



Extraction of Chitosan from *Aristeus antennatus* Shells as a Prior for Biodegradable Plastic Production

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ABSTRACT

Crustacean shells can be used to extract chitin, which is the second most common biopolymer after cellulose (such as crabs, shrimps, prawns, and krills). Chitosan is a biopolymer that can be modified chemically and physically. Deproteinization, demineralization, and deacetylation were employed to extract chitosan from red shrimp shells *Aristeus antennatus* the average total catch per (five-hours-hauls) is about 62 kg. FTIR, SEM and biodegradation were used to characterise the final product; Chitosans deacetylation degree was determined to be around 86 %, which was compared to commercial chitosan's deacetylation degree of 95 percent in the rest of the study. The chitosan yield was 18% with 7.65% moisture content and 32.27% ash containing different minerals. The solubility of extracted chitosan was 98.15%. There are 10 formulations of bioplastic films synthesized based on chitosan extracted from chitin-wastes of locally collected *Aristeus antennatus* were set at a basis of 100% as well as chitosan film. Castor oil was added as a plasticizer. The recovered chitosan's Fourier transform infrared spectrum (FTIR) revealed the expected properties. The produced bioplastic films were characterized via several judging criteria. The biodegradability of the formed bioplastic films was assessed along two weeks of incubation in seawater and marine sediment. Observably, all bioplastic films were decreased in their weights compared to polypropylene (PP) as synthetic plastic, which was not changed.

KeyWords:

Aristeus antennatus, Chitin, Chitosan, Deacetylation, Castor oil, Bioplastic, Biodegradation.

1. INTRODUCTION

Marine species diversity provides a rich source of unique chemicals that could be used in medications, cosmetics, nutritional supplements, molecular probes, agrochemicals, and bioplastics, among other applications. Crustaceans are one of the most diverse groups of marine animals, with over 500 species ranging from shallow seas in the tropics to depths of over 1000 metres on continental slopes. The annual amount of shrimp shells in Egypt is estimated to be 200,000 tonnes. There are many species of shrimps on the coastal waters of Egypt. The 8 shrimp species caught commercially in Egypt included:

Marsupenaeus japonicus, *Metapenaeus monoceros*, *Metapenaeus stebbingi*, *Penaeus semisulcatus*, *Trachysalambria curvirostris*, *Penaeus latisulcatus*, *Solenocera indica*, and *Aristeus antennatus*[1]. *Aristeus antennatus*, one of the most important species with red shrimp, was used as a novel ecofriendly coagulant of model sulfonated azo-dyes. Experiments were conducted utilising extracted chitosan and commercial chitosan (86 % and 95 percent, respectively) to determine the effect of deacetylation degree on the coagulation process[1]. There is no safe way to dispose of this garbage, thus it is frequently deposited in drains or landfills. Other sources of chitosan include crab shells, some fish, and other crustaceans and marine creatures. Crustaceans are economically important species because they recycle nutrients as filter feeders and provide as a food supply for large aquatic mammals. Crabs, lobsters, krills, and shrimps are examples of marine crustaceans. Enzymes, proteins, hyaluronic acid, polyunsaturated fatty acids, hydroxyapatite, chondroitin sulphate, collagen, gelatine, glycosaminoglycans, astaxanthin and chitin have all been extracted from marine crustaceans. The exoskeleton and cephalothorax of marine crustaceans are the main sources of chitin. Most crustaceans' shells are mainly composed of 30-40% protein, 30-50% calcium carbonate and calcium phosphate, and 20-30% chitin [2]. Chitin is the second most abundant natural polysaccharide on the globe, after cellulose. Every year, the aquatic biosphere produces more than 1011 tonnes of chitin. Chitin and its derivatives, particularly chitosan, have a wide range of potential and common applications. Chitin and chitosan, as well as calcium carbonate and pigments, make up a majority of shrimp shells. Chitosan, on the other hand, is a natural polysaccharide with the structural name Poly-N-acetylglucosamine that is a biodegradable biopolymer [3]. Chitosan is converted by deacetylating chitin with a strong alkali at a high temperature for a longer duration [4].

Bioplastics, also known as biodegradable plastic, are plastics that can be produced by extracting chitosan from shrimp and used as food packaging material. As technology advances, particularly in the food technology industry, many alternatives are discovered to be used to extend the storage duration of ready-served food before consumption. One of them is the use of active packaging in packaging. Plastic product is packaging that can prevent disturbance from external environment from affecting packaged food. Bioplastic, on the other hand, is a broad term that encompasses both bio-based plastics and biodegradable polymers (including petrochemical polymers); nevertheless, not all bio-based plastics are biodegradable [5]. Plastics account for 40% of the global consumer packaging market (food and non-food), and plastic packaging is increasing faster than any other material. The developments in material properties are mostly responsible for the growth of the plastics market. Plastics are prized for their lightness, flexibility, design utility, low cost, and ease of use, as well as for their processing capabilities, aesthetic quality, and physio-chemical properties. Polyethylene, polypropylene, polystyrene, and polyethylene terephthalate, the most extensively used food packaging plastics, are currently supplied from petroleum sources. However, an expansion in the use of plastics in packaging has led to environmental difficulties, an energy crisis, global warming and in recent years. As a result, the global civilization seeks to conduct research into finding alternate sources of plastic material that can degrade naturally. Natural polymeric materials have gained in popularity as a result of their commercial potential and applicability, as society's dependence on petroleum-based products has decreased. one of the green technologies interested in plastics production is bioplastics, which have large-scale focal points such as thermostability, versatility in warm and mechanical properties, and in common they are light, less expensive, and allow coordinates forms in an infinite number of line preparations. However, due to natural, financial, and political factors, the development of underutilised biopolymer-based plastics has been a major requirement, as it would allow for partial substitution of petroleum-based plastics [6]. Vegetable oil, maize starch, potato starch, pineapple strands, jute, hemp, henequen clears out, and banana stems are all sustainable sources for bioplastic [7]. The annual production of bioplastics is relatively low, accounting for less than 1% of the over 360 million tonnes of plastics manufactured each year. Their production in 2019 was 2.11 million tonnes [8]. Furthermore, bioplastics output is predicted to reach 2.43 million tonnes by 2024. Bioplastics are also a feasible solution for environmental sustainability because of their biodegradability and the utilisation of biogenic raw materials in their production [5].

Thus, the current study aims at extract by chemical methods and used as food backing as bioplastics for application and characterize the chitosan from the shrimp shells of *A. antennatus*. In addition, some bioplastic films were synthesized from chitosan with filler (starch) and plasticizer (castor oil). Moreover, the biodegradation activity of the formed bioplastic was estimated.

2. MATERIALS AND METHODS

2.1 Collection and procedure of shrimp sample wastes

Red shrimp shells were collected from a local fish market in Port Said, Egypt, to be utilised as substrates for extracting chitin and subsequently converting it to chitosan via a deacetylation procedure. Shell materials were collected from *A. antennatus* waste. The complete cephalothorax and abdominal exoskeleton were retrieved from the discarded flesh sections of shrimp processing. The Marine Science Department, Faculty of Science, Port Said University, Egypt, assisted in its discovery.

Before and during transportation to the laboratory, representative samples of shrimp wastes were collected, sealed in plastic bags, and stored at -20°C . They were rinsed with distilled water, air-dried, and then oven-dried for four days at 60°C [9].

