The Development of Cellulose Nanocrystals Reinforced with Carboxylmethyl Cellulose/Gelatin for Biodegradable Packaging

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Abstract— *It has significant potential to strengthen carboxymethyl cellulose/gelatin nanocomposite with cellulose nanocrystals from plantain stems for the production of bioplastics. Alkaline pretreatment and acid hydrolysis were used to extract cellulose nanocrystals from plantain stem. Films made of carboxymethyl cellulose and gelatin were strengthened using cellulose nanocrystals made from plantain stem fiber. SEM, thermogravimetric analysis (TGA), and water vapour permeability (WVP) were used to characterize the synthetic bioplastic's physical properties. The environmental deterioration of the bioplastic samples was observed over time at regular intervals in soil that was taken from a waste landfill. The results showed that the water vapour permeability of the investigated films was decreased by the addition of CNC from 2.45 x 10^{-6}g/m x h x Pa to 1.73 x 10^{-6}g/m x h x Pa. Additionally, it was discovered that unreinforced films degraded by 0.2% after 35 days, whereas 5wt% and 10wt% CNC reinforced films lost weight as a result of biodegradation by 0.1% and 0.18%, respectively. Overall, the interconnected carboxymethyl cellulose/gelatin bolstered CNC nanocomposite film for making plastics increased the heat and water vapour permeability of the packaging film, which offers the chances of their packaging application*.

Keywords— Plantain stem, packaging material, carboxymethyl cellulose, gelatin, and bioplastics.

I. INTRODUCTION

Hydrocarbon packaging materials currently pose a serious hazard to the environment as they are unable to decompose naturally and the scarcity of petroleum feedstock (Goh et al., 2016). Toxic waste production should be decreased by employing environmentally friendly and renewable methods. About 300 million metric tonnes of synthetic polymer will be discharged into the environment in 2018, with half of that quantity being released without being sorted, based on the assessment conducted by (Ogunola et al., 2018). Recycling plastic is not always easy because end products made from these wastes might not be suitable for use in post-consumer goods and because mixed plastic pollutants might cause problems. The demand for bioplastic as an alternative to traditional plastics has risen exponentially because to its non-toxicity, biocompatibility, renewability, and biodegradability features (Mostafa et al., 2020). Biobased plastics can be degraded by microbial processes using a variety of raw materials (proteins and polysaccharides), largely generated from plants (cellulose-based plastics and starch-derived plastics), as well as algae and bacteria such polyhydroxyalkanoates (PHAs) and polylactic acid (PLA). The amount of the plastic material is significant because it has the potential to be dangerous toward each human, communities, and the entire ecosystem (Gerritse et al., 2020; Mateos-Cárdenas et al., 2020). As a result, an increase in waste volume was caused by an unrestrained population growth and an excessive use of non-renewable resources. Only a few methods exist at the moment for partially eradicating harmful wastes, such as landfills and ocean discharges of an assortment of materials, some of which can decompose in a predetermined amount of time while other garbage cannot decompose for hundreds of years. The bio bags, on the other hand, were expected to differ from conventional plastic bags only little (Fernández-Braa et al., 2019). All these issues with conventional plastic have been addressed by the introduction of biopolymers, which maintains remarkable distinctive qualities and is more reliable today. It could be among the best solutions to fill the void left by the widespread prohibition of regular plastic. Biodegradable plastics are obviously manufactured from renewable biomass resources including vegetable and

fruit garbage, biopolymers, and microorganisms (Yaradoddi et al., 2019). Biodegradable polymers can be broken down into smaller bits through aerobic or anaerobic biological processes. The procedure is frequently explained in terms of the kinds of bioplastics employed, such as starch, cellulose, and materials made of biopolymers.

