Natural Polymers. II. Thermal and Mechanical Properties of Gum Arabic Nanocomposite

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Abstract: The effect of Cloiste 20A (herafter referred to as C20A), an organo-clay nanoparticle, on the thermal and mechanical properties of Gum Arabic(hereafter called GA), a biopolymer, is presented. The study is executed using DSC to obtain the glass transition temperature (T_g), crystalline melting point (T_m), delta specific heat capacity (ΔC_p), enthalpy of melting (ΔH_m) and % crystallinity for the thermal analysis while the tensile strength (TS), initial (Young) modulus (YM), energy at break, (EAB), as well as elongation at break (EB%), for the mechanical properties of both the GA alone and the nanocomposites. Viscometry, UV-visible and FTIR spectroscopy as well as XRD were employed for characterization. The results show that while all the T_g values and generally the ΔH_m decrease, the T_m, % crystallinity and ΔC_p increase, as the loading of the organoclay are increased up to 9.5% (w/w). The TS of the biopolymer is optimally improved at 4.5% loading, YM at 9% loading, the EAB at 7% while EB decreases mostly at 4.5% loading, of the nanoparticle. The studies via viscometry, UV-visible and FTIR show a high level of interaction between the biopolymer and C20A. In addition the XRD indicate an appreciable level of intercalation/exfoliation of the nanoparticles particularly at 4.5% loading.

Key words: Gum Arabic, Cloisite 20A,Tensile strength. Young' modulus, Elongation at break, Energy at break, X-ray diffraction, Infra-red spectroscopy.

1.   Introduction

Gum Arabic (GA) or *Acacia* gum is an edible biopolymer obtained as exudates of mature trees of *Acacia senegal* and *Acacia seyal, Acacia karoo, Acacia polyacantha*, *Acacia sieberana,* to mention a few, which grow principally in the African region of Sahel in Sudan. The exudate is a non-viscous liquid, rich in soluble fibers, emerging from the stems and branches usually under stress conditions such as drought, poor soil fertility, and injury (Williams and Phillips, 2009).

The African gum belt is located north of the Equator and south of the Sahara desert, an arid zone between latitudes 4° and 18°, extending from east-west, continuously, from Somalia, through Ethiopia, Sudan, Chad, Niger, Nigeria, Burkina Faso, Mali, Mauritania, and Senegal. It is also found in parts of Africa South of the Equator, for instance, Tanzania, Zimbabwe, Malawi and South Africa. In Asia, *Acacia senegal* has been found in the Arabian peninsula and India (Glicksman, 1979).

Gum Arabic (GA) has been used for different purposes as in food, pharmaceutical, cosmetics and medical purposes (FAO, 2000; Wirongrong *et al.,* 2011).

The high solubility and relatively low viscosity of GA has limited most its application to the food industry where its ability to stabilize emulsions has been highly utilized. Effective cross-linking of GA has been demonstrated by the use of gamma irradiation up to 20 KGy (Ibrahim *et al.,* 2013). Such process, however, renders the biopolymer more amorphous and less mouldable, more brittle, harder and limits its thermal processibility to useful(non-food) products. What GA needs is enhanced crystallinity, that is, greater crystalline temperature, T_m and ΔC_p to sustain higher thermal processing condition at a moderately reduced glass transition temperature, T_g, that is, plasticization. This would reduce its natural brittleness so that products obtained from GA could have enhanced tensile strength and moderate elongation at break. The possibility of this might transform GA to a semi- thermoplastic system and broaden its industrial base application. Ibrahim *et al* (2007, 2013) plasticized GA with polyvinyl alcohol (PVA) in the absence and presence of CMC thereby increasing the -OH group level. Their findings were based on compatibility of the polymers arising from increased hydrogen bonding level in the blend resulting in little enhancement of the GA tensile strength. The usage of GA and many biopolymers has been limited due to the poor mechanical and barrier properties (Othman, 2014).

This study therefore sets to produce a nanocomposite of GA using Cloisite 20A nanoparticle, and MMT organoclay, with the organic modifier as dimethyl dehydrogenated tallowyl ammonium chloride (quaternary salt, 2M2HT, Southernclay Product). This is with the aim of enhancing the physical, thermal and mechanical

properties of this biopolymer, Gum Arabic, and expands its technological applications.

2. Methods

Materials

Grade 1 Gum Arabic, based on visual neat appearance, was purchased from "Kasuwan-Kurmi" local market, Kurmi, Kano State, Nigeria.

Purification Procedure (Air Drying Method)

The raw gum Arabic was dissolved in distilled water and stirred mechanically for 72h to effect homogeneity of the fairly viscous solution. This was then filtered under vacuum to remove all the suspended fine particles remaining in the solution. Thereafter, visually clean GA films were obtained using a glass mould in order to air dry films. The films were then finally dried in the vacuum desiccator to constant weight. The GA film obtained is now pure and could be quantitatively dissolved in distilled water.

Gum Arabic Nanocomposite Preparation Procedure

Different concentrations of GA-nanocomposite and GA alone were prepared. Each of the weighed amount (w/w, %) of C20A was mixed with its proportion of GA and distilled water just enough to dissolve the mixture was added. The C20A weight % concentrations prepared were; 1%, 1.5%, 2.5%, 3%, 3.5%, 4%, 4.5%, 5%, 5.5%, 6%, 7%, 7.5%, 8%, 8.5%, 9%, 9.5% of Cloisite 20A. GA alone and each composite mixture was stirred using a mechanical stirrer (Gallenkamp App № 6B 8297 B) for 100 minutes to obtain a neat GA alone (control sample, no cloisite 20A) and the GA nanocomposite samples.

