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Improvement of Polypropylene (PP)-Chitosan Nanoparticles (CNP) for Advanced Bio-Composite

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Abstract: This study delves into the augmentation of polypropylene (PP) with chitosan nanoparticles (CNP) to develop bio-composites tailored for multifaceted applications, particularly in the context of environments. The investigation focuses on characterizing these composites concerning their structural, thermal, degradation, and electrochemical properties. Commercial polypropylene waste obtained from the Federal University of Technology, Akure (FUTA), underwent meticulous processing, converting it into pellets of varying sizes. Chitosan nanoparticles were derived from chitin, procured from a Lagos-based seafood company. These fillers were judiciously chosen for their ability to confer heightened conductivity, cost-effectiveness, biodegradability, and availability. The synthesis involved the preparation of nano-chitosan (CNP) through a method wherein chitosan powder underwent dissolution and subsequent reaction with Sodium Tri-Poly-Phosphate (TPP). Composite blends with different weight percentages of PP and CNP were formulated using a solvent casting method. Fourier Transform Infrared Spectroscopy (FTIR) was employed to discern surface functionalities in the PP/CNP bio-composites. The results revealed significant alterations in functional groups upon the introduction of chitosan nanoparticles into the PP matrix, suggesting chemical modifications within the composite structure. Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) elucidated the thermal behavior of the composites, indicating a decrease in thermal stability with increasing CNP content. Water absorption tests displayed variances in absorption rates, with higher CNP content leading to escalated water absorption capabilities due to the hydrophilic nature of chitosan. Soil biodegradability assessments unveiled a direct correlation between chitosan content and degradation rates, evidencing enhanced biodegradability with higher concentrations of chitosan nanoparticles. Electrochemical measurements via Cyclic Voltammetry depicted a marked increase in specific capacitance with 30% CNP inclusion, signifying improved charge storage capabilities in the composite.

***Keywords*:** biocomposite, chitosan, polypropylene, characterization

1. Introduction

Waste management is one of the greatest problems we face in our environment. Various steps are being taken to ensure waste generated does not cause harm to human health and the environment by using them for various applications. One of these developments is the use of waste for energy generation [1]. The depletion of fossil fuel as

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well as its negative effect on human health and the environment has shifted researchers' attention to the search for alternative energy sources that are renewable, cheap and environmentally friendly. Fuel cell technology is one of the ways of generating energy without any special pollution and negative environmental impacts [1, 2]. Microbial Fuel Cell (MFC) technology utilizes agricultural residue, municipal and industrial waste as carbon in order to minimize the emission of greenhouse gases and global warming [3]. It is a sustainable green technology that can facilitate bio-electrochemical conversion. However, MFC still produces a low power output which limits its commercial applications [4, 5]. Nevertheless, this problem could be solved by modifying the electrode surface area of the MFC using conductive materials of higher surface area such as activated carbon and graphene [4, 6]. Proper optimization of the electrode can increase the application of MFC for commercialization [5].

There is a need to use nanostructure polymeric materials with high surface area for the modification of the surface of carbon-based material in order to improve their ability to create effective interfaces with bacterial attachments [7]. Polypropylene products, a common waste found around us, could be used as matrix binders together with these biomass wastes for composite electrode formation [8]. However, polypropylene products may be limited in certain areas to which they can be used owing to some weak properties such as low electrical conductivity and melt viscosity [9]. Conductive carbon fillers can considerably reduce the polymer resistance [10]. Hence, an agro-derived bio composite made from chitosan nanoparticles with a polypropylene matrix was proposed for use in the preparation of highly functional electrodes for use in fuel cell applications.

In this study, polypropylene and chitosan sourced from chitin was used as precursors for the formulation of Polypropylene Nano-Chitosan based bio composite. The aim of this research is to prepare and characterize Polypropylene Nano- based bio-composite for fuel cell application. According to the literature, there has been no report on PP-CNP bio-composite electrodes for fuel cell applications. The biodegradability of the composite as well as its electrical conductivity would be evaluated and compared to obtain the optimal electrode. Also, the effect of the incorporation of chitosan nanoparticles into the polypropylene was examined, and the optimal value, to get a better composite for use as electrode material in fuel cells, was determined. The derivable benefit of this study is the development of electrode material with high conductivity and biodegradability, as well as ensuring an environmentally friendly way of disposing of wastes.

2. Materials and method

2.1 *Experimental materials*

A commercially available plastic waste, a derivative of polypropylene was used in this study. The research objectives narrowed the preliminary resin selection to commodity polymers, which are commonly available, and have excellent application to the fuel cell environment. Fillers from chitosan nanoparticles, derived from chitin, were used in conjunction with a polypropylene matrix to form electrically conductive bio-composites. The choice of fillers for this research is based on their ability to impart high conductivity to the composites, effective biodegradability while still maintaining a relatively low cost and high availability.

2.2 *Sourcing and collection of materials*

Polypropylene waste used in this study was obtained from the Federal University of Technology, Akure (FUTA) community. It was washed thoroughly and shredded into pellets (sizes 1.69 mm and 3.21 mm) at ZL Alliance Global, Alagbaka Akure, Nigeria. Chitosan was obtained from a seafood company in Lagos, Nigeria with the average size of 80 mm and a degree of DE acetylation (DD) of 81%.

2.3 *Sample preparation*

2.3.1 *Preparation of Nano chitosan*

Nano Chitosan CNP was prepared using Daramola and Adelaja's [11] modified method. 30 g of Chitosan powder was dissolved in 2 L of 2% volume of acetic acid. It was stirred for 24 h at 60 °C and TPP solution was prepared by dissolving 73.4 g of Sodium Tri-Poly-Phosphate (TPP) in 2 L distilledwater. Chitosan solution was then added to Sodium

Tri-Poly-Phosphate (TPP) solution in drops togive a final ratio of 1:1 (CS: TPP). The resultant sample (Chitosan Nanoparticle CNP) was then filtered and washed severally with distilled water which was made to stand for a day before being filtered with a sintered glass. Obtained samples were then oven-dried for 48 h and grinded to powder.

2.3.2 *Polypropylene composite blend formulation*

The blend formulation for the preparation of the PP/CNP composite was done by varying the percentage weight of PP and CNP in ratios 100:0, 90:10, 80:20, 70:30, 60:40 to obtain an optimal sample where PP/unfilled (100:0) was used as the CONTROL.

