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Synthesis, Structure and Properties of a Biodegradable Hydrogel Composite from Banana Stem and Collagen Fibre

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ABSTRACT

This study explored the potential of using waste banana stem in the preparation of biodegradable hydrogel composite. A modified carboxymethyl banana stem graft copolymer was synthesized via free-radical polymerization, using potassium persulfate as an initiator, acrylamide as a monomer, and N,N'-methylene bisacrylamide as a crosslinker. Collagen fibre was incorporated as an organic filler to enhance the hydrogel's properties. The reaction was carried out at 70 °C under a nitrogen atmosphere to prevent unwanted oxidation. The resulting hydrogel composite was characterized using Fourier Transform Infrared spectroscopy analysis to confirm the successful grafting of the carboxymethyl group onto the banana stem backbone and the presence of collagen fibers within the hydrogel matrix. Thermogravimetric analysis revealed the improved thermal stability of the hydrogel composite, Carboxymethyl Banana stem-g-polyacrylamide/collagen fibre (CMBS-g-PAm/CGF) compared to the Collagen fibre-free hydrogel sample (CMBS-g-PAm). Scanning electron microscopy illustrated the hydrogel's porous, network structure, which facilitates water permeation. Optimal reaction conditions were determined to achieve the highest water absorbency of 198 g/g. The biodegradation study revealed a moderate degradation rate of 37.18% after 90 days. These results show the potential of developing an eco-friendly banana stem-based hydrogel composite with a good swelling capacity that could be used in agricultural applications.

Key words: Banana stem, biodegradation, carboxymethylation, characterization, collagen fibre, hydrogel

INTRODUCTION

Hydrogels are a class of loosely cross-linked, three dimensional hydrophilic polymers with capacity to absorb and hold as much as hundreds or thousands of times its own weight in water.

The considerable amount of hydrophilic groups and their loose, three-dimensional network structure are responsible for their high hydrophilicity [1, 2]. The super-swelling characteristic of hydrogel makes them suitable for use in water-absorbing applications areas such as hygiene, industry, biomedical, horticulture and pharmaceutical [3-5]. However, synthetic polymer-based hydrogels have been identified with some drawbacks which include poor biodegradability, costly and non-renewable [6]. Therefore, there is an increasing effort to develop new hydrogel composites using natural polymers such as cellulose and its derivatives [7], humic acid, flax yarn waste [8] to render the hydrogels biodegradable, more eco-friendly, and renewable.

At present, Nigeria is among the largest banana producing countries in Africa, providing about 2.8 million tonnes per year [9]. Nearly 90% of the banana stem is discarded after production. This waste can be put into good use. Banana pseudo stem consists of layers of tightly packed overlapping leaf sheaths and contain cellulose, hemicellulose and lignin which can be utilized as skeletal backbone for the monomer to be grafted [10]. The Musaceae family has significant potential as a source of lignocellulosic fibres from the plant pseudostems. These materials, which have traditionally been considered waste, can be used to produce bio-based composites to replace petroleum-derived synthetic plastics in some sectors such as packaging and the automotive industry [11, 12]. The fibres extracted from banana stem have mechanical, thermal, and physicochemical properties that allow them to compete with other natural fibres such as sisal, henequen, fique, and jute, among others, which are currently used in the preparation of bio-based composites [13].

In spite of the potential use of Musaceae residues, there are currently few or no record related to bio-based hydrogel development using banana and plantain pseudostems. The work is expected to offer a new pathway for utilization of banana stem, reduce hydrogel production cost, and improve biodegradation and swellability of the hydrogel.

The aim and objective of this study are to investigate the potentials of utilizing banana stem and collagen fibre for a novel hydrogel synthesis, characterize and determine its physicochemical properties.

MATERIALS AND METHODS

Materials

Acrylamide, (Am), N,N'-methylene bisacrylamide (MBA), and potassium persulphate (APS), were purchased from Fluka. Banana stem was collected from a research farm at the Federal

University of Technology, Akure (FUTA). Monochloroacetic acid and propylene oxides were obtained from Sigma Aldrich. Ethanol, methanol, collagen fiber (CGF) and NaOH were used as purchased. All other reagents used were analytical grade and solutions were prepared with distilled water.

