Natural Polymers .4. Effect of Outdoor Exposure on Gum Arabic Nanocomposites

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Abstract. The effects of outdoor exposure on the neat gum Arabic and its nanocomposite films with cloisite 20A, an organo-modified montmorillonite nanoclay, were studied with a view to extending the non-food application of the biopolymer. Based on the post-processed mechanical properties, four out of many nanocomposites produced containing 2.5,4.5,5.0 and 8.5%(w/w) of cloisite 20A(C20A) were exposed to the natural environment along with the neat polymer separately. The degradation process was monitored by determination if the tensile strength, Young's modulus, elongation at break supported with studies of the UV and FTIR spectroscopy as well as XRD and SEM. The results showed that while the initial outdoor exposure rapidly degraded the mechanical properties of both the neat polymer and some of its nanocomposites(2.5&4.5%C20A) the values of these properties were greater and indeed increased in some(5.and 8.5%C2A) of the latter than the former. The UV and FTIR indicated absence of polyconjugated unsaturation and lower level of formation of oxidation products, mainly hydroxyl and carboxyl groups, in the nanocomposites relative to the neat polymer. The XRD and SEM of a typical nanocompoite sample showed some enhanced crystallinity and intercalation of the nanofiller within the polymer matrix during the period of exposure. The nanocomposites containing 4.5,5.5 and 8.5% C20A were found more resistant to outdoor degradation than the neat biopolymer.

Introduction

In a typical tropical environment the combined effects of thermal, rainfall, solar radiation and energy, harmattan, air/oxygen, among others, suggest the need for complimentary processes that would inhibit or retard polymer degradation(Turoti et al.,1999). The structural requirements for a compound that would be able to combat the diverse outdoor degradants should at least provide thermoxidative and photoxidative stabilization to polymers exposed to outdoor conditions. What is commonly utilized for such stabilization is a blend of additives that would provide synergistic results as employed in some earlier work (Turoti et al., 1999). Our earlier studies have shown that a biopolymer such as Gum Arabic can have enhanced thermal and photoxidative properties when nanocomposited with Cloisite 20A,an organo-clay from montmorillonite(MMT))(Turoti and Chinedu.,2016). Other studies, particularly on synthetic polymers, have shown the effectiveness of nanoclays in improving the thermal, mechanical and chemical properties of some polymers such as nylons and polyethylene (Usuki et al.,1993, Osman et al.,2005, Oya et al.,2000). The major reason attributed to this effectiveness is the ability of nanoclays to undergo exfoliation/intercalation when incorporated into the matrices of the polymers (Ray and Okamoto (2003), Alexandre and Dubois (2000). The fundamental structural characteristics of the nanoclays are their layer high aspect ratio which is in the order 10^3 in a well dispersed state without eaking of layers and the surface area of about $750m^2$ (very small particle size) as well as the existence of interlayer spacing with which they accommodate the polymer chains resulting into polymer nanocomposites (Olad, 2012). The polymer is thus associated with the nanoclay at the inner surfaces between the platelets through some surface bonds including H-bonds, Van der walls forces and dipole-dipole interactions depending on the chemical composition of the polymer. For effective interaction with essentially hydrophobic polymers and the rather hydrophilic clay needs to be modified organically resulting into organoclay as detailed in some earlier work (LeBaron et al.,1999)). The different structural possibilities of the organic moiety results into different organically modified MMT products. Therefore, if the position of the polymer is that of intercalation/exfoliation at the interlayer space of the nanoclay, the naocomposite may

have some protective advantage over the neat polymer particularly when they are exposed to the same environmental conditions such as outdoor.

The present work focuses on the effect of outdoor aging (natural weathering) on Gum Araic (GA) and its nanocomposite films., The nanomaterial engaged is Cloisite 20A(Southern Clay, NY) referred herein as C20A. The previous work(Turoti et al.,2016) have shown that the major technological properties of GA films are improved in the presence of C20A.It may be expected that the outdoor exposure should incur greater damages on both the neat polymer and its nanocomposites than exposure to photoxidation or thermal condition alone due to the greater combined degradants present in outdoor.

EXPERIMENTAL
The procurement, purification, processing and preparation of GA and its nanocomposites of GA-C20A have been detailed earlier (Turoti and Chinedu, 2016., Turoti et al.,2016).

Outdoor aging of GA Samples
The method of outdoor aging was similar to that described in an earlier study (Turoti et al., 1999). The films of both the neat GA and its selected nanocomposites [2.5, 4.5,5 and 8.5% C20A., selection based on performance properties prior to aging as detailed in Turoti and Chinedu 2016) were mounted on specially prepared plywood containing rounded holes of diameter 3.5 cm to allow penetration of light through the films. The plywood was then suspended at an angle of 45^0 to the horizontal.

Characterization of GA Samples
Mechanical property measurement
The mechanical properties of the GA nanocomposite and neat GA films were studied using a computerized Instron tensile testing machine. The cross-head speed was kept constant at $5mms^{-1}$ at maximum load of 120kg during the test. With a gauge length of 7cm, width of 2cm films of similar thickness were employed from which the TS, YM and EB were obtained from the computerized data sheet as detailed earlier(Turoti and Chinedu., 2016).

Infrared spectroscopy measurements.
The FT-IR spectrophotometer used was SHIMADZU FT-IR-8400S, Japan. Apodization; Happ-Genzel, Resolution; 4[1/cm] was used to monitor the development of functional groups during the period of exposure in a similar way described earlier(Turoti et al.,1999,Turoti and Chinedu.,2016).

UV-Visible Spectroscopy
The UV spectrometry of the polymer pure and GA nanocomposite films was carried out using SHIMADZU UV-Visible spectrophotometer Model 1800 series, USA, to obtain the absorbance and λ_{max} of the samples as described earlier(Turoti et al.,2016).

X-Ray Diffractometer (XRD)
GBC EMMA (Enhanced Mini Material Analyser) X-ray diffractometer was used to study the crystallinity and diffraction pattern during the exposure of the biopolymer samples and the Cloisite20A for reference and comparison.

Scanning Electron Microscopy (SEM)
The typical sample used for examination with Scanning Electron Microscope Model ASPEX 3020 series was used to study the surface morphology of the biopolymer and its nanocomposite
films.

Results and Discussion
Table 1 shows that for each sample of either the neat GA and its nanocomposite the λ_{max} generally decreases with exposure time, that is a blue shift or hypsochromic effect is found as exposure progresses (William and Flemming, 1980). This probably suggests the less polyconjugated unsatuation particulary as exposure progresses. The intensity or absorptivity generally shows initial hypochromic effect before an hyperchronic effect as exposure time increases. This may suggest the possibility of formation of higher concentration of unsaturated chromophres due to degradation of the polymer chains during exposure to the outdoor environment.

