Synthesis and Characterization of a Gel-Biopolymer from Cane Sugar and Polymethyl acrylate

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Abstract: The use of cane sugar for the preparation of gel biopolymer was studied as an alternative to petroleum based gels due to their biodegradability. The sugar used was in the form of syrup obtained from evaporation of extracted cane juice. Polymethyacrylate(PMA) was obtained by polymerizing methylacrylate monomer(MA). This was copolymerized with the syrup from the cane sugar to obtain the sugar-based acrylate biopolymer (Sugar-g-PMA) via graft copolymerization of PMA using acidified potassium permanganate as initiator at 90^0C. The product obtained was a dark brown gel. FTIR and ^{1}H-NMR were used to characterize the sugar, PMA and the copolymer. The percentage of cane sugar juice extracted was 47.94% while percentage syrup obtained from the extracted cane juice was 15.22%. FTIR spectrum prominent bands found in the cane sugar were $3365.00cm^{-1}$ and $1052.00cm^{-1}$ for O-H stretch and C-O stretch respectively. The PMA shows the C-O stretch, C=O peak and CH_2 bend respectively at $1165.47cm^{-1}$, $1737.37cm^{-1}$ and $3426.00cm^{-1}$ to confirm ester functional group moiety . The disappearance of the carbonyl peak at $1737.37cm^{-1}$ in the new Sugar-g-PMA gel copolymer confirm the grafting process. The ^{1}H-NMR spectrum prominent peaks found in the cane sugar were 4.04ppm, 3.81ppm and 3.66ppm which confirmed the OCH_2 and O-H group in the sugar moiety. The PMA showed important signals at 3.87ppm, 3.79ppm and 3.64ppm that confirm the presence of ester functional group. The ^{1}H-NMR spectrum of the Sugar-g-PMA showed a novel peak at 9.52ppm that confirm grafting process. The FTIR and ^{1}H-NMR results showed that the graft copolymerization reaction was successful. The Sugar-g-PMA gel produced represents an additional contribution to sustainability and production of environmentally friendly bio-based polymeric material.

Keywords: Biodegradability, Cane-sugar, gel biopolymer, polymethylacrylate, copolymer

I. INTRODUCTION

Polymers are among the most important largely produced materials in the world. The usefulness of synthetic polymers are so numerous that humans cannot do without them. They are involved in the production of medical devices for improving life quality (Agarwal *et al.*, 2008), high-tech devices for communication and information processing (Bujak *et al.,* 2013; Tomlinson *et al.,* 2014), fibres for textiles (Weng *et al.,* 2016), building and construction materials (Worthington *et al.,* 2017), sustainable power generation and energy storage (Serrano *et al.,* 2009), materials for transportation and infrastructure, packaging materials, agricultural tools (Worthington *et al.,* 2017). Manmade

polymers spread through virtually every aspect of modern society. The factors that have contributed to the widespread of these materials include monomer cost, synthetic ease and excellent properties. Synthetic polymers are largely derived from petroleum which is a finite resource (Zhu *et al.,* 2016). This resource is exhaustible because petroleum sources are limited and non-renewable. Many studies have predicted that fossil will be depleted with less than a century (Rass-Hansen *et al.,* 2007). Therefore, alternative feed stocksare required for sustainable production of polymers. The exhaustible nature of the oil reserves has intensified interest in natural renewable resources for the chemical synthesis of polymers.The growing reliance on synthetic polymers has raised a number of environmental and human health concerns. The use of some polymers poses serious ecological problems, mainly because of their non-degradability. When fossil resources and their derivatives are used for the synthesis of some polymers, they release poisonous by-products that are toxic to the environment. Also by disposal, they contribute to the generation and accumulation of waste leading to landfills and green house effects (Madkour *et al.,*2016). Synthetic-based polymers have natural resistance to degradation and has induced the accumulation of plastic in our environment, pollution sources of atmospheric, visual, and also contamination of soil and marine environments (Shah *et al.,* 2008; Webb *et al.,* 2013). This has led to the introduction of new polymers that are sustainable and environmentally friendly. Moreover, the problem associated with the production and use of polymers which are basically environmental pollution and unsustainable feed stocks can be addressed by the synthesis of polymers that will align with the principle of Green chemistry (Omotoso and Akinsanoye, 2017).