Preparation of Pulverized Chemically Modified Banana Stem (PBS)

The banana stem was chopped, washed and then dried at 70 °C. The dried banana stem was milled and screened to obtain the pulverized banana stem (PBS). PBS was weighed and put in a 2000 mL beaker with 20% sodium hydroxide solution. The suspension was heated and agitated at 70 °C for 5 h. The sample was filtered using microcloth, and washed with 90% ethanol then transferred into a beaker with 15% sodium hydroxide solution in water bath and interfused by appropriate amount of monochloroacetic acid. The mixture was stirred and heated at 70 °C for 60 minutes, then filtered with 75% ethanol solution. The resulting chemically modified banana stem (CMBS) was dried in an open atmosphere [14].

Preparation of CMBS-g-P(Am)/CGF

CMBS was dispersed in an 50 mL of distilled water. The suspension was then added into a 250 mL three-necked flask equipped with magnetic stirrer, reflux condenser, and nitrogen line in a water bath. A series of samples with different amounts of CMBS, MBA, KPS and CGF were prepared by the following steps: Nitrogen gas was bubbled into the solution for a few minutes. An appropriate amount of KPS was added with vigorous agitation and temperature was maintained at 70 °C. After about 20 minutes, appropriate amount of Am, MBA and CGF were successively added under vigorous stirring and nitrogen atmosphere [15]. After reaction for about 50 minutes, the obtained gel (CMBS-g-P(Am)/CGF) was washed with distilled water and 90% ethanol several times, cut into pieces and dried at 70 °C. The dried polymer product was milled, screened and kept in a desiccator prior to use.

Swelling Measurement

The dry hydrogel composite powder was accurately measured and soaked in 500 mL tap water at room temperature for a day to reach swelling equilibrium. The unabsorbed water was removed from the swollen samples by filtering through a mesh screen. The weight of the swollen samples was measured and recorded. The water absorbency was calculated according to Equation 1 in triplicate (three replicate) as follows;

$$Q_{eq} = \frac{M_2 - M_1}{M_1} \qquad (1)$$

where Q_{eq} is the water absorbency per gram of dried sample (g/g); M_1 and M_2 are the weights of the dry and swollen samples respectively [16].

Characterization

FTIR spectra were recorded on a FTIR Spectrometer in 4000 cm^{-1} – 350 cm^{-1} region using KBr pellets. The surface morphology and the structures of the prepared polymer gel were examined using scanning electron microscopy (SEM). Thermogravimetric analysis/Differential thermal analysis (TGA/DTA) was employed to thermally characterize the hydrogel.

Biodegradation Test

The biodegradation test was carried out using the following procedures [17]. The soil was collected from the FUTA university campus and was mixed with 6 g/kg of urea to increase the activity of microbial flora. The processed soil was then taken in a polyethylene bag (180 mm x 115 mm) and 100 ml of water was added. A 1 g of synthesized hydrogel (CMBS-g-PAm/CGF) in a bag was dipped in water for 24 h, then entirely buried in the moist soil and left in the chamber for 60 days at room temperature. The CMBS-g-PAm/CGF was transferred to a glass petri dish and dried at 60 °C in a vacuum oven. The polymer degradation percentage was then calculated using Equation 2. A similar experiment was conducted for 90 days

$$\%\ \text{Hydrogel Degradation} = \frac{W_1 - W_2}{W_1} \times 100 \qquad (2)$$

where W_1 and W_2 are the initial and the final weight of the hydrogel respectively [17].

