

Natural Polymers 3. Photooxidation and Mechanical Properties of Gum Arabic Nanocomposite Exposed to UV Irradiation

Turoti M^{*1}, Oti C¹. and Achi S.S²

¹. Department of Chemistry, Obafemi Awolowo University, Ile-Ife, Nigeria.

². Department of Chemistry, Kaduna State University, Kaduna, Nigeria.

muyiwa5552@yahoo.com

Abstract: The unavailable information on the mechanical properties of Gum Arabic(GA) and its nanocomposites under exposure to UV irradiation has been obtained through this study. The nanocomposite consists of GA and Cloisite 20A(C20A), an organoclay of montrimorillonite. Based on the preliminary studies of the mechanical properties involving 16 nanocomposite samples with varying weight fractions, the films of four of them at 2.5,4.5,5 and 8.5% were selected and exposed to 365nm UV radiation at room temperature. The early exposure mechanical properties including tensile strength (TS), Young's modulus (YM), and elongation at break (EB,%) were determined. The concurrent chemical changes were monitored using FTIR and UV spectroscopy. The results showed that the rather low mechanical properties of GA polymer films could be improved significantly by nanocompositing the polymer with 4.5% C20A. The TS and YM improved by 90 and 100% respectively while the EB decreased by 40 %. The unchanged infrared absorptions and reduced λ_{max} as well as higher absorptivity of the UV spectra during photooxidation at this loading compared to the control and other loadings most probably accounted for the effectiveness of the nanocomposite sample. The study shows the importance of nanocomposite in the technology of Gum Arabic.

[Turoti M, Oti C and Achi S.S. **Natural Polymers 3. Photooxidation and Mechanical Properties of Gum Arabic Nanocomposite Exposed to UV Irradiation.** *Nat Sci* 2016;14(10):6-14]. ISSN 1545-0740 (print); ISSN 2375-7167 (online). <http://www.sciencepub.net/nature>. 2. doi:[10.7537/marsnsj141016.02](https://doi.org/10.7537/marsnsj141016.02).

Key words: Gum arabic, Cloisite 20A, Nanocomposite, Photooxidation, Tensile strength, Young's modulus, Energy at break, Elongation at break.

Introduction

Acacia is a tree from which Gum Arabic(GA) is produced as an extrudate as a result of harsh climatic condition e.g. drought, poor soil, wound or deliberate production by tapping involving removal of the bark of the tree only. The trees grow widely across the Sahelian belt of Africa situated north of the equator up to the Sahara desert and from Senegal in the west to Somalia in the east. There are two commercial trees of the Acacia species known as *Acacia Senegal* and *Acacia Seyal* that produce GA. The gum from the former is a pale to orange-brown solid which breaks with a glassy fracture and the latter is darker, more friable and rarely found as lumps in export consignments. The sticky gummy substance dries on the branches or stem to form hard nodules which are picked manually and separated according to colour and size. The chemical composition of GA is complex depending on origin, climate, harvest season, tree age, soil environment and processing conditions, such as spray drying(Al-Assaf, et al., 2005 (a,b); Flindt et al., 2005; Hassan et al., 2005; Idris et al., 1998; Karamalla et al., 1998; Siddig et al., 2005; Verbeke et al., 2003). It consists of a group of macromolecules characterized by a high proportion of carbohydrates (~97%), which are predominantly composed of D-galactose and L-arabinose units and a low proportion of proteins (<3%)

(Islam et al., 1997). The backbone is composed of 1,3-linked- β -D-galactopyranosyl units while the side chains are composed of two to five 1,3-linked - β -D-galactopyranosyl units, joined to the main chain by 1,6-linkages. Many researchers recognized that GA as a highly heterogeneous material that could be separated into three major fractions by hydrophobic affinity chromatography(Randall et al., 1989).

Clay minerals are belonging to the nanoplatelet structured filler particles used in polymer composite technology. Montmorillonite, hectorite and saponite are the well-known smectites which are most commonly used in the preparation of polymer nanocomposites (Pavlidou and Papaspyrides,2008). Montmorillonite (MMT) has the widest acceptability for use in polymer nanocomposites due to its easy availability, well known intercalation/exfoliation chemistry, high surface area of about 750 m²/g., high surface reactivity and high aspect ratio which can be in the range 1000 in well dispersed state without breaking of layers. The clay known as montmorillonite ($M_x(Al_{4-x}Mg_x)Si_8O_{20}(OH)_4$, M: monovalent, usually Na, cation, x: degree of cations isomorphous substitution in octahedral sheets), abbreviated as MMT, consists of platelets with an inner octahedral layer sandwiched between two silicate tetrahedral layers (Huang and Paul, 2007). In its natural state, this

clay exists as stacks of many platelets. The X-ray d-spacing of completely dry sodium montmorillonite is 0.96 nm while the platelet itself is about 0.94 nm thick (Olphen (1963), Fornes, 2001).