The synthesis of biopolymers from renewable sources must be able to provide polymers that can easily replace the existing macromolecules. Biocompatible and biodegradable materials are currently emerging as valuable alternatives to conventional synthetic petroleum-based polymers (Thomas and Lutz, 2011). Several parameters have been reported to influence the degradation behaviour of biodegradable polymers; the most important factors are the chemical composition, the molecular weight and molecular-weight distribution, the crystallinity, the structure of the polymer and glass transition temperatures. Recent studies have also evidenced the strong influence of ordered monomer sequences

on degradation properties (Li *et al.,* 2011). Among the various renewable resources for polymers, carbohydrates are particularly more suitable. Carbohydrate polymers are becoming materials of high importance in diverse fields of applications due to their non-toxicity, cost-effectiveness, accessibility, ease of modifying physical and chemical properties (stereochemical diversity) and their renewability. Some of these materials and their many derivatives are currently being employed for applications such as corrosion inhibition, catalysis, drug delivery, fuel cell and adsorption (Galbis, 2016).

Furthermore, the incorporation of sugar-derived units into step-growth polymers (synthetic sugar-containing polymers) have become more attractive because of their role as biomimicry analogues and their potential for industrial applications (Fleet *et al.,* 2011). The main reasons for this interest are the great abundance of natural sugars, structural diversity, multiple functionalities, innocuousness for human health, and the hydrophilic nature of the resulting materials (Rop *et al.,* 2019). The resultant products are biodegradable and biocompatible materials and have been utilized in medicine, biotechnology and other sectors of greater consumption, such as foodstuff packaging (Acik, *et al.,* 2017). The use of sucrose as raw material has attracted special attention for the production of surfactants and bio-based polymers for several reasons. Sucrose is a cheap raw material obtained directly from sugar cane and sugar beets (Eggleston, 2018) and it is a reactive molecule having eight free hydroxyl(OH) groups and two anomeric carbon atoms which enables several chemical transformations (Rop *et al.,* 2019).The presence of hydroxyl groups in sugar reduces its utilities in many applications hence, the need for modification (Queneau *et al.,* 2007). Several studies have been accomplished to modify and increase the uses of biopolymer through grafting. Grafting is used to introduce synthetic polymers into the main saccharide chain through chemical modifications by covalent bonding, and thus confer specific addition properties to the biopolymer. Graft copolymerization of acrylic monomers such as methyl acrylate onto sugar backbone is a technique of obtaining materials having wide range of applications due to the merging properties of the sugar and the synthetic polymer. Grafting is one of the best methods of copolymerizing methyl acrylate onto sugar. Sucrose attach to methyl acrylate by covalent bonding with free radical mechanism (Kohut-Svelko, 2009; Irshad *et al.,* 2018). Methylacrylate, a strongly hydrophobic monomer containing vinyl group is of interest in this work.

This monomer contains reactive carbon-double bonds, allowing radical polymerization, which is usually not only relatively simple to perform but also provides high yields of polymers with low polydispersities and high molecular weight (Acik, *et al.,* 2017). Moreover, the sucrose monomer is strongly hydrophilic and hence impart water-solubility. The combination of these monomers with hydrophobic ones like methyl acrylate can lead to amphiphilic copolymers with a wide range of properties and applications. Typically, amphiphilic polymers, such as sugar-based polymers, are widely used in applications that require biocompatibility and/or biodegradability (Feng *et al.,* 2010).Few work has been reported on copolymerization of sugar with methyl acrylate. This research examined the production of a biopolymer that is useful as gel from graft copolymerization of methyl acrylate and cane sugar which is a renewable source, using acidified potassium permanganateas initiator.

