coefficients and smaller standard errors than those based on intercepts of plots. The values of the *intrinsic* viscosities resulting from these models differed, but showed similar trends, the intrinsic viscosity values calculated by using Tanglertpaibul and Rao plot was chosen as the best model for intrinsic viscosity determination because it showed a better linear fit, with higher correlation ( $R^2$ ) for all blends. The intrinsic viscosity calculated for the blend AO:KS (20:80) had the highest intrinsic viscosity value at 44.31 dl/g, the value was seen to be lower than the intrinsic viscosity of a pure Khaya gum, but significantly higher than that of a pure cashew gum, which was found to be 6.31 dl/g this trend was found to decrease slightly as the composition of cashew gum was added. This shows that at precise blend combinations a synergism is archived which could have been as result of some interaction between the polymeric materials found within both gums.





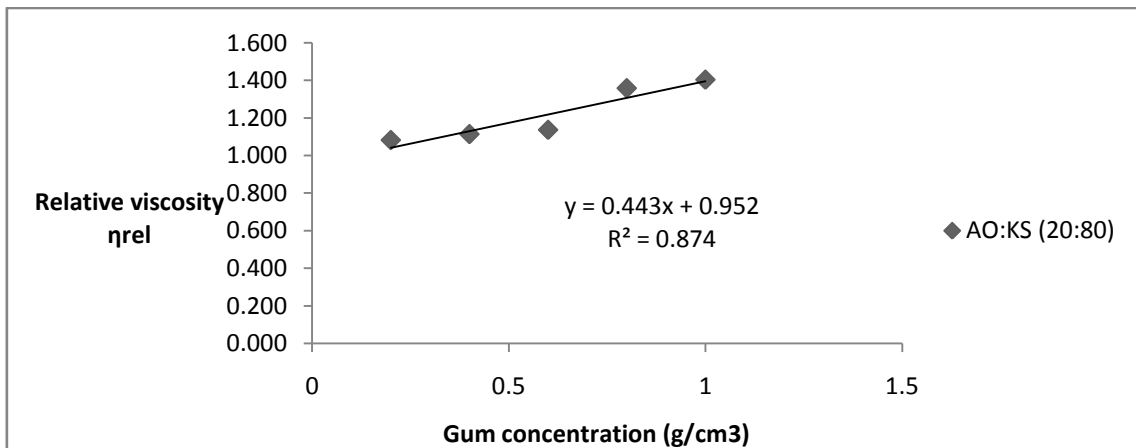
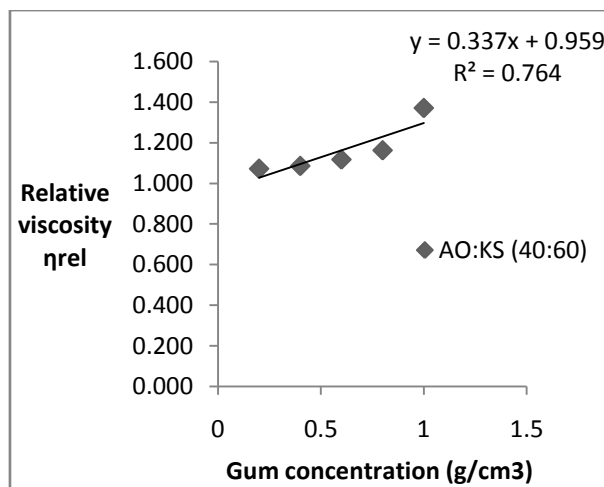
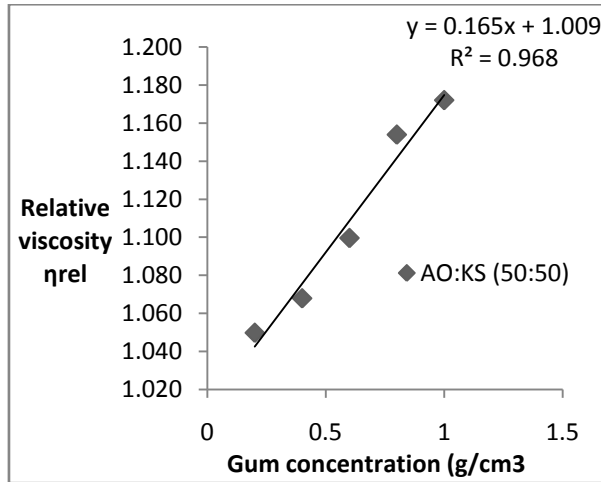


Fig. 6: Tanglertpaibul and Rao plot for the blends of AO:KS with concentration

**Table 1:** The intrinsic viscosity calculated from the slope of Tangelertpaibul and Rao (1987) plot are given below as

GUM BLENDS	INTRINSIC VISCOSITY (dl/g)	R2
AO	6.31 ± 0.01	0.915
KS	59.02 ± 0.02	0.912
AO:KS (80:20)	41.41 ± 0.01	0.809
AO:KS (60:40)	36.37 ± 0.14	0.689
AO:KS (50:50)	16.52 ± 0.02	0.968
AO:KS (40:60)	33.71 ± 0.01	0.764
AO:KS (20:80)	44.31 ± 0.01	0.874