As appealing alternatives to synthetic-based plastic packaging materials, biopolymers derived from a variety of natural resources, such as cellulose, chitosan, starch, soy, zein, and other proteins from plant and animal sources, have been considered (Tang et al., 2012). Due to their advantageous characteristics, these natural polymers packaging materials increase the quality and shelf life of the packed commodities (Han and Gennadios, 2005). One of the components that is utilized the most frequently in the production of bioplastics is carboxymethyl cellulose (CMC). It is a translucent, non-toxic synthetic polymer with a top standard of biocompatibility as well as biodegradability. It has excellent film-forming capabilities, is highly polar, highly soluble in water, and causes a number of beneficial associations with hydroxyl groups (Naduparambath et al., 2018). The prospect of interaction and blending with other polar polymers is thus suggested (Ismaiel et al., 2018). Gelatin is used to make biodegradable films, but it is also a soluble, pleasant, and renewable material. It is an animal protein that is made from collagen through acid hydrolysis or alkaline hydrolysis.

It is widely used in the food and pharmaceutical industries (Alves et al., 2015). Gelatin is employed in packaging for a number of reasons, including its accessibility, cost, versatility, as well as protective action towards gas flow (Ramos et al., 2016). Furthermore, cellulose nanocrystal is among the most studied bio-based reinforcements (CNC). According to Moon et al., (2011), cellulose nanocrystal particles typically have a crystallinity index that fluctuates around 54 to 88%, a width of 20 to 50 nm, and fiber lengths of 100 to 250 nm. The CNC is created by acid or enzymatic hydrolysis of cellulose fibers. They are used as replacements in polymeric composites because of their unique properties, such as high modulus, the ability to generate a highly porous structure, huge surface area, biodegradability, as well as environmental benefits (Mariano et al., 2016; Ferreira et al., 2017). It is possible to separate cellulose nanocrystals from a variety of natural sources of cellulose. The most accessible and prolific of these sources is plant biomass. They therefore have the greatest potential for mass producing CNCs. Shape, size, and degree of polymerization are a few properties of nanocellulose that rely not only on the isolation techniques used in addition to origin through which they were derived (Habibi et al., 2010). One of the cellulose-containing natural fibers is found in the plantain stem (Musa paradisiaca). It is a substantial staple food in Nigeria and other humid tropical countries in Africa, America, and the Caribbean (Ketiku, 1973; Baiyeri and Unadike, 2007). It is a natural fiber product whose potential has not yet been fully realized. Thus, processing plantains can boost product variety, market price, and usage whilst still positively contributing. The use of CNC to improve the properties of popular film-forming mixtures like gelatin/CMC is not well supported by research. This approach is based on the idea that a bothersome plantain stem fiber can be given value in order to assist speedy deconstruction and packaging of meals for on-the-go eating. The results of the study should provide new applications for plantain stems and contribute to addressing pressing environmental issues associated with the usage of petroleum-based and non-biodegradable plastics in food packaging, especially for goods that need to be consumed on the go.

II. MATERIALS AND METHODS

2.1 Materials

The Onitsha Bridge-head Chemical Market in Anambra State, Nigeria, provided the ingredients. The analytical grades of gelatin (bloom strength 185), glycerol (98%), sulphuric acid (99%), sodium hydroxide, sodium chlorite, acetic acid (98%), benzene (99%), ethanol (99%), calcium chloride (96%) and potassium sulphate (99%). The analytical grades of carboxylmethyl cellulose (molecular weight, 115 000 g/mol; degree of polymerization, 1700-1800). The plantain stem fiber came from Okeanyanwu's plantation in Awka Town, Awka South Local Government Area, Anambra State, Nigeria.

2.2 Extraction of cellulose pulp

Cellulose was extracted from the plantain stem fibre (PSF) using a similar technique by EL Miri et al., (2015), with a little alteration. Carefully selected, cleaned, and dried fiber was used. The fiber was ground into a powder, sieved to a thickness of 150 m, and diced to a length of about 10 mm before being cooked in a sodium hydroxide solution. For this treatment, 17.5% (w/v) sodium hydroxide was employed for 1 hour at 80 °C. The generated fibers were thoroughly cleaned with distilled water before being dried in an oven at 100 °C to a constant weight. A previously documented bleaching procedure involved bleaching 1 g of dry fiber for 1 h at 75 °C using 0.6 g sodium chlorite, 0.5 ml acetic acid, and 65 ml distilled water (EL Miri et al., 2015). Due to the continuous injection of extra bleaching solution at 1-hour intervals, the fibers had gone white after 4 hours. After properly cleaning them with distilled water, the fibers were left to air dry to their ultimate weight.