II   METHOLOGY

Materials: The materials used for this experiment are freshly harvested cane sugar (*Saccharum officinarum*) from a farm at Owode-Ede, Osun state. The reagents used are: methyl acrylate, ethanol, hydroquinone, potassium permanganate, sodium sulphate and sulphuric acid. These chemicals are of Analar grade. The analytical instruments are Perkin-Elmer (Waltham, USA) FTIR Spectrum Two Spectrometer and Nanalysis NM Ready PRO 60 60MHz Nuclear Magnetic Resonance Spectrometer.

Methods

Extraction of sugar

Freshly harvested cane sugar were carefully scraped to remove the coloured outermost layer and then cut into smaller pieces for easy crushing and juice extraction. Cane sugar juice was extracted by mechanically crushing the canes to release the juice using cane juice extractor. The remaining pulp was again crushed and pressed. This was done to ensure that almost all the juice was extracted. The juice obtained was filtered to remove dirt and debris from the harvesting process and was kept in a closed clean container. The extracted juice was measured by gravimetric method and calculated as percentage on the basis of fresh cane sugar weight. The weight of the remaining pulp was determined and the juice from each pressing step was then thickened into syrup. This was done using a water bath to evaporate most of the water in the juice for 2hours at 110^0C. The cane juice had a light tan colour. It was stored in an air tight metallic container placed in a freezer to prevent sucrose inversion. The syrup was analysed using FTIR and ^{1}H-NMR.

Percentage juice extracted was calculated as

Weight of extracted juice × 100
Weight of sugarcane

Percentage of the cane sugar syrup was calculated as

Weight of sugarcane syrup × 100

Weight of sugarcane juice

Polymerization of Methyl acrylate (MA)

The polymerization was carried out in a 3 necked 1.5Litres batch reactor equipped with a mechanical stirrer, a temperature regulator and an inlet for the introduction of nitrogen gas. 400ml of methyl acrylate monomer was transferred into the reactor and 13.50ml of acidified

potassium permanganate solution was added as catalyst. The mixture was thoroughly stirred for 30minutes and the reaction was allowed to proceed for 3hours at 90°C. At the end of the reaction time, the reaction mixture was terminated by adding 4ml of $0.1mol/dm^3$ of hydroquinone. The reaction mixture was allowed to cool to room temperature. The final product was washed with methanol to remove the unreacted methyl acrylate and the initiator. It was then dried over sodium sulphate for 48 hours. The final product was stored in a close container for analysis and other applications.

Grafting Poly (methyl acrylate) [PMA] on cane sugar backbone

560ml of the sugar syrup and 28ml of acidified potassium permanganate were charged into the batch reactor. The mixture was homogenized for 20minutes with a mechanical stirrer. 100g of the prepared poly(methyl acrylate) was added and the mixture was homogenized again for 25minutes in an inert environment. The reaction was allowed to continue for 8hours at 90°C. The reaction was terminated by adding 10ml of $0.1mol/dm^3$ hydroquinone with continuous stirring for 10 minutes. The product obtained was a highly viscous dark brown-like biopolymer. The gel was allowed to cool at room temperature for 30minutes. Thereafter, it was washed with methanol to remove the unreacted sugar, poly (methyl acrylate) and the catalyst from the grafted copolymer (sugar-g-PMA). The sugar-g-PMA product was dried on sodium sulphate for a period of 48 hours. It was then stored in a closed container until the period of analysis.

Instrumental Analysis

IR spectra were recorded in a Perkin-Elmer (Waltham, USA) FT-IR Spectrum Two FT-IR spectrophotometer using KBr cells. KBr pellets were obtained from 1:10 weight ratios of specimens and KBr powder under a specific hydraulic pressure. Spectra were recorded at room temperature. The wavelength number range was 4000-400cm^{-1}. ^{1}H-NMR spectra were recorded by a Nanalysis NM Ready PRO 60 at an operating frequency of 60MHz Nuclear Magnetic Resonance Spectrometer. Solvent used was deuterated water (D_2O).