The Results are expressed as mean ± SD for three replications. The means were found to be significantly different (p < 0.05)

**IX. Thermodynamic Parameters And Polymer Conformation:**

Temperature has an important influence on the flow behavior of plant gum sample content hydrocolloids. Since different temperatures are usually encountered during processing of hydrocolloids, their rheological properties are studied as a function of temperature. The Arrhenius equation to a great extent explains the relationship between the temperature and viscosity. The viscosity is dependent up on the intermolecular distances. As the temperature is increased, the intermolecular distances increase and therefore the viscosity will decrease for these main reasons. The viscosity is a function of temperature and the equation is given below

$$\ln \eta = \ln A + \frac{E_F}{RT} \dots\dots\dots 19$$

Equation 19 revealed that a plot of  $\ln \eta$  versus  $1/T$  should be linear with slope and intercept equal to  $E_F$  and  $\ln A$  respectively. Activation parameters deduced from the plots are presented in Table 2. The results obtained indicated excellent correlation through  $R^2$  values. The calculated values of  $E_F$  were 6.28 and 10.05 kJ/mol for AO and KS pure gums respectively. The activation energy for the blend flow was found to be highest in (80:20) with the value of 8.424KJ/mol, this value was found to decrease with increase in composition of khaya gum, but a change in trend was noticed from the 40:60 to 20:80 of the AO:KS blend. It has been found that low activation energy of flow indicates few inter- and intra-interactions between polysaccharide chains in the concentration range investigated and that the higher the value of  $E_F$ , the less sensitive is the polymer to temperature change (Shaikh *et al.*, 2011; Nair *et al.*, 2002). Hence the change in trend maybe associated with some other polymeric constituent of the KS gum that promoted interaction within the blend as its composition was increased, this result suggests the use of the blends (40:60 and 20:80) at higher temperature in food or drugs application.

According to Acevedo and Katz (1990), thermodynamic parameters of viscous flow can be calculated using the Frenkel-Eyring equation in the form,

$$\ln \eta = \left( \ln A - \frac{\Delta S_V}{R} \right) + \frac{\Delta H_V}{RT} \dots\dots\dots 20$$

where A is the pre-exponential factor, R is the universal gas constant, T is the absolute temperature,  $\Delta S_V$  and  $\Delta H_V$  are the entropy and enthalpy changes of viscous flow. From equation 20, a plot of  $\ln \eta$  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. Values of Frenkel-Eyring flow parameters deduced from the plots are also presented in Table 2. Calculated values of  $\Delta H_V$  were found to be positive. This indicates the attainment of the transition state for viscous flow is accompanied by bond breaking.

The enthalpy change and activation energy of melt flow were accounted for using the Arrhenius-frenkel and frenkel-eyring model respectively (Ravindranatha, 2002)

Table 2: shows the values for  $\Delta H$  and  $E_f$  for the gums and their blends

GUM BLENDS	$\Delta H$ (KJ/mol)	$E_f$ (KJ/mol)	Gum Conformation	$b_{law}$
AO	14.477	6.2872	rod-like	0.730
KS	23.160	10.0581	random coil	1.715
AO:KS (80:20)	19.398	8.4244	random coil	1.414
AO:KS (60:40)	13.657	5.9316	random coil	1.482
AO:KS (50:50)	8.816	3.8293	rod-like	0.809
AO:KS (40:60)	14.156	6.1480	rod-like	0.889
AO:KS (20:80)	19.040	8.2691	random coil	1.028

The power-law equation is used to estimate the exponent  $b$  from the slope of double logarithmic plot of against concentration, which provides an indication of the **conformation of polysaccharides** (Lai, tung, and lin, 2000), If  $b > 1$ , then suggest random coil conformation (lapasin and pricl, 1995) and when  $b < 1$  is for rod-like conformation (lai and chiang, 2002). Khaya gum molecule has a random coil conformation, while the pure cashew gum had a rod-like conformation, the conformation of the blends changes from a random coil conformation to rod-like conformation as the composition of Khaya gum was increased. This trend was found to confirm the formation of a blend or an existing interaction within the dilute solution of the blends.

Table 3: Shows the calculated Huggins parameter and hydrodynamic interaction of the gums.