For the blending, the solvent casting method as carried out by Siemann [12] was employed. Polypropylene (PP) was dissolved in 0.067 g/ml Xylene at 164 °C using a magnetic stirrer hot plate. Fillers (CNP) were added to the dissolved PP. It was allowed to cool down and was poured into a mold [13]. The resulting blend; bio-composite was sundried to drain the organic solvent left in the sample. This method was carried out for the entire formulations as shown in Table 1. The optimized sample was then selected after being subjected to analytical tests.

Table 1. Blend formulation for PP/CNP composite sample

Designation	Sample
A0	PP
A1	PP/CNP 10%
A2	PP/CNP 20%
A3	PP/CNP 30%
A4	PP/CNP 40%

2.4 *Material characterization of bio-composites*

2.4.1 *Fourier transform infrared spectroscopy (FTIR)*

This was used for the physiochemical characterization of the composite. It was used to identify the surface functionalities of the prepared PP/CNP bio-composite samples. 0.5 g of the sample was mixed with 0.5 g of potassium bromide (KBr powder), after which 1mL of nujol (a solvent for preparation of sample by Buck 530 IR-spectrophotometer) was pipetted into the sample with the aid of a syringe to form a paste before introducing it into the instrument sample mould and allowed to scan at a wavelength of 600-4,000 cm^{-1} to obtain its spectra height.

2.4.2 *Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)*

Thermogravimetric analysis (TGA) is a technique to determine the change in weight as a function of temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change. Differential Scanning Calorimetry (DSC) measures the heat flow into or out of a sample as it is heated or cooled. TGA/DSC analysis can provide information on the thermal stability, decomposition behavior, and phase transitions of materials [11]. Here, TGA and DSC were conducted following the method of Zhang [14] using UW_MSE TA Instruments TGA Q50 for the analysis with dynamic drift of < 50 ug from 50-1,000 °C at 20 °C/min with an empty Pt pan and an instrument temperature precision of +/- 0.1 °C.

2.4.3 *Water absorption characteristics*

The water absorption test of PP/CNP bio-composites was carried out according to the modified method of Raheem

[15]. Each sample of PP/CNP was cut and weighed on an electric balance capable of reading 0.0001 g. 250 mL of distilled water was measured and poured into a plastic cup and the samples were submerged into the water and kept at 25 °C. The samples were removed after 24 h for seven days and the weight gain of the samples was measured at different time intervals using Equation 1.

$$Increase\ in\ weight\ (\%) = \frac{Wet\ Weight - Condition\ Weight}{Condition\ Weight} \times 100 \tag{1}$$

2.4.4 *Biodegradability test*

The PP/CNP bio-composite samples obtained were evaluated for their biodegradability using soil burial, a modified method in Adelaja and Babaniyi [16]. The soil used in this test was assessed for its composition/profile. The acidic, salinity and moisture content of the soil was determined respectively. 3 kg of the soil sample was used for the soil degradation test. PP/CNP bio-composites were weighed and buried into already filled pots with soil 2 cm beneath the surface under laboratory conditions. The soil was regularly irrigated with clean water to maintain stable humidity. After a predetermined degradation time (30 days, 60 days and 90 days), the samples were carefully removed from the soil, cleaned with water and dried. The dried samples were weighed to calculate the weight loss using Equation 2.

$$\%Mass\ loss = \frac{Mi - Mf}{Mi} \times 100 \tag{2}$$

Where Mi = initial mass; and Mf = final mass.

2.4.5 *Electrochemical measurement*

Electrical conductivity which is the ability of the bio composite to conduct an electrical current over a defined area, was evaluated to determine its conductive capacity in aqueous environment using a Cyclic Voltammetry. It was carried out using a conventional three-electrode cell, with Pt rod and Ag/AgCl electrode as counter and reference electrodes, respectively. Cyclic voltammetry (CV) was performed on an Autolab potentiostat/galvanostat at a scan rate of 100 mV/s in 0.5 M H_2S electrolyte, with a potential window of -1 to 1 V. The corresponding specific capacitance (Csp) of the PP/CNP electrode can be calculated by the equation below:

$$C_{sp} = \frac{A}{2mkV} \tag{3}$$

Where A = current; m = mass; k = scan rate; V = potential window.

3. Results and discussion

3.1 *Fourier transform (FTIR) spectroscopy*

The FTIR spectrum for the pristine sample (A0) is shown in Figure 1. The FTIR spectrum has absorption peaks at 1,714.6 cm^{-1} due to the carbonyl stretch (C = 0) which is typical of aldehydes, ketones, esters and carboxylic group; 2,967.0 cm^{-1} to C-H bonds in alkanes and alkyls groups; 1,576.7 cm^{-1} to C=C stretch of the aromatic compounds such as benzene rings; 1,457.4 cm^{-1} to bending vibrations of methyl (CH_3); 1,241.2 cm^{-1}, 1,095.8 cm^{-1}, and 1,017.6 cm^{-1} to C-O bonds.

The propylene monomer, from which polypropylene (PP) is derived, contains a functional group known as an alkene or a carbon-carbon double bond (C=C). Although PP itself does not contain any additional functional groups, these functional groups are likely incorporated through the chemical processes involved during the preparation of the composite. After the introduction of chitosan nanoparticles (CNP) to the polypropylene (PP) as the polymeric matrix for the synthesis of the PP/CNP composite, the following FTIR spectra were seen as shown in Figure 2-5. In sample A1 (as shown in Figure 2: A1), the following additional peaks were found to be present: 1,505.8 cm^{-1} which is attributed to the N-H bending vibration, indicating the presence of amine functional groups; 2,959.5 cm^{-1} to C-H stretching vibration of aliphatic hydrocarbons; 1,449.9 cm^{-1} to CH_2 bending vibration; 1,408.9 cm^{-1} to C-N stretching vibration, typically found in amine or amide groups, which was confirmed by the peak at 1,088.4 cm^{-1}; 1,237.5 cm^{-1} and 1,013.8 cm^{-1} to C-O stretching vibration, indicating the presence of ether or ester functional group. The introduction of chitosan nanoparticles in sample A1 has led to the emergence of additional functional groups, such as amine groups (N-H bending vibration) from chitosan, as indicated by the appearance of peaks at 1,505.8 cm^{-1}. The presence of ether or ester functional groups is also suggested by the appearance of peaks at 1,237.5 cm^{-1} (C-O stretching vibration) and 1,013.8 cm^{-1} (C-O stretching vibration). These changes in functional groups may be attributed to the incorporation of chitosan nanoparticles into the polypropylene matrix [11].