III. RESULTS AND DISCUSSIONS

Extraction parameters

Percentage extraction of the cane juice was 47.94% while the percentage yield of the cane syrup was 15.22%. The PMA percentage was calculated to be 72%.

IR Analysis

IR Analysis of Cane Sugar Syrup

Figure 1 shows the IR spectrum of cane sugar syrup. The bands at 3365.00cm^{-1} and 3303.00cm^{-1} are due to O-H group. Bands occurring at 1052.00 cm^{-1} and 1261.38 cm^{-1} occurred due to C-O bonds commonly found in sucrose. C-H stretching vibrational frequency occurred at 2934. 36cm^{-1}. These peak are characteristic peaks of saccharide configurations as found in sugars, such as sucrose, fructose, glucose, maltose, lactose galactose and a number of others. Similar result was earlier reported by Patil and Netravali 2019 and Chao *et al.,* 2017 about the peaks found in simple sugars. The peak seen at 928.47cm^{-1} corresponds to the C-H bending in sucrose. Other prominent bands were found at 1639.27cm^{-1} and 1417.80cm^{-1} which corresponds to substituted C-C in sucrose. The IR analysisshows the characteristic bands found in sugar generally.

IR Analysis of Methyl acrylate and Poly(Methyl Acrylate)

Figure 2 presents the FTIR spectrum of methyl acrylate. The spectrum shows prominent absorption peaks at 3368.00 cm^{-1}. and 2963.83cm^{-1} to confirm C-H stretching vibrations, C=O stretch of the ester group present in methyl acrylate was found at 1754.11cm^{-1}. The peaks at 1637.71cm^{-1} and 1407.42cm^{-1} are characteristics of vinyl bond. C=C stretching frequency is at 1637.71cm^{-1} while CH$_2$= (scissor) bend is assigned to the peak at 1407.42cm^{-1} . The peak occurring at 1440.86cm^{-1} is as a result of CH$_2$ bending vibration in methyl acrylate. The sharp peaks found at 1282. 30cm^{-1} and 1281,95 cm^{-1} are due to C-O stretch vibrations. The band along with others confirm the ester functional group present in the methylacrylate monomer. The identification of C=C bond in the structure of this material shows it can undergo polymerization via chain reaction mechanism in the presence of an initiator.

Figure 3 shows the FTIR spectrum of Polymethylacrylate. The major bands found in PMA spectrum are at 2929.13cm^{-1} and 2860.52cm^{-1} which occurs as a doublet. The peaks are due to the presence of C-H stretching vibrations. The sharp peak at 1737.37cm^{-1} corresponds to ester carbonyl group (C=O) stretching vibration. The broad peak at 1374.23cm^{-1} and 1165. 47cm^{-1} appeared are due to C-O stretching vibrations of ester. The peak found at 1453cm^{-1} shows the CH$_2$ bending vibrations in PMA. The major evidence of homopolymerization is the reduction in the characteristic peaks of vinyl band which are C=C stretch and CH$_2$ bend vibrational frequencies. Although, there is presence of C=C in Polymethylacrylate spectrum which is also found in methyl acrylate spectrum at 1638.00cm^{-1}, the reduction of C-H stretch from 3368. cm^{-1} to 2929.13cm^{-1} and reduction of CH$_2$ bend from 1407cm^{-1} to 1374.23cm^{-1} are evidences for the homopolymerization process. The existence of some of these peaks confirm that it is not all the unsaturation in the monomer units that were polymerized because the presence of some vinyl and CH$_2$ bend in the PMA homopolymer. Therefore, polymerization of the methyl acrylate monomeric units to form polymethyl acrylate occurred by chain growth mechanism at the vinyl bonds. The mechanism can be explained via the initiation, propagation and termination stages. Authors like Ghosh *et al.,* 2010; Omotoso and

Akinsanoye 2017 and Ferreira *et al.,* 2000 had similar reports.