GA-Nanocomposite Films Preparation.

The composite solution obtained was then applied separately onto each glass mould of 14 cm × 10 cm × 0.2 cm and evenly spread in order to obtain a composite film of uniform thickness in length and breadth by placing each on a plumed horizontal concrete slab(180^0), and left to air-dry at room temperature(26 ± 0.1^0C) for 48 hrs. At this point the films obtained possess an elastic property which makes it to be easily removed from the glass substrate.

Characterization of GA Nanocomposite

Differential Scanning Calorimetry

The DSC/DTA investigation of the biopolymer and its nanocomposites were carried out using NETZSCH model DTA 404 PC at the Centre for Energy Research and Development (CERD), Obafemi Awolowo University, Ile-Ife, Nigeria. Thermal parameters were obtained including the T_m, T_g, ΔCp and ΔH_m and % crystallinity.

Mechanical Properties

Tensile properties of the GA nanocomposite films were studied using a computerized Instron tensile testing machine at the CERD, Obafemi Awolowo University, Ile-Ife, Nigeria. The cross-head speed was kept constant at 5mms^{-1} at maximum load of 120kg.

With a new neat cutting razor blade, films of 20mm by 70mm gauge length and 2mm thick (approx.) were cut and used for characterization. The stress-strain curves were obtained from which the tensile properties, YM, TS, EB and EAB were determined using standard procedures as described earlier (Turoti et al., 2015).

Determination of intrinsic viscosity

The intrinsic viscosity, $\overline{M_V}$, of each GA sample was determined by dilute-solution viscometry as described and determined by Arthur et al., (2014).

X-Ray Diffractometry (XRD)

GBC EMMA (Enhanced Mini Material Analyser) X-ray diffractometer at the Energy and Material Development Institute, Akure, Nigeria, was used to determine the diffraction pattern of, Cloisite 20A, GA alone and the GA-nanocomposites. The values of d spacing of some selected samples were computed.

UV-Visible Spectroscopy

The UV spectrometry of the polymer nanocomposite films was carried out at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria, using SHIMADZU UV-Visible spectrophotometer Model 1800 series, USA, to obtain the absorbancies of the samples.

FTIR Spectra of GA Nanocomposites

The FT-IR spectrophotometer used was SHIMADZU FT-IR-8400S, Japan. Apodization; Happ-Genzel, Resolution; 4[1/cm] at the Redeemers University, Ede, Osun State. Each chemical group was determined at its established IR absorption frequency.

3. Results and Discussion

Table 1 shows the effect of the presence of varying concentrations of C20A on some of the thermal parameters of GA. It is clear that C20A exerts both plasticizing and crystallizing effects on the host biopolymer. This is why the T_g and T_m generally decreases and increases respectively in the presence of the C20A nanofiller. The decreasing effect on the T_g shows This might probably be due to greater linear arrangements of the GA polymer chains to each other in the presence of the nanoparticles. This claim is evident from the generally greater values of the % crystallinity of the nanocomposite when compared with the GA alone. For instance, it can be seen that the nanocomposite with the highest % crystallinity gives the highest ΔH_m and one of the highest T_m values above 150^0C (Table 1).

Table 1: The Characteristic Values of DSC Analysis of the GA Nanocomposite Samples

%Concentration	ΔHc(J/g*k)	% Crystallinity	Tg (°C) (mid)	Tm (°C) (peak)	ΔHm (J/g) (Area under peak)
0%	0.068	0.00	82.7	146.7	*111.00*
1%	0.379	81.84	56.9	148.2	*85.93*
1.50%	0.295	76.75	53.2	147.1	*80.58*
2%	4.782	17.90	50.0	141.0	*18.79*
2.50%	1.823	80.53	44.7	149.6	*84.56*
3%	2.400	51.92	53.8	153.9	*54.52*
3.50%	1.702	80.06	59.0	154.4	*84.06*
4%	2.226	68.59	46.0	149.6	*72.02*
4.50%	1.434	29.85	43.3	153.0	*31.35*
5%	2.902	90.67	41.8	153.5	*95.20*
5.50%	1.054	108.19	48.7	153.3	*113.60*
6%	0.959	78.07	56.9	152.8	*81.97*
6.50%	0.748	93.72	54.2	155.9	*98.40*
7%	5.208	78.35	51.3	152.3	*82.26*
7.50%	2.876	71.27	55.1	153.7	*74.83*
8%	1.131	78.43	68.9	150.7	*82.35*
8.50%	2.264	48.99	40.1	148.1	*51.43*
9%	1.422	93.35	50.5	158.2	*98.02*
9.5%	3.684	62.12	42.9	149.0	*62.23*

It can also be seen that all the nanocomposites all have greater ΔH_c values than that of the neat biopolymer. The non-uniform change in T_m, as well as other heat parameters as observed can be explained by a bimodal process of melting which is typical of polymers made up of more than one different monomeric unit (Song *et al.,* 2013). The primary technological implication of these thermally connected parameters is that C20A could be a suitable plasticizer for a hard and brittle polymer, such as GA, and also it enhances heat capacity that is important for heat sustainability in the need of processing the biopolymer into commercial articles. These features of the nanofiller would be particularly desired if the mechanical properties of the polymer are also improved.