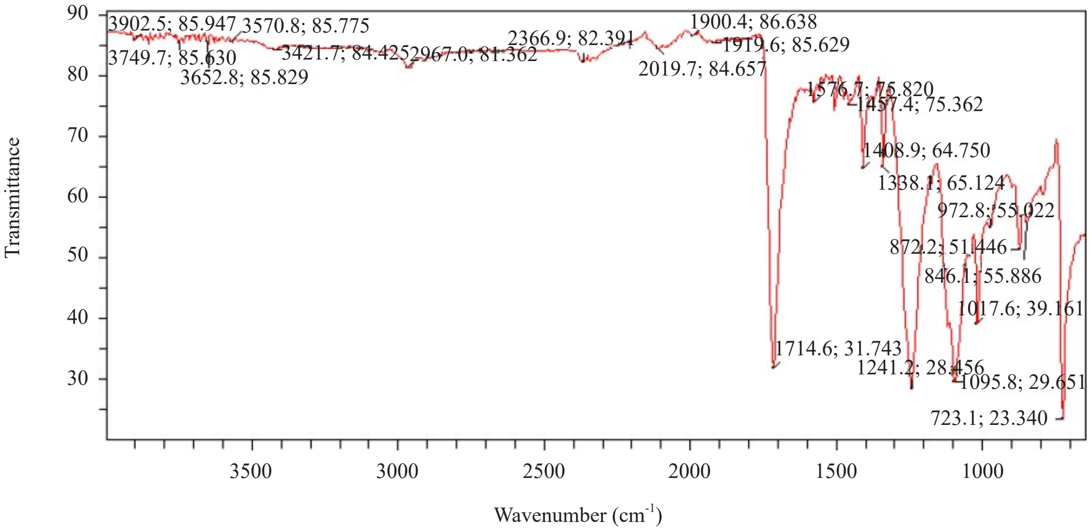


Figure 1. FTIR diagram of sample A0

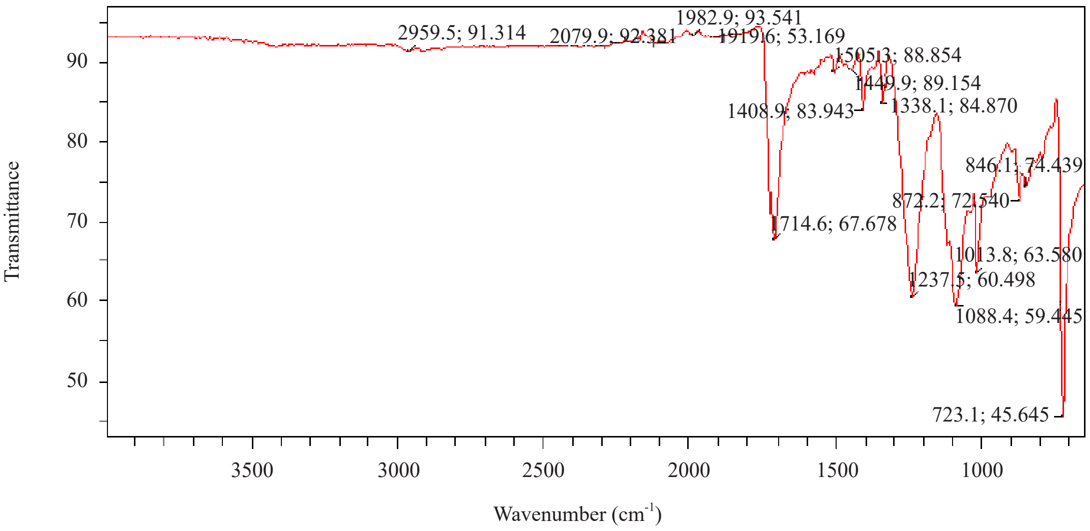


Figure 2. FTIR diagram of sample A1

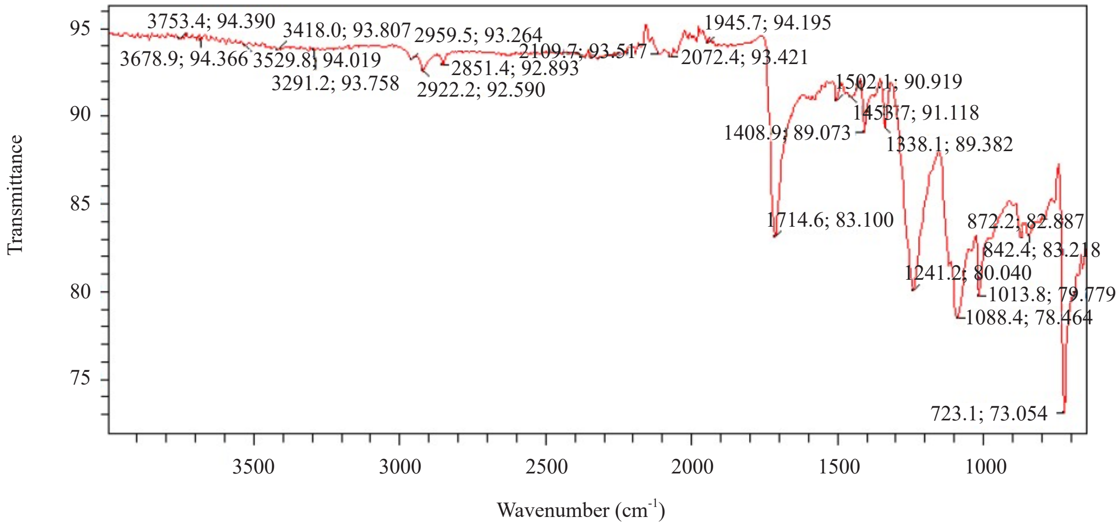


Figure 3. FTIR diagram of sample A2

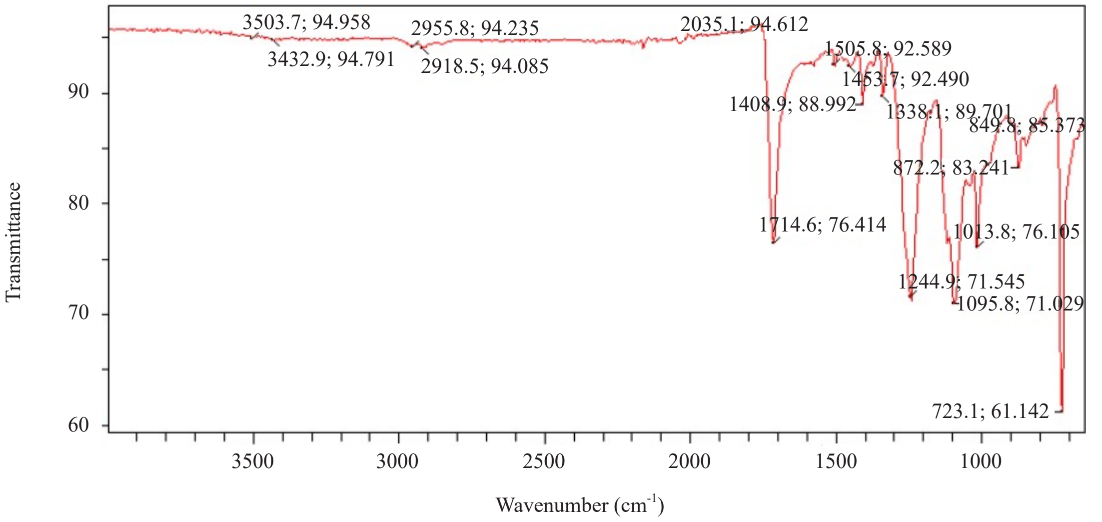


Figure 4. FTIR diagram of sample A3

More so, in the sample A2, additional wavenumbers were found within the sample. The peak at 1,502 cm^{-1} corresponds to the N-H bending vibration, indicating the presence of amine functional groups; 2,851.4 and 2,959.5 cm^{-1} correspond to the C-H stretching vibration of aliphatic hydrocarbons, which was confirmed by the C-H bending vibration of aliphatic hydrocarbons found at 1,338.1 cm^{-1}. The peak at 1,408.9 cm^{-1} reveals the C-N stretching vibration, typically found in amine or amide groups, which was confirmed by the peak at 1,088.4 cm^{-1}; 1,241.2 cm^{-1} and 1,013.8 cm^{-1} to C-O stretching vibration, indicating the presence of ether or ester functional groups. The introduction of 20% chitosan nanoparticles in A2 results in the emergence of additional functional groups compared to the control sample (A0). These changes in functional groups observed in A2 compared to A0 are likely attributed to the incorporation of chitosan nanoparticles into the polypropylene matrix. The presence of chitosan introduces new functional groups, such as amine groups, ether or ester groups, and potentially other unidentified groups [17]. These changes in functional groups can have implications for the properties and performance of the polypropylene-chitosan composite.

Also, when the amount of chitosan nanoparticle was increased to 30% as observed in sample A3, the following additional functional group were found: 1,505.8 cm^{-1} to N-H bending vibration, indicating the presence of amine functional groups; 1,408.9 cm^{-1} to C-N stretching vibration, typically found in amine or amide groups; 2,918.5 cm^{-1} and 2,955.8 cm^{-1} to C-H stretching vibration of aliphatic hydrocarbons; 3,503.7 cm^{-1} and 3,432.9 cm^{-1} to O-H stretching vibration of hydroxyl groups; 1,453.7 cm^{-1} to CH_2 bending vibration; 1,244.9, 1,095.8 and 1,013.8 cm^{-1} attributed to C-O stretching vibration associated with ether or ester functional groups. The introduction of 30% chitosan nanoparticles in sample A3 leads to the appearance of additional functional groups compared to the control sample (A0). These changes in functional groups are a result of incorporating chitosan nanoparticles into the polypropylene matrix, contributing to the modified chemical composition and potential interactions between chitosan and polypropylene.