IR Analysis of the Graft Copolymer

The IR spectrum of the graft copolymer, sugar-g-PMA is shown in Figure 4. The spectrum shows sharp band at 3389.11cm^{-1} confirming the presence of O-H stretch from the sugar. The peaks at 1100.50cm^{-1}, 1076.09cm^{-1} and 1037.20 cm^{-1} are evidences of C-O stretch from cane sugar. They showed the presence of the C-O-C stretch in glycosidic linkage of sugar. The peak at 2934.97cm^{-1} corresponds to the C-H stretch vibrational frequency of polymethylacrylate and cane sugar (sucrose). The peak found at 1643cm^{-1} shows the presence of substituted anomeric ring of sucrose from the cane sugar syrup. Carbonyl stretching vibration peak at 1737.37cm^{-1} found in the polymethylacrylate homopolymer had almost disappeared in the graft copolymer. The peak is now faintly appearing as 1703.30cm^{-1}. The broad O-H band of sugar became sharp at 3389.11 cm^{-1} (Figure 4). The presence of these two peaks confirms the presence of carboxylic acid. This serve as a major evidence for the graft polymerization process. The likely formation of carboxylic acid may be as a result of oxidation of some of the –CH$_2$OH ends in sugar to carboxylic acid (COOH). Similar fact has also been reported by Nandi in 2015. He reported that acidified $KMnO_4$ can oxidize CH_2OH of sucrose to carboxylic acid (CO_2H) without breaking up of the molecule.

The carboxylic acid could also have been formed from caramelization of the cane sugar. The presence of the new functional group confirm a new reactive group on the graft copolymer. The gel like nature of the copolymer is evident from the hydrophilic and hydrophobic layers. The new CO_2H and O-H groups ensures the new polymeric material is more reactive than the starting materials. These carboxylic acid group makes the copolymer a suitable hydrogel. This is because the copolymer has the ability to undergo hydrogen bonding and permanent dipole-dipole interactions which could result into stronger intermolecular interactions.
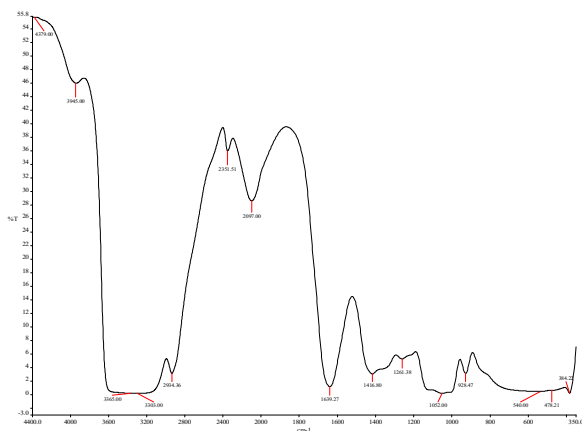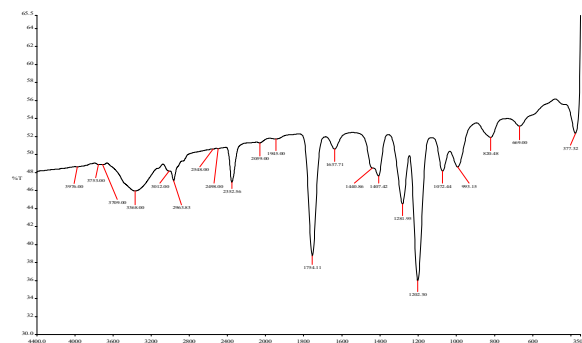

Figure 1: IR spectrum of cane sugar syrup.