Figure 1 shows that as small as 4.5% (w/w) C20A can increase the tensile strength of GA from 3.7 to 6.4 x 10^6 Nm^2, almost 100% enhancement. Figure 2 demonstrates that 9% of the nanoparticle is capable of increasing the Young's modulus of GA by about 1,400%. Padua (2012) observed increases in TS and YM of a biopolymer nanocomposite when incorporated with cellulose nanofibers (CNFs) at higher concentration.

Figure 3 shows a relatively progressive increase in EAB as the concentration of filler in the GA nanocomposite increases, with the maximum energy at break observed at 7 % concentration of the nanofiller. Thus toughness and resilence of GA could be improved by the presence of the organoclay nanoparticle.

Padua (2012) and Othman (2014) both reported that, generally, mechanical properties of bionanocomposites are significantly dependent on the amount of nano-fillers.

Addition of fillers generally decreases the ductility of polymers (example, the EB, %. This is well known and expected as has been observed for some nanocomposites (Fornes *et al.,* 2001; Shah *et al.,* 2005). Many studies have demonstrated that the tensile strength and modulus of biopolymer-nanocomposite materials increase while elongation at break decrease with an increase in the amount of nanofillers (Rhim, 2011; Rhim *et al.,* 2011,2013; Tang *et al.,* 2012). Generally, there is longer EB than GA alone and this could be attributed to the penetration of the polymer chains into the gallery of C20A as attested by the lower T_g with increasing concentration of the nanofiller, as discussed in the earlier section (see Table 1).

This similar trend is observed in this work with samples 4.5 %, 4 % and 2.5 % which show high TS, but low EB. The EB of the nanocomposite was longest at 5% where the TS has the least value (see Figs 1 & 4.).

With the general observations of some of the thermal and mechanical results, some selected samples of the nanocomposites and the control (GA alone) were further subjected to some analysis.
Viscosity Average Molecular Weight (M_v)

The slope obtained from the plots of specific viscosity (η_{sp}) against concentration (g/dl) in Fig. 5 is substituted for [η] to obtain the values of the M_v

for the different selected samples of the GA nanocomposite in line with earlier studies (David *et al*., 2015. Arthur *et al*; 2014, Taglerpaibut and Rao, 1987, Lai *et al.,* 2000, Sornsrivichai, 1990, *Mc* Millan,1974). The slope obtained for the samples are as follows.GA alone = 0.655, sample 2.5% = 0.806, sample 4.5%: = 1.170, sample 5% = 0.677 and sample 8.5% =0.601. The variation of calculated M_v with concentration of C20A is in Fig.6.
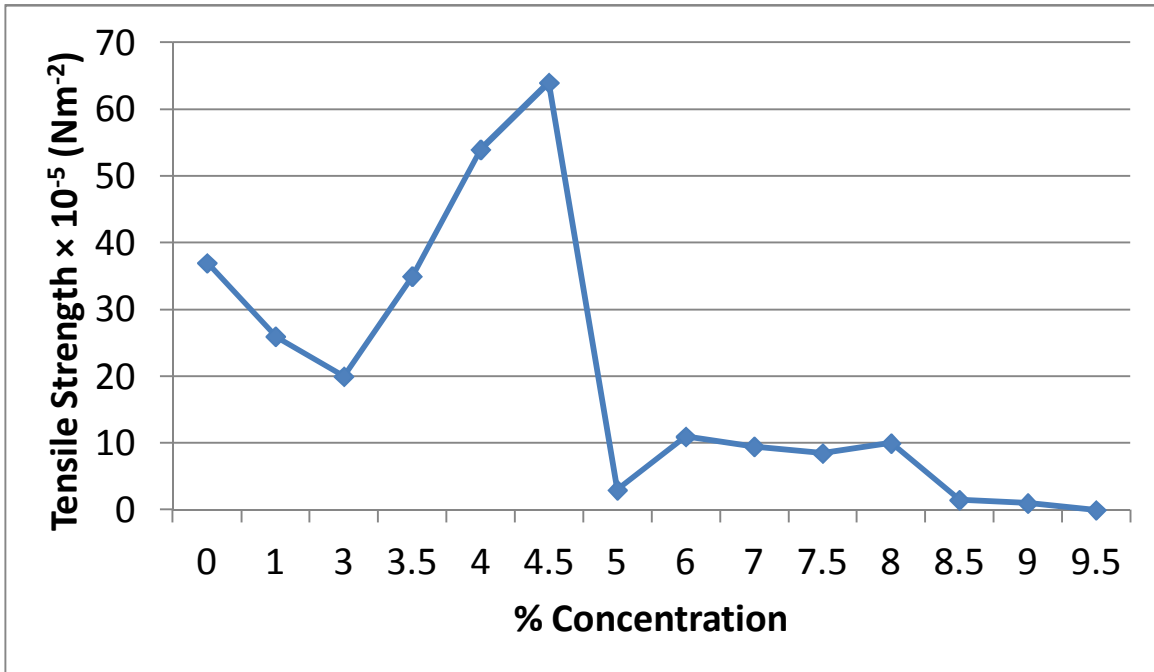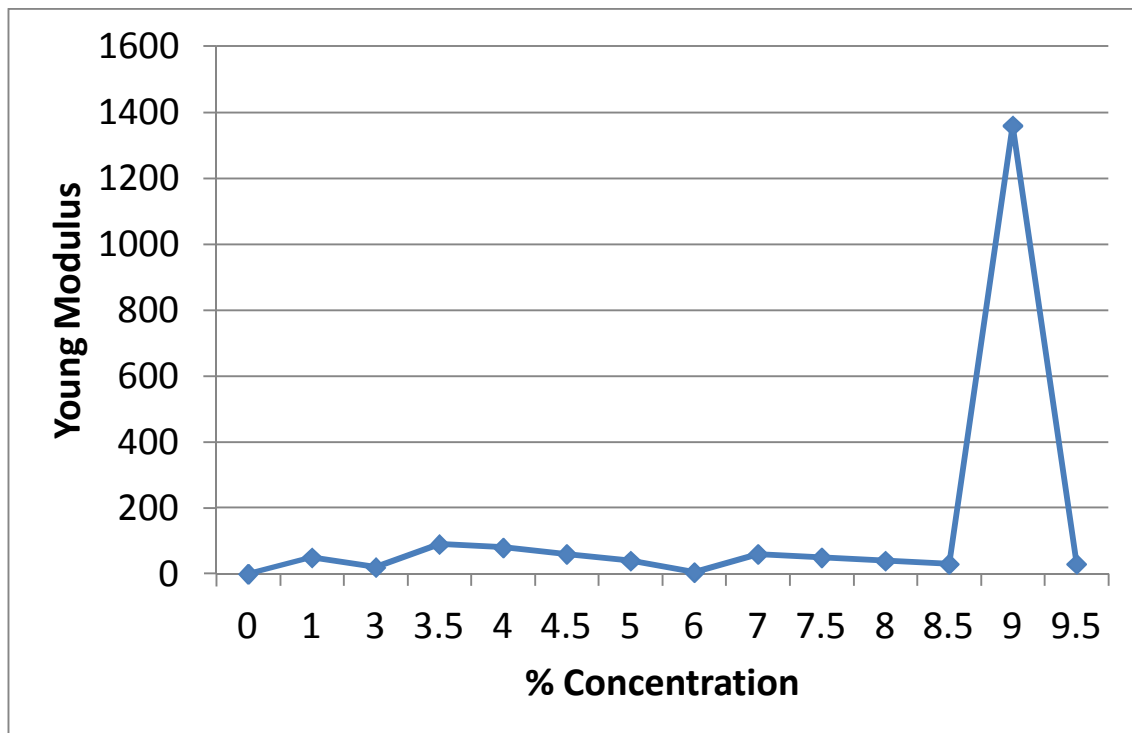