Table 1:UV absorption for Outdoor Exposed GA-Nanocomposite

Sample weight %	Outdoor Exposure Time (hr)	λ_{max}(nm)	Absorptivity
MMT		200.40	0.155
GA alone	0	200.20	0.894
GA alone	1. 45	193.00	2.267
GA alone	3. 30	191.00	1.722
2.5	0	200.20	0.492
2.5	1. 45	192.00	2.137
2.5	3. 30	197.00	2.980
4.5	0	194.05	1.069
4.5	1. 35	193.70	1.567
4.5	3. 10	190.70	0.831
5	0	200.20	0.760
5	2. 5	194.00	2.469
5	4. 15	191.00	2.119
8.5	0	200.20	0.383
8.5	2. 25	194.00	2.492
8.5	5. 55	192.00	2.215

Mechanical Properties of GA Nanocomposites

The GA nanocomposites and the neat polymer were exposed to outdoor condition containing at least rainfall, dew, sunlight, night were characterized using their tensile strength, Young's modulus and elongation at break.

Tensile Strength (TS)

Figure 1 shows that the TS of the control, samples of 2.5% and 4.5% C20A decrease progressively with outdoor exposure time. This effect could be as a result of scission of polymer backbone of the GA. With increasing nanofiller concentration in the nanocomposite an observed. increase in TS was noted with 5% and 8.5%. This may probably be attributed too the fact that as the polymer chain degrades there is need for more of the C20A required for greater intercalation/exfoliation to interact with the chains resulting into concomitant increase in the TS (Shao-Yun Fu et al., 2008, Ray and Okamoto, 2003). The nanocomposite samples have greater TS and less rate of degradation than the untreated polymer during the short-lived exposure to the devastating weather conditions. For instance, whereas the TS of the neat GA declines rapidly by 84% that of the 4.5 % GA declines by 52% while nanocomposites of 5 and 8.5% GA increase significantly. Increase in the TS of other polymers by C20A has earlier been demonstrated

Young modulus(YM)

Figure 2 shows that neat GA films can be sustained during early outdoor service life where stiffness is required only by the intervention of C20A at 5% loading which shows a remarkable increase in its YM. This parameter increases for sample 2.5 and 4.5% C20A while that of 8.5% decrease progressively with increasing outdoor exposure time.

Elongation at break (EB,%).

From the results in Figure 3 EB (%) of the GA nanocomposites decreased on outdoor exposure particularly with samples 5% and 8.5%. This could also be as a result of reduced polymer chain mobility due to its interaction with the nanofiller.
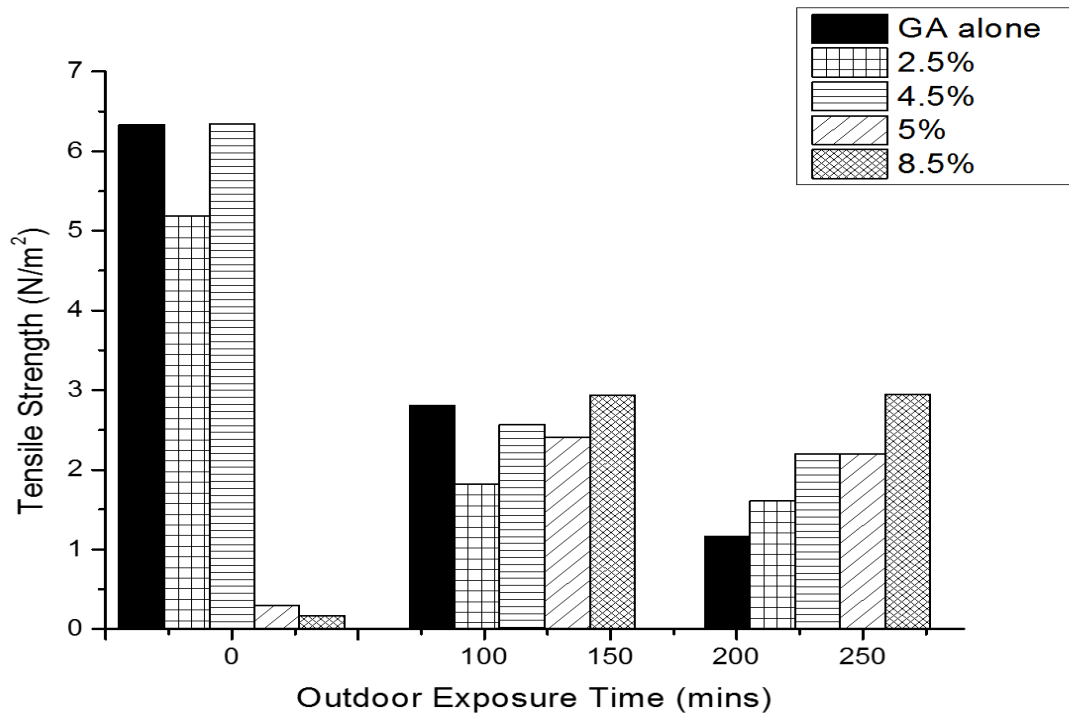
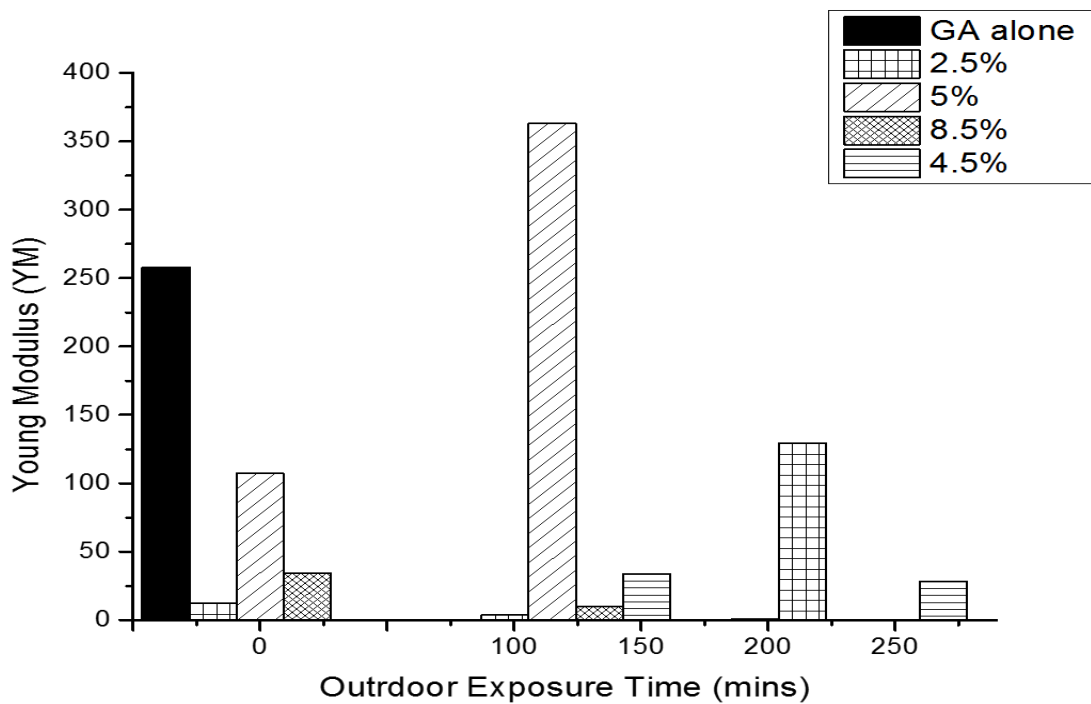Fig.1.Outdoor Exposure Gum Arabic. Effect of exposure time on the TS of GA-Cloisite 20A nanocomposite.