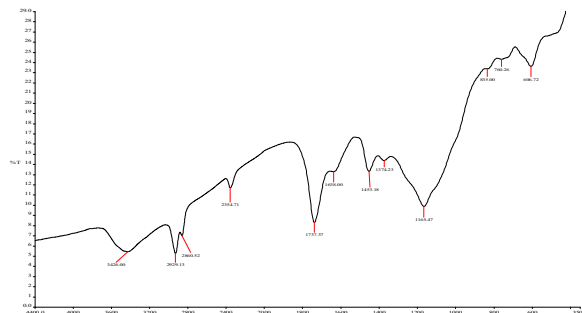Figure 2: IR Spectrum of Methylacrylate monomer

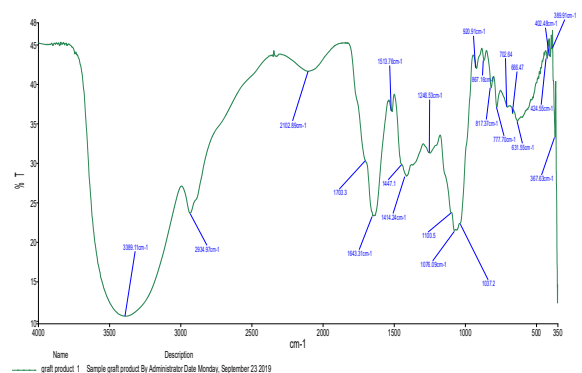Figure 3: IR Spectrum of Polymethylacrylate

Figure 4: IR Spectrum of graft product (Sugar-g-PMA)

^{1}H NMR Analysis of cane sugar syrup

Figure 5 shows the ^{1}H-NMR spectrum of cane sugar syrup. The peaks at δ 5.41ppm and 5.38 ppm appear as doublet. The signal shows the presence of α-anomeric proton of the glucopyranosyl ring in sucrose. This is because the proton NMR values resonates more downfield than what is commonly found in ß-anomeric protons. The anomeric centre of a sugar is a stereocentre created from the intramolecular formation of acetals or ketals of a sugar hydroxyl group and an aldehyde or ketone group (Ferreira *et al.,* 2000). The various anomeric groups are formed when carbohydrates undergo cyclization process. This usually leads to formation of the new centres which are the α,ß- anomeric carbon centres. Signals at δ4.16ppm, 4.04ppm, 3.81ppm and 3.66ppm and 3.57 ppm correspond to the OCH$_2$ protons attached to fructose ring in sucrose. The signals 3.42ppm and 3.26 ppm is an evidence for the existence of ß-anomeric protons in the

structure of the sugar. The peak at 2.22 ppm shows the presence of alkyl proton (–CH) next to glucose and fructose rings in the sugar. The solvent peak is seen at 4.79 ppm. The proton NMR of the simple sugar therefore revealed that that the sugar is a ring shape and not a straight chain molecular. This confirm that it has a high stability.

^{1}H NMR Analysis of Polymethyl acrylate

The ^{1}H-NMR spectrum of PMA is in Figure 6. The spectrum showed signals at 3.87ppm, 3.79ppm, 3.64ppm. These peaks confirm the protons on the methyl group attached to oxygen atom, (O-CH$_2$-)group in the structure of PMA. Peaks occurring at 3.42 ppm, 3.36ppm, 3.29ppm, 3.24ppm, 3.20ppm, 3.15ppm, 3.10ppm, 3.06ppm, 3.04ppm and 3.00ppm, 2.94ppm, 2.90ppm, 2.85ppm, 2.80ppm, 2.75ppm, 2.36ppm and 2.29ppm confirm protons next to carbonyl group. the peaks confirm that the ester function group found in the methylacrylate is still present in the PMA. The peak at δ 1.96ppm and 1.26ppm serve as evidences for the presence of CH$_2$ (methylene) protons while the peak at δ 6.64 ppm is characteristic of acrylic proton. The peak found at δ 0.81ppm which is due to end-standing methyl group (Chen and Qu, 2005). The signals at δ 4.05ppm and 5.86ppm are evidences of vinyl protons in the PMA moiety. They suggest the presence of unsaturation in the homopolymer. These peaks were similar to those observed from the FTIR spectrum of polymethyl acrylate. The peaks suggests that the new homopolymer still possess a level of unsaturation in its structure. (Ghosh et al., 2010).