RESULTS AND DISCUSSION

Graft Reaction:

Graft copolymer base on banana stem and collagen fiber was synthesized by grafting acrylamide onto polysaccharide molecules by a free radical polymerization in the presence of KPS and MBA as the initiator and cross-linker respectively. Polymerization mechanism involved in hydrogel synthesis is given in Scheme 1

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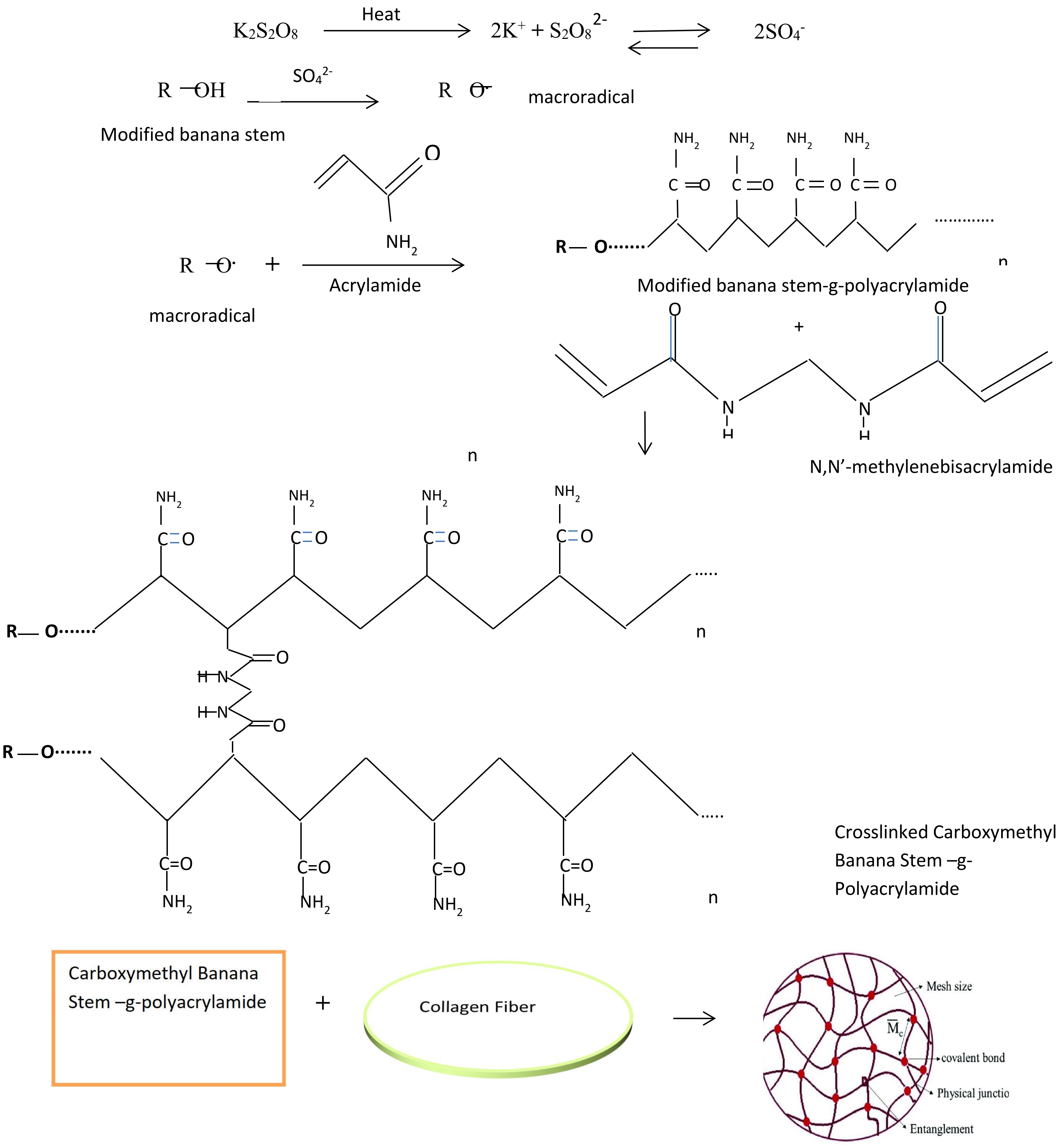

Scheme 1: Proposed Reaction Mechanism for the Synthesis of CMBS-g-P(Am)/CGF ▬ CMBS-g-P(Am)/CGF

