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Thermal and Morphological Studies on Biosynthesized Chitosan-Silver Nanocomposites

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Abstract: The environmental pollution originating from the persistence and improper disposal of seashell wastes has led the stakeholders in food industries across the globe to migrate to the sustainable use of the wastes, whose components need to be studied for proving their nature and to confirm their usefulness. For this reason, the treatment of the wastes was assessed which demonstrates that the wastes contain chitosan as a polymer in their formulation. The thermal stability of the chitosan was found to be influenced by polar groups, such as O-H bonds. The morphological characteristics of rod-liked were detected. A series of chitosan–silver (CHS-Ag) nanocomposites with different weight ratios of silver were obtained by biosynthesis using *Nicotiana tabacum*. Thermogravimetric analysis (TGA) studies of the nanocomposites were performed in order to establish the mode of their thermal degradation. The TGA Thermograms showed that the thermal degradation of CHS-Ag nanocomposites was found to proceed in two steps. The surface morphology of the CHS was analyzed by scanning electron microscopy (SEM) before and after biosynthesis.

Keywords: *Biopolymer; Environmental Sustainability; Thermal Stability;* Nanostructure; *Biosynthesis*

1. Introduction

Biopolymers have gotten a lot of attention from both theoretical and practical perspectives. Chitosan is a prospective agent for its industrial significance due to its eco-friendliness and potentially attractive economy among biopolymers (Mariana *et al*., 2021). Chitosan's drawbacks, such as thermal instability, aggregation, and hence poor surface area, frequently limit its possible applications. To overcome these drawbacks, researchers have attempted to create biopolymer-based blends/composites with metal nanoparticles as the dispersion phase (Thakur *et al*., 2022). Silver nanoparticles, on the other hand, have outstanding morphological and thermal properties (Khodashenas and Ghorbani, 2019). Thermogravimetric analysis has been used by several studies to investigate the thermal stability

of chitosan in polymers and composites (Abdurrahim, 2019). Polymer scientists need to know about their thermal stability and thermal history in order to understand their processing behaviour and choose the best material for a given application (Feist, 2015). Thermal stability and degradation behaviour are important to know when modifying polymers for novel uses. As a result, research into the thermal stability of biopolymers and their composites is critical (Izwan *et al*., 2021). The biosynthesis of chitosan-silver nanocomposites, as well as their thermal and morphological characterizations, has not been explored, according to a review of the literature (Verma *et al*., 2021). Also, A composite in film form was prepared from the biomaterial hydroxyapatite, chitosan and glycerol using the dissolution/recrystallization method. A nanoparticle-based film with a homogenous and smooth surface was produced and tested as promised for removal Cd^{2+} and Zn^{2+} in waste industrial waters (Akartasse *et al*., 2022). The use of silver Nanoparticles find more applications in industrial fields (antioxidant, antibacterial activities (Gunawan & Sardjono (2022), Apriliani *et al*., 2020; Basuliman *et al*., 2023;) The thermal stability of chitosan-silver nanocomposites was evaluated using thermogravimetric analysis (TGA) and surface morphology was examined using scanning electron microscopy in this study.

2. Methodology

2.1 Materials and Samples Treatment

Crab shells were obtained from a local fish market at New Bussa, Niger State, Nigeria. Fresh Tobacco (*Nicotiana tabacum*) leaves were randomly collected from different locations in Tunga Awuje Paiko, Niger State Nigeria. The shells were carefully washed using tap water to remove dirt, sand and other impurities. The washed shells were air-dried for two weeks and pulverized using mortar and pestle. The resulting particles were filtered to < 1mm fine sizes for easy extraction. The sieved shell sample was stored in an opaque glass bottle for further analysis. The leaves of Nicotiana tabacum were washed with tap water and then distilled water, air-dried for one week and ground into powdery form by using a mortar and pestle. The powdered samples were sieved and stored at room temperature in an opaque polythene bag prior to use. Reagent grade glacial acetic acid (Sigma Aldrich), hydrochloric acid, and sodium hydroxide (BDH Chemicals England) were used as received.

2.2 Experiments

2.2.1 Biosynthesis of Silver Nanoparticles

The biosynthesis of silver nanoparticles was achieved by the addition of 30.00 cm^3 of the *Nicotiana tabacum* leaf extract into a 250.00 cm^3 conical flask. To the conical flask, 20.00 cm^3 of 1.00 $mmoldm^{-3}$ $AgNO_3$ solution was added and heated at 60^0C for 10.00 minutes. After this, the flask was incubated at room temperature for 24.00 hours after which a colour change of silver nitrate to brown which signified the formation of silver nanoparticles was observed. The maximum wavelength and absorbances of the silver nanoparticles were recorded using a Shimadzu UV spectrophotometer (UV-1800).