Fig. 1: Effect of concentration of Cloisite 20A on TS of GA

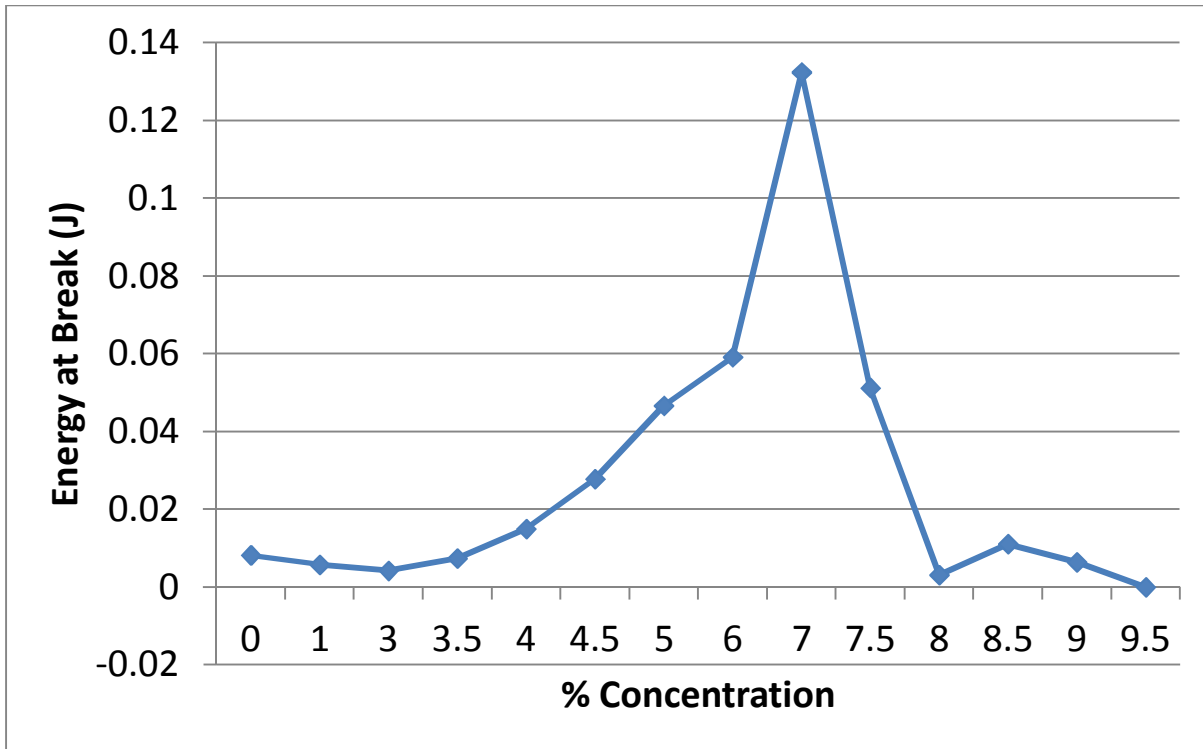Fig. 2: Effect of concentration of Cloisite 20A on YM of GA