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of PBS, CMBS, and CMBS-g-P(Am)/CGF are presented in Figure 1. In Fig 1a, the FTIR spectrum of pulverized banana stem exhibits characteristic absorption bands at 3785 cm^{-1}, 3406 cm^{-1} (-OH stretching of hydroxyl groups from cellulose and hemicellulose). 2919 cm^{-1} (C-H stretching of alkyl groups), and indicating the presence of methylene groups, 1442 cm^{-1} (CH_2 bending vibration). Also, 1038cm-^{1} (stretching vibrations of C-O-C from glucosidic band of cellulose structure) is a characteristic absorption in cellulose [18, 19]. Upon carboxymethylation, the CMBS spectrum in Fig. 1b shows the appearance of a new band at 1712 cm^{-1} (C=O stretching of the carboxyl groups), confirming the introduction of Carboxymethyl groups. Other notable bands were observed at 2919 cm^{-1} (C-H stretching), 2848 cm^{-1} (C-H stretching of methoxy groups), 1604 cm^{-1} (COO- asymmetric stretching), 1034cm^{-1} (β 1,4 glycosidic bond) [20]. The FT-IR spectrum of the Carboxymethyl banana stem-g-P(acrylamide)/CGF hydrogel displays bands at 3457 cm^{-1}(N-H stretching, overlapping with O-H stretching). 1712 cm^{-1} (C=O stretching from both CMBS and acrylamide), 1632 cm^{-1} (Amide I band, C=O stretching in acrylamide), 1445 cm^{-1} (C-H bending), and 1275 cm-^{1} (Amide III band, C-N stretching and N-H bending). The presence of amide bands confirms the successful grafting of polyacrylamide onto the CMBS/collagen matrix [20, 21].

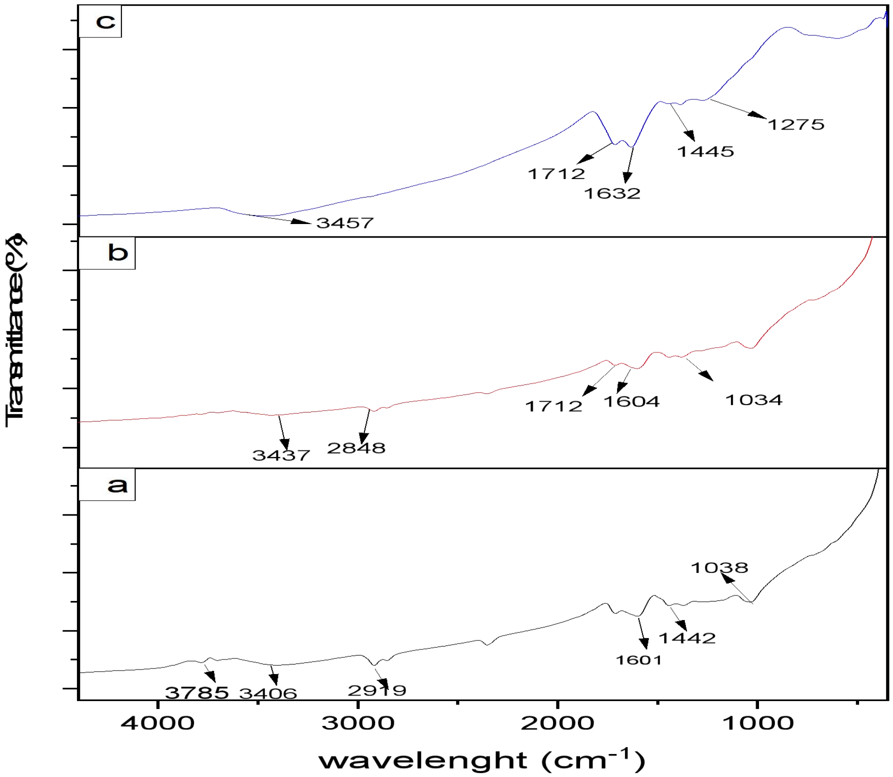

Figure 1: FTIR spectra of (a) Pulverized Banana stem (PBS) (b) Carboxymethyl banana stem (CMBS) and Carboxymethyl banana stem-g-Polyacrylamide/Collagen fibre (CMBS-g-PAm/CGF)

Scanning Electron Microscopy (SEM) Analysis

As presented in Figure 2, CMBS-g-PAm/CGF shows an interlaced network and highly porous structure. The pores are homogenously distributed in the hydrogel matrix. These pores are the regions of water permeation and interaction sites of external stimuli with the hydrophilic groups in the synthesized graft copolymers. The surface roughness of the hydrogel could be attributed to the introduction of the organic filler, CGF. In addition, the uniformity of the hydrogel surface appearance might suggest evenly dispersed CGF within the polymer matrix.