The sodium ions can be exchanged with organic cations, such as those from an alkyl ammonium salt, to form an organo-clay (LeBaron and Wang *et al.*, 1999) when the ammonium cation have unsubstituted or substituted hydrocarbon (HCB) tails., it is referred to as a “surfactant” owing to its amphiphilic nature. The HCB moiety modifies the naturally hydrophilic inorganic MMT to its hydrophobic forms which are more compatible with hydrophobic polymers. The possible different substituted derivatives of the hydrocarbon moiety give rise to many forms of organo-clay montmorillonite nanoparticles. Among these are the commercial Cloisite, 10A, 20A, 30A, 30B manufactured by Southern Clays, New York. Polymer nanocomposites consist of polymer matrixes and the nanomaterials e.g. MMT or its organo-clay forms.

The employment of UV irradiation to improve or degrade properties of polymers have long been recognized (Turoti 1998, Ranby and Rabek 1975). Generally polymers suffer greater deterioration of their important technological properties the smaller the wavelength of the UV light. For instance, polymers such as PMMA, PVC and PS degrades faster when exposed to UV light at 254nm than 365nm as evident from detection of carbonyl, unsaturated and cross-linked compounds among others with the attendant changes in their useful mechanical properties (Turoti *et al.*, 1998, 2015).

There are few studies on photooxidation of natural polymers than synthetic polymers and there are generally more damages to the former than the latter under UV irradiation (Sionkowska *et al.*, 2013). The level of research work on the effect of UV irradiation on biopolymer nanocomposites seems unavailable.

The present study concentrates on finding the effect of UV light at 365nm on the mechanical properties of Gum Arabic nanocomposite.

Experimental Materials

Gum Arabic was obtained from “Kasuwan-Kurmi” local market, Kurmi, Kano State, Nigeria. MMT clay modified by dimethyl, dehydrogenated tallow, quaternary ammonium from Southern Clays, NY).

Purification and Processing of Gum Arabic

The raw GA was manually broken into smaller pieces and the solid contaminants such as dirt, barks and stones were removed manually and cleaner smaller pieces of GA were obtained. An appreciable quantity of the raw GA was used at a time (although,

this is a function of the container used). This dissolution of gum arabic was effected in distilled water for 72 hrs.

The GA solution cast on a glass mould to obtain film. The films were then dried in the desiccator to constant weight.

Gum Arabic Nanocomposite Formulation and Exposure Procedure

Preliminary investigations involving carefully prepared 16 different concentrations of GA-nanocomposite and studies on their thermal/mechanical properties led to the selection of four different concentrations detailed in an earlier work (Turoti *et al.*, 2016). These were 2.5, 4.5, 5 and 8.5 w/w% of C20A loading.

The films of GA alone (control) and the GA-nanocomposite samples were subjected to UV-irradiation in a UV cabinet (Universal UV Lampe, Typ TL-900/U, CAMAG) at room temperature and in air using low-pressure mercury vapor lamp emitting 365 nm radiation. The range of the exposure time for all sample films was within 1– 6 hrs 30 mins, corresponding to 115 – 747.5 kJ/m² doses. The distance between each of the samples and the light source was 11 cm, at which irradiation intensity equals 2.04 mW/cm² (Kaczmarek and Andrzej, 2007).

Characterization of GA Nanocomposite Tensile Testing of GA Nanocomposite

Tensile properties of the GA nanocomposite films were studied using the universal Instron tensile testing machine. The cross-head speed was kept constant at 5mm/s at maximum load of 120kg during the test.

With a new neat cutting 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 namely, YM, TS and EB were determined as detailed elsewhere (Turoti, 1998).

The TS was calculated using the formula:

$$TS = \frac{\text{Maximum Load (N)}}{\text{Cross-sectional Area (m}^2\text{)}}$$

The YM was calculated from the slope of the graph which is also equal to tangent over the range for which the stress-strain curve was constant. The EB (%) was determined using the equation:

$$EB(\%) = \frac{l - l_0}{l_0} \times 100 \quad (\text{where; } l - l_0 = \text{Extension at break and } l_0 = \text{gauge length} = 0.02\text{m})$$

Infrared Spectroscopy.

The FT-IR spectrophotometer used was SHIMADZU FT-IR-8400S, Japan, Apodization; Happ-Genzel, Resolution; 4[1/cm] at Redeemers University, Ede, Osun State, Nigeria.

XRF Elemental Analysis

UV-Visible Spectroscopy

The UV spectrometry of the polymer nanocomposite films was carried out at the Central Science Laboratory, OAU Ile-Ife, using SHIMADZU UV-Visible spectrophotometer Model 1800 series, USA.