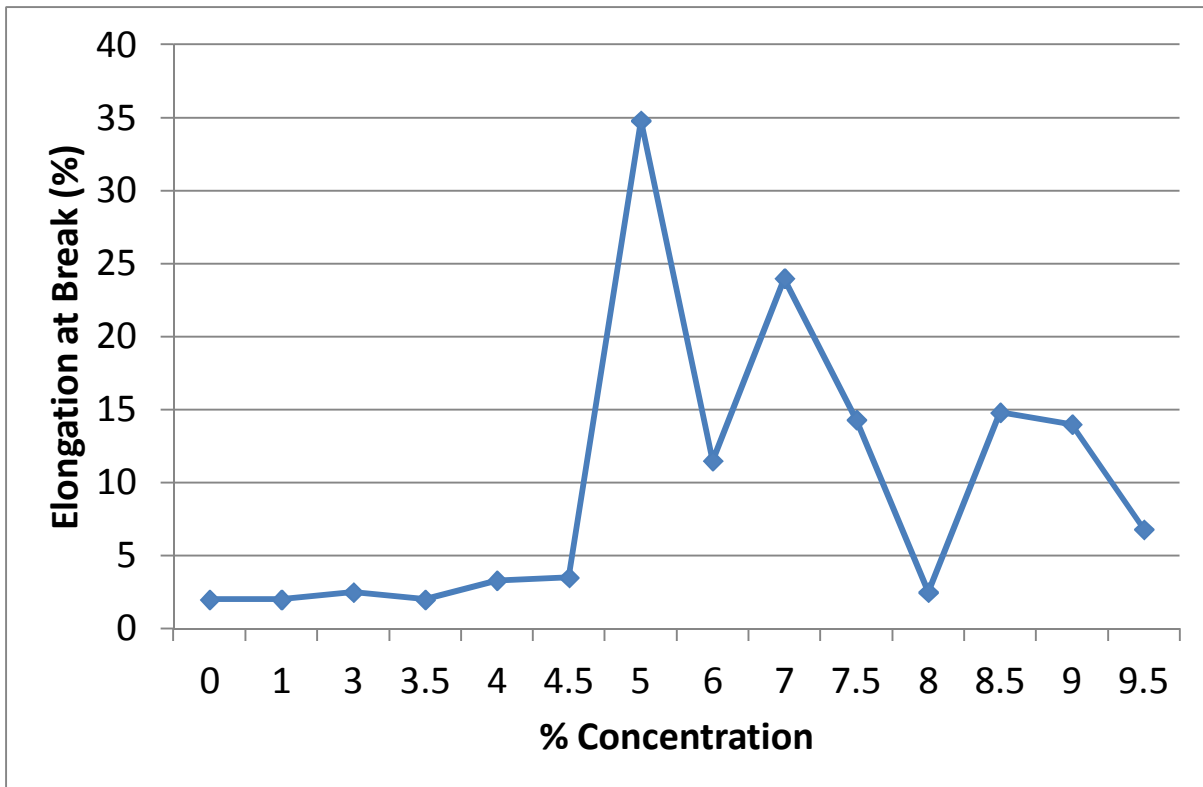Fig. 3: Effect of concentration of Cloisite 20A on EAB of GA

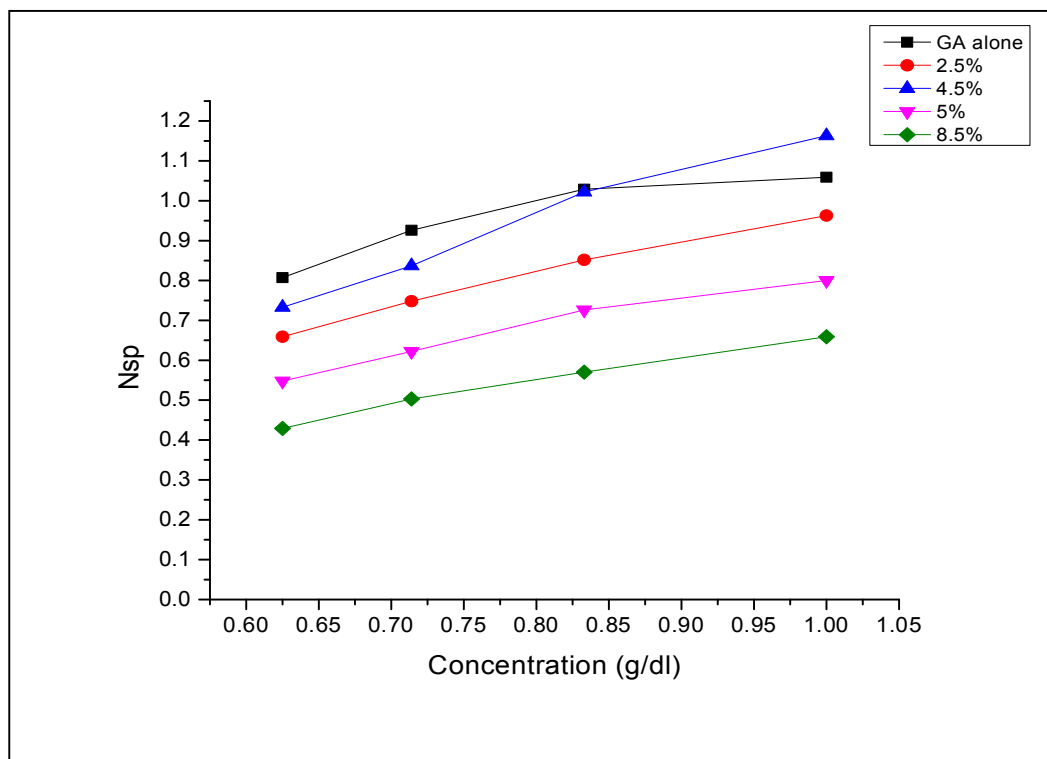Fig. 4: Effect of concentration of Cloisite 20A on EB of GA.