2.3 Plantain stem cellulose nanocrystal (CNC) preparation

The CNC was produced by controlled sulphuric acid hydrolysis using 8.75 mL of 64 weight percent sulphuric acid (H_2SO_4) and 1g of dried cellulose pulp. The mixture was vigorously stirred at 45°C for 30 minutes, according to earlier findings (Csiszár and Nagy, 2017; Kargarzadeh et al., 2017). When the timer went off, ten rounds of ice-cold deionized water were used to stop the reaction. The cold solution was centrifuged for 10 minutes at 8500 rpm, and the liquid supernatant was decanted. The solid was centrifuged and diluted constantly until it became murky. To achieve a pH of around 6.5–7.0, the turbid suspension was dialyzed for a whole week against demineralized water. The recovered solution was refrigerated until use, and the weight fraction of CNC concentration in the solution was determined using the gravimetric method.

2.4 Preparing nanocomposite films

The films were produced using a process called solution casting, just like Mohammadi et al., (2020). A predetermined amount of CMC was dissolved in distilled water at 90°C for 30 minutes while being constantly agitated to produce a 100 g solution. Furthermore, gelatin was dissolved in a distinct batch of distilled water at 60 °C with a specified weight (per the design). Then the mixture of CMC and gelatin was heated to 90 °C for 30 minutes while being stirred continuously. The necessary quantity of CNC was dissolved in glycerol (30 wt% of the total solid content of the gelatin and CMC), and the mixture was combined at 90 °C while droplets were added to the CMC/Gelatin solution. The liquid was added to a 130 mm diameter petri dish after 30 minutes of stirring, and air dried for 48 hours to ensure the solvent evaporated gradually. The resultant films were separated from the plate and stored for analysis in a desiccator.

2.5 Analyzing the morphology of nanocomposite films

A scanning electron microscope was utilized to examine the distribution of the CNC fillers in the polymer matrix on a VEGA 3 TESCAN at 5 kV. The film samples were vacuum dried overnight at 40°C and then cryogenically shattered to uncover their cross section for analysis. Before examination, the samples were coated with a 5nm layer of platinum to improve clarity in the scanning electron microscope (SEM).

2.6 Analysis using thermoradimetry

The heat decomposition of cellulose nanocrystals and nanocomposite films was evaluated using an SDT Q600 thermogravimetric analyzer. The samples were cooked in a nitrogen atmosphere from 0°C to 500°C at a rate of 10°C/min for a total of 3.8 mg.

2.7 Determination of WVP

WVP was calculated using the gravimetric method in accordance with ASTM E96/E96M-05 (2005). 4g of anhydrous calcium chloride ($CaCl_2$) was placed in a glass container with the specified diameter and depth in order to achieve a relative humidity (RH) of 0. In a desiccator with potassium sulfate (K_2SO_4) at a temperature and relative humidity of 98%, the glass bottle was covered in the nanocomposite film, weighed, and placed. The sample was measured once every 24 hours in order to determine how the weight of the glass bottle changed over time. Slopes were produced using a linear regression (weight change versus time). The water vapour transfer rate was calculated by dividing the diameter of the plastic bottle opening (m^2) by the gradient of the straight line (g/h) (WVTR). Following that, the WVP (g/(m x h x Pa)) was calculated as stated in the equation below.

$$\text{WVP} = \frac{WVTR}{S(R_1 - R_2)} X \quad (1)$$

where X is the film's thickness in meters, S is the saturated water vapour pressure in pounds at the test temperature of twenty-five degrees Celsius, and R_1 and R_2 are the relative humidity in the climate chamber and the glass bottle, respectively.