2.2.2 Preparation of Chitosan and its Nanocomposites

The extraction of chitosan was achieved by deproteinisation, demineralization and deacetylation of the powdered crab shells using 1.25M NaOH at 30^0C for 3 hours, 1.25M HCl at 80^0C for 5 hours to obtain chitin and 0.5M HCl at 100^0C for 2 hours to produced chitosan respectively. The preparation of the nanocomposites (COMP 1:1, COMP 1:2 and COMP 2:1) was done by varying the amounts of acetic acid solutions of chitosan and aqueous solutions of silver nitrate as shown in Table

1. Nanocomposite COMP 1:1 was prepared by the addition of 10cm^3 aqueous leaf extract of *Nicotiana tabacum* to the mixture of 40.00 cm^3 of 1% chitosan and 40.00 cm^3 of 1.00 mmoldm^{-3} silver nitrate solutions, stirred at 100.00 rpm for 1.00 hours and subsequently allowed to age for 24.00 hours. The changes in colour from colourless to pale brown and then to dark brown signified the formation of the nanocomposites. The obtained chitosan/silver nanocomposite film was freeze-dried at -42^{0}C for 3.00 hours and then further characterized. The other experimental runs to prepare nanocomposites COMP 1:2 and COMP 2:1 was carried out using the conditions set out in Table 1.

Table 1: Experimental Runs for the Preparation Chitosan–Silver Nanocomposites

Run	Amount of Chitosan (wt %)	Amount of silver nitrate (mmoldm^{-3})	Sample
1	1.00	1.00	COMP 1:1
2	1.00	2.00	COMP 1:2
3	2.00	1.00	COMP 2:1

2.3 Characterization of the Prepared Chitosan and its Nanocomposites

To determine the thermal stabilities of the prepared samples, 5.00 mg of each of the samples of chitosan and chitosan-silver nanocomposites were heated from ambient temperature 30 to 600°C, at a heating rate of 10°C/min under a nitrogen atmosphere using TGA-STA 449F3 NETZSCH5 analyzer. To determine the surface morphologies of the prepared samples, 0.10 g of the dry samples of chitosan and chitosan-silver nanocomposites were ground and placed on a carbon adhesive tape followed by coating with gold under vacuum conditions using a sputter coater. Then, their morphologies were visualized using HRSEM (ZEISS Auriga Crossbeam 550) operating at a resolution of 0.5 nm, voltage of 5 kV and 50.00 KX magnification level.

3. Results and Discussion

3.1 Thermal Description of the Biosynthesized Chitosan and its Nanocomposites

The thermal stabilities of the prepared samples were determined using thermogravimetric analysis (TGA) and the results are shown as TGA and DTG curves in Figures 1a and b respectively. Information obtained from the curves is presented in Table 2.

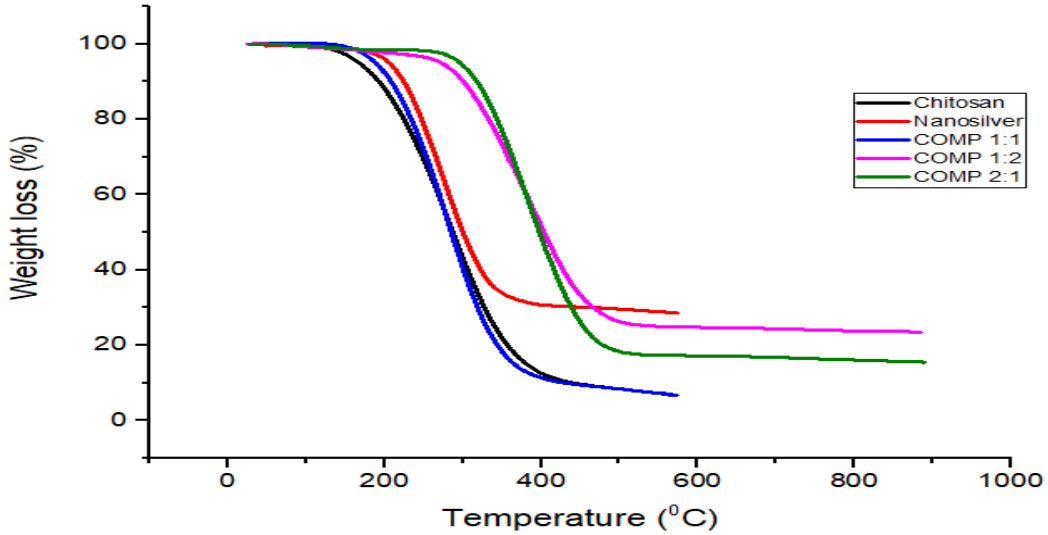


Figure 1a: TGA curves of the prepared chitosan, silver nanoparticles and chitosan-silver nanocomposites

