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RESEARCH PAPER

Synthesis of nanochitosan from oyster pearl shell (Pinctada maxima) as renewable energy candidate

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Abstract: The increase in energy needs must be balanced by environmentally friendly technological innovations. Chitosan polymer is one of the technological innovations of energy materials that are being developed by many developed countries. This research aimed to identify the potential of oyster pearl shell waste as a source of electrolyte polymers. The study was conducted experimentally by synthesizing chitosan nanoparticles from chitosan using the ionic gelation method. Chitosan is obtained through the isolation method from Pinctada maxima oyster pearl shell waste. The isolation method is carried out by three processes: deproteination, demineralization, and deacetylation. Several characterizations were carried out to analyze the material from the synthesis, including a proximate test, FTIR analysis, and PSA analysis. Isolated chitosan was identified to have a deacetylation degree that reached 88.63% with the formation of OH and NH2 functional groups. In general, the proximate tets data has shown that the obtained chitosan already meets the Indonesian standard SNI 7949:2013. PSA analysis resulted in differences in size distribution, PDI, and zeta potential between chitosan and chitosan nanoparticles. The results were obtained by the average distribution of chitosan particle size of 52.043 µm and chitosan nanoparticle size of 2.3365 µm—the analysis of the potential zeta of chitosan -3.9 mV and chitosan nanoparticle -21,6 mV. Thus, changes in the size of the chitosan material affect its potential PDI and zeta values. The change of these two values is a good indicator of the initial data and the potential of the material as an energy material. Therefore, chitosan polymer is an electrolyte material that can be used as a candidate for environmentally friendly renewable energy materials.

Keywords: Degree of deacetylation, electrolyte polymer, zet potential.

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INTRODUCTION

Energy is an essential need required by society. The battery is one of the important sources of energy used in most electronic devices. The continuous use of energy accompanied by population growth in Indonesia has increased battery consumption. Batteries are currently widely used and are made from heavy metals that can use chemicals that pollute the environment by making environmentally friendly technological innovations [1]. Environmentally friendly technology, known as renewable energy, is starting to be developed by researchers to reduce the use of fossil energy that can cause pollution.

Bio-battery is an innovative product of renewable energy technology produced from organic materials. Electrolytes are a component of batteries that are widely produced from organic materials. One of the organic materials that can be utilized as a source of electrolytes is the natural polymer chitosan. Chitosan has the potential to be used as an electrolyte polymer because chitosan has a free amine functional group that can exchange ions and hydroxy groups that can be modified.

Chitosan is a derivative of chitin which is abundant is nature [2], [3], [4], [5]. Crustaceans such as crab shells, shrimp shells, pigeon shells, and oyster pearl shells are the primary sources of chitin [6], [7], [8]. Oyster pearl shells are composed of chitin, protein, glycoproteins, peptides, lignin, and pigments, with chemical constituents of Ca, Mg, Na, P, Fe, Cu, Ni, B, Zn, dan Si. The high chitin content in oyster pearl shells makes oyster shells a good source of chitosan. The shell of the oyster-type *Pinctada maxima* was successfully isolated into chitosan with a deacetylation degree of 81,50% [8].

Chitosan is generally modified into nanoparticles to produce better physical and chemical properties. Modification of chitosan is done using the crosslink agent method using sodium trypolyphosphate (STPP) compound. The smaller particle size increases the conductivity of the material. Chitosan with a smaller particle size can increase proton conductivity by 4,7×10-5 S/cm where high conductivity can facilitate the process of moving protons from the anode to the cathode [9].

Based on previous research, chitosan sourced from oyster shells is more focused on its utilization as a medical material. The shell of the oyster type *Pinctada maxima* used is abundant in West Nusa Tenggara (NTB) because it is a superior commodity. However, the shell part is not optimally utilized, so it becomes waste that can interfere with environmental cleanliness. Several studies have also stated that chitosan can be used as a mixture to make environmentally friendly natural batteries. Nano-sized chitosan has better conductivity characteristics than micro-size. Synthesis of nano chitosan from oyster pearl shells (*Pinctada maxima*) has never been done. So, this study aims to determine the potential of oyster pearl shells (*Pinctada maxima*) synthesized into nano chitosan to be used as electrolyte polymers for bio-battery candidates. The result of this study is expected to be an innovation in utilizing oyster pearl shell weights for the environment.