Fig.2. Outdoor Exposure Gum Arabic. Effect of exposure time on the YM of GA-Cloisite 20A nanocomposite.
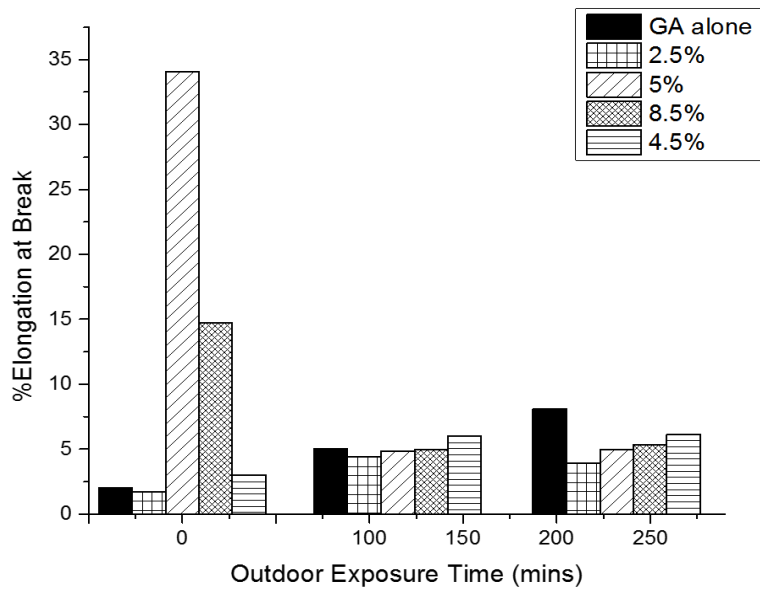
Fig.3. Outdoor Exposure Gum Arabic. Effect of exposure time on the EB of GA-Cloisite 20A nanocomposite.

Figure 4 shows the energy the films have before deaths. The energy at break(EAB) generally increase with time of exposure both for the untreated and the nanocomposits. The 4.5% sample particularly increases to the extent of having the greatest EAB and hence the sample with highest level of **toughness** whish this mechanical parameter determines in polymeric materials.
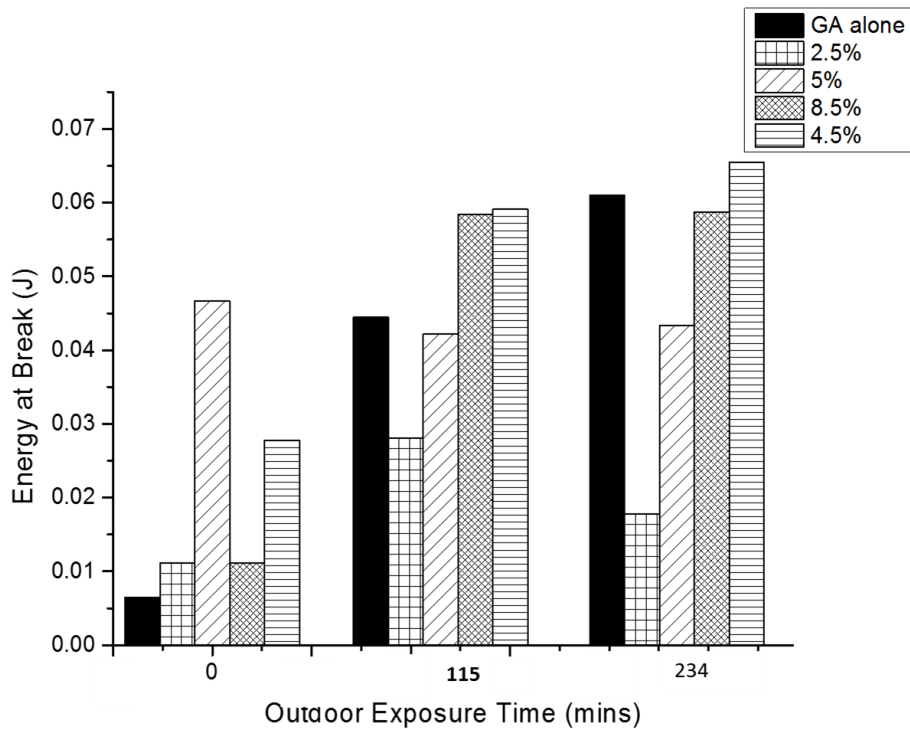

Fig.4: Outdoor Exposure Gum Arabic. Effect of exposure time on the EAB of GA-Cloisite 20A nanocomposite.

The net observation on the mechanical properties is that the nanocomposite samples having greater resistance to tensile deformation and stiffness would necessarily be less ductile than the neat GA during the outdoor exposure as has been demonstrated in earlier studies (Turoti et al,.1999,2010). These provide some evidence of some level of interaction between the polymer matrix and the nanoparticles even as exposure progresses.

FTIR Spectroscopy
Figures 5-8 show the FT-IR results of the GA nanocomposite indicating some prominent peaks like the broad and intense peak for the bonded and free hydroxyl functional group between $3200cm^{-1}$ – $3650cm^{-1}$and another peak between $1710cm^{-1}$– $1750cm^{-1}$ of carbonyls.
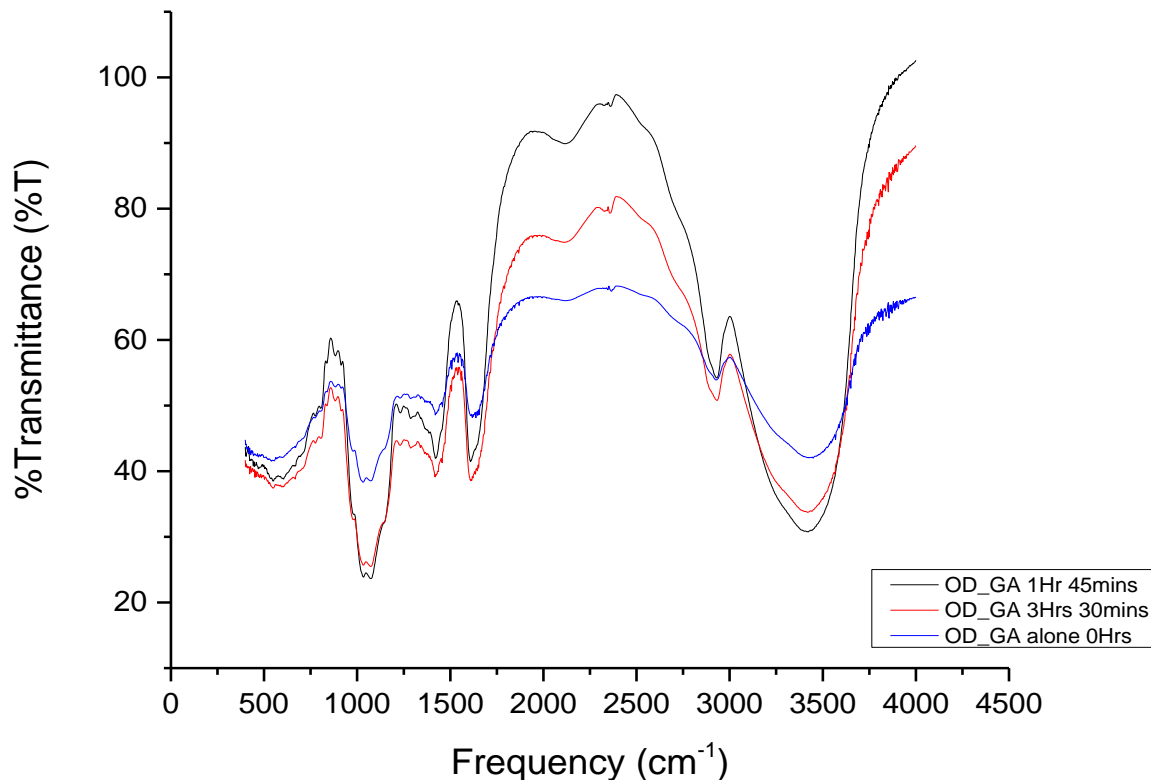