^{1}H-NMR analysis of Grafted copolymer (Sugar-g-PMA)

The ^{1}H-NMR spectrum of grafted sugar is shown in Figure 7. The ^{1}H-NMR spectrum of sugar-g-PMA showed signals at δ 3.63ppm, 3.80ppm, 3.67ppm corresponding to OCH$_3$ group, peaks at 3.48pp and 2.28ppm shows the presence of proton on carbon next to a carbonyl group, 1.26 ppm is an evidence of methine proton and the peaks at 0.80ppm, 0.76 ppm and 1.38 ppm confirm the presence aliphatic protons. These peaks were similarly found in the polymethylacrylate used for the copolymerization process. The main observation is that the methyl protons are reduced and the aliphatic protons had massively increased in the grafted biopolymer. This suggests that some of them may have been polymerized (Figure 4). Peaks at δ 5.41ppm, 4.16ppm, 3.80ppm, 3.67ppm and 3.48ppm are from (OCH$_2$ and OCH$_2$) groups in the sucrose unit. The signalat δ 9.52ppm is an evidence of carboxylic acid proton in the new grafted copolymer.

The peak is an entirely new peak since it was not found in the sugar and PMA utilized in the polymerization process. This peak must have occurred due to oxidation of hydroxyl group on sucrose during copolymerization reaction (Quintas et al., 2007),. The peak at δ4.79ppm is the solvent peak. The peak can also result from the caramelization of the sucrose. Caramelization involve the decomposition of sucrose in the presence of acids/ bases and heat to form some

aromatic compounds like furan, furanones, hydroxyl furfural, maltol and so on (Quintas et al., 2007). The hydrolysis of the sucrose to fructose and glucose units could have occurred first followed by their degradation in this particular polymerization process. Also, the presence of acidified KMnO$_4$ in the reaction could have triggered the occurrence of caramelization reaction of some of the sucrose units in the sugar syrup. The weak signal at 6.87 ppm is assigned to the acrylic group in the new copolymer. All the split peaks of the ^{1}H-NMR spectrum of polymethylacrylate and some of the sugar split peaks appear in the ^{1}H NMR spectrum of sugar-g-PMA. Based on the ^{1}H NMR results, the grafting reaction between the Polymethyl acrylate and sugar can be confirmed. The results are also consistent with the FTIR results earlier discussed.

Proposed mechanism for the Polymerization reaction

The formation of radicals during the polymerization reaction occurred through acidified KMnO$_4$ leading to the reduction of Mn (VII) to Mn (II). This is shown in equation 1. The proposed mechanism for grafting PMA unto cane sugar (CS) under the catalytic influence acidified KMnO$_4$ is explained below. The mechanism follows three steps.

Formation of a free-radical species (Initiation stage) occurs as shown in equations (1) and (2).As shown in equation (3), when free radical species are created (R$^\bullet$), they generate sugar macroradicals which are active centres (Propagation stage):CS macroradicals may also be formed by direct attack of Mn (VII) ion on the CS molecule via abstraction of a hydrogen atom (Equation 4):In equation (5), the CS macro-radicals are reacted with polymethylacrylate with the creation of the free radical. The reaction was proposed to be terminated by combination of radicals to form the copolymer. This occurs as a result of the introduction of hydroquinone. The chemistry of the process is shown in Appendix 1. .