MATERIALS AND METHODS

Tools and Materials

Isolation of chitosan and synthesis of chitosan nanoparticles using several tools and materials in the manufacturing process. The tools used were magnetic stirrer with hot plate (IKA-CMAG HS7, Indonesia), grinder (SY-150 Pulp Grinder Yamamoto, Indonesia), miller (FGD-Z100 Fomac, Indonesia), LLPA-C10 (Laser Particle Sizer Analyzer) (Labtron, United Kingdom), and PSA SZ-100 (Particle Size Analyzer) (Horiba, Singapore). The materials used were *Pinctada maxima* oyster pearl shells, distilled water, NaOH pro analyst (Merck, Jerman), HCl 1 M pro analyst (Mallinckrodt, USA), CH3COOH 0.1% pro analyst (Mallinckrodt, USA), STPP 0.1% pro analyst (Xilong Scientific, China), and tween 80 0.1% pro analyst (Sigma Aldrich, Germany).

Methods

This research was conducted using laboratory experimental methods. The oyster pearl shell isolation method was used to form chitosan by changing the amine group into an acetyl group. The method used to reduce the particle size of chitosan into nano chitosan is the ionic gelation method.

The research procedure generally includes shell preparation, isolation of chitosan, synthesis of nano chitosan, and characterization. The sample was prepared by washing, drying, and grinding. The results of the sample preparation process obtained oyster shell flour, which was then sieved using a 100 mesh sieve.

Chitosan isolation is carried out through three stages, including deproteination, demineralization, and deacetylation. The chitosan isolation process is a modification of the research conducted by Nurmaulida et al. (2023) by modifying the NaOH concentration at the deacetylation stage. In the deproteination stage, 80 grams of oyster shell flour was mixed with NaOH in a ratio of 1:10 (w/v). The mixture was then homogenized for 1 hour at 80℃; the homogeneous solution was then washed to neutralize the pH. The neutral solution was then precipitated and oven-dried at 80℃ for 3 hours. The deproteinated powder then underwent demineralization by mixing with 1 M HCl solution in a ratio of 1:15 (w/v), then homogenized for 3 hours at room temperature. The homogenized solution was washed until the pH was neutral and then precipitated and dried using an oven at 80℃ for 3 hours to produce chitin powder. Chitin powder undergoes deacetylation to convert acetyl groups into amine groups to form chitosan. Chitin powder was mixed with 80% NaOH in a ratio of 1:15 (w/v) at 120℃ for 3 hours. The mixture was neutralized, precipitated and dried at 60℃ for 5 hours to produce chitosan powder [8].

Nanochitosan synthesis combined previous research conducted by Handayani et al. (2018) and Ali et al. (2018). The nano chitosan synthesis process is divided into three stirring processes. The first stirring was done by

dissolving 3 g of chitosan using 60 mL of CH3COOH 0.1% (w/v), then 1 L of distilled water was added and stirred for 1.5 hours at 1000 rpm. The second stirring was carried out by adding 25 mL of 0.1% tween 80 dropwise for 1 hour at 1000 rpm. The third stirring was done with the addition of 0.1% STPP and stirred for 2 hours at 1000 rpm. The stirred sample was then neutralized and dried at 60℃ for 5 hours to produce nano chitosan powder [10], [11].

Data Analysis

Chitosan that has been successfully isolated is analyzed for physiochemical properties in the form of functional group analysis using FTIR testing and proximate testing. Based on the FTIR testing results, the absorption band's spectrum data in wave numbers (cm-1) and transmittance (%T) were obtained. FTIR data analysis can identify functional groups, qualitative crystallinity, and degree of deacetylation. Analysis of the chitosan functional groups of the research results was carried out by matching the FTIR spectrum obtained with the FTIR spectrum of Nurmaulida et al.'s research results. The formation of hydroxy functional groups (OH) and amine functional groups (NH2) is a sign of the was carried out by looking at the OH and NH2 spectrum peaks formed. Analysis of the degree of deacetylation peaks formed. The degree can be analyzed using the baseline equation by comparing the absorbance of the amine group wave number in the range. The baseline equation for calculating the degree of deacetylation is found in equation (2).

$$A = log\frac{r_0}{r} \quad (1)$$

$$DD\ (\%) = \left[100 - \left(\frac{A_{1655}}{A_{3450}} \times \frac{100}{1{,}33}\right)\right] \quad (2)$$

Description:

r_0 = Distance between baseline and tangent

r = Distance between the baseline and the lowest valley

A_{1655} = Absorbance value at 1655 cm^{-1}

A_{3450} = Absorbance value at 3450 cm^{-1}

$1{,}33$ = A_{1655}/A_{3450} ratio for fully acetylated chitosan

The level of chemical composition of a material can be determined by conducting proximate testing that refers to the Official Methods of Analysis of the Association of Official Analytical Chemists (AOAC). Data from proximate testing is in the form of chemical composition percentage data close to the actual composition [12]. In this study, proximate testing was carried out to determine the chitosan content from the research results. The composition tested included moisture, ash, protein, and fat content.