Fig.5: Effect of Cloisite 20A concentration on viscosity average molecular weight GA nanocomposite.
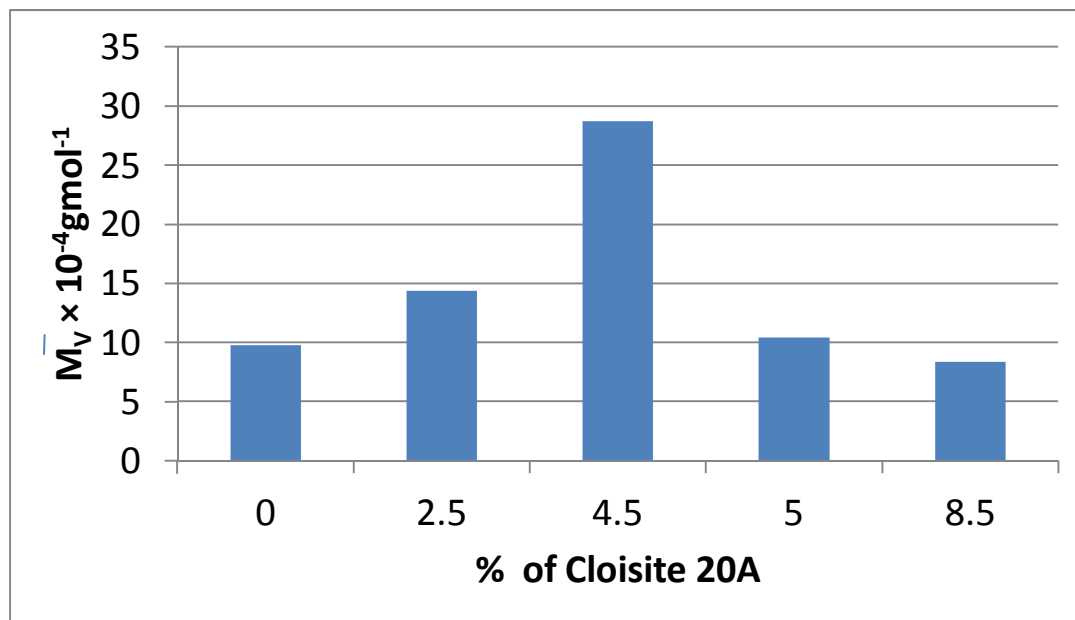

Fig. 6: Effect of Cloisite 20A concentration on the viscosity average molecular weight.

The sample 8.5% has the least M_v value of 8.364 x 10^4 g mol^{-1} as compared with the value for GA alone having 9.802 x10^4g mol^{-1}. This observed decrease in M_v value could probably be attributed to less association of the nanoparticles with GA at such higher nanofiller concentration. This might be accepted since the samples were thoroughly filtered to obtain a homogenous solution for the viscometry experiment. This probably indicates some chemical interactions might be existing between GA and C20A at some nanofiller concentration such as 4.5%.

Anderson *et al.,* (1968), who reported that the average weight molecular weight, M_w, of GA lies between 260,000g and 1,160,000g and that the

variation depends on the gum specie and source. The M_v is usually smaller than the M_w for a particular polymer and as such the M_v values of 9.802×10^4g mol^{-1} obtained for neat GA would probably be realistic. But significant to note are the increasing values peaking at 4.5% and thereafter decreasing gradually to lower values of 8.364×10^4 gmol^{-1} at 8.5%. This result is suggestive of some bonding between GA and C20A at 2.5 and 4.5% and probable declining effect of the nanofiller on the biopolymer at some higher concentration such as 5 and 8.5%..We posit a progressive intercalated to exfoliated and seggregative states of the nanofiller as its concentration increases, from 2.5-8.5%, within its host GA matrix. The concentration dependent H-bonding between the nanofiller platelets at the edges, where the OH group of the known Si-OH exists, might be very strong to allow GA chains to penetrate into the gallery of the C20A at the higher concentrations beyond 4.5%.

UV-Visible Spectroscopy

The data obtained for the UV-Visible spectroscopic analysis of both the neat GA and the bionanocomposite can be seen in Table 3.