2.8 Deterioration of nanocomposite films in soil

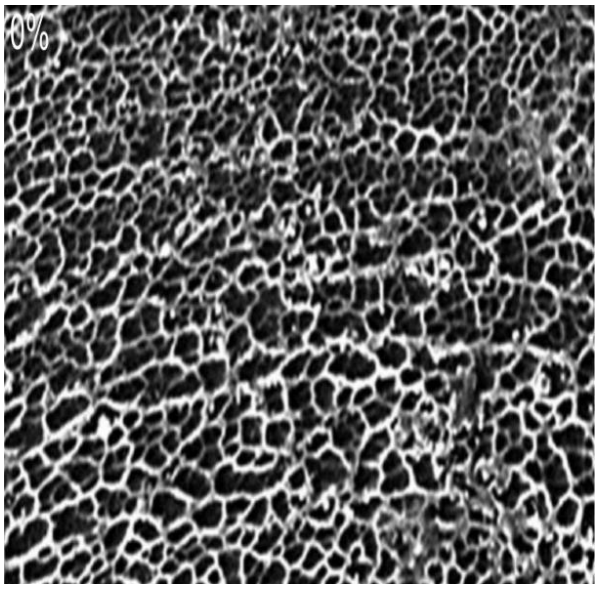
The soil degradation test was conducted as described by Salisu et al., (2012) with a few minor adjustments. The test films were weighed and positioned at a depth of 6 cm in a container filled with sand. The samples were carefully taken out of the soil every five days for 40 days in order to determine the weight loss.

III. RESULTS AND DISCUSSION

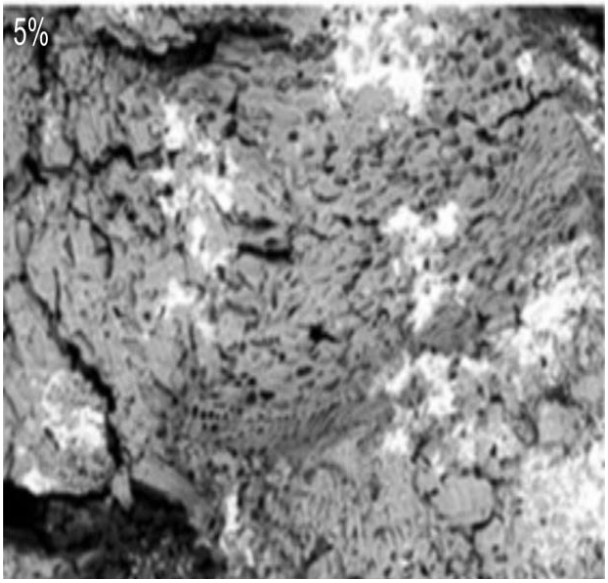
The CNC arrangement in the CMC-gelatin mixture as observed under an electron microscope scanning is depicted below. In the micrograph of the unstrengthened film, there were a few boundless aggregates and a few abrupt fractures that may have been caused by inadequate smoothness during the film-making operation (Ma et al., 2017). As a result, for films enhanced using five weight percent cellulose nanocrystal, interconnectivity as well as stable nanostructures composed of cellulose

nanocrystal and matrices were observed. However, the CMC-Gelatin film supplemented with 10% cellulose nanocrystals showed some superficial inhomogeneity and substantial splitting. This might be due to increased CNC strengthening, which causes more agglomeration and decreased dispersibility. The compact aggregation of CNCs, as per Kumar et al., (2020), shows that the chains of CNCs display potent hydrophilic contacts with intermolecular hydrogen bonds. In addition, consistent nanostructures made of cellulose nanocrystal and networks were observed for films enhanced using 5 wt% cellulose nanocrystal, with a diameter of approximately of 31 nm for the isolated CNCs and sizes spanning between 20 nm to 50 nm.