2.2 Chitin extraction from shrimp waste

Kumari *et al.* (2016) [10] devised a method for extracting chitin. 10 kg of shrimp shell trash was treated with 4% NaOH for 24 hours at room temperature. The alkali was washed out of the shells several times with distilled water until the PH=4 was back to normal. As a result of this process, shells were deproteinized. To make chitin, the deproteinized shells were demineralized for 12 hours at room temperature with 4 % HCl. After draining the acid from the chitin, it was rinsed with distilled water and dried at room temperature. Then treated with 2 % NaOH and 1 % HCl, the operation was repeated. The obtained chitin was slightly pink in colour. It was further decolorized by soaking it in 1% potassium permanganate (KMnO_4) for 30 minutes, followed by 1% oxalic acid for 30 minutes to 2 hours.

2.3 Deacetylation of chitin for chitosan formation

To convert the decolorized chitin to chitosan, it was deacetylated with 86 percent (w/v) NaOH for three days at 30°C . Centrifugation at 4000 rpm for 15 minutes separated the alkali fraction in chitosan, and the excess alkali was drained and rinsed with distilled water until the pH reached neutral. The chitosan fraction obtained was dried overnight at 40°C and stored at room temperature until further analysis [11].

2.4 Characterization of extracted chitosan

2.4.1 Moisture content

Kumari *et al.* (2016) technique, [10] was used to determine moisture content, residue on ignition, and ash content. The loss on drying of the generated chitosan will be calculated using the gravimetric method. By drying the sample to a constant weight and measuring it after and before drying, the water mass loss will be estimated. The difference between the wet and oven dry sample weights will be the water mass (or weight).

$$\text{Moisture content} = \frac{\text{Wet weight} - \text{Dry weight}}{\text{Dry weight}} \times 100 \quad (1)$$

2.4.2 Degree of deacetylation (DD)

Chitosan homogenous solution was prepared with 0.01 mol/L diluted HCl and titrated against 0.1M NaOH. The pH inflections were used to identify the endpoint. There were two separate inflections noted. The first is for HCl neutralisation, and the second is for chitosan ammonium ion neutralisation.

DD % = 100-DA % [11] indicates the quantity of amino groups in the chitosan chain, also known as the degree of deacetylation.

2.4.3 Solubility of chitosan

Chitosan dissolves entirely in 1% glacial acetic acid. One gramme of chitosan was dissolved in 99 ml of distilled water with 1% glacial acetic acid. A magnetic stirrer was used to mix it for 30 minutes. The

sample was extracted, the residue was filtered out using Whatmann No. 1 filter paper, and then the sample was weighed [10].

2.4.4 Fourier transform infrared analysis of chitosan (FTIR)

The specimens were rinsed in water for 4 minutes to eliminate any unreacted acid before being dried for the FTIR examination. The functional groups on the surface of the materials were observed using FTIR in the attenuated reflection (ATR) mode. The spectra were acquired using a Nicolet Series II Magna-IR System 750 with 32 scans at a resolution of 4 cm^{-1} in the wavenumber range of 4000 and 600 cm^{-1} [12].

2.5 Bioplastic synthesis

2.5.1 Formulation and production of bioplastic composites

Chitosan and maize starch were weighed with varied predefined masses to create bioplastics. The chitosan is then dissolved in glacial acetic acid while being stirred with a magnetic stirrer. The same action is taken with maize starch until all of it dissolves. Both solutions are combined in a beaker with varying amounts of castor oil, which is employed as a plasticizer to increase flexibility.

After the sample begins to gel, it is put into the mould and dried over a hotplate at $75\text{-}80^\circ\text{C}$ with a magnetic stirrer at 75 rpm for $20\text{-}30$ minutes, until all of the solvents evaporate and plastic films form [13].

The formulation of starch-chitosan/oil composition will be set at a basis of 100 for several details, as shown in Table 1. The gels were created by dissolving 1g of chitosan in 99 mL of 1% glacial acetic acid ($\text{pH } 4$). The gels were then homogenised for 6 hours at 60°C with moderate stirring. To make a starch suspension, dissolve 5g of starch in 100 mL of distilled water while stirring on a hotplate at 50°C for 20 minutes. Castor oil was applied as a plasticizer in ten various ratios, as shown in Table 1. Furthermore, the dope solution was cast on a glass plate (Petri dish) with a depth of 2 mm , and it will be baked in an oven at 60°C for 5 hours. Following oven drying, the bioplastic will be separated from the casting and stored in desiccators. Following that, preliminary evaluation of the generated bioplastic using FTIR analysis and scanning electron microscopy is performed (SEM).

Table 1: Different formulations of bioplastic synthesized based on chitosan extracted from chitin-wastes of locally collected *A. antennatus*.

Cast film (Composite no.)	Polymer suspension (%)		Plasticizer (%) Castor oil
	Chitosan	Starch	
1	10	45	45
2	30	35	35
3	50	25	25
4	70	15	15
5	75	10	15
6	78	5	18
7	79	1	20
8	85	5	10
9	94	1	5
10	97	2	1

3. RESULTS AND DISCUSSION

3.1. Physico-chemical parameters

3.1.1 Degree of chitin deacetylation (DD)

Due to its low solubility, chitin is frequently converted to chitosan, which has a higher solubility and more biological applications than chitin [14,15]. Since the acetyl group is removed from the amino groups

by using a deacetylation method from the chitin molecular chain, the adaptability of chitosan is determined by the degree of chemical reaction [16]. The acetyl group is removed from the amino groups by using a deacetylation method from the chitin molecular chain, leaving a complete amino acid. The alkaline deacetylation of chitin [17] is the most essential step for turning chitin to chitosan. As a result of the strong alkaline solutions used in this experiment, the chitin collected was converted to chitosan using NaOH. According to sigma-Aldrich, the recovered chitosan and commercial chitosan were found to be 86 and 75-85 percent deacetylated, respectively. The DD must be taken into account, as well as reaction time, temperature, and alkali concentration. Chitosan solubility is one of the most important factors regulating chitin particle size [18]. Incomplete deacetylation is indicated by a lower solubility rate, according to Brine and Austin (1981), [19]. The solubility of chitosan is proportional to its effectiveness. The process of eliminating the acetyl group is known as deacetylation [20]. Mucha *et al.* (2005), [21] found that as the DD level rises, so does the water level. Chitosan films' propensity to absorb water was lowered. In this investigation, the DD of the isolated chitosan was 86 percent, as indicated in Table 2 The DD value, which is the most important feature of chitin, is determined by the crude material and the forms used for deproteinization and demineralization. Higher DD values were found to be due to a higher protein sum, which influences the chemical, physical, and natural properties of chitosan, such as adsorption and covalent connecting. It was also discovered that the method of DD depends on the source of chitin, as well as the time, temperature, and soluble concentration used.

3.1.2 Moisture of chitosan

The influence of concentrations of NaOH (10 M) and HCl (0.5 M) on chitosan yield extraction. This is because a lower quantity of HCl was unable to extract minerals from shrimp shells, resulting in a higher yield [49]. However, Table 2 shows the yield calculated for chitin removed from shrimp trash. Furthermore, the isolated chitin had an 86 percent degree of deacetylation (DD). In comparison to other workers, this percentage is reasonable. The DD of chitosan, for example, was discovered to be 83.23 percent [50]. The DD is normally between 30 and 95 percent, depending on the chemicals employed in the production [51]. In the present study, however, the chitosan production was 18 percent, with 7.65% moisture content Table 2. This could be related to chitosan polymer depolymerization, sample mass/weight loss due to excessive removal of acetyl groups from the polymer during deacetylation, and chitosan particle loss during washing [52].