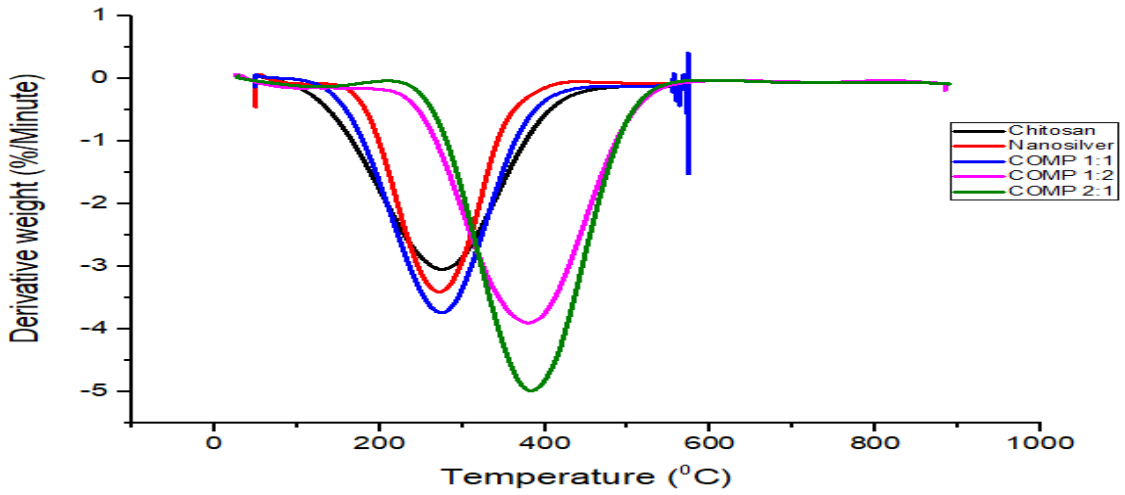


Figure 1 b: Thermograms of the prepared chitosan, silver nanoparticles and chitosan-silver nanocomposites

Table 2: Thermal behaviours of Chitosan, Silver Nanoparticles and their Composites

Sample	Moisture content (%)	Ash content (%)	Onset degradation temperature (^{0}C)	Peak degradation temperature (^{0}C)
Chitosan	10.21	6.67	192.96	398.92
Nanosilver	8.50	6.43	203.14	384.57
COMP 1:1	3.56	28.57	199.20	366.70
COMP 1:2	4.54	23.27	266.68	503.57
COMP 2:1	3.40	15.47	287.98	503.07

It can be seen that the TG curves are smooth, with only two weight loss steps which show the thermal degradation of chitosan, nanosilver and chitosan-silver nanocomposites (COMP1:1, COMP1:2 and COMP 2:1) in a nitrogen atmosphere is simple and is a one-step reaction apart from the loss of moisture. The first weight loss at a temperature around 100^{0}C for chitosan, nanosilver, COMP1:1, COMP1:2 and COMP 2:1 respectively is associated with the loss of moisture and components of the plant moisture that bonded physically to them (Hassan *et al.,* 2018). From Table 2, 3.56, 4.54 and 3.40% moisture contents for COMP1:1, COMP1:2 and COMP 2:1 respectively were observed at higher temperatures than for chitosan. It implies that they contained less bonded moisture which can be attributed to the interaction of silver nanoparticles that are less hydrophilic materials. The variation in the moisture content could be connected to the different amounts of silver nanoparticles present in the nanocomposite polymer chains via amine and hydroxyl groups. It has been reported that the moisture content in a polymer is determined by the number and nature of ionic groups in the polymer matrix (Rajendra, 2019). Furthermore, it is believed that, due to the distinct hydrophilic nature of chitosan, a nanocomposite with more amount of chitosan is expected to be more hydrophilic (MujeebRahman *et al.,* 2018). But this assertion was not however observed for the prepared nanocomposites. This may be due to the even distribution and reduced agglomeration of nanosilver across the polymer matrix. The second weight-loss stages 192.96 to 398.92°C, 203.14 to 384.57°C, 199.26 to 366.70°C, 266.68 to 503.57°C and 287.98 to 503.07°C, depict the thermal breakdown of chitosan, nanosilver, chitosan-silver nanocomposites (COMP 1:1, COMP 1:2 and COMP 2:1) respectively were observed.