IV. CONCLUSION

This environmentally friendly process provides an attractive method for modification of sugar into useful industrial biopolymer. The proton NMR and FTIR showed that this method is efficient for graft copolymerization. The use of sugar as one of the starting materials for producing the gel contributes to the reduction of the quantity of polymethyl acrylate consumed in the reaction. Hence, there is reduction in the dependency on methyl acrylate obtained from petroleum as feedstock. The glycosidic linkages in sugar and the ester groups represent points of attack by the enzymes of microorganisms that promote their decomposition. This suggests that the synthesized sugar-g-Polymethylacrylate gel can decompose on exposure to microorganisms in soil, compost and marine sediment at high temperatures. The decayed materials can then return to the earth as useful nutrients. As a result of this, carbon (IV) oxide gas emitted is reduced thus, reducing global warming. Therefore, this research is an additional knowledge to synthesis of
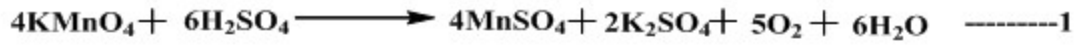
biopolymers from renewable resources like sugar which is tune with the principle of Green Chemistry.
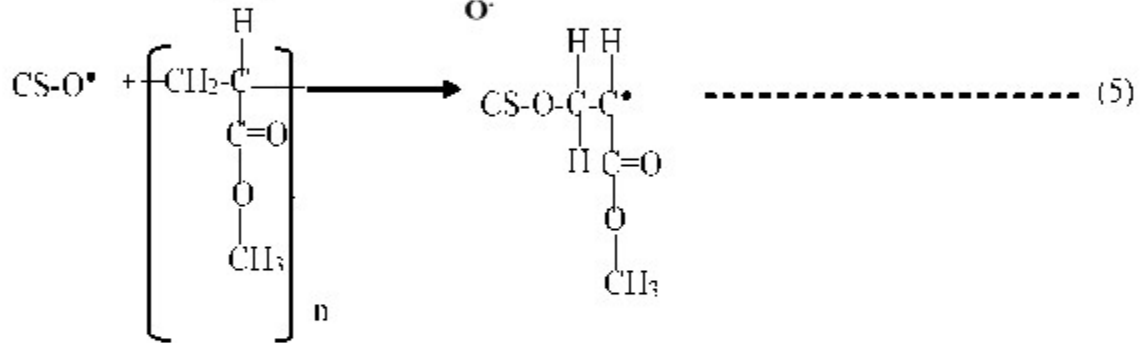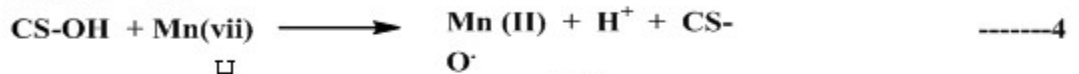
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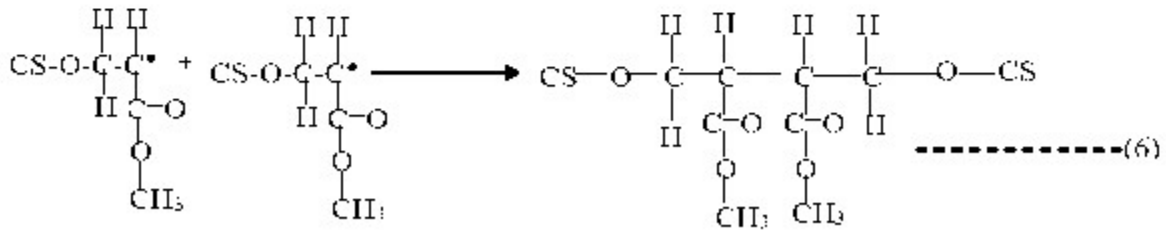Appendix 1: Proposed mechanism for polymerization reaction.

Initiation stage

$$4KMnO_4 + 6H_2SO_4 \longrightarrow 4MnSO_4 + 2K_2SO_4 + 5O_2 + 6H_2O \qquad \text{--------1}$$

$$Mn\ (vii) + HR \longrightarrow Mn\ (II) + H^+ + R^· \qquad \text{--------2}$$

Propagation

$$\text{--------3}$$

$$CS\text{-}OH + R^· \longrightarrow CS\text{-}O^· + RH$$

$$CS\text{-}OH + Mn(vii) \longrightarrow Mn\ (II) + H^+ + CS\text{-}O^· \qquad \text{------4}$$

Termination process.

Graft copolymer