Table 2: Physio-chemical and functional properties of chitosan.

Chitosan yield %	Moisture chitosan %	Degree of deacetylation %	Solubility of chitosan %
18	7.65	86	98.18

3.1.3 Solubility of chitosan from *A. antennatus* shell

Table 2 demonstrates that isolated chitosan has a solubility of 98.18 %. Samar *et al.* (2013), [22] found that chitosan has a high solubility, ranging from 83.28 to 99.05 %. At varied temperatures and NaOH concentrations, Hossain and Iqbal (2014) [18], discovered that chitosan solubility ranged from 48.3 to 97.65 percent. Deacetylation temperature and time, alkali content and ratio to chitin, prior treatments employed for chitin isolation, and particle size are all important factors that influence chitosan solubility. The solubility of chitosan increases as the DD increases, with samples treated with 50 and 60 % NaOH having solubilities ranging from 96.01 to 97.2 %. By partially eliminating the protein and the acetyl group, lower solubility levels can be attained. It is soluble in inorganic acid due to the strongly protonated free amino group, which attracts ionic molecules [22]. However, solubility, which is a crucial criterion for evaluating the quality of chitosan, is affected by deacetylation duration, temperature, NaOH solution content, and particle size [18].

3.1.4 FTIR spectrum of chitosan

Figure 1 shows the FTIR spectrum analysis of chitosan. The stretching of OH groups in chitosan corresponds to the broadband at $3360\text{--}3480\text{ cm}^{-1}$. The amide I and amide II bands absorption bands in the chitosan spectrum were around 1650 and 1587 cm^{-1} , respectively. The ethylene group's scissoring band was also seen at 1418 cm^{-1} . The absorption bands around 1065 and 890 cm^{-1} correspond to vibration C-O-C bonds, confirming monomer bonding via -glucosidic links.

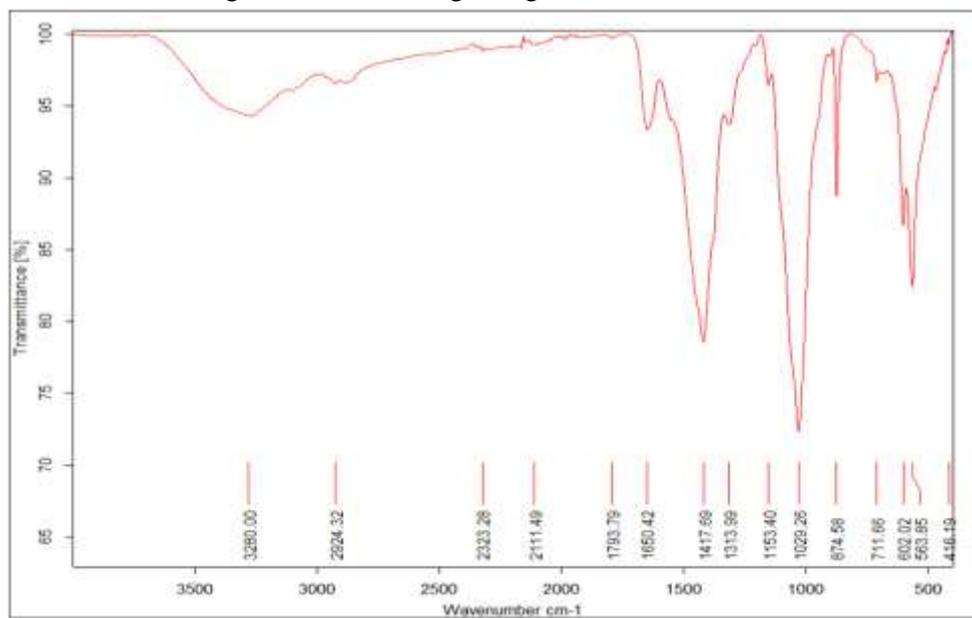


Figure 1: FTIR spectrum of the extracted chitosan

Shown in Figure 1. The O-H and N-H bands were extending, as evidenced by a peak around 3280 cm^{-1} . The 1793 cm^{-1} peak in the spectrum represents the carbonyl group vibrations (amide band I). At 1650 cm^{-1} , N-H bending may be visible (amide II). Amide I and amide II, which were found at 1793 and 1650 cm^{-1} , respectively, are separate bands for chitosan. This unique band is generally attributed to the stretching of the CO group hydrogen connected to the amide group of the neighbouring intra-sheet chain [53]. At 1153 cm^{-1} , Amide III was assigned to the band. Peaks for the CH_2 groups in CH_2OH spiked at 3280 and 1650 cm^{-1} for the separated chitosan samples. The oxygen stretching of glycosidic linkage was found to be 1153 cm^{-1} . The C-O stretching of the structure was identified at 1029 and 874 cm^{-1} . The CH_3 group of NHCOCH_3 (amide bond) can be seen at 1313 cm^{-1} . The pyranose ring was discovered at 874 cm^{-1} . The FTIR spectrophotometry results of the extracted chitosan samples used in this study were confirmed by those of previous investigations [23-25]. Because chitosan presented in this work is of animal origin, contamination by glycosaminoglycans (GAGs), another form of polysaccharide prevalent in these species, is always a possibility that, the functional group is an amino acid for chitosan which are presents a strong peak at 3280 cm^{-1} , while it can be seen in Figure 1 print region two strong peaks at 1417.69 and 1029.26 cm^{-1} .

3.1.5. Production and characterization of bioplastic films

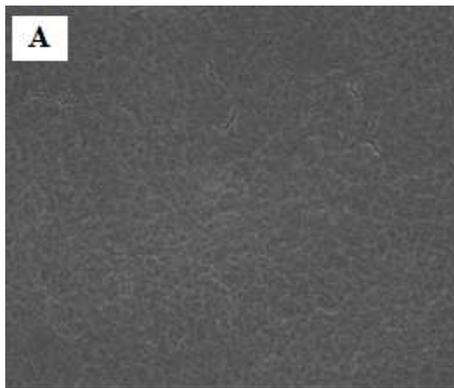
The optimal proportion from triers are castor 5 , 20 %. Because of its multifunctional qualities, chitosan, a polysaccharide derived from chitin, has gained a reputation in a variety of fields, ranging from biomedical and biopharmaceutical applications to waste water treatment and the food industry [26].

As a result, chitosan has long been touted as a natural and biodegradable alternative to petroleum-based plastics in a variety of applications, most notably in the food packaging industry as consumable films or coatings, to improve the preservation and quality of food by creating a barrier against stickiness, oxygen, and carbon dioxide [27-28]. The goal of bioplastic is to emulate the life cycle of biomass, which includes fossil asset preservation, CO_2 generation, and water. For the time being, there is a massive request to explore the various suitable plants available for this purpose [29]. Indeed, a few factors influence the characteristics of chitosan films, including the atomic mass [30] and DD of chitosan, as well as the presence or absence of plasticizers [29,31]. Plasticization of chitosan by thermo-mechanical medicines,

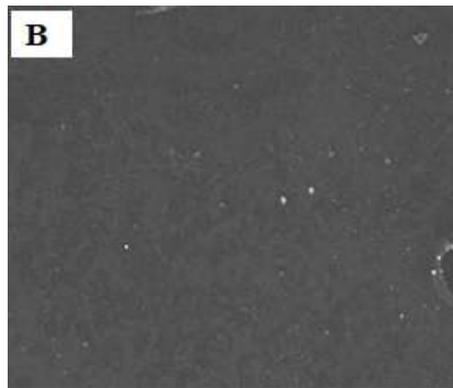
on the other hand, can be a fascinating alternative to the traditional casting technique, allowing for larger-scale chitosan film arrangements [32-33]. Melt-mixing and thermo-compression [27], dissolve expulsion [35], and blown expulsion [36] all produced thermoplastic starch/chitosan films.