Fig. 5: Outdoor exposure of Gum Arabic. Effect of outdoor exposure time on the FTIR absorption peaks of neat GA(control).

, - A medium alkanes C-H CH$_2$- and -CH$_3$ stretch between $2880cm^{-1}$ to $2845cm^{-1}$as well as those of between $2975cm^{-1}$ to $2915cm^{-1}$.Also, the intense and sharp carboxylate O-C=O asymmetric stretch of the GA around $1660cm^{-1}$– $1580cm^{-1}$. As can be seen, for most samples there is a general initial increase in concentration of the functional groups as time of exposure increases, particularly the –OH group, followed by a decrease except for the sample containing 4.5% where some level of constant absorption peaks are maintained throughout the the

short period of investigation. This probably could be attributed to hydrolysis of the glycosidic group after an initial photooxidation by the solar UVB(290-315nm) responsible for the photochemical effects in polymers under outdoor exposure(Belder Koldijk,1996). Also, there is a general tendency towards lower formation of these functional groups with increasing loading of C20A.With the general lower content of these oxidation compounds it is more appropriate to observe more stability of the nanocomposites than the neat GA
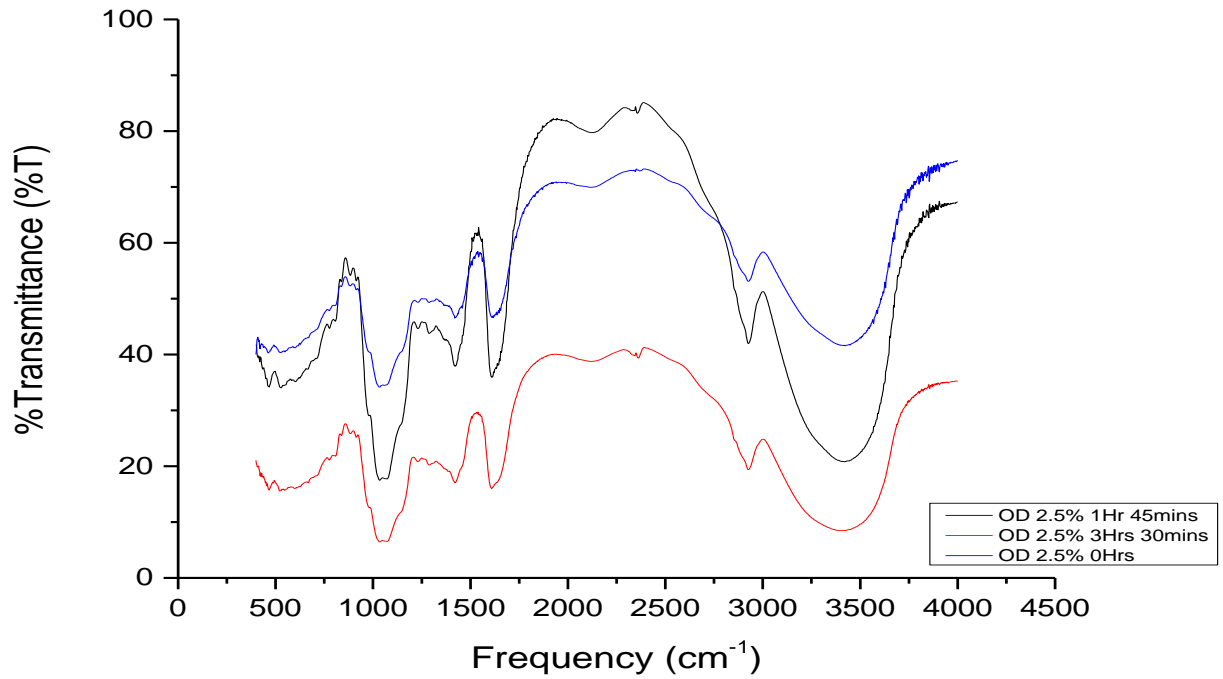
 Fig.6: Outdoor exposure of Gum Arabic. Eff ect of outdoor exposure time on the FTIR absorption peaks of GA-2.5%C20A nanocomposite.
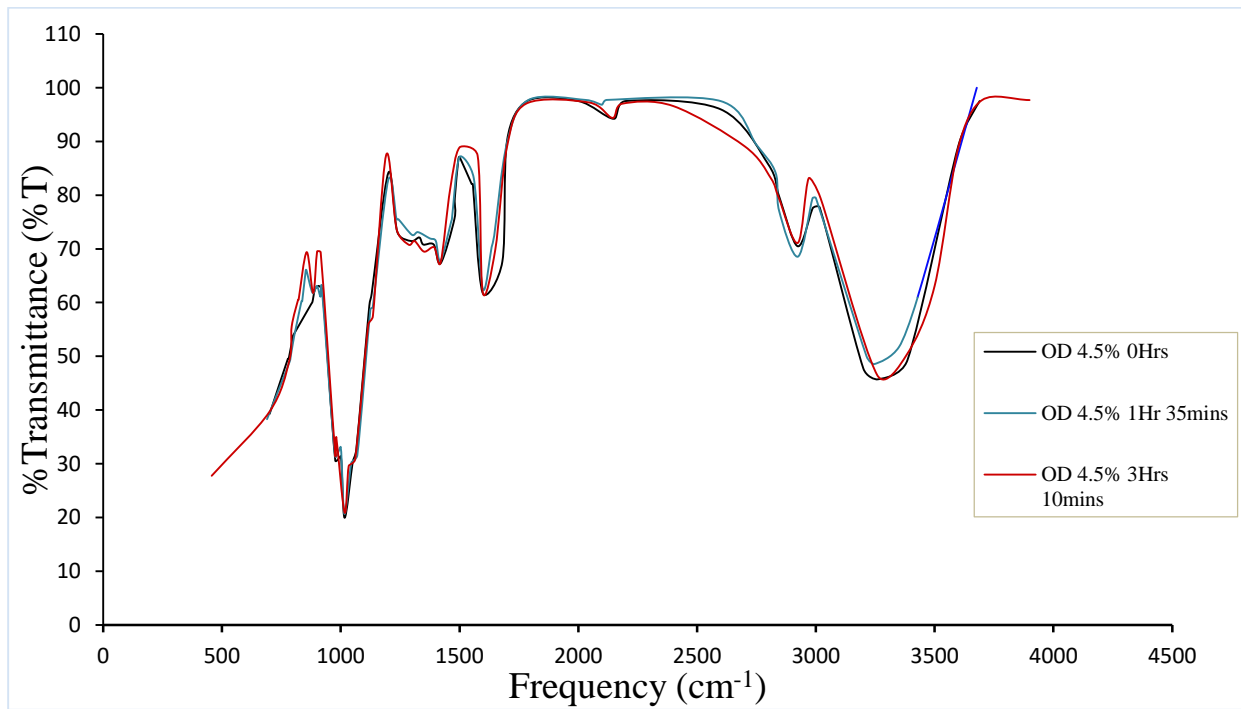