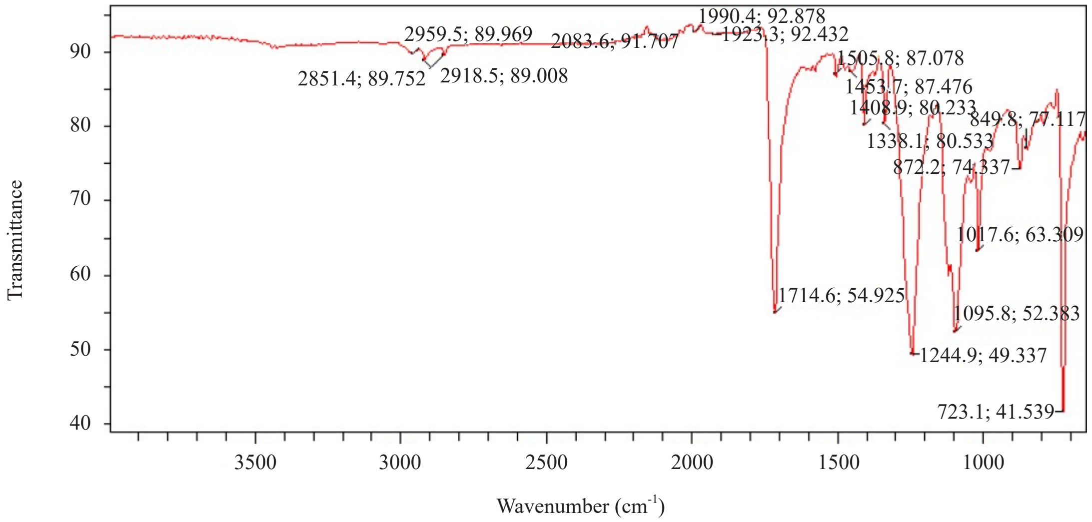


Figure 5. FTIR diagram of sample A4

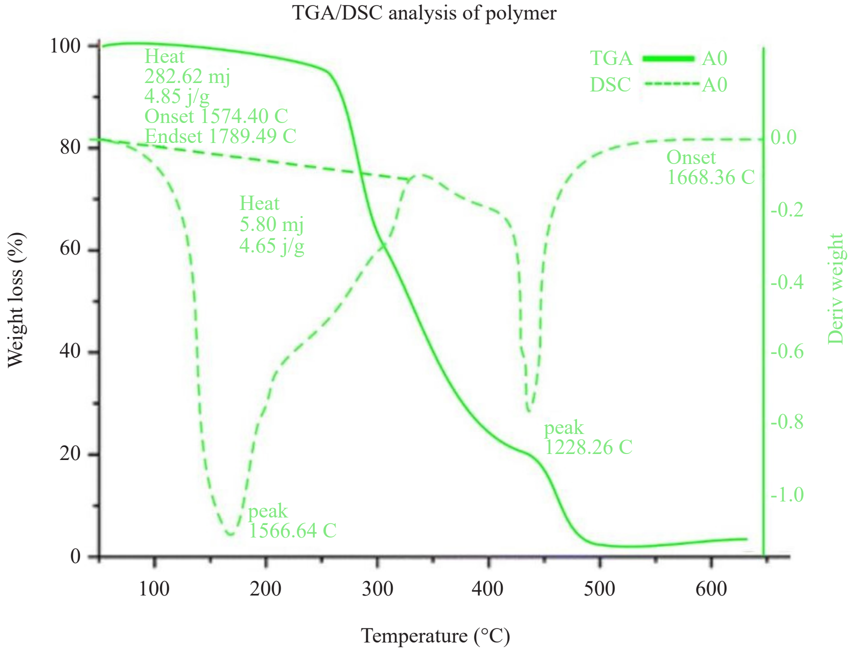
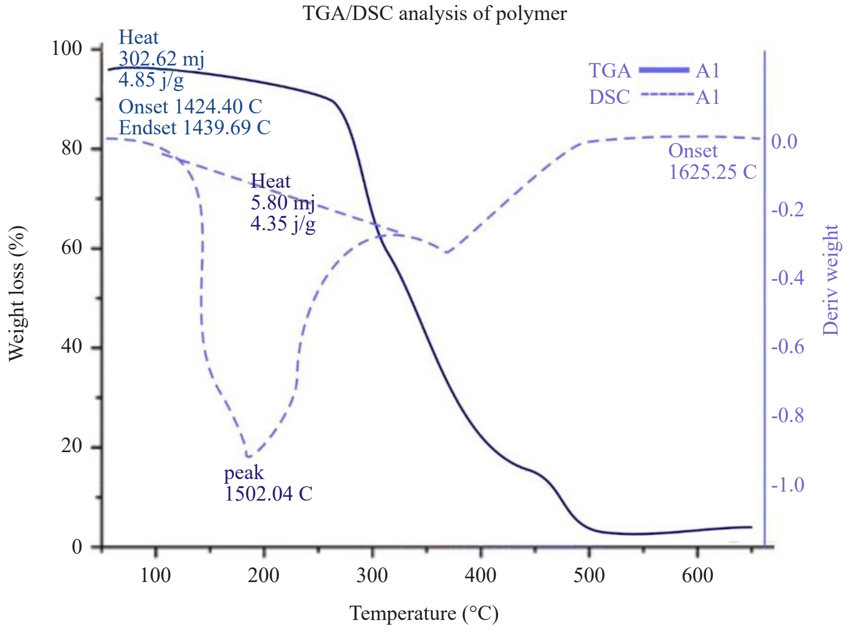
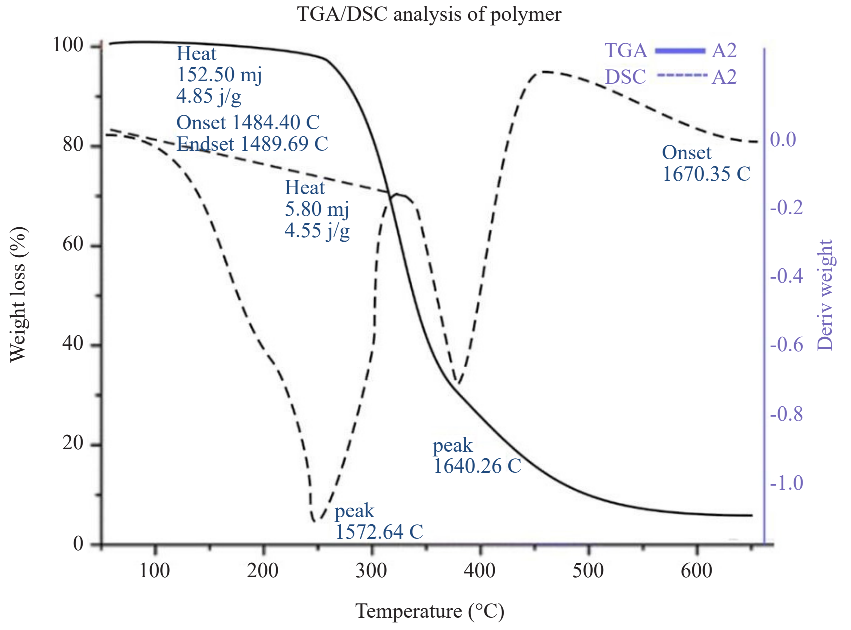


Figure 6. TGA/DSC analysis of the pristine (A0) sample

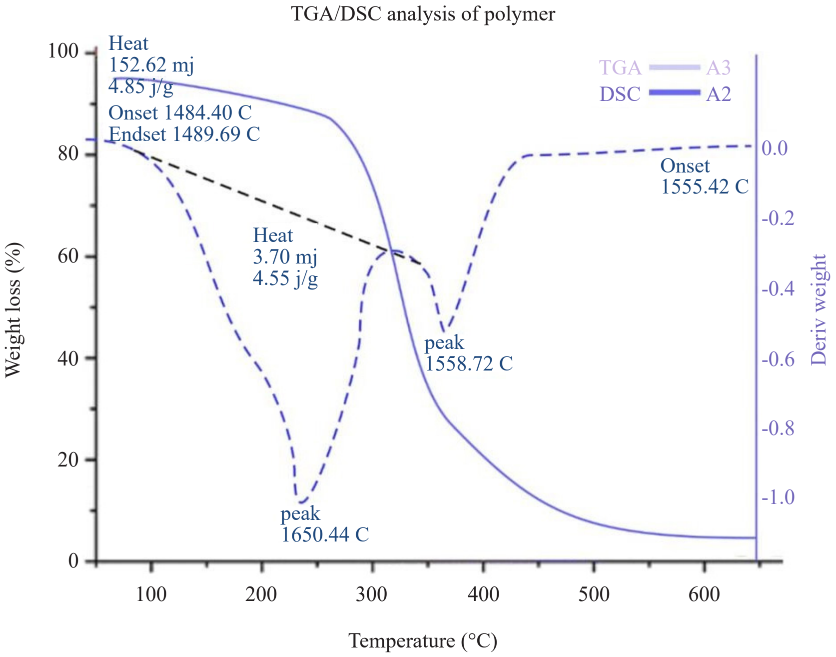
In sample A4 (shown in Figure 5), the peak with wavenumber 1,505.8 cm^{-1} corresponds to N-H bending vibration, indicating the presence of amine functional groups, while 2,959.5 and 1,338.1 cm^{-1} reveals the C-H stretching and bending vibration of aliphatic hydrocarbons, respectively. Wavenumber 1,408.9 cm^{-1} can be attributed to C-N stretching vibration, typically found in amine or amide groups; 1,244.9 cm^{-1} to C-O stretching vibration, indicating the presence of ether or ester functional groups; 1,449.9 cm^{-1} reveals CH_2 bending vibration. The changes in functional groups observed in sample A4, compared to A0, can be attributed to the incorporation of a higher percentage of chitosan nanoparticles in the polypropylene matrix. The presence of chitosan nanoparticles introduces amine or amide groups and potentially other unidentified functional groups, leading to modifications in the chemical composition and properties of the polypropylene- chitosan composite.