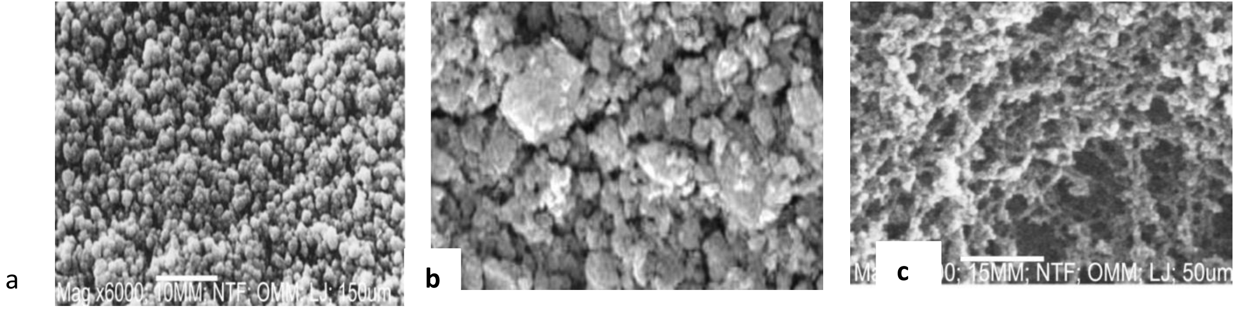

Figure 2: (a), (b) CMBS-g-PAm/CGF SEM micrograhps at different magnifications (c) CGF.

Thermal Analysis

TGA and DTA were used to determine the thermal stability of the synthesized hydrogels, CMBS-g-PAm/CGF and CMBS-g-PAm as illustrated in Figure 3. In Fig. 3 (a), three stages of degradation were observed for the hydrogel matrix. The first stage of degradation in Figure 3(a) and (b) occurred at 121 °C and 128 °C with a weight loss of 42% and 22% respectively. The weight losses were related to the elimination of physiosorbed water. The loss in mass, at 402 °C and 396 °C in CMBS-g-PAm and CMBS-g-PAm/CGF respectively can be attributed to decarboxylation (CO elimination) [22]. The loss of SO_2 and methyl amine groups from the interaction of collagen fiber with the graft copolymer chain could cause decomposition at 476 °C. The weight losses, 5% and 12%, at 680 °C and 712 °C (a) and (b) respectively are attributed to the destruction of the crosslinked network structure of the hydrogels. Overall, the results reveal an improved thermal stability in collagen incorporated hydrogel with lower weight loss than the CMBS-g-P(Am).