Fig. 7. Outdoor exposure of Gum Arabic. Effect of outdoor exposure time on the FTIR absorption peaks of GA-4.5%C20A nanocomposite.

polymer as evident from the relatively high mechanical properties observed in the previous section with increasing C20A concentration. However the stability of the nanocomposites lie decreasingly between those containing 4.5-8.5% of C20A. The increasing outdoor degradation due to increasing hydrolysis demands more of the nanofiller for greater polymer-organoclay interaction as exposure time increases. The sample containing 4.5% C20A apparently shows the greatest resistance towards outdoor degradation as the peaks of functional groups such as,–OH >CO and >C=C<, that are commonly used for etermining oxidation indices remain unchanged during the period of exposure. Generally there is a decreasing changes in concentration of these oxidation (functional) groups in

samples containing 0% to 0-4.5% C20A and followed by increase in the concentration of these groups as one proceeds to sample containing 8.5% of the nanofiller. It may be probably true from these results that the smaller the change in these functional groups as the exposure progresses the greater the stability of the nanocomposite. This trend of the degradation/stability replicates the trend of initial viscosity average molecular weight with respect to the concentration of the C20A, that is, M_v of samples containing 4.5> 2.5>5>0>8.5% of these nanocomposite in an earlier study (Turoti and Oti,2016).This probably shows that for the GA-20A nanocomposite system the greater the molecular weight the greater the stability towards outdoor degradation.
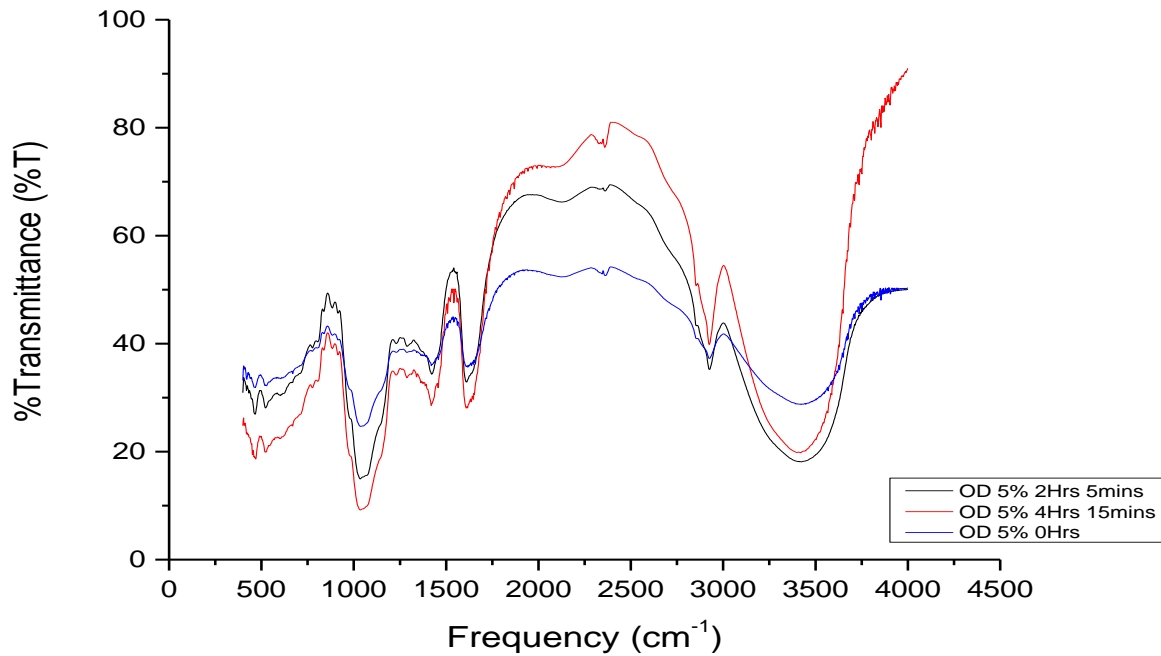

Fig. 8. Outdoor exposure of Gum Arabic. Effect of outdoor exposure time on the FTIR absorption peaks of GA-5%C20A nanocomposite.
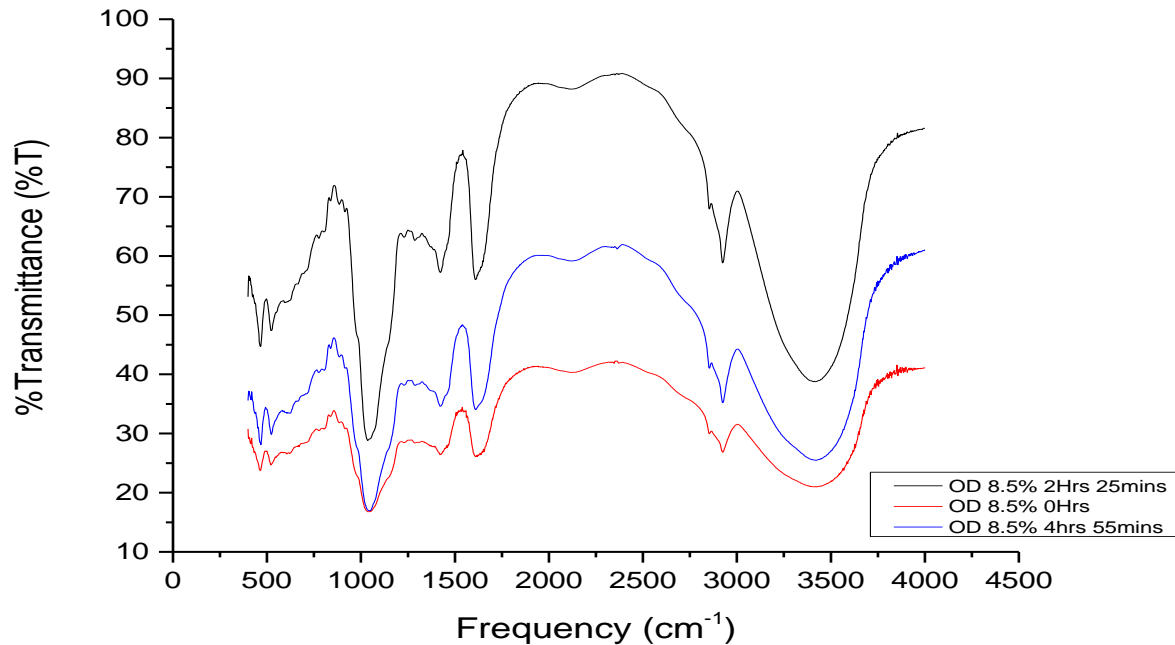
Fig. 9: Outdoor exposure of Gum Arabic. Effect of outdoor exposure time on the FTIR absorption peaks of GA-8.5%C20A nanocomposite.