Results And Discussion

UV spectroscopic studies

Table 1 shows that UV irradiation executes early degradation of the GA alone and the polymer

nanocomposites as indicated by the varying absorptions probably due to formation of new chromophores as irradiation progresses. Almost all the samples absorb at about the same λ_{\max} except for the sample containing 4.5% C20A with generally rather relatively low λ_{\max} and higher absorption values. This may suggest that the absorptions of the 4.5% sample probably contains less of the unsaturated compounds.

Table 1: UV absorption for UV-irradiated GA-Nanocomposite

Sample weight % (%)	UV-Exposure Time (hrs, mins)	λ_{\max}	Absorptivity $E^{1\% 1\text{cm}}$
MMT		200.40	0.155
GA alone (control)	0	200.20	0.894
GA alone	2.30	200.20	1.044
GA alone	5.15	200.20	0.648
2.5	0	200.20	0.492
2.5	2.30	200.20	0.586
2.5	5	200.20	0.466
4.5	0	194.05	1.069
4.5	2.20	204.35	1.340
4.5	4.40	190.50	1.027
5	0	200.20	0.760
5	2.20	200.20	0.625
5	4.30	200.20	0.900
8.5	0	200.20	0.383
8.5	2	200.20	0.690
8.5	4	200.20	0.958

Tensile Strength of UV-Irradiated GA Nanocomposites

Figure 1 shows that UV irradiation decimates the TS of all the samples within the few hours of exposure

affecting the control (GA alone) more adversely than the GA nanocomposites.

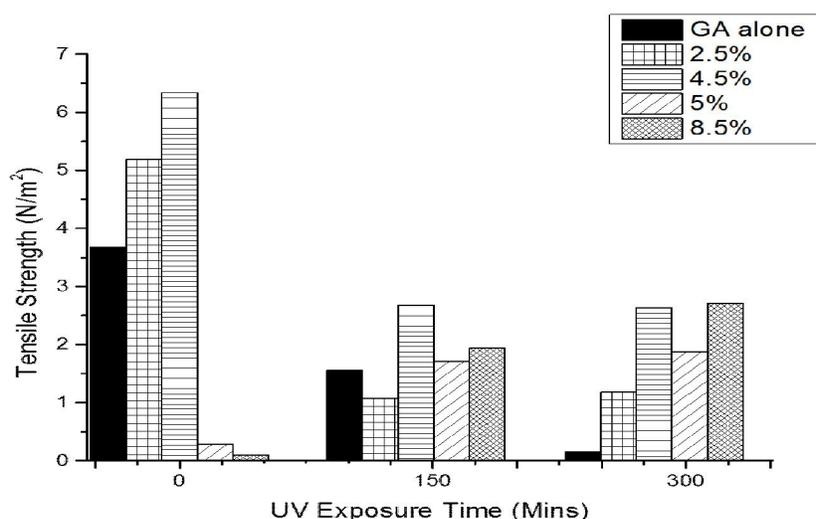


Fig.1: Photooxidation of Gum Arabic. Effect of UV Exposure time on TS of GA-C20A nanocomposites.

The improvement in the mechanical properties classifies the clay (C20A) used in this work as a reinforcement agent. When the rigid clay platelets are combined with the soft GA, the former which is of higher resistance and module carry the major portion of applied load to the polymer matrix under stress conditions. This depends on the level of adequate interfacial interactions between the filler and matrix. (Fornes et al., 2001). The nanocomposite containing 4.5% C20A has the highest TS of about 90% above

that of the neat polymer during the early exposure of the samples to UV irradiation at 365nm.

Fig.2 shows that at 2.5% C20A loading the YM of GA can be effectively improved over that of the neat polymer only after 150 hr exposure to UV irradiation. This shows if tougher/stiffer GA is required, it may be nanocomposited with 2.5% C20A and then irradiate with 365nm UV light for 150minutes. While the YM of the GA alone suffers.