Figure 1b indicates the thermogram of the prepared samples and from this, thermal stability for silver nanoparticles up to a temperature of 203.14°C, followed by a drastic loss of weight in the temperature range of 203.14 to 384.57°C, which is within the range of temperature reported by Khalil

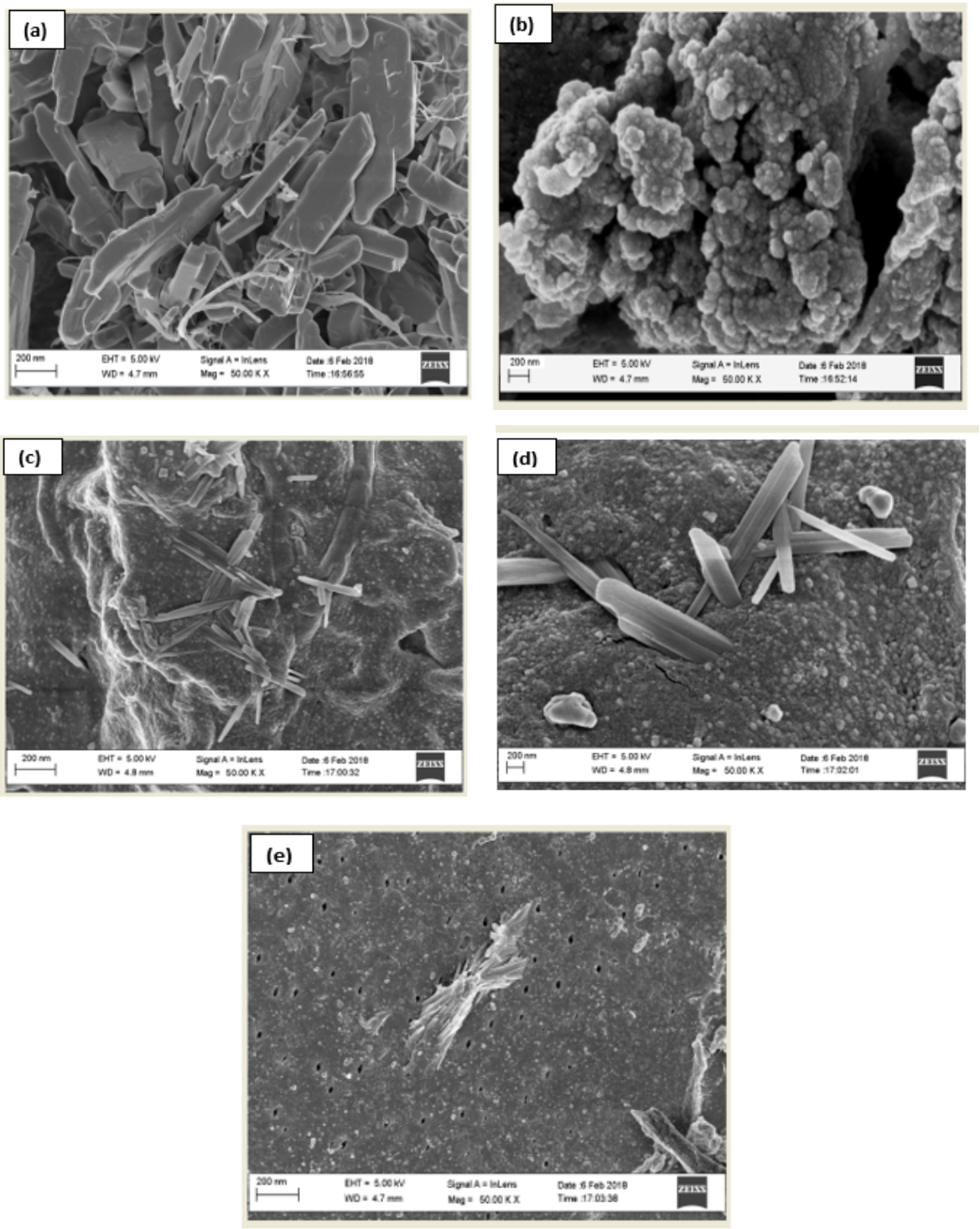
et al. (2014) for silver nanoparticles biosynthesized using olive leaf extract. For the sample, an ash content of 6.43% due to the oxidation of silver nanoparticles to silver oxide (Ag_2O) was observed for the silver nanoparticles. Hence, the prepared silver nanoparticles are more thermally than chitosan. Obviously from the thermal information in Table 2, a higher amount of ash contents of 28.57, 23.27 and 15.47% was obtained for nanocomposites (COMP 1:1, COMP1:2 and COMP 2:1) were respectively obtained at temperatures above 500°C. This means that the incorporation of nanosilver may have increased the thermal stability of silver doped chitosan.From Table 2 it can be seen that the peak degradation temperatures (503.57 and 503.07°C) for a complete breakdown of composites (COMP1:2 and COMP 2:1) were obtained were higher than that of chitosan. This implies that COMP 1:2 and COMP 2:1 had to withstand an additional temperature of about 105°C to completely degrade. This may be attributed to the presence of silver nanoparticles which are known to be high thermal stability (Zhang *et al.,* 2016). Apparently, the TGA results showed that the thermal properties of the nanocomposites are not only dependent on the proportion of the stabilizing agent present but also on the choice of metal nanoparticles as stabilizing agents. Rationally, during the incorporation of stabilizing agent or filler such as nanoparticles into a polymer matrix, rearrangement of the polymer chain usually take place depending on the ratio of the stabilizing agent which tends to affect the inter-plane and intra-plane hydrogen bonds that play an important role in the thermal degradation of the polymer (Yue *et al.,* 2012).