3.1.6. SEM of produced bioplastic films

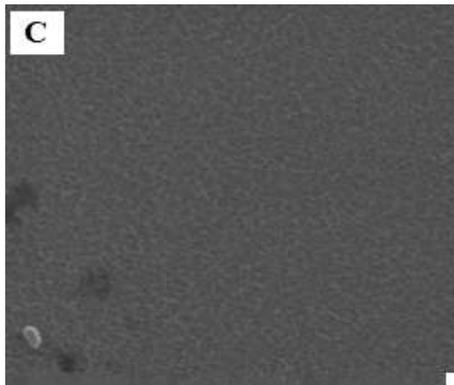
SEM micrographs of chitosan surfaces and variably formed biofilms, demonstrating surface and cross-section morphology, are shown in Figure 2. With only a few straps, the chitosan film was homogeneous and continuous. The surface morphology of the chitosan blend films was homogeneous, with a high basic keenness and no interface layer. This demonstrates the consistency with which chitosan chains are conveyed throughout the films, as well as their compatibility. The homogenous mixes of chitosan and oils (Castor with varied percent's; 5 and 20%) were generally due to hydrogen bonding between the functional bunches of the mixed component (-Gracious and -NH₂ bunches in chitosan).



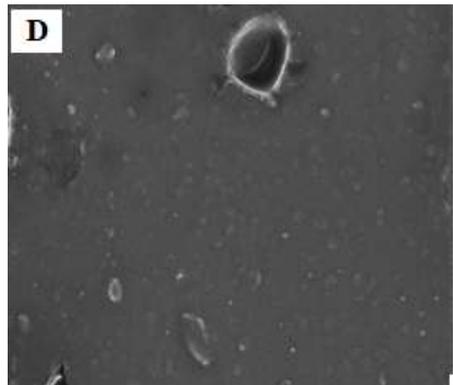
SED 20.0 kV WD 16.2 mm Std.-PC 24.0
HighVac. x250 STD 5202



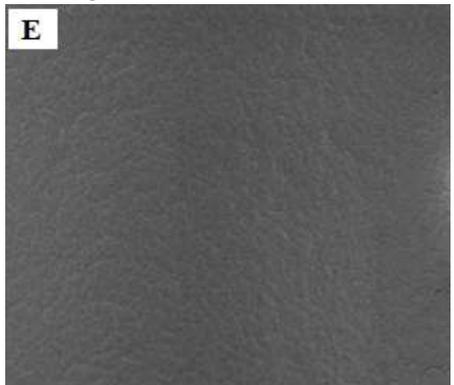
SED 20.0 kV WD 16.2 mm Std.-PC 24.0
HighVac. x25,000 STD 5201



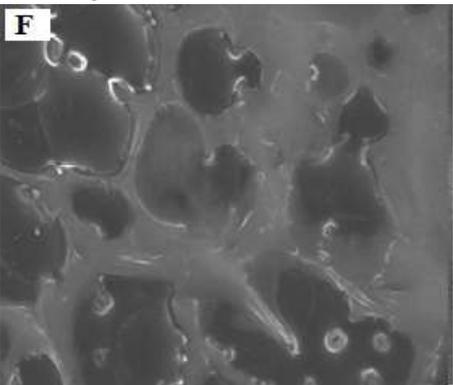
SED 20.0 kV WD 15.5 mm Std.-PC 24.0
HighVac. x250 STD 5211



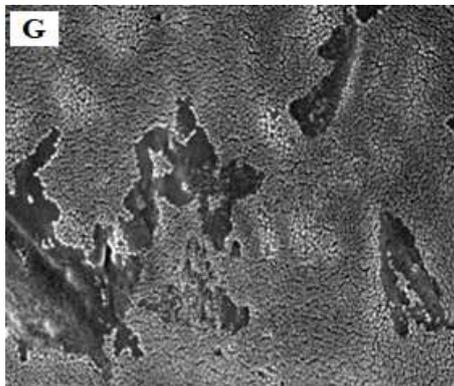
SED 20.0 kV WD 15.6 mm Std.-PC 24.0
HighVac. x25,000 STD 5213



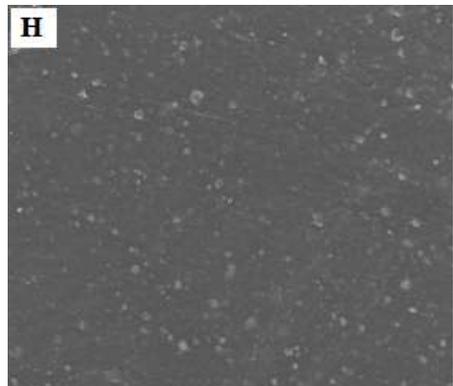
SED 20.0 kV WD 17.0 mm Std.-PC 24.0
HighVac. x25,000 STD 5209



SED 20.0 kV WD 15.9 mm Std.-PC 24.0
HighVac. x250 STD 5211



SED 20.0 kV WD 16.3 mm Std.-PC 24.0
HighVac. x250 100 pm STD 5197



SED 20.0 kV WD 16.3 mm Std.-PC 24.0
HighVac. x25000 pm STD 5200

Figure 2. SEM images for the bioplastic films formed from chitosan and castor oil. A and B show chitosan pure with different magnifications 25×10^3 and 250×10^3 respectively, (C, D) presented Castor 5% mixed with starch and chitosan complex with 25×10^3 and 250×10^3 dramatically, (E, F) also castor oil different concentration 20% with the same complex as 25×10^3 and 250×10^3 magnifications, finally (G, H) given as standard polypropylene bag at 25×10^3 and 250×10^3 consequently.

Figure 2 shows that chitosan starch and castor oil 20 percent bioplastic could not mix well with starch in (E and F), but chitosan bioplastic in (A and B) is more acidic due to the state of the chitosan solution employed in the experiment. Because starch solubility is highly influenced by acidity, it appears that chitosan has a different affinity with the starch-castor oil 5 percent matrix, resulting in lumps visible on the surface and in the cross-section of bioplastics. Both bioplastics have rough surfaces, resulting in limited transparency. The cross-section of starch-chitosan-castor oil 5 percent bioplastics revealed a more compact matrix than that of starch-chitosan castor oil 20 percent oil, indicating that starch-chitosan castor oil 20 percent oil has low mechanical characteristics. Figure 2 (G and H) illustrates the shattered surface for polypropylene is flat due to brittle fracture and is used to analyse the changes in characteristics. With the addition of polypropylene (PP) particles, as illustrated in Figure 2, the impact energy absorbed decreases, resulting in fractures to prevent ballooning due to imposed strain [37].