Table 3: UV-Visible spectroscopy of GA/Cloisite 20A Nanocomposite.

Sample weight % of C20A	λ_{max}	Absorbance
0	200.20	0.894
2.5	200.20	0.492
4.5	194.05	1.069
5	200.20	0.760
8.5	200.20	0.383

The low λ_{maxa} (blue shift or hypsochromic effect) and high intensity (hyperchromic effect) at 4.5% C20A compared to those of the other samples including the GA alone suggest some interaction between the two components of the nanocomposite. This may probably be responsible for the optimum values of many of the parameters obtained for the composite at 4.5% C20A as found in this study.
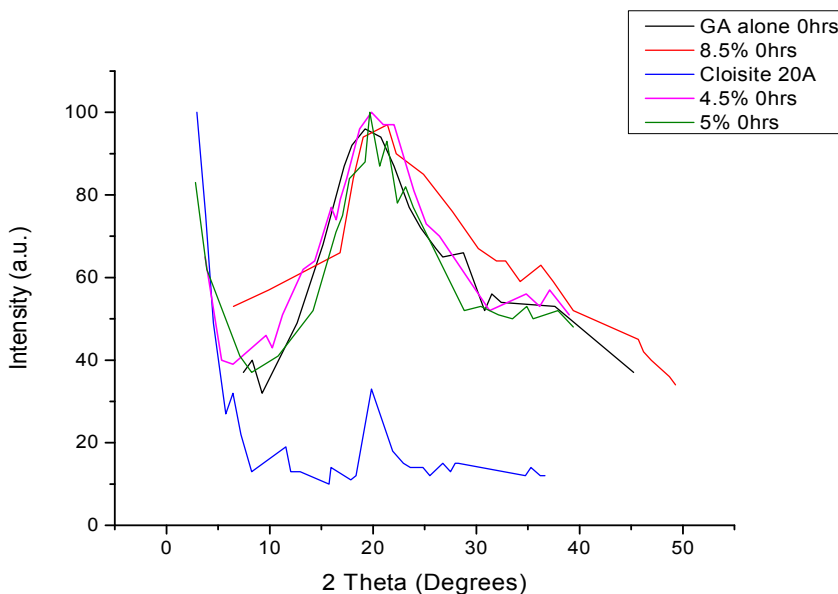
X-Ray Diffraction

Fig. 7: XRD patterns of pure GA,C20A and GA/C20A nanocomposites

Figure 7 shows the XRD patterns of C20A alone, neat GA and GA/C20A nanocomposites. The intensities of the neat GA and the nanocomposites samples are not only greater than that of the Cloisite20A but many of the diffraction peaks present in the latter are absent and/or new ones now emanate in the former. For instance, the XRD pattern of the C20A shows two reflection peaks at about $2\Theta = 6.48^o$ corresponding to a basal spacing of 1.14 nm, characteristic of MMT nanoparticles (Wang *et al.*,

2005), and a base peak at $2\Theta = 19.85^0$. The XRD pattern of GA alone shows a prominent peak at about $2\Theta = 20.95^o$ and a little broad peak at about $2\Theta = 28.4^o$. This suggests some amount of crystallinity in GA alone (Nara and Komiya, 1983). There is observed variation in the observed 2Θ values after incorporating C20A within the GA matrix. The basal plane of C20A at about $2\Theta = 6.48^o$ disappeared in the nanocomposite indicating that oriented layers in C20A were disrupted by GA chains leading to possible

intercalation/exfoliation. The absence of that peak in the XRD probably signifies that either the d-spacing of the clay becomes too large or highly disordered such that it is non-detectable by XRD and fails to produce a Bragg's diffraction peak (Kaushik *et al.,* 2011). The second prominent base peak at $2\Theta =$ 19.92^o broadens in the nanocomposite, appearing at 19.06^o indicative of the formation of an intercalated nanostructure in the nanocomposite, while the peak broadening and intensity decrease most likely indicate the disordered intercalated or exfoliated structure of the C20A in the nanocomposite (Wang *et al.*, 2005). This is in conjunction with the calculated inter-planar d-spacing values of some other peaks as shown in Table 4.

However, it is well known that evidences from XRD alone are not sufficient to indicate exfoliation of the C20A nanoparticles (Morgan and Gilman, 2003 and Eckel *et al.,* 2004). We further seek some evidences from FTIR spectra.

Figure 8 shows that some of the absorbances present in C20A are either absent or stronger with few new peaks in the GA nanocomposites. For instance, the sharp fingerprints absorbance in C20A between 500-600 cm^{-1} have disappeared in all the nanocomposites spectra. Similarly, the absorptions shown by C20A between 1250-1490cm^{-1},2800 and2900 as well as the last last stretching vibration at 3740cm^{-1} of C20A are absent in the spectra of the nanocomposites. However, there is the conspicuous broadening of the –OH stretching vibration at 3450

cm^{-1}characteristic of the glucosidic ring in the presence of C20A. The requisite changes in absorbances in the composite compared to either the C20A or GA alone may be explained from Fig. 9. 1 in line with Kaczmarek and Andrzej (2007).