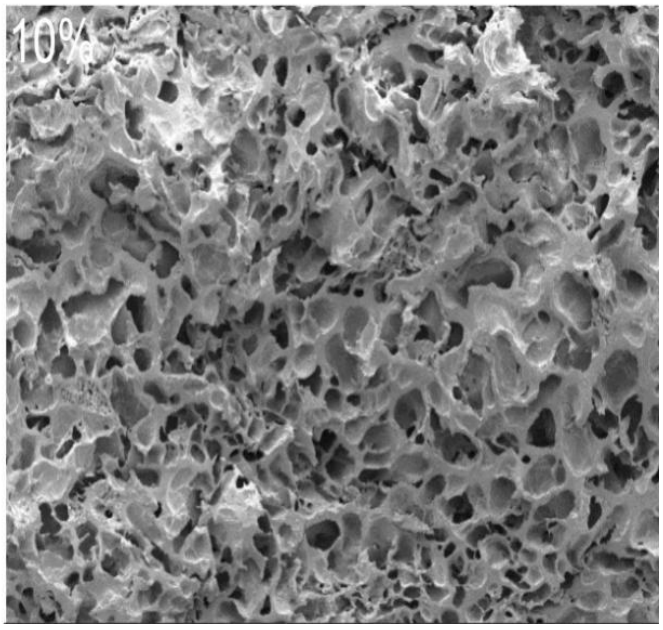
The 10 wt% CNC augmented CMC-Gelatin film, however, showed substantial fracturing and some superficial imperfections. It could be due to increased CNC fortification, which causes greater clumping and decreased miscibility. The tight assemblage of CNCs, as per Kumar et al., (2020), shows that the networks of CNCs display potent aqueous contacts and strong hydrogen bonds. The segregated CNCs were found to have sizes spanning between 20 nm to 50 nm, with a mean size of 31 nm. Although this region is similar to that shown by Agustin et al., (2013) utilizing onion shoots (30-50 nm). Zhou et al., (2017) observed ranges around 10 nm as well as 50 nm for CNC synthesized using silk plant, and Benini et al., (2018) documented 10-60 nm with CNC utilizing Imperata brasiliensis vegetation. According to Kargarzadeh et al., (2017), the width of rice husk fiber was lowered by 15-20 nm.



(a) 0% CNC film



(b) 5% CNC reinforced film



(c) 10% CNC reinforced film

FIGURE 1: Scanning electron micrograph of the nanocomposite films; (i) 0 wt% CNC, (ii) 5 wt% CNC, and (iii) 10 wt% CNC

3.1 Thermal evaluation

Thermogravimetric analysis (TGA) as well as differential thermogravimetric analysis was implemented to investigate the thermal properties of the CNC and nanocomposites (DTG). The results show that below 284°C, the nanocomposites remained thermostable. Because of this, neither CNC nor the nanocomposites was capable of maintaining upwards of 90% of their original weight at this temperature. Its depolymerization, dewatering, as well as disintegration of glycosylation units are assumed to be the main contributors to CNC degradation between 284°C and 286°C. Zhou et al., (2017) found a 245°C beginning decomposition temperature, which really is equivalent to the findings of this study. Early on in the heating process, the weight of the CNC experiment progressively dropped since the sample contained free water (Xu et al., 2017). The CNC's highest temperature of deterioration, as indicated by the DTG curve, was 407°C.

The maximal degrading temperature of 364°C for CNC has indeed been recorded (Benini et al., 2018). The major thermal decomposition threshold for cellulosic materials is typically thought to vary between 200°C and 400°C, and so this optimum degeneration temperature fits in that range (Agustin et al., 2014).

The weight loss was reasonably steady above 400°C and produced a 32% char residue. The sulphate groups formed after sulphuric acid hydrolysis could have had an influence on the amount of residue that was left following the breakdown. The curve patterns with in CMC-gelatin nanocomposite films both with and without reinforcing were similar, however the addition of CNC improved their thermostability. The 5 wt% as well as 10 wt% CNC strengthened films declined at 285°C as well as 286°C, respectively, while the unreinforced film started to deteriorate at 284°C.

According to the DTG graph, the deterioration temperature of such nanocomposite films considerably rose from 390 °C for the unstrengthened film to 400 °C and 407 °C with both the inclusion of 5 wt% as well as 10 wt% CNC, respectively. CNCs showed that they marginally improved the thermostability of the nanocomposite by serving as just an insulation as well as mass transport barrier towards the volatile compounds released upon decomposition (Benini et al., 2018).