Moreover, the degradation of COMP 2:1 at a higher temperature than COMP 1:2 can also be attributed to the presence of high good dispersion of silver nanoparticles in the sample than in the latter (Borsoi *et al.,* 2016; Sofla *et al.,* 2016). This means that the less agglomerated nanoparticles of silver were better dispersed and incorporated in the chitosan polymer matrix of COMP 2:1 and bound by it more firmly via Lewis acid-base interaction than in the COMP 1:2. As a result, COMP 1:2 was more prone to thermal decomposition than COMP 2:1. More so, even if COMP 1:2 had more proportion of silver nanoparticles than COMP 2:1, proper dispersion is the leading issue (Crews *et al.,* 2016). The results obtained in this work regarding the enhancement of thermal stability of chitosan using nanoparticles agrees with the findings of Fernandes *et al.* (2010) and Liu *et al.* (2015). Similarly, MujeebRahman *et al.* (2018) reported an improvement in thermal stability of the chitosan-based films using metal nanoparticles. This type of higher thermal stability was not observed for chitosan nanocomposites after incorporation with zinc nanoparticles by Subhani *et al.* (2018). This may be attributed to the less thermal stability of zinc nanoparticles compare to silver (Siddiqi *et al.,* 2018). From Table 2, the values of weight loss are not the same for chitosan-silver nanocomposites. The variation in the weight loss could be connected to the different amounts of silver nanoparticles present in the chitosan polymer chains. The results obtained from this study show that the doping of chitosan with nanosilver increases its thermal stability (as shown in initial degradation temperatures). for example, COMP 1:1, COMP 1:2 and COMP 2:1 have initial degradation temperatures of 199.26, 266.68 and 287.98°C respectively, which are higher compared to the 192.96°C obtained for chitosan. Also, the values of degradation temperatures obtained for the nanocomposites show that a small amount of nanosilver is actually required to improve the thermal stability of chitosan.

3.2 Surface Morphology of the Biosynthesized Chitosan and its Nanocomposites

The extracted chitosan alongside biosynthesized silver nanoparticles, as well as the chitosan-silver nanocomposites (COMP 1:1, COMP 1:2 and COMP 2:1), prepared from the combination of both chitosan and silver nanoparticles in different ratios, were analysed using high-resolution scanning electron microscopy (HRSEM) and their micrographs are presented in Plate I (a-e) {(a) Chitosan, (b)

COMP1:1, (c) COMP 1:2, (d) COMP 2:1 and (e) Silver nanoparticles}.From the micrographs in Plate I (a-e), it can be observed that the chitosan and silver nanoparticles which are the starting materials for the formation of the nanocomposites, showed needle-like crystalline structures with smooth surfaces and a cluster of spherical beads-like structures with uniform distribution respectively. The COMP 1:1 on the other hand had a micrograph shown in Plate I (c). The micrograph shows irregular rough surfaces of blended chitosan-silver nanoparticles, with remnants of chitosan on the surfaces.