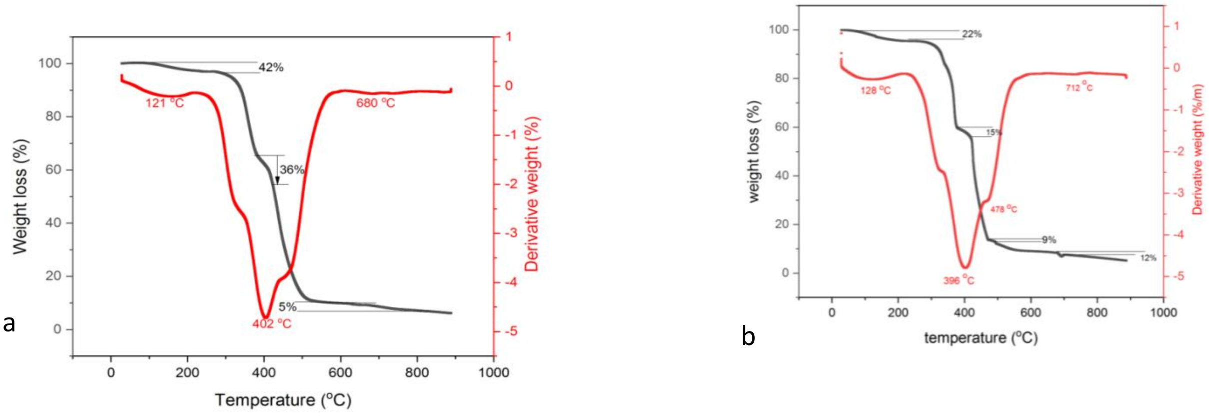

Figure 3: TGA/DTA curves of (**a**) CMBS-g-PAm (**b**) CMBS-g-PAm /CGF

Optimization of the Grafting Variables

In this work, the various variables affecting the grafting conditions were systematically optimized to obtain a hydrogel with maximum water absorbency.

Effect of Crosslinker Content

Fig. 4 shows the effect of crosslinker (MBA) on the swelling capacity of the synthesized hydrogel. It is obvious that when the concentration of crosslinker was increase from 0.078% to 0.16% there was an initial increase in absorbency of CMBS-g-PAm/CGF hydrogel from 146 g/g to 197 g/g. Further increase in the amount of the crosslinker resulted in a decrease in the water absorbency. For example, an increase in the ratio of crosslinker from 0.16% to 0.39% resulted in corresponding decrease in water absorbency of the composite. An explanation for this behavior is that when the amount of crosslinker is less, the formation of the network of the CMBS-g-PAm/CGF is inefficient due to few crosslink points rendering it semi-soluble and hardly capable of absorbing water. On the other hand, excess crosslinker generates excessive nodes in the polymeric network and results in a highly cross-linked, rigid structure which restrict free space for water penetration [23]. Therefore, the synthesized hydrogel showed a low swelling capacity.

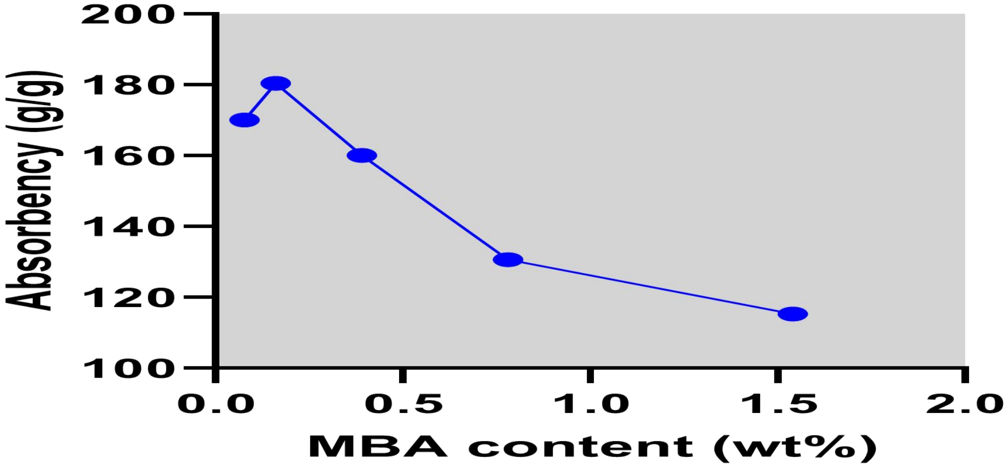

Figure 4: Effect of cross-linker on the swelling capacity

Effect of Initiator Content

The effect of amount of the initiator (KPS) on the swellability of the hydrophilic gel in tap water was presented in Fig. 5. It was observed that the water absorbency was increasing as the amount of KPS increased and then decreased with a further increase in KPS mass ratio. This might be attributed to the generation of many free radical reactive sites by the initiator which produced a lot of growing polymer chains before equilibrium is reached, and raising the hydrogel water absorbency capacity. The swelling decreased because excessive initiator concentration produced excess free radicals, which lead to increase in terminating step reaction, and production of low molecular weight polymers. Excess concentration of initiator has also been reported to increase the ratio of homopolymerization [24].