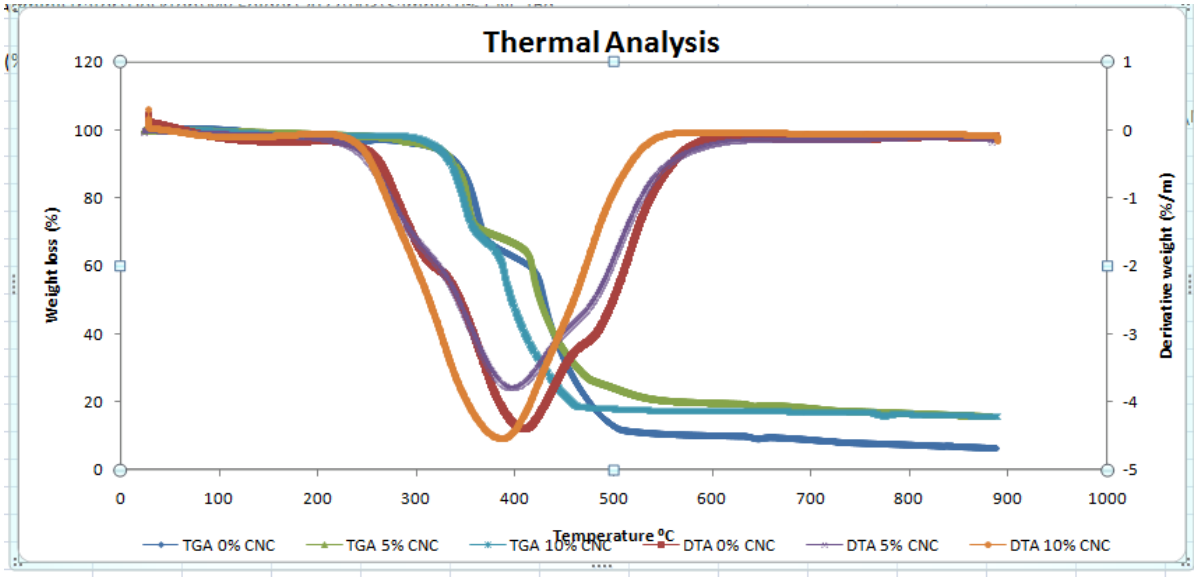


FIGURE 2: Thermal degradation of the nanocomposites

3.2 Water Vapour Permeability

For applications such as packaging, films are expected to at the absolute least lessen gaseous transmission across wrapped items and the environment. This important factor is necessary for avoiding product contamination or packaging-related environmental pollution. The WVP of unstrengthened CMC-gelatin film, 5 wt%, as well as 10 wt% CNC strengthened CMC-gelatin films were examined and reported. The WVP of unstrengthened CMC-gelatin film was calculated to be 2.45 x 10^{-6} g/(m x h x Pa), while for 5 wt% and 10 wt% CNC strengthened films, it was reduced to 1.99 x 10^{-6} g/(m x h x Pa) and 1.73 x 10^{-6} g/(m x h x Pa), respectively.

There is unmistakable proof that the addition of CNC to the CMC-gelatin combination improved the films' WVP. This decrease in WVP can be attributed to the impermeable CNCs, which were evenly dispersed throughout the mix matrix to produce a

circuitous pathway and prolong overall effective diffusion pathway for water vapour transmission (Kanmani and Rhim, 2014; Yadollahi et al., 2014; Bai et al., 2015). The WVP result obtained from this investigation, however, is lower than that reported by Noshirvani et al., since 15% CNC (6.79 x 10^{-7} g/(m x h x Pa)) were introduced to the starch-PVA mixture Noshirvani et al., (2018). Additionally, WVP of 3.7 x 10^{-11} g/(m x h x Pa), which is much lower than the results obtained in this study, was recorded in chitosan/gelatin plasticized using sorbitol as well as glycerol for food containers with a thickness of 0.8 mm (Arvanitoyannis et al., 1998). Similarly, it is assumed that the permeability of a film to water vapor is unrelated to its thickness; yet, hydrophobic films usually exhibit a strong association between their susceptibility and thickness as a result of their attraction to water (Patricia-Miranda et al., 2004). Our research has shown that biodegradable films created by strengthening CMC-gelatin using plantain stem CNC possess excellent WVP for food packaging, in contrast to standard synthetic polymer packaged food films, which are stated to also have WVP in the region of 2.3 x 1014 to 8.7 x 1014 g/(m x h x Pa) (Bastarrachea et al., 2011).