3.1.7. FTIR profiles of produced bioplastic films

The FTIR profiles were used to identify produced bioplastic films in comparison to the profile of polypropylene. Based on the FTIR spectra below Figure 3, after the mixing process with the castor oil diluted 5%, its curve shows the new peak related to O-H stretch on 3280 cm^{-1} and also the characteristic carbonyl stretching was observed at 1417 and 1029 cm^{-1} . At 1623 cm^{-1} , the characteristic carbonyl stretching was detected. While in 3257 cm^{-1} the carbonyl group was presented. The FTIR spectra of polypropylene are displayed in Figure 3. Bending out of the plane of the N-H bond is associated with the absorption band 559.92 cm^{-1} . The elongations of the carbonyl group C=O have been attributed to the absorption bands at 1623.47 cm^{-1} , while the asymmetric and symmetric elongation vibrations of the N-H group characteristic of the main amide have been assigned to the bands at 3429 and 3108.06 cm^{-1} , respectively.

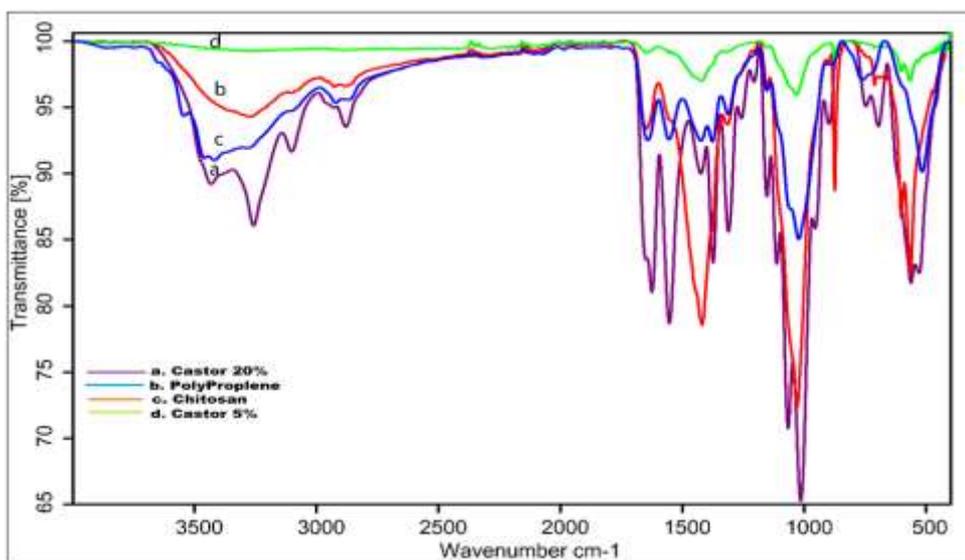


Figure 3: Different FTIR spectra of the extracted bioplastic films; (a) 20% castor oil composite film, (b) the synthetic plastic (polypropylene), (d) 5% castor oil composite film, and (c) 100% chitosan.

To determine the importance of the band corresponding to the carbonyl group to the possible interaction with the hydroxyl groups of anhydroglucose units of the starch, the deconvolution technique was used to clarify the overlapping effect of the bands, where the contribution of each one can be separated. A signal peak at 1623.47 cm^{-1} is mostly associated with the vibration of the amide carbonyl group, whereas the

band at 1555.96 cm^{-1} is associated with both the flexion vibration of the N-H bond and the vibration of the C-N bond. The band at 1555.96 cm^{-1} is assigned to stretched bonds $\text{CH}=\text{CH}_2$, showing that, in addition to functionalization, disproportional collateral processes are generating unsaturation in the PP chain [38]. Furthermore, data in Figure 3 depict the results of FTIR spectra analyses of pure chitosan bioplastic and added plasticizer castor 5%. The spectra in this Figure show certain functional groups that are identical to those identified in chitosan and castor 5 percent. A high absorption at wavenumber 3357.46 cm^{-1} in the infrared spectra of starch indicates the stretching vibration of OH groups. A large, high-intensity signal indicates the hydrogen bonding in the castor 5 percent molecule. Peaks that appear below 1421.60 cm^{-1} suggest that the methylene group is bending. The CH stretching vibration of alkanes is indicated by the peak at 2916.54 cm^{-1} . The presence of ether and alcohol C-O bonds is indicated by the peaks at 1375.24 and 1028 cm^{-1} . In FTIR spectra, the acetamido from chitosan was identified at 1640.98 cm^{-1} . The width and strength of the resultant peaks associated with pure chemical and mixing ratio are different in the FTIR spectra of the bioplastic that has been added plasticizer mixture, according to Helwati *et al.* (2019) [39]. Castor 5% is a substance with an OH group and CH alkanes. The spectra revealed that the amino groups of chitosan interact with the hydrogen atom of the hydroxyl group from castor 5% to create an increase in the peak intensity and width of the stretching vibrations of the OH group of bioplastics.

3.1.8. Swelling capacity of produced bioplastic films

The fractional water up takes curves as a function of synthetic plastic (polypropylene), and types of content chitosan pure and chitosan with castor 5%, chitosan with 20% castor are shown in Figure 4. As the figure observed the chitosan with 20% castor the most weight in 20 min, while the synthetic plastic (polypropylene) had the same time stable weight. While in chitosan pure and chitosan with 5% castor take up the same rate approximately water in 20 min that mean the chitosan wase increased, the water up-take decreased. This was an expected result since chitosan is hydrophobic and it's considered the same explanation of M. Correlo [40].

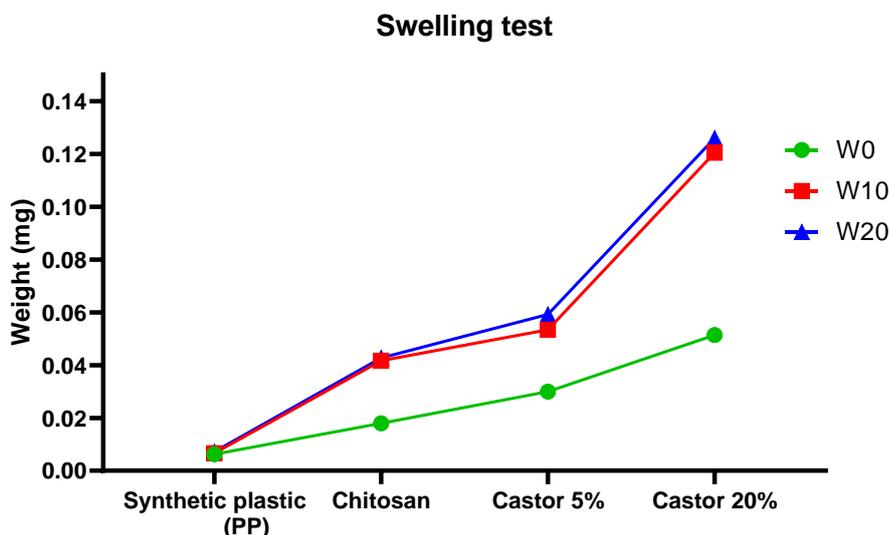


Figure 4: Absorbance of water effect on bioplastic film.

3.2. Biodegradation of the formed bioplastic films

To evaluate the eco-friendly properties of the formed bioplastic films, their biodegradability was assessed. Data presented in Table 3 confirmed the biodegradability of the bioplastic films; from four main formulations, along two weeks of incubation in both seawater (SW) and marine sediment (MS). The assessment included their weight (g) before incubation with (SS) and (MS) samples and after incubating

them at 4, 7 and 14 days. Finally, the net bioplastic film's status with 2 x 2 cm² dimensions was described well.

Table 3: Biodegradability of the formed bioplastic films (2 × 2 cm²) from different formulations along two weeks of incubation in different treatments of both seawater and marine sediment.