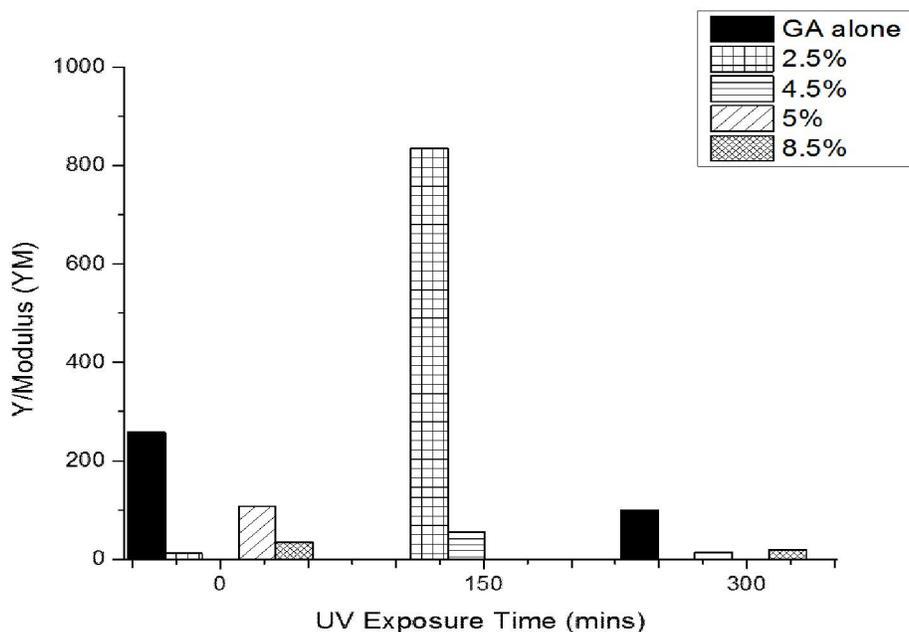


Fig.2: Photoxidation of Gum Arabic. Effect of UV Exposure time on YM of GA-C20A nanocomposites.

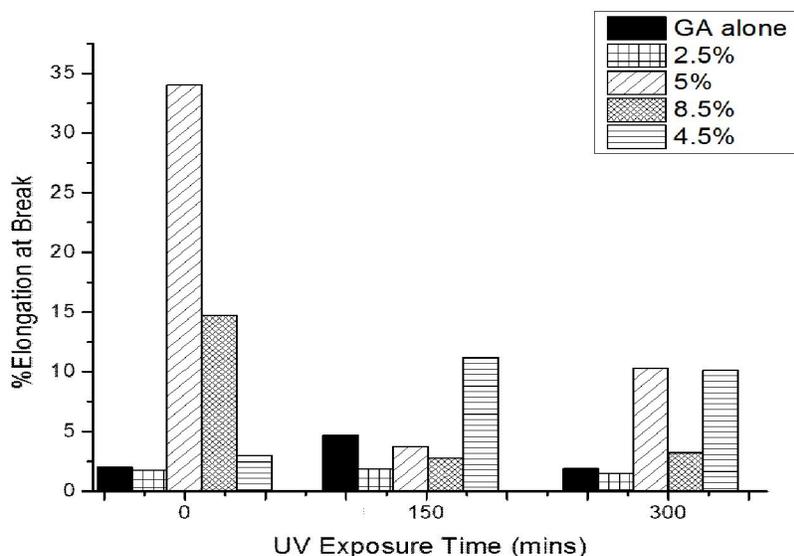


Fig.3: Photoxidation of Gum Arabic. Effect of UV Exposure time on EB of GA-C20A nanocomposites.

Extinction the 2.5% GA nanocomposite has improved value of about 800 times at the end of 150minutes of irradiation. The improved elastic modulus of the nanocomposite is 800 times that of the control at this early period of exposure. This could have resulted from the level of particle loading and higher aspect ratio of the organoclay nanoparticles particularly since the modulus of the particles is usually much higher than that of the polymer matrices in line with earlier work. (Shao-Yun Fu et al,2008).

As can be seen from Fig.3, the EB(%) of all the GA nanocomposites decrease on UV-irradiation. This is attributed to reduced polymer chain mobility and increased crystallinity due to its interaction with the nanofiller. Eqbal et al (2013) has recently showed that



Table 2: XRF Analysis Results of Gum Arabic

Elements	Conc. Value	Conc. Error
Cl	0.3393	±0.1010
K	18.3221	±0.4007
Ca	34.2689	±0.5450
Sc	0.8610	±0.0881
Ti	0.0826	±0.0225
Fe	1.2522	±0.0440
Ni	0.3326	±0.0186
Cu	0.3609	±0.0180
Zn	0.1241	±0.0100
Br	0.0528	±0.0059
Rb	0.0496	±0.0063
Rh	3.6376	±0.3864
Cd	15.7126	±0.5706
Sn	21.3178	±0.7162
Gd	0.5692	±0.0605
Dy	2.0303	±0.1019
Ta	0.6864	±0.0457

the structure of GA contains $-\text{NH}_2, -\text{CO}_2\text{H}$ of the amino acids along with the main chain which are capable of forming H-bonding with the -O- of the clay limiting the mobility of the polymer and reduce the EB. Such bondings facilitate the intercalation of the polymer within the gallery of the nanoclay groups.

However, GA can be rendered more ductile and flexible by incorporating low quantities, such as 4.5% of C20A, into the polymer matrix and irradiate with UV light at 365nm.

Table 2 shows that there are significant levels of some metals such as Fe and transition metal capable of accelerating the rate of initiating catalytic photodecomposition of hydroperoxide to form free radicals (ROO) as in equation 1.

These radicals have contributed to the rapid early photodegradation of the biopolymer at 365nm (Marston 2005). There the presence of C20A may have provided a non-radical or ion formation alternative which reduce the formation of alkylperoxyl or alkoxy radicals.