GUM BLENDS	Huggins Parameter K	Interaction Type	$bm1$	A
AO	0.3066	no aggregation		
KS	0.0001	no aggregation		
AO:KS (80:20)	0.0048	no aggregation	8.3452	-0.155
AO:KS (60:40)	0.0075	no aggregation	5.2399	4.760
AO:KS (50:50)	0.0035	no aggregation	3.9570	-3.007
AO:KS (40:60)	0.0035	no aggregation	2.8539	1.176
AO:KS (20:80)	0.0024	no aggregation	1.1872	3.612

when  $bm1 \geq 0$ , whereas they are repulsive when  $bm1 < 0$  (Wang, Sun, and Wang, 2001)

Table 3 summarizes the nature of interaction as well the hydrodynamic behavior of the blends, it shows that for all the blends the calculated value of the Huggins parameter was found to be less than unity, which according to Higuro *et al.*, indicates that no aggregation exists in the blends, but their affinity for water increased as the composition of cashew gum (AO) gum was increased, this was found to be evident in the interaction parameter  $bm1$

## X. FTIR STUDY OF THE GUMS:

The use of infrared spectroscopy for the characterization of polymer blends is extensive, coleman *et al.*, 1991. The IR spectra fig 7, shows the graphical representation of the frequencies of radiation absorbed and the percentage transmittance. Very strong bands which occur at  $2854-3008\text{cm}^{-1}$  in the gums can be mostly attributed to absorption of CH stretch and  $\text{CH}_2$ - asymmetric stretch in aliphatic groups closer to those bands. C-O stretch vibration due to carboxylic acid, alcohol and ester was noticed at  $1054.13\text{cm}^{-1}$  and the characteristic peak at  $1381\text{cm}^{-1}$  was attributed to O- $\text{CH}_3$  deformation, while the peak at  $755\text{cm}^{-1}$  was due to the  $\text{CH}_2$  rocking mode of vibration. The (C-C) vibrational mode appeared at  $1514\text{cm}^{-1}$ , while peak at  $1083\text{cm}^{-1}$  was attributed to C-C-C bending vibrational modes. The FTIR spectra of AO:KS blends (80:20, 60:40, 50:50, 40:60 and 20:80 %w/w) composition respectively showed that the blends did not indicate the existence of any chemical interaction between the components, although thorough analysis of the IR spectra for these blends showed a decrease in the transmittance of the carbonyl group, as well as other vibrational modes in the blend when the composition of khaya gum in the blend was increased

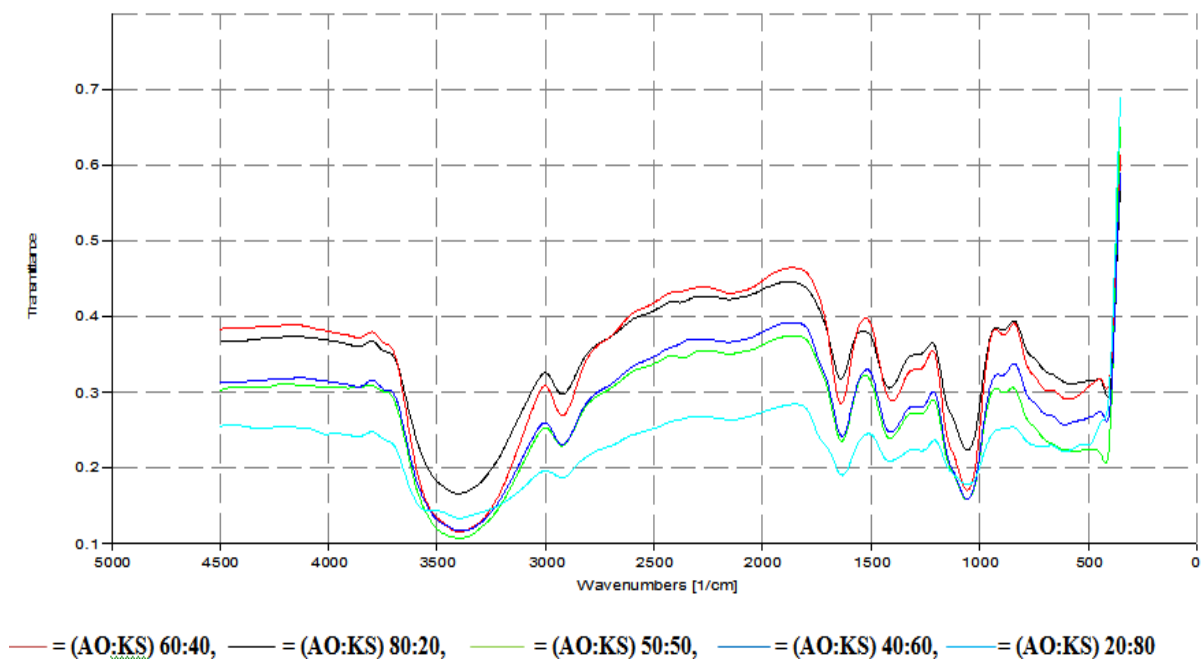


Fig. 7: FTIR spectrum of the gum blends of *Khaya senegalenses* and *Anacardium occidentale* gum

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