The formula of bioplastic films	Evaluation parameter (daily)	Treatment	
		Seawater (SW)	Marine sediment (MS)
Chitosan 100% (Extracted in this study).	at zero day	9.1	7.5
	after 4 days	8.9	6.3
	after 7 days	3.1	3.5
	after 14 days	2.8	2.2
	Status description of biofilm after 14 days	Transparent and easy to cut.	It became lighter and more transparent.
Castor oil 5%, 1% starch and chitosan 94%.	at zero day	4.1	0.0319
	after 4 days	4.0	0.067
	after 7 days	3.1	0.110
	after 14 days	2.3	0.0847
	Status description of biofilm after 14 days.	Bleached	Color bleached, It became lighter and soft with pores.
Castor oil 20%, 1% starch and chitosan 79%,	at zero day	6.0	0.0628
	after 4 days	6.2	0.099
	after 7 days	3.8	0.0892
	after 14 days	2.5	0.0571
	Status description of biofilm after 14 days.	Bleached	Transparent and easy to cut.
Market Plastic Polypropylene (PP).	at zero-days	3.3	3.7
	after 4 days	3.3	3.7
	after 7 days	3.2	3.5
	after 14 days	3.0	3.5
	Status description of biofilm after 14 days.	No change	No change

The results in Table 3 indicated that, in the case of chitosan alone (100%), the bioplastic film became lighter and more transparent at the end of the experiment. In the case of formula (castor oil 5% and 95% chitosan), biofilm color got bleached as well as it became lighter and soft with pores. The biofilm formula of castor oil 20 and 80% chitosan became transparent and easy to cut. Observably, all previous bioplastic films were compared to polypropylene as synthetic plastic which was not changed at all. Periodically, all tested bioplastic films decreased in their weights except the synthetic one (Market polypropylene PP), which nearly kept its weight in both treating media (SW and MS).

According to Harrison *et al.* (2018) [42], as the number of bioplastic materials has increased, qualities like as flexibility, durability, printability, transparency, barrier, heat resistance, biodegradability, and many others have improved dramatically. Plastic waste concerns have prompted the creation of biodegradable polymers. Biodegradable bioplastics, in particular, are polymers that are mineralized into carbon dioxide, methane, water, inorganic chemicals, or biomass via the enzymatic action of specific microorganisms. As a result, they may be an acceptable and environmentally benign alternative to traditional petrochemical plastics [3].

Biodegradability testing points are used to determine the amount of resistance of bioplastics to the impact of breaking down microorganisms, soil moisture, temperature, and physico-chemical components found in soil. The most influential elements in biodegradation are the physicochemical qualities of the biopolymers, the environmental circumstances, and the microbial populations to which the bioplastics are exposed. This process can occur in both natural and industrial settings, in aerobic and anaerobic conditions, with the latter receiving the least attention. Compost, soil, and some aquatic settings were studied as aerobic environments, while anaerobic environments included anaerobic digestion plants and a few aquatic habitats [3].

The chemical and physical structure of the materials, rather than the origin of their resources or the manufacturing method, affects the degradability of bio-polymers. Endres (2017) [43], on the other hand, stated that "degradability is a functional attribute or a disposal option at the end of the material's life cycle." The degradation process is influenced by a combination of abiotic (UV, temperature, moisture, and pH) and biotic (microbial activity) processes and factors [42]. According to Mohee *et al.* (2008) [44], the leftovers of bioplastic biodegradation are not normally harmful and can be ingested by other living species. However, several difficulties have been raised in recent research regarding the inclusion of fossil resins in the composition of bioplastic goods. According to Wahyuningtiyas and Suryanto (2017) [45], the biodegradation process is influenced by parameters such as humidity, temperature, oxygen content, pH, time, nutrient availability [42], UV radiation [44], and the presence of microorganisms [45]. The thickness of the biodegradable material also influences the pace of biodegradation: the thicker the product, the longer its biodegradability, according to Rujni-Sokele and Pilipovi (2017) [46]. Biodegradability tests were used to precisely assess bioplastics, which had to be chopped into $10 \times 10 \text{ cm}^2$ and buried under the soil (12 cm profundity) stored in plastic jugs for 14 days before being carried out according to Zulferiyenni *et al.* (2014) [47-48].

Finally, according to the European Bioplastic Organization, bioplastic can be classified as bioplastic based on renewable sources or plastic that is biodegradable and/or compostable. Vegetable oil, maize starch, potato starch, pineapple strands, jute, hemp, henequen clears out, and banana stems are all renewable supplies for bioplastics [5].

4. CONCLUSION

There is no doubt that widespread use of biodegradable plastics in packaging will lower the burden of rubbish, particularly in emerging nations, and will move money away from solid waste management and toward educational and health service projects. The current study estimated the cost and yield of chitosan extraction. The bioplastics were created using the phase inversion approach after being cast on a glass plate. The bioplastics are created from a combination of chitosan and Castor oil, and they produce clear

films with good degradability and picture quality in a scanning electron microscope. The best bioplastic compositions contained 20% (w/w) Castor oil and 5% (w/w) Castor as a plasticizer. To change its mechanical properties, castor oil was utilised as a plasticizer. The addition of 5% (w/w) castor created a bioplastic with a modest uptake absorption of water that took up to 30 minutes. There are some difficulties encountered when producing bioplastic from shrimp chitosan. Hopefully, more study will be undertaken to turn the mixture of chitosan and organic matter additions into an useful substance for industrial manufacturing.