PlateI: HRSEM micrographs of (a) chitosan, (b) silver nanoparticles (c) COMP1:1, (d) COMP 1:2, (e) COMP 2:1

This is almost the same as COMP 1:2 presented in Plate I (d) except that the surface of the COMP 1:2 are more regular with a broad phase of chitosan embedded in the nanoparticles of silver.

The COMP 2:1 on the other hand has a micrograph shown in Plate I (e). The micrograph shows a series of holes across the surface with remains of chitosan clumped together on the surface. The holes may be attributed to the permeation of the surface by nanoparticles of silver (Slavin *et al.,* 2017).

In general, the HRSEM image of chitosan in Plate I (a) shows a smooth and uneven surface but, after the formation of nanocomposite with silver nanoparticles, the surface becomes rough and porous which signifies that a change had taken place; this trend aligns with a result from a previous study (Jeevanandam *et al*., 2018). In a study by Krishnaveni and Ragunathan (2015), the morphology of chitosan prepared from *F.solani* was portrayed as a needle-shaped semi-crystalline structure with a smooth surface. Meanwhile, the HRSEM image presented in Plate I (b) reveals the formation of a cluster of spherical bead-like nanosilver particles with uniform distribution. Usually, silver nanoparticles are known to exhibit spherical shapes (Lee and Jun 2019). The results for the silver nanoparticles obtained in this study are in agreement with the micrographs obtained by Loo *et al.* (2012), Vanaja *et al.* (2013) and Nazeruddin *et al*. (2016) for biosynthesized nanosilver particles. The presence of some large spherical particles observed may be due to the high surface activity and aggregation of smaller particles of the nanosilver over time (Verma and Mehata, 2016).

Electron dispersive spectroscopy (EDS) is a technique used to examine the presence of elements through the amplitudes of the wavelength of the x-rays emitted after their electrons have been hit by some electron beam (Swapp, 2012). For X-ray to be emitted, the atoms must contain a minimum of K-shell and L-shell where the electron is allowed to dislodge from shell to shell. Therefore, hydrogen, being the only element in the periodic table with only K-shell is not detectable with EDS (Swapp, 2012). Figures 2 a, b, c, d and e show the EDS of chitosan, nanosilver and chitosan–silver nanocomposites (COMP 1:1, COMP 1:2 and COMP 2:1) respectively prepared in this study.

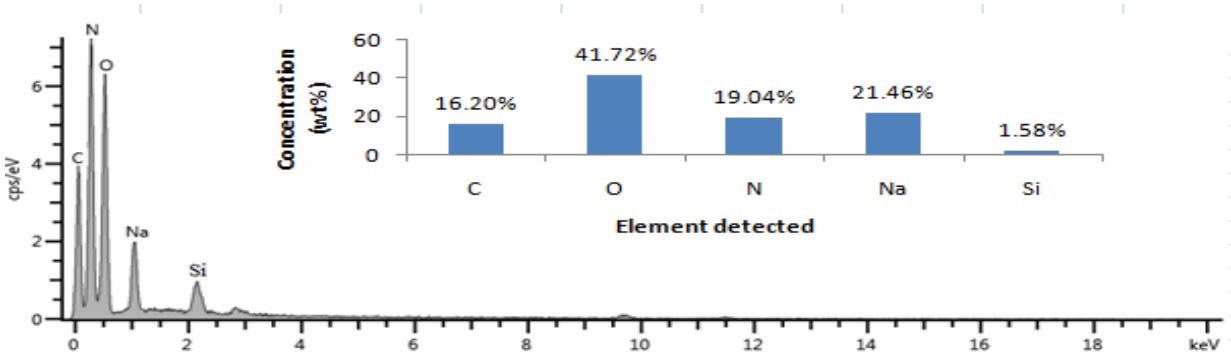


Figure 2a: EDS spectrum of chitosan. The inset is a histogram showing percent distribution of elements.