FTIR spectroscopy of UV-Irradiated GA samples

GA main chain is made up of monomeric sugar units which indicates the presence of C-OH stretch of both 1° and 2° alcohol as observed in the IR spectra of GA alone (Fig. 4).The broad

-OH absorption at 3445cm^{-1} increases with exposure time. This may be due to increase in photooxidation with time and production of unstable hydroperoxides that can decompose easily to hydroxyl groups in a similar manner to an earlier work (Turoti et al, 1998). In such situation the secondary product from the hydroxyl group, that is, $>\text{C}=\text{O}$ would also be formed probably in a non-quantitative yield as it is at 1695cm^{-1} (Fig.4).

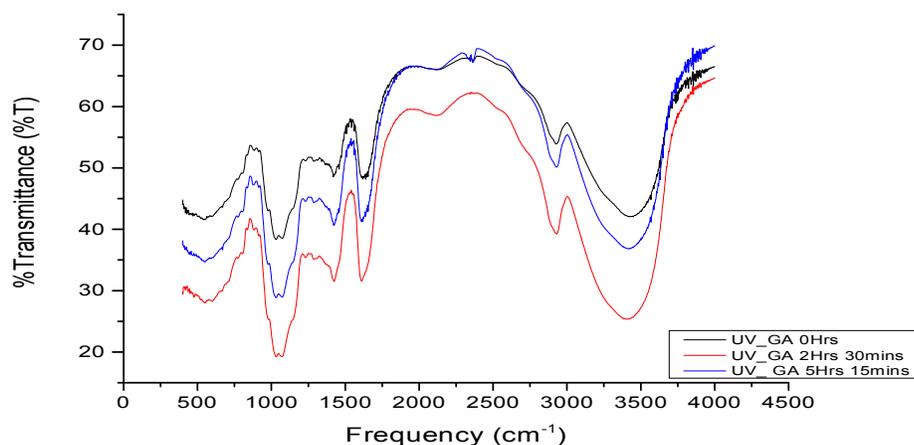


Fig.4. Photooxidation of Gum Arabic. Effect of UV Exposure time on FTIR absorptions of neat GA.

In Figs.5-8 the level of $-OH$ and hence the $>CO$ are generally smaller in the GA-C20A nanocomposites than in GA alone during photooxidation. The features in the FTIR spectra of the nanocomposite sample containing 4.5% C20A show fewer, sharper and unchanging absorption peaks during exposure to the UV light (compare fig.6 to figs.5, 7 & 8). The features depict (i) more association (interaction) between the biopolymer and the nanofiller resulting into loss of

some absorption peaks at and below 500cm^{-1} unlike in others, (ii) photostabilization as there are no changes in the absorption peaks and (iii) absence or less of intermolecular H-bonding between the $-OH$ groups of the matrix, as indicated by less broad probably broken by the strong interacting nanofiller through the Si-O- of the clay by H-bonding (Kaczmarek and Andrzej, 2007, Ferreiro, 2006).

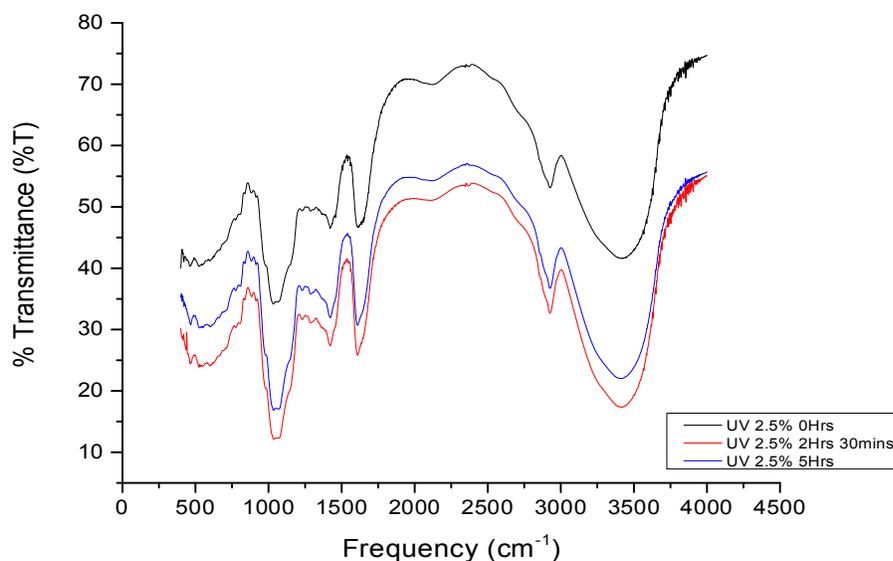


Fig.5. Photooxidation of Gum Arabic. Effect of UV Exposure time on FTIR absorptions of GA-2.5%C20A nanocomposites.