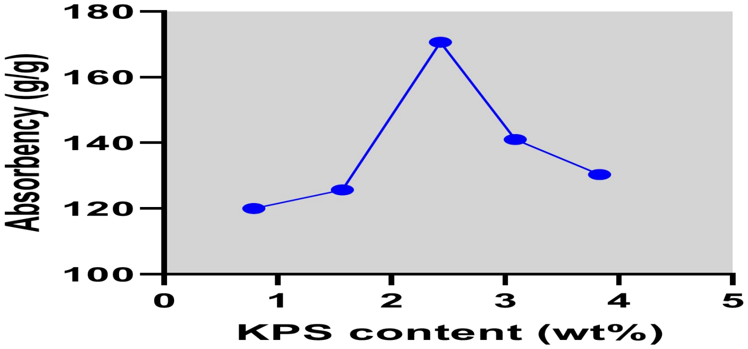

Figure 5: Effect of initiator on the swelling capacity

Effect Lignocellulose Content

Polysaccharide content has notable effect on the water absorption capacity of hydrogel and gel strength. In Fig. 6, it was revealed that the water absorbency of CMBS-g-PAm/CGF increases with the increasing of the lignocellulose content until equilibrium is attained and decline with further increase in the mass ratio of the polysaccharide. This is so because lignocellulose biomass (LB) made available more –OH groups interacting with acrylamide in the reaction system, thereby promoting the extent of graft polymerization which can consequently enhances the water absorbency of the hydrogel. However, presence of excess of LB could make the system too viscous to undergo graft polymerization efficiently thereby producing excessive crosslink nodes and crosslink density, leading to reduction in the space of the polymeric material and hence, in its water absorption capacity [25].

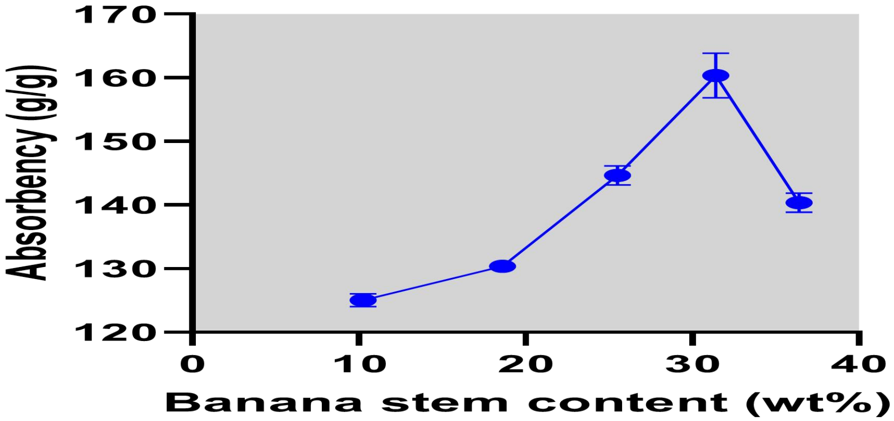

Figure 6: Effect of lignocellulose content on the swelling capacity

Effect of Collagen Fiber Content

The effect of collagen fiber content on the water absorbency is indicated in Fig. 7. The water absorbency increased with the increase of the mass ratio of CGF until it reached a maximum at 198 g/g of 10.85% mass ratio of CGF. Further increase of the amount of CGF resulted in a noticeable decrease in water absorbency. One explanation for this observation could be interaction between the initiator and functional groups in collagen fiber such as –OH, -COOH, or NH_2 to liberate free radicals on which the graft polymerization would observation could be interaction between the initiator and functional groups in collagen fiber such as –OH, -COOH, or NH_2 to liberate free radicals on which the graft polymerization would take place. The grafting of Am onto CGF improved the network structure of the hydrogel polymer matrices. At weight ratio of CGF less than 13.97%, graft efficiency increased which in turn led to an increase in water absorbency [26]. On the contrary, when the weight ratio was above 10.85%, the excess CGF increases the network points in the hydrogel matrices causing an increase in cross-linking density of CMBS-g-PAm/CGF which resulted in a decrease in absorbency.