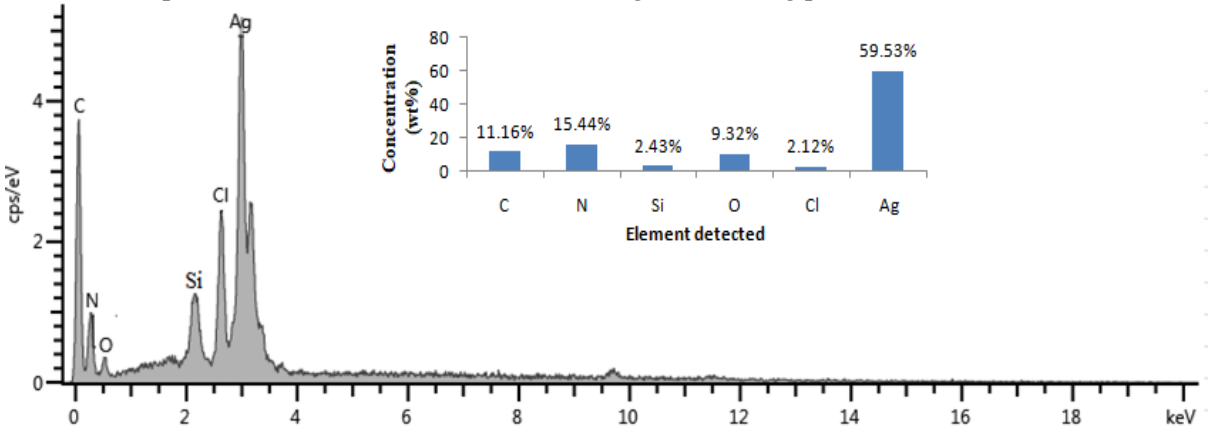


Figure 2b: EDS spectrum of silver nanoparticles. The inset is a histogram showing percent distribution of elements.

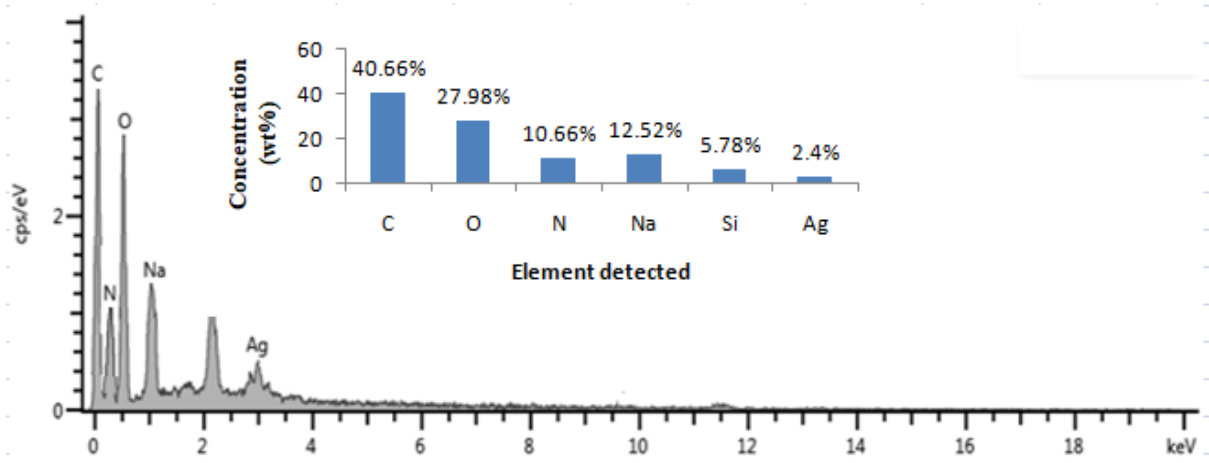


Figure 2c: EDS spectrum of chitosan–silver nanocomposite (COMP 1:1). The inset is a histogram showing percent distribution of elements.

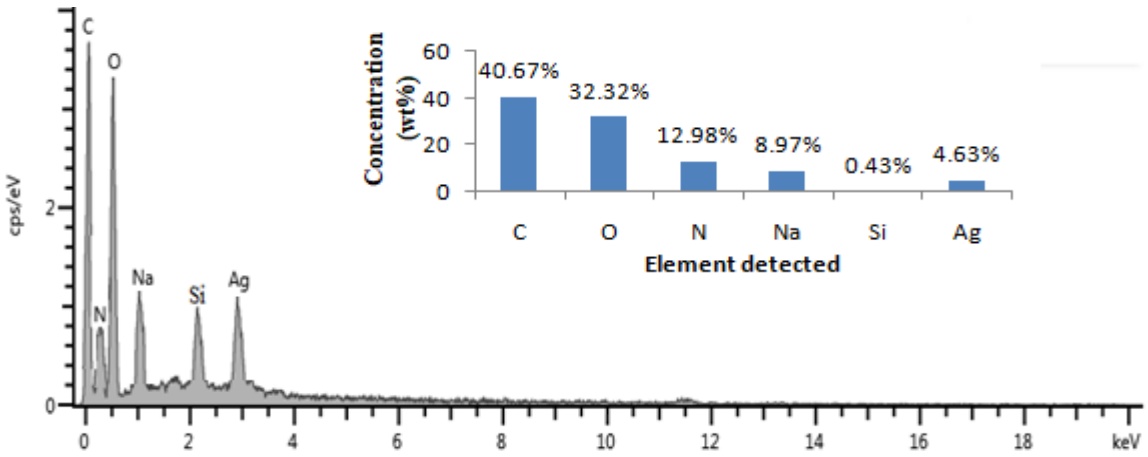


Figure 2d: EDS spectrum of chitosan–silver nanocomposite (COMP 1:2). The inset is a histogram showing percent distribution of elements.