REFERANCES

- [1] L. B. Holthuis, FAO species catalogue vol. 1: Fao, 1980.
- [2] H. O. Ahmed, F. A. A. Razek, A. R. Khafage, M. Sarhan, T. Soliman, H. Aly, et al., "A new record of the Jinga shrimp *Metapenaeus affinis* (H. Milne Edwards, 1837)(Decapoda, Penaeidae), on the Egyptian Coasts, the Mediterranean Sea," Egypt. J. Aquat. Res., vol. 47, pp. 143-150, 2021, doi.org/10.1016/j.ejar.2021.04.001.
- [3] D. R. G. Fouad, "Chitosan as an antimicrobial compound: modes of action and resistance mechanisms," Bonn, Univ., Diss., 2008, 2008, doi:de/diss_online elektronisch publiziert.
- [4] S. Kumari and P. K. Rath, "Extraction and characterization of chitin and chitosan from (*Labeo rohita*) fish scales," Procedia Manuf., vol. 6, pp. 482-489, 2014, doi.org/10.1016/j.mspro.2014.07.062.
- [5] A. Folino, A. Karageorgiou, P. S. Calabrò, and D. Komilis, "Biodegradation of wasted bioplastics in natural and industrial environments: A review," Sustainability, vol. 12, p. 6030, 2020, doi.org/10.3390/su12156030.
- [6] V. Siracusa, P. Rocculi, S. Romani, and M. Dalla Rosa, "Biodegradable polymers for food packaging: A review," Trends in Food Sci. Technol. Res., vol. 19, pp. 634-643, 2008, doi.org/10.1016/j.tifs.2008.07.003.
- [7] S. Chaliha and K. G. Bhattacharyya, "Catalytic wet oxidation of 2-chlorophenol, 2, 4-dichlorophenol and 2, 4, 6-trichlorophenol in water with Mn (II)-MCM41," Chem. Eng. J., vol. 139, pp. 575-588, 2008, doi.org/10.1016/j.cej.2007.09.006.
- [8] L. G. Hong, N. Y. Yuhana, and E. Z. E. Zawawi, "Review of bioplastics as food packaging materials," AIMS Mater. Sci, vol. 8, pp. 166-184, 2021, doi: 10.3934/matserci.2021012.
- [9] M. H. Mohammed, P. A. Williams, and O. Tverezovskaya, "Extraction of chitin from prawn shells and conversion to low molecular mass chitosan," Food Hydrocoll., vol. 31, pp. 166-171, 2013, doi:10.1016/j.foodhyd.2012.10.021.
- [10] S. Kumari, P. Rath, and A. S. H. Kumar, "Chitosan from shrimp shell (*Crangon crangon*) and fish scales (*Labeorohita*): Extraction and characterization Suneeta," Afr. J. Biotechnol., vol. 15, pp. 1258-1268, 2016, doi: 10.5897/ajb2015.15138.
- [11] P. Premasudha, P. Vanathi, and M. Abirami, "Extraction and characterization of chitosan from crustacean waste: A constructive waste management approach," Int. J. Sci. Res. vol. 6, pp. 1194-1198, 2017, doi:10.21275/art20175408.
- [12] A. A. El-Zahhar, A. M. Idris, K. F. Fawy, and M. Arshad, "SEM, SEM-EDX, μ -ATR-FTIR and XRD for urban street dust characterisation," Int. J. Environ. Anal. Chem., vol. 101, pp. 988-1006, 2021, doi.org/10.1080/03067319.2019.1674849.
- [13] M. Hasan, M. Zufadli, R. Rahmayani, G. Fajri, and H. Fansuri, "Thermomechanical and morphology of biodegradable film made of taro starch and chitosan plasticized by castor oil," Rasa. J. Chem., vol. 12, pp. 1390-1399, 2019.
- [14] Y. N. Tan, P. P. Lee, and W. N. Chen, "Microbial extraction of chitin from seafood waste using sugars derived from fruit waste-stream," AMB Express, vol. 10, pp. 1-11, 2020, doi.org/10.1186/s13568-020-0954-7.
- [15] I. Younes and M. Rinaudo, "Chitin and chitosan preparation from marine sources. Structure, properties and applications," Mar. Drugs, vol. 13, pp. 1133-1174, 2015, doi: 10.3390/md13031133.

- [16] M. R. Hussain, M. Iman, and T. K. Maji, "Determination of degree of deacetylation of chitosan and their effect on the release behavior of essential oil from chitosan and chitosan-gelatin complex microcapsules," *Int. j. adv. eng.*, vol. 6, pp. 4-12, 2013.
- [17] L. Manni, O. Ghorbel-Bellaaj, K. Jellouli, I. Younes, and M. Nasri, "Extraction and characterization of chitin, chitosan, and protein hydrolysates prepared from shrimp waste by treatment with crude protease from *Bacillus cereus* SV1," *Appl. Biochem. Biotechnol.*, vol. 162, pp. 345-357, 2010, doi:10.1007/s12010-009-8846-y.
- [18] M. Hossain and A. Iqbal, "Production and characterization of chitosan from shrimp waste," *J. Bangladesh Agric. Univ.*, vol. 12, pp. 153-160, 2014, doi:10.3329/jbau.v12i1.21405.
- [19] C. J. Brine and P. R. Austin, "Chitin variability with species and method of preparation," *Comp. Biochem. Physiol. B, Biochem. Mol. Biol.*, vol. 69, pp. 283-286, 1981, doi:10.1016/0305-0491(81)90242-X.
- [20] H. K. No, S. H. Lee, N. Y. Park, and S. P. Meyers, "Comparison of physicochemical, binding, and antibacterial properties of chitosans prepared without and with deproteinization process," *J. Agric. Food Chem.*, vol. 51, pp. 7659-7663, 2003, doi:10.1021/jf030226w.
- [21] M. Mucha, S. Ludwiczak, and M. Kawinska, "Kinetics of water sorption by chitosan and its blends with poly (vinyl alcohol)," *Carbohydr. Polym.*, vol. 62, pp. 42-49, 2005, doi:10.1016/j.carbpol.2005.07.008.
- [22] M. M. Samar, M. El-Kalyoubi, M. Khalaf, and M. Abd El-Razik, "Physicochemical, functional, antioxidant and antibacterial properties of chitosan extracted from shrimp wastes by microwave technique," *Ann. Agric. Sci.*, vol. 58, pp. 33-41, 2013, doi:10.1016/j.aoas.2013.01.006.
- [23] E. B. Ibitoye, I. H. Lokman, M. N. M. Hezme, Y. M. Goh, A. B. Z. Zuki, and A. A. Jimoh, "Extraction and physicochemical characterization of chitin and chitosan isolated from house cricket," *Biomed. Mater.*, vol. 13, p. 025009, Jan 30 2018, doi: 10.1088/1748-605x/aa9dde.
- [24] A. Kucukgulmez, M. Celik, Y. Yanar, D. Sen, H. Polat, and A. E. Kadak, "Physicochemical characterization of chitosan extracted from *Metapenaeus stebbingi* shells," *Food Chem.*, vol. 126, pp. 1144-1148, 2011, doi:10.1016/j.foodchem.2010.11.148.
- [25] T. K. Varun, S. Senani, N. Jayapal, J. Chikkerur, S. Roy, V. B. Tekulapally. "Extraction of chitosan and its oligomers from shrimp shell waste, their characterization and antimicrobial effect," *Vet. World*, vol. 10, p. 170, 2017, doi: 10.14202/vetworld.2017.170-175.
- [26] Y. S. Puvvada, S. Vankayalapati, and S. Sukhavasi, "Extraction of chitin from chitosan from exoskeleton of shrimp for application in the pharmaceutical industry," *Int. Curr. Pharm. J.*, vol. 1, pp. 258-263, 2012, doi:10.3329/icpj.v1i9.11616.
- [27] M. Z. Elsabee and E. S. Abdou, "Chitosan based edible films and coatings: A review," *Mater. Sci. Eng.: C*, vol. 33, pp. 1819-1841, 2013, doi:10.1016/j.msec.2013.01.010.
- [28] A. Quirós-Sauceda, H. Palafox-Carlos, S. Sáyago-Ayerdi, J. Ayala-Zavala, L. A. Bello-Perez, E. Alvarez-Parrilla, E., De La Rosa, L.A., González-Córdova, A.F. and González-Aguilar, G.A., "Dietary fiber and phenolic compounds as functional ingredients: interaction and possible effect after ingestion," *Food & function*, vol. 5, pp. 1063-1072, 2014, doi:10.1039/c4fo00073k.
- [29] R. Jabeen, R. Goswami, O. Awe, A. Kulkarni, E. T. Nguyen, A. Attenasio, Walsh, D., Olson, M.R., Kim, M.H., Tepper, R.S. and Sun, J., "Th9 cell development requires a BATF-regulated transcriptional network," *J. Clin. Investig.*, vol. 123, pp. 4641-4653, 2013, doi:10.1080/23311932.2015.1117749.
- [30] V. G. L. Souza, J. R. A. Pires, C. Rodrigues, I. M. Coelho, and A. L. Fernando, "Chitosan Composites in Packaging Industry—Current Trends and Future Challenges," *Polymers*, vol. 12, p. 417, 2020, doi:10.3390/polym12020417.
- [31] J. R. Rodríguez-Núñez, T. J. Madera-Santana, D. I. Sánchez-Machado, J. López-Cervantes, and H. Soto Valdez, "Chitosan/hydrophilic plasticizer-based films: preparation, physicochemical and antimicrobial properties," *J Polym Environ.*, vol. 22, pp. 41-51, 2014, doi 10.1007/s10924-013-0621-z.