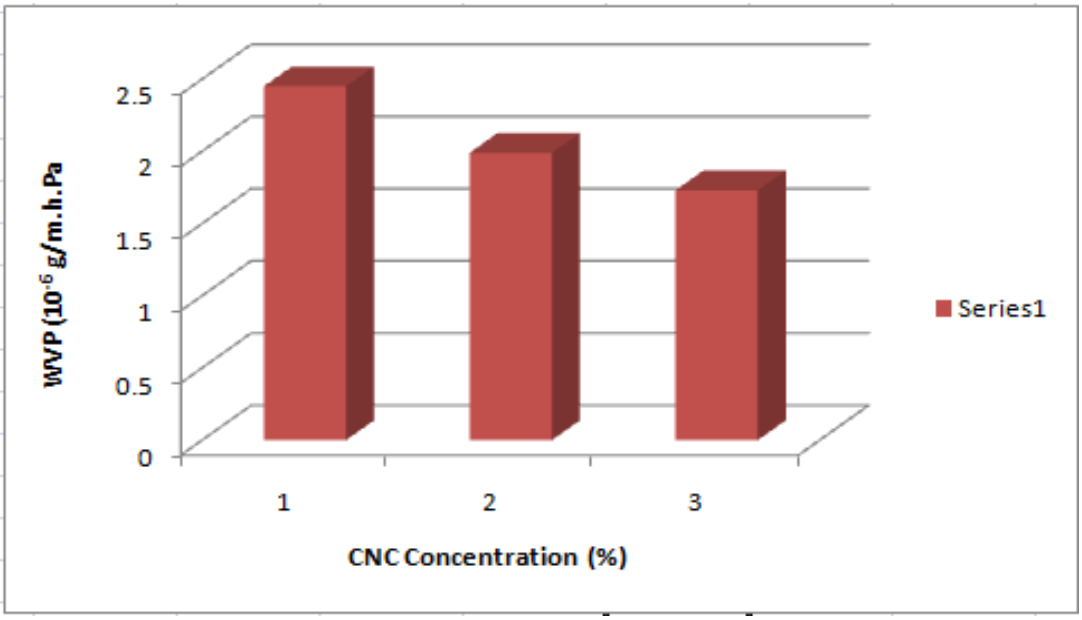


FIGURE 3: Water vapour permeability of the nanocomposite films

3.3 Degrading of the soil

Common polymers including polystyrene, polypropylene, polyethylene terephthalate, and polyethylene are all well recognised for their environmental resistance.

Biodegradability therefore has gained significance when assessing overall environmental impact of polymer in areas such as packaging. The biodegradation behaviors of the 0%, 5%, and 10% CNC strengthened CMC-gelatin films were investigated utilizing the earth immersion strategy. The microbial degradation was studied in regards to the weight loss upon interment in wet soil. The study indicate that the specimen degraded faster compared to the other specimens, despite the fact that significant deterioration wasn't really seen throughout the study period. The degradation of the nanocomposite after first few days of soil burial was essentially similar for both the strengthened and the unreinforced CMC-gelatin films. After 25 days, the unreinforced film showed a higher degree of biodegradability 0.3%, while the 5 wt% as well as 10 wt% CNC strengthened films experienced weight losses of 0.4% as well as 0.5%, correspondingly, attributable to degradability. A superior three-dimensional (3D network) might have resulted from 5 wt% CNC dispersing more evenly in the CMC-gelatin matrix than 10 wt% CNC. Their structural rigidity is readily jeopardized since composites' poor dissemination encourages pressure areas to form in their structure. Although it's crucial to note that equilibrium degradation was not reached in the 35-days timeframe, it's probable that the inclusion of CNC retarded those biodegradation of the films. The strengthened films showed the possibility of continuous deterioration if the disintegration timeframe were protracted, despite the fact that the deterioration rate of the unstrengthened films fell dramatically. After being buried in earth, films quickly disintegrate (Goheen and Wool, 1991; Danjaji et al., 2002); nevertheless, strengthened films have a higher likelihood of ongoing complete breakdown than unstrengthened films, which might also decay gradually beyond 1 month.