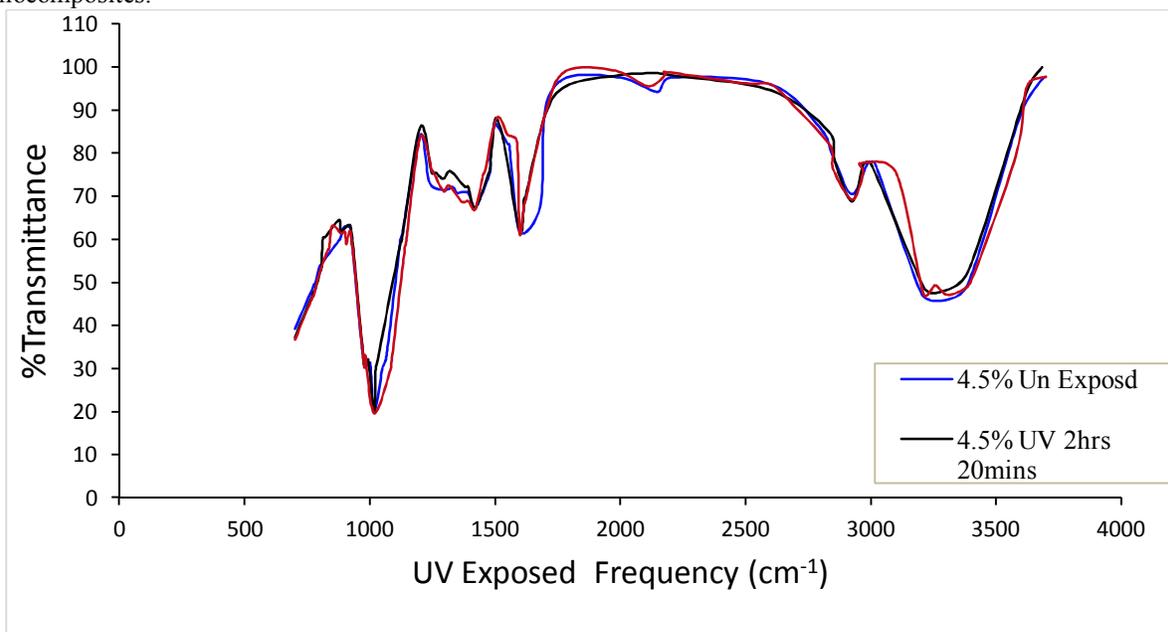


Fig.6. Photooxidation of Gum Arabic. Effect of UV Exposure time on FTIR absorptions of GA-4.5% C20A nanocomposites.

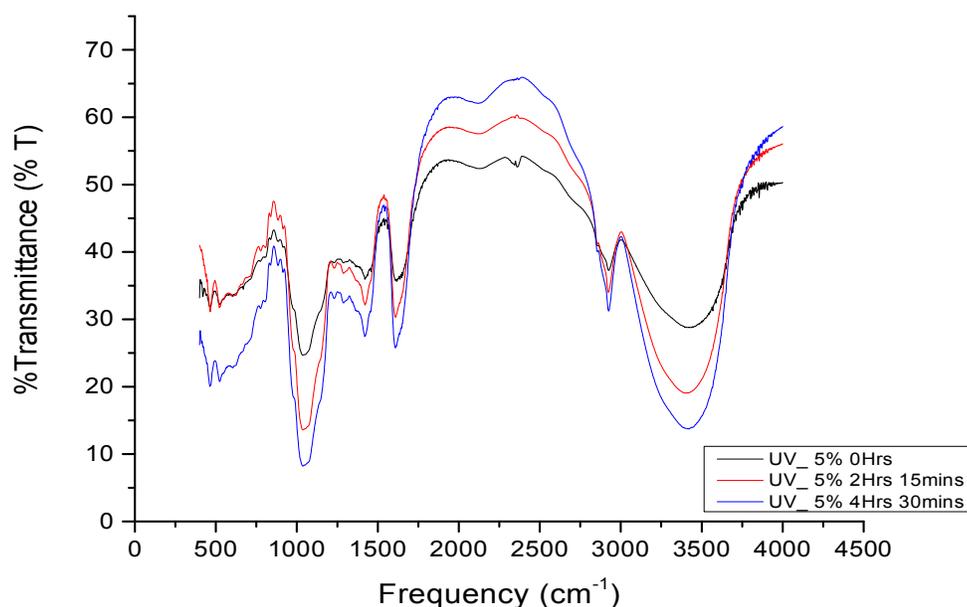


Fig.7. Photoxidation of Gum Arabic. Effect of UV Exposure time on FTIR absorptions of GA-5.5% C20A nanocomposites.