In pursuance of these observations the XRD pattern and SEM images of one of these nanocomposites were investigated.

XRD of GA Nanocomposites
Figure 10 is the XRD patterns of unexposed C20A (for reference) and for exposed neat GA while fig.11 shows exposed GA-8.5% C20A nanocomposites in comparison to its unexposed and also the unexposed C20A.It is clear that the XRD peaks at the lower angles of the C20A disappear with C20A nanofiller in the polymer whereas at the wider angles there are more peaks after exposure of the neat GA and nanocomposite samples. In addition, the intensity of the peak of the C20A at $2\Theta = 19.92^o$ is increased from about 30 in the C20A to 100 a.u in both the unexposed and exposed GA samples but sharper in the exposed nanofilled sample than in the neat biopolymer. It is not clear why the reflection angle($2\Theta = 19.92^o$) is almost the same for both C20A and neat GA except that it suggests there is probably a common crystal present in both materials but stronger/greater in the neat GA and also augmented by the nanofiller. The XRD pattern of the C20A shows three reflection peaks at about $2\Theta = 6.48^o$corresponding to a basal spacing of 1.14 nm, characteristic of MMT based product (Wang *et al.,* 2005), $2\Theta = 11.5^0$ and a base peak at $2\Theta = 19.92^o$.However, the observed variation indicates that the GA molecules have possibly intercalated into the layers of the silicates in the nanocomposite samples, resulting in intercalated/exfoliation of some of the nano-particles, while few particles remained as non-intercalated evident from the presence of small random peaks in the GA nanocomposite (Voorn, *et al.,* 2006), The XRD pattern of the outdoor exposed GA- 8.5% showed four distinct peaks at $2\Theta = 19.65^o$ (max), 27.07^o , 33.04^o and 35.29^o while the XRD plot of the pre-exposure GA-8.5% C20A shows two distinct peaks at $2\Theta = 21.30^o$ and 36.24^o.
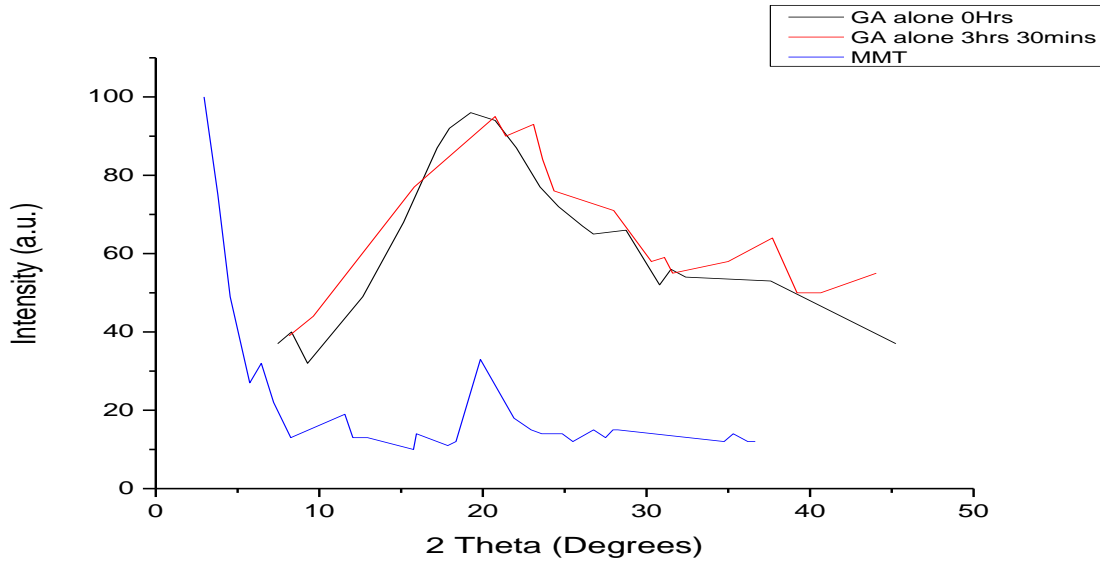
Fig.10: Outdoor Exposure of Gum Arabic. XRD of GA alone during outdoor exposure and unexposed Cloisite 20A.

The C20A base peak decreased a little from 19.925° to 19.59° in the nanocomposite, and appears more intense indicates the formation of an intercalated nanostructure in the nanocomposite, while the peak broadening and intensity increase in this case, most likely indicates the ordered intercalated or exfoliated structure of the GA nanocomposite on exposure to outdoor. (Wang *et al.,* 2005). Thus, in this case, it is observed that its outdoor exposure has further improved its crystallinity, as indicated from the XRD plot of the outdoor exposed sample, which shows less broad and sharper peaks that clearly indicates enhanced crystallinity. The