Table 4: XRD Peak ntensity and d spacing for GA/Nanocomposites compared to Cloisite 20A

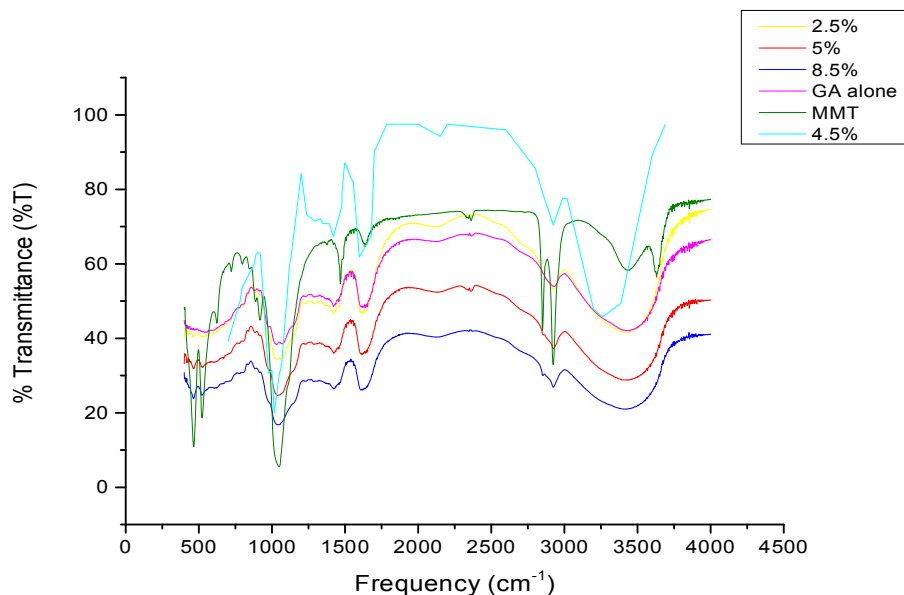| Sample	Peak(2θ)^0	d-spacing(nm)
C20A(alone)	3.8	23.23
	5.75	15.36
	19.85	4.47
GA alone	7.358	12.0
	20.95	4.24
	28.4	3.14
4.5%	3.75	23.54
	9.65	9.15
	15.95	5.55
	19.85	4.47
5%	3.9	22.64
	19.7	4.50
	23.15	3.84
	34.9	2.57
8.5%	19.8	4.48
	22.95	3.87
	36.2	2.479

Fig. 8: FTIR spectra of neat Cloisite 20A, GA alone and GA/Cloisite 20A nanocomposite at 2.5,4.5,5 and 8.5% Cloisite 20A loading.
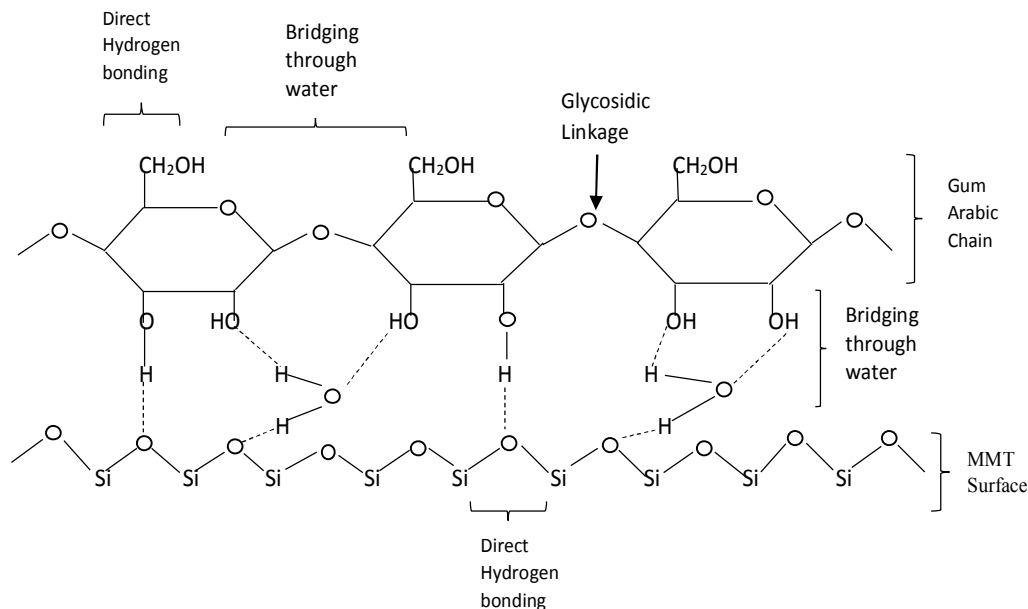
Fig. 9: Schematic illustration showing the formation of hydrogen bonds in GA chains and Cloisite 20A

4. Conclusion

Gum Arabic, a natural polymer, can be converted to engineering materials by incorporating appropriate quantities of cloisite 20A nanoparticles, at levels below 10% (w/w) of the polymer. The nanocomposites resulting from such combination have enhanced thermal properties through improved crystallinity, heat capacity, crystalline melting point, plasticization by moderate reduction of glass transition temperature, that are required during thermal processing conditions otherwise impossible with the brittle, hard and amorphous untreated biopolymer. The results from XRD, viscometry and FTIR spectroscopy provided some evidence for, at least, intercalation of the organoclay by the polymer chains along with compatibility between the two components of the nanocomposites. These resulted in enhanced tensile strength, Young's modulus and energy at break using different effective loading of the nanomaterial with the expected decrease in elongation at break.

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