This suggests that some level of photostabilization occurs in the nanocomposites where the level of formation of macroalkoxyl radicals precursors to hydroxyl groups has been reduced in the presence of the nanoclay (C20A) particles. This could

arise if there is interaction of the nanoclay with the GA chains by the intercalated nanoparticles providing some protection from the degrading effects of photoxidation.

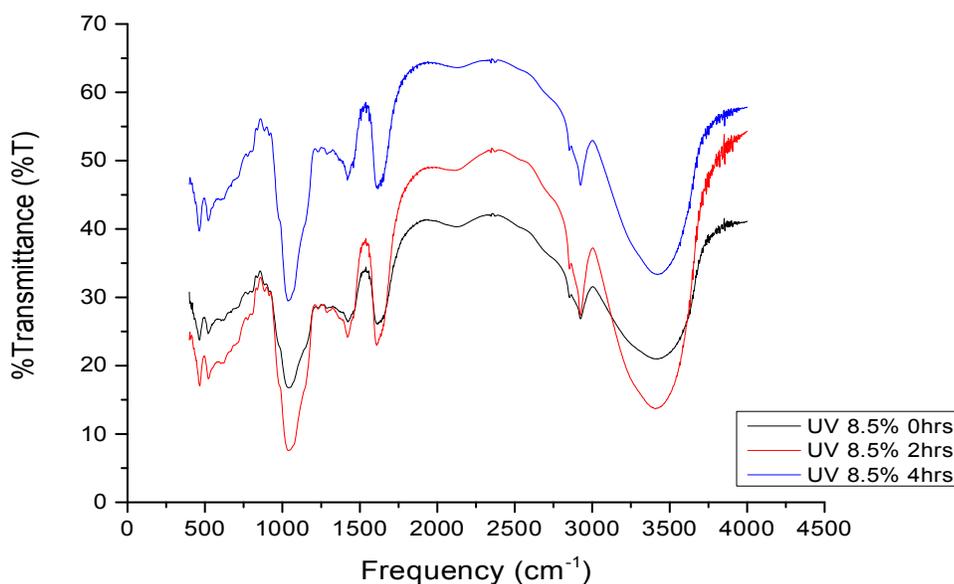


Fig.8. Photoxidation of Gum Arabic. Effect of UV Exposure time on FTIR absorptions of GA-8.5% C20A nanocomposites.

If some of the chromophores in the biopolymer are involved in the interaction, the level of UV light

absorption and hence photodegradation would be reduced. The foregoing discussion may be clearer

from a probable mechanism of photooxidation of gum Arabic under the relatively low energy effect at 365nm (Fig.9). This resulted into formation of more –OH groups as the spectra of figures 4,5,7 and 8 unlike fig.6 show.

Fig.9 Proposed Photooxidation of Gum Arabic (not shown).

Conclusion

From this study, it can be concluded that photooxidation of gum Arabic using 365nm is very fast and this leads to rapid degradation of its mechanical properties. The incorporation of 4.5% cloisite 20A into the biopolymer significantly reduces the level of photooxidative degradation and hence improves its important mechanical properties during the early period of exposure to the UV light.

Acknowledgement

The authors are very appreciative of the kindness of the Management of Centre for Energy Research and Development, Obafemi Awolowo University, Ile-Ife for their permission to use their equipment in this study. We are also grateful to the Management of Southern Clays, New York, for the free supply of cloisite 20A that is helpful in this work.