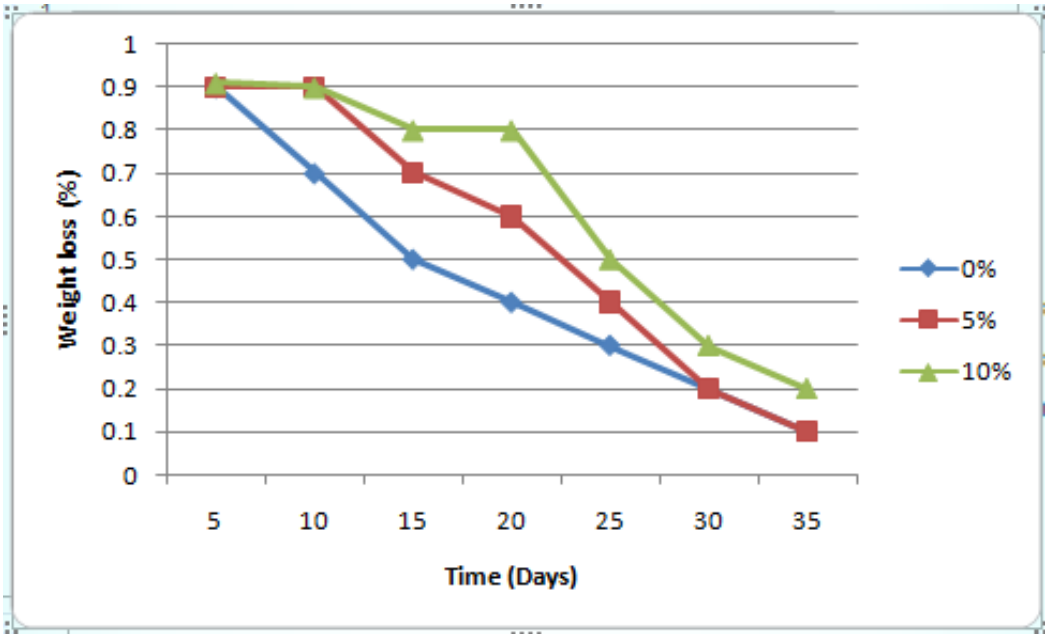


FIGURE 4: Soil burial test of the nanocomposites

IV. CONCLUSIONS

Plantain stem fiber was used to make cellulose nanocrystals with sizes varying from 20 to 50 nm with both the aim of fabricating as well as strengthening nanocomposite films with CMC and gelatin as the matrix for upcoming packaging applications. Interestingly, the thermal efficiency of the CMC-gelatin matrix performed better with the inclusion of CNC. The thermal conductivity of the film was increased to 390–407°C. The enhancement in thermal properties shows that the plantain stem CNC's act as an insulator shielded the volatile compounds released during disintegration from mass transfer. The water vapour permeability of the films under investigation also showed that the inclusion of CNC to the CMC-gelatin matrix decreased the water vapour permeability from 2.45 x 10^{-6} g/(m x h x Pa) to 1.73 x 10^{-6} g/(m x h x Pa). Although hydrophobic, CNC has a higher water barrier property due to its capacity to create a compact three-dimensional framework with the matrix and have less water particle accessibility. The demonstrated findings support the use of plantain stem CNC strengthened CMC-gelatin films as potential sustainable packaging materials, notably for on-the-go food containers.

V. CONFLICT OF INTEREST:

There are no interests in conflict.

AUTHOR CONTRIBUTIONS:

The experiment design was done by E. C. Nwanna; P. C. Eze; L. C. Orakwe; C.P. Nwachukwu; A. E. Ekpo; and J. I. Maduegbuna. The experiment execution was done by E. C. Nwanna; P. C. Eze; C.P. Nwachukwu[1]; and A. E. Ekpo. The data analysis and interpretation was done by E. C. Nwanna; P. C. Eze; L. C. Orakwe and J. I. Maduegbuna. E. C. Nwanna; P. C. Eze; L. C. Orakwe and A. E. Ekpo served as the scientific co-ordinators. All authors reviewed, edited, and approved the manuscript.

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