(a)



(b)



(c)

Figure 7. TGA/DSC analysis of the synthesized composites. (a) TGA/DSC analysis of the PP/CNP 10% composite (sample A1), (b) TGA/DSC analysis of the PP/CNP 20% composite (sample A2), (c) TGA/DSC analysis of the PP/CNP 30% composite (sample A3)

Overall, the addition of chitosan nanoparticles in samples A1, A2, A3, and A4 introduces specific functional groups associated with chitosan. The presence of chitosan-related functional groups (introduced by the addition of chitosan nanoparticles), along with the observed peaks related to carbonyl groups (possibly from the polypropylene matrix or other components used in the samples), ether or ester groups, and aliphatic hydrocarbons, suggests that the addition of chitosan nanoparticles has modified the chemical composition of the polypropylene matrix. These changes in functional groups can potentially influence the properties and performance of the polypropylene-chitosan composite. The presence of chitosan in the composite material can potentially enhance its mechanical, thermal, and barrier properties due to the unique properties of chitosan, through the formation of new bonds, such as ether or ester linkages, which can affect the material's properties. The FTIR analysis provides valuable information about the functional groups present in the polypropylene-chitosan composites and the potential chemical interactions occurring within the material. This information is essential for understanding the structure-property relationships and tailoring the properties of the composite material for various applications.

3.2 *Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC)*

Thermogravimetric analysis (TGA) and Differential Scanning Calorimetry (DSC) were used to investigate the thermal behavior of the pristine sample (A0) and the synthesized PP/CNP composites (A1, A2, and A3) and are shown in Figure 6 and Figure 7, respectively. The TGA curves show the weight loss of the samples as they are heated from room temperature to 600 °C under a nitrogen atmosphere, while the DSC curves show the heat flow of the samples as they are heated from room temperature to 200 °C under a nitrogen atmosphere. Figure 6 shows the TGA/DSC results of the pristine sample (A0). The TGA curve shows that the sample undergoes a single stage of weight loss, which can be attributed to the decomposition of the material. The DSC curve shows a single endothermic peak, which can be attributed to the melting of the material. The TGA/DSC results of the pristine sample provide a baseline for comparison with the synthesized PP/CNP composites. Figure 7 shows the TGA/DSC results of the synthesized PP/CNP composites (A1, A2, and A3).

The TGA curves show that the weight loss of the composites increases with increasing CNP content. This indicates that the thermal stability of the composites decreases with increasing CNP content. The TGA curves also show that the composites undergo two stages of weight loss, which can be attributed to the decomposition of the CNP and the PP matrix, respectively. The DSC curves show two endothermic peaks, which can be attributed to the melting of the PP matrix and the decomposition of the CNP, respectively. The melting temperature of the PP matrix decreases with increasing CNP content, which indicates that the addition of CNP affects the crystallization behavior of the PP matrix.

The TGA/DSC results of the synthesized PP/CNP composites provide valuable information on their thermal behavior, which can have implications for their performance in different applications. The decrease in thermal stability with increasing CNP content suggests that the composites may not be suitable for high-temperature applications. The effect of CNP on the crystallization behavior of the PP matrix may also affect the mechanical properties of the composites. This result is similar to the findings of Adeniyi et al. [11, 18].

Overall, the TGA/DSC analysis can help optimize the composition and processing conditions of PP/CNP composites for specific applications by providing insights into their thermal behavior. The use of waste materials as a substrate for microbial fuel cells can provide a sustainable source of energy while also addressing the issue of waste management. This technology has the potential to contribute to the development of a circular economy, where waste is transformed into a valuable resource.

3.3 *Water absorption*

The water absorption test measures the amount of water absorbed by the samples over time. In this case, Table 2 shows the result of the five composite samples (A0, A1, A2, A3, and A4) and their respective weights in grams on each day of the test. The water absorption test results provide valuable insights into the behavior of the samples regarding their ability to absorb water [19]. Understanding the water absorption characteristics of materials is crucial in various fields, including construction, manufacturing, and materials science.

Table 2. Water absorption of the PP-CNP composite

Sample	Weight gain (g)							
	Day 0	Day 1	Day 2	Day 3	Day 4	Day 5	Day 6	Day 7
A0	3	3.01	3.02	3.03	3.04	3.04	3.05	3.05
A1	3	3.03	3.06	3.07	3.09	3.1	3.11	3.11
A2	3	3.03	3.05	3.09	3.1	3.1	3.11	3.11
A3	3	3.03	3.03	3.05	3.06	3.07	3.07	3.07
A4	3	3.04	3.07	3.09	3.1	3.11	3.11	3.11

From the result, all samples show an increase in weight over time, indicating water absorption. The rate of water absorption varies between the samples, with some samples absorbing water at a faster rate than others. The observed variations can be attributed to factors such as material composition, structural characteristics, porosity, surface properties, and environmental conditions [1].

Sample A0 shows a gradual increase in weight over the course of the test. The weight increases by 0.01 g on each consecutive day, suggesting a consistent water absorption rate. This behavior indicates that the sample may have a uniform structure or a relatively homogeneous distribution of pores or voids, allowing water to penetrate at a steady pace. Pristine polypropylene (sample A0) typically exhibits low water absorption due to its hydrophobic nature [20]. The water absorption test data for sample A0 was used as a baseline to evaluate the impact of chitosan nanoparticle content on water absorption.

Sample A1 contains 10% chitosan nanoparticles in the polypropylene matrix. Chitosan nanoparticles have hydrophilic properties, which can enhance the water absorption characteristics of the composite material [21]. The incorporation of 10% chitosan nanoparticles into the polypropylene matrix led to an increase in the water absorption capacity of the composite, by functionalizing the hydrophobic polypropylene with the hydrophilic chitosan [20]. The weight of sample A1 gradually increases over the seven-days, reaching 3.11 g on Day 7. This indicates that the composite material can absorb and retain water over time. Sample A2 contains 20% chitosan nanoparticles, further increasing the chitosan nanoparticle content in the polypropylene matrix. The higher concentration of chitosan nanoparticles enhances the hydrophilicity of the composite material, promoting greater water absorption. This trend was also observed in samples A3 and A4, thus demonstrating that the incorporation of a higher percentage of chitosan nanoparticles into the polypropylene matrix results in a greater water absorption capability. The hydrophilic nature of chitosan nanoparticles promotes water absorption by creating additional pathways for water molecules to enter the composite material [22]. The porous structure of chitosan nanoparticles allows for water penetration and retention within the composite matrix, leading to an increase in weight over time. These trends are similar to those obtained by literature [19, 20, 23].