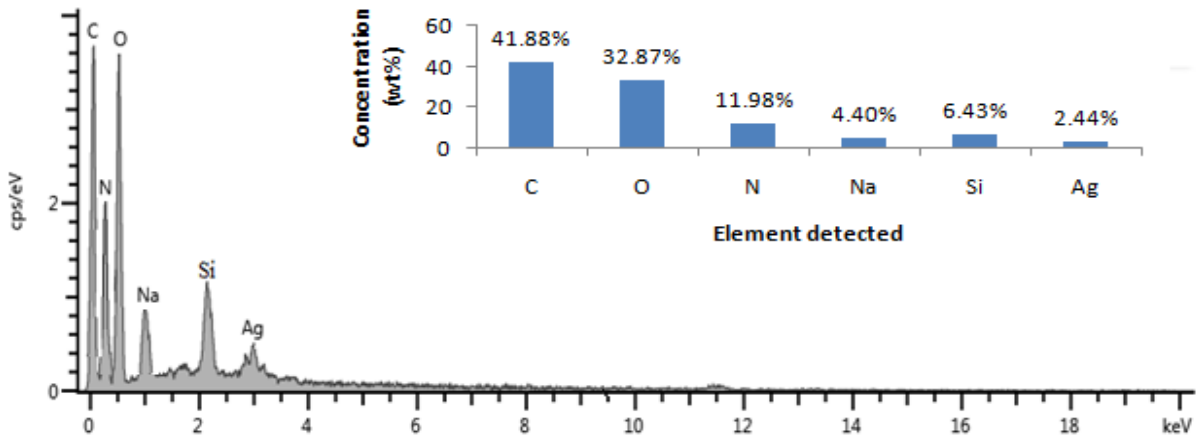


Figure 2e: EDS spectrum of chitosan–silver nanocomposite (COMP 2:1). The inset is a histogram showing percent distribution of elements.

Figure 2a is the EDS for the prepared chitosan showing carbon, nitrogen and oxygen in the surface chemical structure. Figure 2b is the EDS spectrum of the prepared silver nanoparticles. The spectrum shows the presence of the strong signal characteristic of elemental silver around 3 keV which is typical of metallic silver as a result of surface plasmon resonance. The EDS spectra (Figure 2c, d

and e) of chitosan–silver nanocomposites show the peaks for the elements (C, N, O and Ag) that make up both chitosan and silver nanoparticles and their respective percentage weights.

The presence of strong signals of Na in the EDS of chitosan and its nanocomposites is attributed to the strong bond formed by Na as a macronutrient commonly found in both chitosan and plant extracts used in the preparation of nanocomposites (Gaikwad *et al.,* 2015). The EDS result of nanosilver (Figure 2c) shows signals similar to that of chlorine which might have originated from the biomolecules of the leaf extract that are bound to the surface of silver nanoparticles (Ullah *et al.,* 2018). The signal for Cl was not observed in chitosan–silver nanocomposites. This shows that it has been removed through the downstream treatment of the chitosan–silver nanocomposite. Also observed in the EDS of prepared samples are signals similar to silicon which may be attributed to interferences of debris of silicon–lithium detector and hot tungsten filament as components of the machine used for a long time (Teli and Sheikh, 2012).

The presence of nanosilver on the chitosan surface confirmed the successful preparation of the chitosan-silver nanocomposites. The EDS histograms displayed the percentage weight ratios of the elements found on the chitosan surface and the nanosilver concentrations (weight %) on the nanocomposites increased from 0 to 4.63% depending on the preparation ratios.

Conclusion

The thermal stability of chitosan is improved after blending with silver nanoparticles. TGA curves show two significant thermal degradation steps for all chitosan- silver nanocomposites. The surface morphology reveals that the aggregation of silver nanoparticles is decreased with increase in chitosan content and the phase separation occurs due to saturation of silver nanoparticles in chitosan matrix. Pores were observed on the surface of the chitosan blends after formation of nanocomposites.

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Compliance with Ethical Standards: This article does not contain any studies involving human or animal subjects.

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