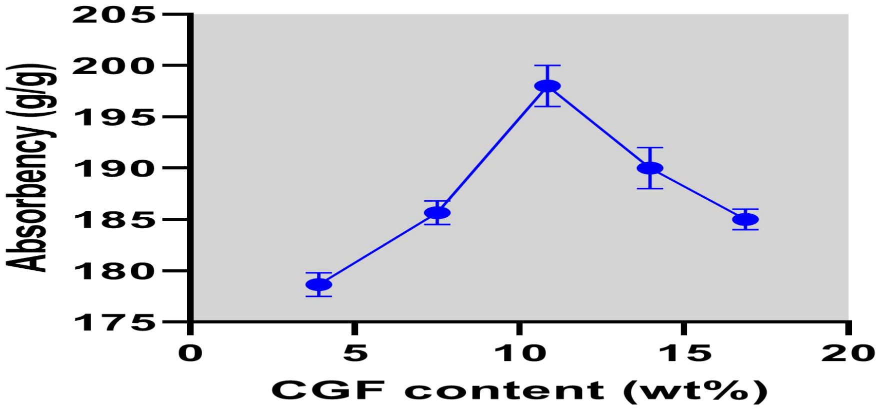

Figure 7: Effect of organic filler on swelling capacity of hydrogel

Biodegradation

The degradation rate of the synthesized hydrogel composite from chemically modified banana stem is illustrated in Fig. 8.

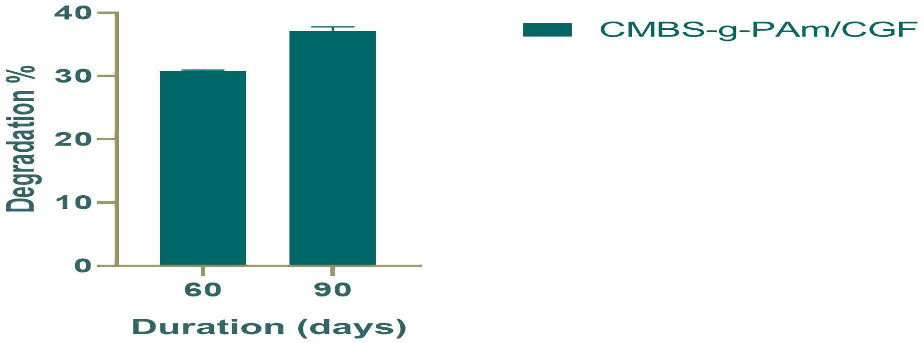

Figure 8: Degradation percentage of the hydrogel composite in the Soil

The principal goal of CMBS-g-PAm/CGF hydrogel in the present work is to function as water reservoir in a manner to meet the sequential water requirement of plant in order to increase crop yields. The result shows that after 60 days the percentage by mass of degraded modified banana stem hydrogel was 30.82%. This result clearly showed decrease in the rate of biodegradation of the CMBS-g-PAm/CGF sample after 90 days. This might be attributed to the number of lignocellulosic and collagen moieties in the hydrogel decreasing over time during the biodegradation process [27]. One explanation for this observation could be that the carboxymethyl modification introduces negatively charged carboxymethyl group which can attract positively charged enzymes such as cellulases and hemicelluloses. This can increase the binding affinity of enzymes to the modified banana stem enhancing their activity and leading to faster biodegradation at the initial stage. In all, the experiment reveals collagen-modified hydrogel is biodegradable.

CONCLUSION

In this work, a novel superabsorbent hydrogel, CMBS-g-P(Am)/CGF was successfully synthesized at 70 °C under N_2 atmosphere via graft copolymerization of acrylamide (Am) onto polysaccharide backbone in an aqueous solution in the presence of KPS, MBA and CGF as initiator, crosslinking agent and organic additive respectively. The formation of superabsorbent hydrogel was confirmed by characterization such as FTIR, SEM and TGA. The optimum reaction conditions to obtain maximum water absorbency (198 g/g) were found to be: MBA 0.16wt%, KPS 2.43wt%, CGF 10.85wt%, and CMBS 31.40wt%. Biodegradation was about 30.82% of the initial weight of the HGs after 60 days. After 90 days, 37.19% biodegradation was observed. The findings suggest that CMBS-g-PAm/CGF hydrogel composite is a safe, green functional material with promising use as a water reservoir system in agricultural application.

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