Furthermore, the constant weight observed at certain points in each sample during the water absorption test, regardless of the duration in water, could be indicative of the saturation point being reached or the presence of a water-impeding barrier which can create a barrier or hinder the diffusion of water molecules into the polypropylene matrix. These could result in a slower rate of water absorption, causing the weight to remain relatively constant during certain periods. It is important to note that the saturation point and the rate of water absorption can be influenced by factors such as the size, distribution, and surface characteristics of the chitosan nanoparticles, as well as the processing conditions used to prepare the composites.

These findings are consistent with previous studies on chitosan-based composites, which have shown that the incorporation of chitosan nanoparticles improves the water absorption properties of polymer matrices. The hydrophilicity, biocompatibility, and porous structure of chitosan nanoparticles contribute to their water absorption capabilities [20, 24]. It's worth noting that the water absorption behavior can be influenced by various factors, including the size and morphology of chitosan nanoparticles, the processing techniques used to prepare the composites and environmental conditions such as temperature and humidity. Additionally, the duration of the water absorption test may impact the observed weight changes and the saturation point of the composites [23]. Understanding the water absorption behavior of chitosan-polypropylene composites is crucial for applications where water resistance or controlled water absorption is desired.

3.4 *Soil biodegradability test*

Soil biodegradability tests are typically performed to evaluate the degradation or breakdown of a material in soil environments. In the case of a polypropylene-chitosan composite, this test assessedthe biodegradability of the composite material when exposed to soil conditions. The weight loss method of assessment (as shown in Table 3) is an indication of the extent of biodegradability ofthe polypropylene-chitosan composites in soil [25].

Table 3. Soil biodegradability of the PP-CNP composite samples

Sample	Initial weight (WB)	Final weight after being buried (WA)		
		30 days	60 days	90 days
A0	3 g	2.61 g	2.4 g	1.84 g
A1	3 g	2.54 g	1.74 g	1.09 g
A2	3 g	2.44 g	1.68 g	1.02 g
A3	3 g	2.42 g	1.69 g	1.04 g
A4	3 g	2.31 g	1.64 g	1.01 g

The results from the table indicate the weight loss of the composite samples over 90 days. Weight loss is often considered an essential parameter to assess the biodegradability of materials, as it reflects the extent of degradation and breakdown in a particular environment. Comparing the weight loss values, it is evident that the pristine polypropylene sample (A0) experienced the least weight loss, indicating slower degradation compared to the composite samples. This can be attributed to the absence of chitosan nanoparticles, which are known for their biodegradable properties. The data suggests that the pristine polypropylene retains its mass more effectively in the soil environment compared to the composite samples containing chitosan nanoparticles.

In contrast, samples A1 to A4, which contain increasing percentages of chitosan nanoparticles, demonstrate higher weight loss (Figure 8). This indicates that the incorporation of chitosan nanoparticles contributes to the enhanced biodegradability of the composite materials. Chitosan, a natural polymer derived from chitin, has been widely investigated for its biodegradable properties and has shown potential in various biomedical and environmental applications [25]. The increasing weight loss trend with higher chitosan nanoparticle content suggests that chitosan plays a significant role in promoting the degradation of the polypropylene-chitosan composites in the soil environment. The biodegradation process is likely facilitated by the microbial activity present in the soil, which interacts with the chitosan component of the composites. Chitosan, being a natural polysaccharide, is known to be susceptible to microbial degradation [26]. Furthermore, the rate of biodegradation can be influenced by various factors such as soil composition, temperature, moisture content, and the presence of microorganisms. Understanding the effects of these factors on the biodegradation behavior of polypropylene-chitosan composites can provide valuable insights into their performance in different soil environments.

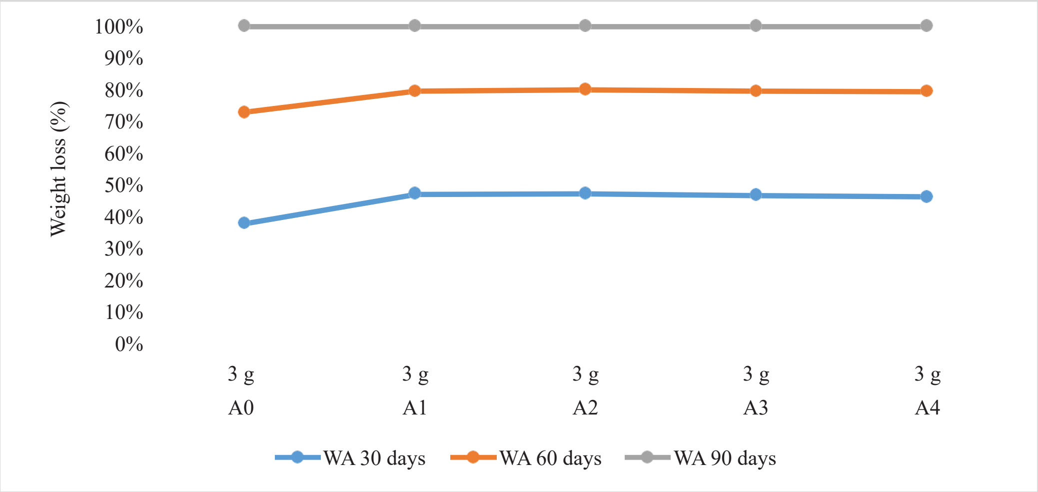


Figure 8. Percentage weight reduction of the buried PP-CNP composite

The percentage weight loss at 30 days indicates the initial degradation of the composite samples. Higher percentages suggest a higher degree of degradation. In this case, Sample A4 exhibits the highest weight loss at 30 days, indicating faster degradation compared to the other samples. At 60 days, the degradation process continues, and the percentage of weight loss increases further. Samples A1, A2, A3, and A4 demonstrate significantly higher weight loss compared to the control sample (A0). This indicates that the addition of chitosan nanoparticles in varying concentrations accelerates the degradation process. After 90 days, the percentage of weight loss reaches its peak, indicating the extent of degradation. All samples show substantial weight loss compared to the initial weight. Notably, samples A1, A2, A3, and A4 exhibit significantly higher weight loss compared to the control sample (A0). This suggests that higher concentrations of chitosan nanoparticles contribute to enhanced biodegradability.