References

1. Al-Assaf, S.; Phillips, G.O. & Williams, P.A.(2005 a). Studies on acacia exudate gums. Part I: the molecular weight of Acacia senegal gum exudate. *Food Hydrocolloids*,19, (4), 647-660.
2. Al-Assaf, S.; Phillips, G.O. & Williams, P.A. (2005 b). Studies on Acacia exudate gums: part II. Molecular weight comparison of the Vulgares and Gummiferae series of Acacia gums. *Food Hydrocolloids*,19,(4) 661-667.
3. Eqbal, D. and Aminah, A. (2013). Utilization of gum Arabic for Industries and Human Health. *American Journal of Applied Sciences*10 (10): 1270-1279.
4. Ferreira, E.A. and De Bussetti, S.G. (2006). Adsorption of 1,10-phenanthroline on Montmorillonites poly (vinyl alcohol) complexes as a function of pH. *Applied Clay Science*, 31, 142-153.
5. Flindt, C., Al-Assaf, S., Phillips, G.O. and Williams, P.A. (2005). Studies on acacia exudate gums. Part V. *Structural Features of Acacia seyal*. *Food Hydrocolloids*, 19, (4) 687-701, ISSN: 0268-005X.
6. Fornes, T.D., Yoon, P.J., Keskkula, H. and Paul, D.R. (2001). Nylon 6 nanocomposites: Effect of Matrix Molecular Weight. *Polymer*, 42(25) pp. 9929-9940.
7. Hassan, E. A., Al-Assaf, S., Phillips, G.O. and Williams, P.A. (2005). Studies on Acacia gums: Part III molecular weight characteristics of Acacia seyal var. seyal and Acacia seyal var fistula. *Food Hydrocolloids*, Vol. 19, No. 4, pp. 669-677.
8. Huang Y and Paul, D.R.(2007). Hydrocolloids in emulsions: particle size distribution and interfacial activity. *Food Hydrocolloids*, 15, 533-42.
9. Idris, O.H.M., Williams, P.A. and Phillips, G.O. (1998). Characterization of gum from Acacia Senegal trees of different age and location using multi-detection gel permeation chromatography. *Food Hydrocolloid*. 12, 379–388.
10. Islam, A. M.; Phillips, G. O.; Sljivo, A.; Snowden, M. J. & Williams, P.A. (1997). A review of recent developments on the regulatory, structural and functional aspects of gum arabic. *Food Hydrocolloids*, Vol. 11, No. 4, 493-505.
11. Kaczmarek, H and Andrzej, P. (2007). The effect of UV-irradiation on poly (vinyl alcohol) composites with Montmorillonite. *Journal of Photochemistry and Photobiology A: Chemistry* 191 209–215.
12. Karamalla, K.A., Siddig, N.E., Osman, M.E., 1998. Analytical data for Acacia senegalva senegal gum samples collected between 1993 and 1995 from Sudan. *Food Hydrocolloid*. 12, 373–378.
13. Siddig, N.E.; Osman, M.E.; Al-Assaf, S.; Phillips, G.O. & Williams, P.A. (2005). Studies on acacia exudate gums, part IV. Distribution of molecular components in Acacia seyal in relation to Acacia senegal. *Food Hydrocolloids*, 19,. 679-686.
14. LeBaron, P.C., Wang, Z. and Pinnavaia, T.J. (1999). Polymer-layered silicate nanocomposites: an overview. *Applied Clay Science*,15, 11-29.
15. Marston, N. J. (2005). Effects of UV Radiation on Building Materials. BRANZ Ltd, Judgeford, New Zealand.
16. Olphen, V. H. (1963). An introduction to clay colloid chemistry. *Journ. of Inter Science*. New York.
17. Pavlidou, S. and Papaspyrides, C.D. (2008). A review on polymer-layered silicate nanocomposites. *Prog. Polym. Sci.*,32, 1119-1198.
18. Ranby B. and Rabek J.F. (1975). Photo degradation, Photo oxidation and Photo stabilization of Polymer., Wiley. Interscience, New York.

19. Randall, R.C., Phillips, G.O., Williams, P.A., 1989. Fractionation and characterization of gum from *Acacia senegal*. *Food Hydrocolloid*. 3, 65–75.
20. Renard, D., Lavenant-Gourgeon, L., Ralet, M. and Sanchez, C. (2006). *Acacia Senegal Gum: Continuum of Molecular Species Differing by Their Protein to Sugar Ratio, Molecular Weight, and Charges*. *Biomacromolecules*, 7, 2637–2649.
21. Siddig, N.E., Osman, M.E., Al-Assaf, S., Phillips, G.O. and Williams, P.A. (2005). Studies on acacia exudate gums, part IV. Distribution of molecular components in *Acacia seyal* in relation to *Acacia senegal*. *Food Hydrocolloids*, 19,(4) 679-686.
22. Shao-Yun Fu, A., Xi-Qiao, Feng, B., Bernd, L.C. and Yiu-Wing, M. (2008). Effects of particle size, particle/matrix interface adhesion and particle loading on mechanical properties of particulate–polymer composites, *Composites: Part B* 39; 933–961.
23. Sionkowska A., Planecka A., Lewandowska K., Kaczmarek B., Szarszewska P.(2013). Influence of UV-Irradiation on molecular weight of chitosan. *Progress on Chemistry and Application of Chitin*, vol.XVII,2013.
24. Turoti Muyiwa, Olayemi J.Y., Adeniyi J.B., Peters Olufemi. (1998). The photooxidative degradation of poly-(vinyl chloride)-2. The stabilizing action of dibutyltin maleate and trisnitro (1,3-dihydroxyl-2-hydroxylmethyl-2-nitropropane) on PVC from ultraviolet light radiation. *Polymer Degradation and Stability*, 61, (2) 297-302.
25. Turoti Muyiwa, Gimba C.E. (2015). Effect of Exposure On Mechanical Properties Of Polymers. I. Poly(Methylmethacrylate). 87-95.
26. Turoti M, Oti Chinedu. (2016). Natural Polymers. II. Thermal and Mechanical Properties of Gum Arabic Nanocomposite. Accepted paper in Nature and Science Journal. In press. Marsland Press, USA.
27. Verbeken, D., Dierckx, S. and Dewettinck, K. (2003). Exudate gums. Occurrence, production, and applications. *Appl. Microbiol. Biotechnol.* 63, 10–21.

7/7/2016