- [32] J. F. Fundo, A. L. Amaro, A. R. Madureira, A. Carvalho, G. Feio, C. L. Silva, C.L. and Quintas, M.A., "Fresh-cut melon quality during storage: An NMR study of water transverse relaxation time," *J. Food Eng.*, vol. 167, pp. 71-76, 2015, doi:10.1016/j.jfoodeng.2015.03.028.
- [33] W. Janik, A. Wojtala, A. Pietruszka, G. Dudek, and E. Sabura, "Environmentally Friendly Melt-Processed Chitosan/Starch Composites Modified with PVA and Lignin," *Polymers*, vol. 13, p. 2685, 2021, doi:10.3390/polym13162685.
- [34] J. Lopez-Calderon and S. J. Luck, "ERPLAB: an open-source toolbox for the analysis of event-related potentials," *Front. Hum. Neurosci.*, vol. 8, p. 213, 2014, doi:10.3389/fnhum.2014.00213.
- [35] J. Mendes, R. Paschoalin, V. Carmona, A. R. S. Neto, A. Marques, J. Marconcini, J.M., Mattoso, L.H.C., Medeiros, E.S. and Oliveira, J.E., "Biodegradable polymer blends based on corn starch and thermoplastic chitosan processed by extrusion," *Carbohydr. Polym.*, vol. 137, pp. 452-458, 2016, doi:10.1016/j.carbpol.2015.10.093.
- [36] K. M. Dang and R. Yoksan, "Morphological characteristics and barrier properties of thermoplastic starch/chitosan blown film," *Carbohydr. Polym.*, vol. 150, pp. 40-47, 2016, doi:10.1016/j.carbpol.2016.04.113.
- [37] G. O. Akalin, O. Oztuna Taner, and T. Taner, "The preparation, characterization and antibacterial properties of chitosan/pectin silver nanoparticle films," *Polym. Bull.*, pp. 1-18, 2021, doi: 10.1007/s00289-021-03667-0.
- [38] A. B. Linares Veliz, J. C. Jiménez García, P. López, and B. R. de Gáscue, "Biodegradability study by FTIR and DSC of polymers films based on polypropylene and Cassava starch," *Electron. J. Chem.* 2019, doi:10.17807/orbital.v11i2.1360.
- [39] H. Helwati, S. Saleha, and T. Iqbalsyah, "Development of bioplastic from wheat Janeng starch for food packaging," in *IOP Conference Series: Mater. Sci. Eng.*, 2019, p. 012015, doi:10.1088/1757-899X/523/1/012015.
- [40] V. M. Correlo, E. D. Pinho, I. Pashkuleva, M. Bhattacharya, N. M. Neves, and R. L. Reis, "Water absorption and degradation characteristics of chitosan- based polyesters and hydroxyapatite composites," *Macromol. Biosci.*, vol. 7, pp. 354-363, 2007, doi:10.1002/mabi.200600233.
- [41] M. Chen, T. Runge, L. Wang, R. Li, J. Feng, X.-L. Shu, and Q.S. Shi, "Hydrogen bonding impact on chitosan plasticization," *Carbohydr. Polym.*, vol. 200, pp. 115-121, 2018, doi: 10.1016/j.carbpol.2018.07.062.
- [42] J. P. Harrison, C. Boardman, K. O'Callaghan, A.-M. Delort, and J. Song, "Biodegradability standards for carrier bags and plastic films in aquatic environments: a critical review," *R. Soc. Open Sci.*, vol. 5, p. 171792, 2018. doi.org/10.1098/rsos.171792.
- [43] H.-J. Endres, "Bioplastics," *Biorefin.*, pp. 427-468, 2017.
- [44] R. Mohee, G. Unmar, A. Mudhoo, and P. Khadoo, "Biodegradability of biodegradable/degradable plastic materials under aerobic and anaerobic conditions," *J. Waste Manag.*, vol. 28, pp. 1624-1629, 2008, doi:10.1016/j.wasman.2007.07.003.
- [45] N. E. Wahyuningtiyas and H. Suryanto, "Analysis of biodegradation of bioplastics made of cassava starch," *J. Mech. Sci. Technol. (JMEST)*, vol. 1, pp. 24-31, 2017, doi:10.17977/um016v1i12017p024.
- [46] M. Rujnić-Sokele and A. Pilipović, "Challenges and opportunities of biodegradable plastics: A mini review," *Waste Manag. Res.*, vol. 35, pp. 132-140, 2017, doi:10.1177/0734242X16683272.
- [47] Z. Zulferiyenni, M. Marniza, and E. N. Sari, "Pengaruh konsentrasi gliserol dan tapioka terhadap karakteristik biodegradable film berbasis ampas rumput laut *Eucheuma cottonii* [The effects of glycerol and tapioca concentration on the characteristics of *Eucheuma cottonii* seaweed dreg-based biodegradabl," *Jurnal Teknologi & Industri Hasil Pertanian (edisi elektronik)*, vol. 19, pp. 257-273, 2014, doi:10.23960/jtihp.v19i3.257%20-%20273.
- [48] M. Abu-Saied, A. Fahmy, N. Morgan, W. Qutop, H. Abdelbary, and J. F. Friedrich, "Enhancement of poly (vinyl chloride) electrolyte membrane by its exposure to an atmospheric dielectric barrier

- discharge followed by grafting with polyacrylic acid," *Plasma Chem. and Plasma Processing*, vol. 39, pp. 1499-1517, 2019, doi: 10.1007/s11090-019-10017-6.
- [49] M. Abu-Saied, T. H. Taha, N. M. El-Deeb, and E. E. Hafez, "Polyvinyl alcohol/Sodium alginate integrated silver nanoparticles as probable solution for decontamination of microbes contaminated water," *Int. J. Biol. Macromolecules.*, vol. 107, pp. 1773-1781, 2018, doi: 10.1016/j.ijbiomac.2017.10.047.
- [50] S. Abirami, D. Nagarajan, A. Samrot, A. M. Varsini, A. Sugasini, and D. A. Anand, "Extraction, characterization, and utilization of shrimp waste chitin derived chitosan in antimicrobial activity, seed germination, preservative, and microparticle formulation," *Biointerface Res. Appl. Chem.*, vol. 11, pp. 8725-8739, 2021, doi:10.33263/briac112.87258739.
- [51] A. Di Martino, M. Sittinger, and M. V. Risbud, "Chitosan: A versatile biopolymer for orthopaedic tissue-engineering," *Biomaterials*, vol. 26, pp. 5983-5990, 2005, doi: 10.1016/j.biomaterials.2005.03.016.
- [52] F. Nessa, S. M. Masum, M. Asaduzzaman, S. Roy, M. Hossain, and M. Jahan, "A process for the preparation of chitin and chitosan from prawn shell waste," *Bangladesh J. Sci. Ind. Res.*, vol. 45, pp. 323-330, 2010, doi.org/10.3329/bjsir.v45i4.7330.
- [53] F. Al Sagheer, M. Al-Sughayer, S. Muslim, and M. Elsabee, "Extraction and characterization of chitin and chitosan from marine sources in Arabian Gulf," *Carbohydr. Polym.*, vol. 77, pp. 410-419, 2009, doi:10.1016/j.carbpol.2009.01.032.