Overall, the results demonstrate that as the concentration of chitosan nanoparticles increases in the polypropylene-chitosan composites (from A1 to A4), the percentage weight loss and rate of degradation also increase. These findings align with previous studies that have reported the positive influence of chitosan on the biodegradation of polypropylene composites [27, 28]. These findings have practical implications for the development and optimization of biodegradable composite materials. By adjusting the chitosan nanoparticle content, it is possible to tailor the composite's biodegradability to meet specific requirements or environmental considerations.

3.5 *Electrochemical characterization*

The electrochemical performance of the PP-Chitosan composite samples was examined using Cyclic Voltammetry (CV) and the result of the CV profile is presented in Figure 9 (a and b). The CV profile of the pristine sample (A0) displayed a distinctive spiral shape with two peaks at the cathode (reduction) side. The spiral shape suggests an irreversible redox reaction, indicating that the reactants undergo an irreversible transformation at the electrode surface. The presence of two cathodic peaks at the reduction side indicates a two-step reduction process, which likely involves different redox reactions occurring sequentially.

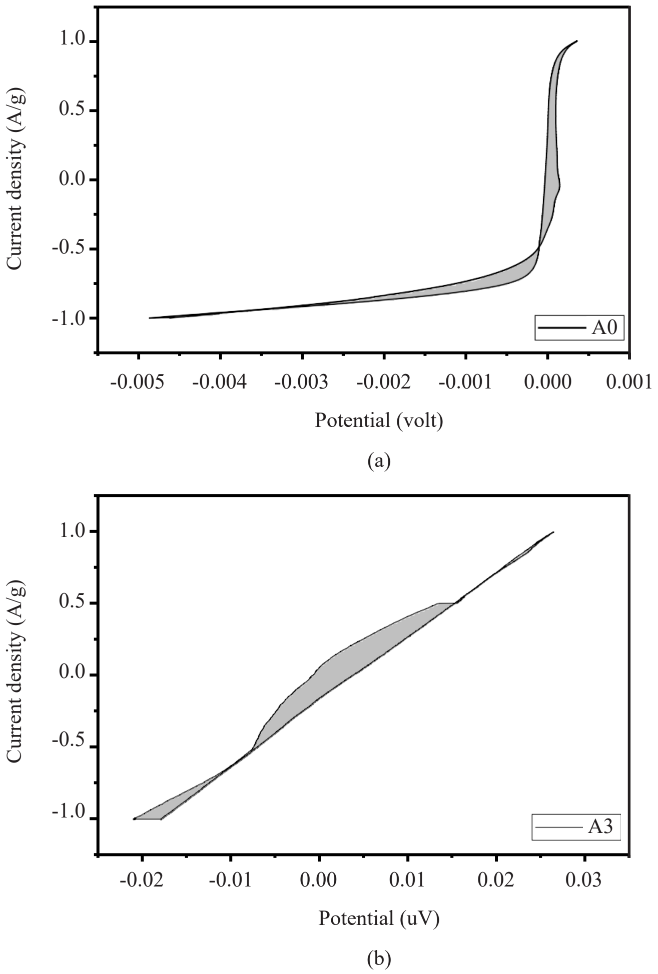


Figure 9. Cyclic voltammetry plot of the synthesized composites. (a) CV profile of the pristine (A0) sample, (b) CV profile of the optimized PP-chitosan composite sample (A3)

On the other hand, the CV profile of the composite sample (A3) exhibits a truncated semi-circle shape, with a sharp peak at the oxidation (anode) side and a smaller peak at the reduction (cathode) side. Additionally, there is a wide separation in electrochemical potential between the oxidation and reduction peaks. The truncated semi-circle shape in the CV profile indicates a reversible redox reaction, suggesting that the reactants can easily interconvert between their oxidized and reduced states at the electrode surface. This behavior is often associated with a capacitive charge storage mechanism, where charge accumulation and release occur without significant changes in the material's structure.

The presence of asymmetric peak heights and the wide electrochemical potential separation between the oxidation and reduction peaks imply a quasi-reversible behavior. This suggests that the forward and reverse redox reactions have different rates, likely due to factors such as slow electron transfer kinetics, concentration gradients of the reactants, or adsorption effects at the electrode surface.

Furthermore, the results of the cyclic voltammetry (CV) analysis for samples A0 (pristine polypropylene) and A3 (polypropylene with 30% chitosan nanoparticle) show a significant difference in specific capacitance. Sample A3 exhibited a much higher specific capacitance of 215.4 F/g, whereas sample A0 displayed a lower specific capacitance of 0.644 F/g. The presence of a specific capacitance in the pristine polypropylene sample (A0), which is generally considered non-conductive, may be attributed to the existence of impurities, surface functional groups, or defects in the polypropylene film. These factors could lead to some degree of electrical conductivity, resulting in the detection of a small but detectable specific capacitance value. In contrast, the enhanced specific capacitance observed in sample A3 can be attributed to the inclusion of chitosan nanoparticles. Chitosan, being a conductive biopolymer, can improve the electrical conductivity of the composite material, leading to an increased specific capacitance value. The chitosan nanoparticles may provide additional active sites for redox reactions and facilitate charge transfer kinetics, thereby boosting the overall electrochemical performance.

4. Conclusion

The use of waste materials such as polypropylene and chitosan nanoparticles for the synthesis of composite electrode materials has the potential to revolutionize the field of sustainable energy production. By transforming waste into a valuable resource, the environmental impact of waste disposal can be reduced while also providing a sustainable source of energy. More so, the results of this study demonstrate that the incorporation of chitosan nanoparticles into the polypropylene matrix can improve the electrical conductivity and biodegradability of the composite, making it an ideal material for use in fuel cells. This suggests that the use of nanofillers in composite materials can enhance their performance and sustainability, opening up new possibilities for the development of advanced materials for energy applications. Furthermore, the findings of this study highlight the importance of sustainable waste management practices and the potential of using waste materials as a source of renewable energy. By adopting a circular economy approach to waste management, a more sustainable and resilient energy system could be created that benefits both the environment and society. This requires a shift in mindset from waste as a problem to waste as a resource and a commitment to innovation and collaboration across different sectors and disciplines.

Confilict of interest

The authors have no relevant financial or non-financial interests to disclose.

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