crystallinity apparently increases with increasing exposure time and particularly with addition of the C20A as can be seen in fig.11 compared to fig.10. The observed enhanced crystallinity during exposure to outdoor most probably manifests in the enhanced mechanical property reported in the earlier section. For instance, the GA-8.5% has a pre-exposure TS of $0.1 \times 10^5 Nm^{-2}$ which increases to $3.0 \times 10^5 Nm^{-2}$ (2900% increase) by the end of exposure whereas that of the neat GA decreased by 588%(see fig.1).
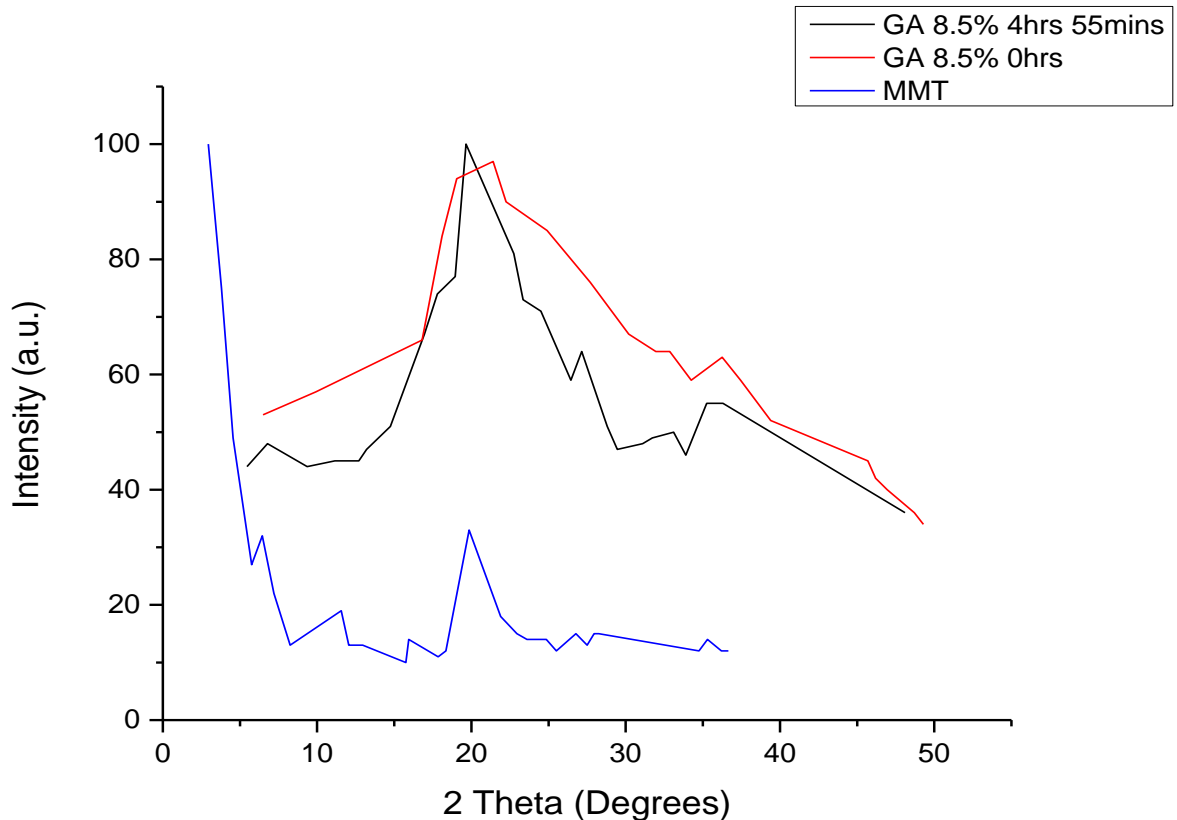
Fig.11: Outdoor Exposure of Gum Arabic. XRD of GA-8.5%C20A during outdoor exposure.
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Such highly increased mechanical strength compared to the pure polymer matrix could be attributed to uniform dispersion of the nano-sized clay particles producing an ultra-high interfacial interaction and possibly polar/ ionic bonds between the GA and C20A in line with an earlier study (Phan *et al.*, 2009).

SEM of GA samples.
The SEM images of the pre-exposed and exposed pure GA in figs 12 and 13can be used to support the rapid decline in the mechanical properties as exposure progressed. There are obvious fragmentation of the polymer chains indicated by the many white speckles or spots in the SEM of the exposed which are absent in the image of the unexposed pure GA sample. The latter only shows bigger and few white spaces/regions most probably indicating the usual amorphous regions of neat GA. The delayed decline or improved in the mechanical properties of the nanocomposite relative to the neat GA indicates that some penetration/intercalation, with some degree of exfoliation of macromolecules into the C20A. This interactions can be further explained by the possible formation of hydrogen bonds between the hydroxyl (-OH) groups from GA units and the silanol (Si–O) groups from the C20A sheets (Kaczmarek and Andrzej, 2007). With more of H-bonds during outdoor exposure then more interaction yielding more crystallinity during exposure is feasible.
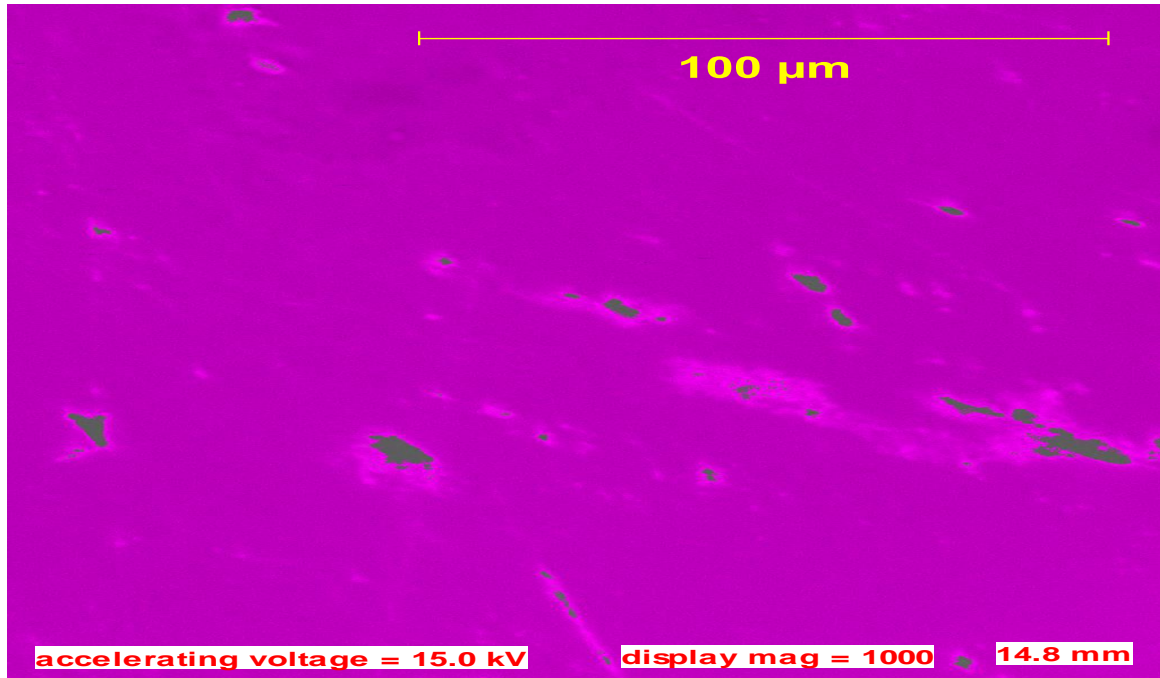
Fig. 12:Outdoor exposure of Gum Arabic.SEM of Unexposed   neat GA.
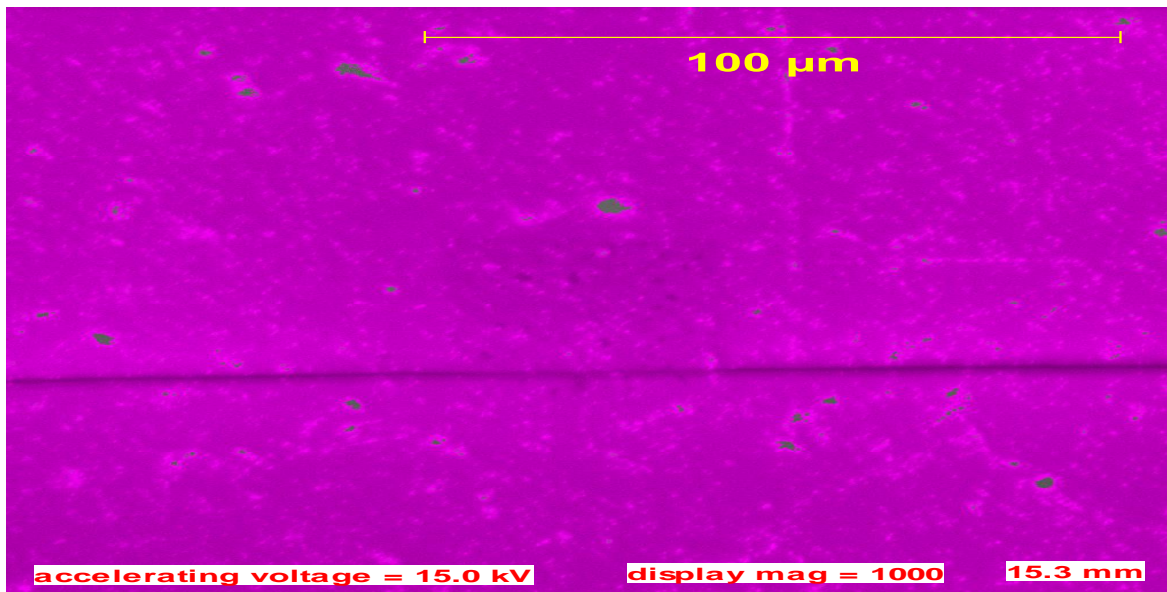

Fig. 13: Outdoor exposure of Gum Arabic. Effect of outdoor exposure of   neat GA

On the contrast, the SEM image of the nanocomposite prior to exposure shows a denser packing of the polymer chains (cf. figs 12 and 14) with few agglomerates of the nanofiller, C20A. These could have become more dispersed into the polymer matrix and enhance greater polymer-nano-particulate interaction as exposure to outdoor continues.
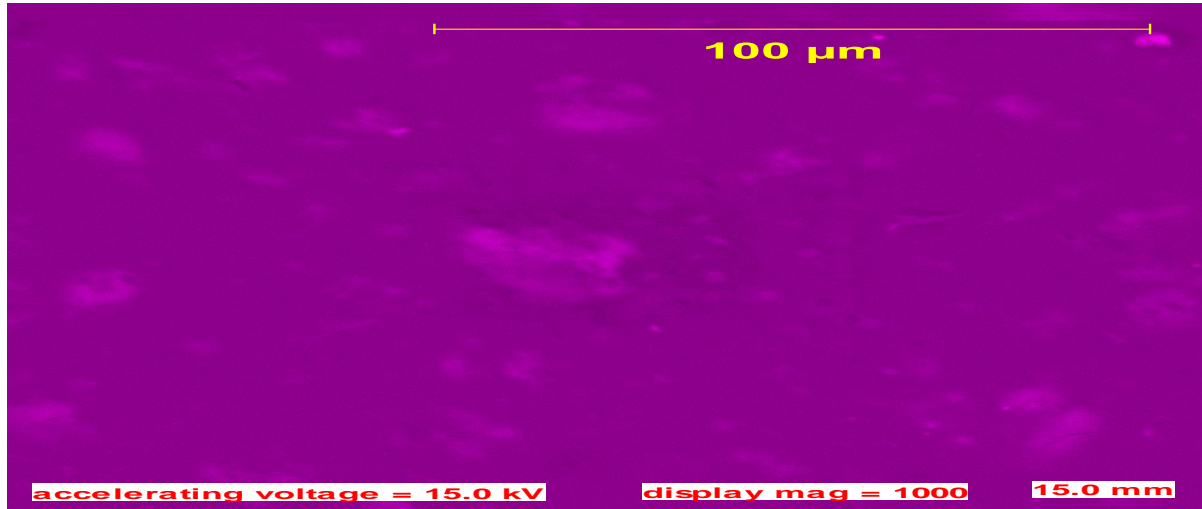
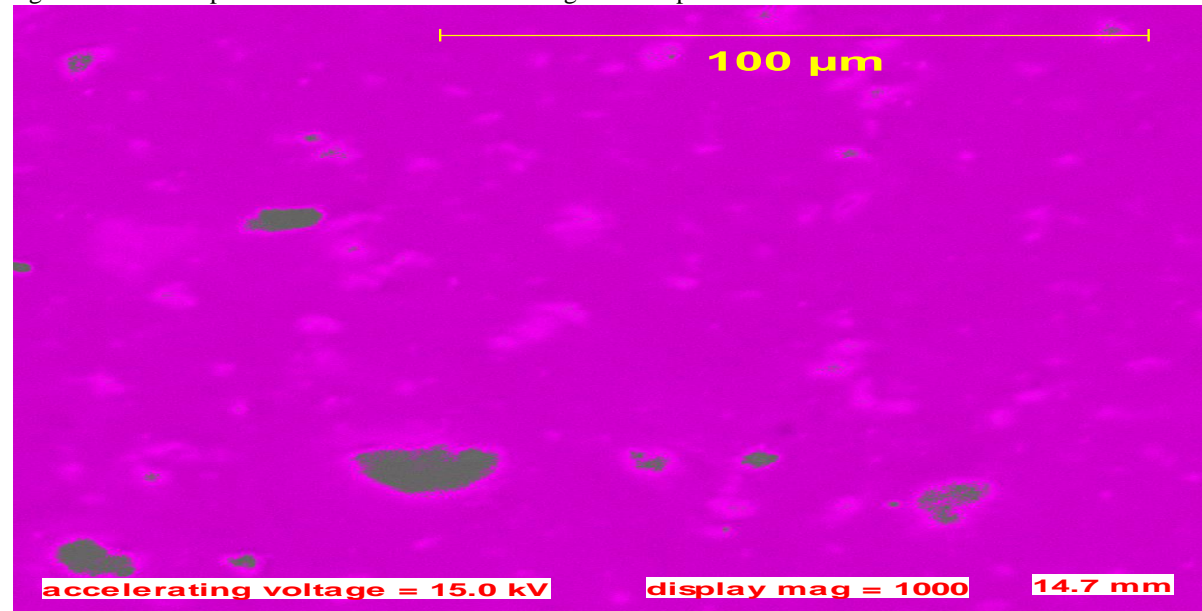Fig.14: Outdoor exposure of Gum Arabic. SEM image of unexposed GA-8.5%C20A

Fig. 15: Outdoor Exposure of Gum Arabic.SEM of exposed GA-8.5%C20A

With the presence of few fragmented chain particles as in the exposed neat polymer the sizes of most of the white particles are bigger than those in the latter indicative of the presence of the nanofiller which are better featured in the exposed sample. These observations from the SEM images most probably explain the substantial improvement in the mechanical properties of the GA nanocomposites.

Conclusion
The results obtained from this study show that the mechanical properties of Gum Arabic films can be substantially improved by producing and employing its nanocomposite containing 4.5-8.5% cloisite 20A nanopartcles when exposed to a tropical outdoor condition. However, due to the well known devastating effects of the outdoor solar thermooxidative, photooxidative and hydrolytic degradation reactions, an effective stabilizers that can significantly combat these effects could be developed, as it is being done to other polymeric systems, so as to enhance durability. The degradation of the pure biopolymer is mainly due to scission of the polysaccharide backbone resulting into formation of non-conjugated oxidation groups that were suppressed in the nanocomposite. The improvement in the mechanical properties of the biopolymer is attributed to intercalation of the nanomaterial by the polymer chain which enhances interaction between the two components showing an exposure-time dependence as the concentration of the nanofiller increases within the above range.

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