Chitosan and nanochitosan samples were subjected to Particle Size Analyzer (PSA) testing to determine particle size and polydispersity index (PDI). Particle size and PDI testing are done using a light scattering technique called dynamic light scattering (DLS). Chitosan can be sad to be nano-sized if the chitosan particles are 1-1000 nm in size [13]. From the results of particle distribution, the type of particles formed can also be seen. The types of particles formed can be seen in Table 1.

Table 1. Types of particles by size

Particle Type	Particle Size (μm)
Coarse particle (PM10)	≤10
Fine Particle (PM2.5)	≤2.5
Ultrafine Particle (PM0.1)	≤0.1

The PDI value of DLS can be calculated by comparing the standard deviation squared with the mean distribution squared. PDI is used to determine the range of particle distribution or particle uniformity. PDI is categorized into two types, namely monodispersion and polydispersion [14], [15].

Testing using the Zeta Potential Analyzer (ZPA) obtained data on the potential zeta value of a material. Zeta potential is the surface charge of a particle that can be used to determine the interactions between particles. The zeta potential value also affects the particle suspension's stability, as seen in Table 2.

Table 2. Effect of zeta potential value on particle stability

ZPA Value(mV)	Stability
0 to ±5	Rapid agglomeration
±10 to ±30	New stability begins
±30 to ±40	Medium stability
±40 to ±60	Good stability
> ±60	Excellent stability

RESULTS AND DISCUSSION

Through deproteination, demineralization, and deacetylation stages, chitosan was successfully isolated. The successfully isolated chitosan was analyzed for the degree of deacetylation and functional groups using FTIR. The results of the FTIR test are in the form of absorption band spectra expressed by wave number (cm-1) on the X-axis and percentage transmittance (%T) on the Y-axis. The FTIR test data of chitosan can be seen in Figure 1.

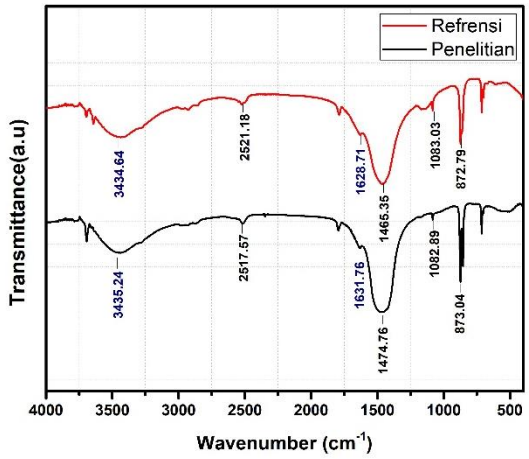


Figure 1. FTIR spectrum of chitosan

Qualitative and quantitative analysis can be carried out based on the results of FTIR testing. Based on Figure 1, qualitative analysis can be carried out, namely the determination of functional groups and crystallinity of chitosan. Functional groups can be seen more clearly in Table 3.

Based on the spectrum formed, chitosan functional groups have stretching and bending vibrational modes [16]. The results of the IR spectrum in Figure 1 and Table 1 show that there are OH (hydroxy) and NH2 (amine) spectra indicating that chitosan has been formed [17]. Both typical functional groups of chitosan form sharp peaks, indicating that isolated chitosan has high crystallinity [6]. The hydroxy and amine functional groups contained in chitosan can form hydrogen bonds with water to reduce the water content in the electrolyte material so that it is not flammable [18]. The functional groups of the research results with the reference have different wave numbers in each functional group. This difference is due to a shift in the spectrum, which differences in the concentration of NaOH can cause.

Tabel 3. Functional groups of reference chitosan and research results

Functional Group	Wave numbers (cm^{-1})	
	Nurmaulida et al., (2023)	Current Research
O-H (stretching)	3434.64	3435.24
C-H (stretching)	2521.18	2517.57
N-H_2 (stretching)	1628.71	1631.76
C-H_3 (bending)	1465.35	1474.76
C-O-C (glucosamine ring)	1083.03	1082.89
B-1,4-glycosidic	872.29	873.04

From the spectrum that has been formed, the degree of deacetylation can be analyzed using equation (2). The value of the degree of deacetylation of chitosan indicates the more acetyl groups of chitin that change into amine groups due to the many hydroxy groups produced by NaOH [19], [20]. The successfully isolated chitosan sample has an absorbance value at wave number 3450 cm-1 of 0.1910 while at wave number 1655 cm-1 of 0.0289. So, the value of the degree of deacetylation of chitosan is 88,63%. The resulting deacetylation degree percentage meets the chitosan standard set by the Indonesian Standard BSN (SNI 7949, 2013) [21].

Proximate analysis was also carried out on chitosan samples that had been successfully isolated. The results of the proximate analysis of chitosan can be seen in Table 4.

Tabel 4. Proximate Chitosan

Parameters	Value ± SD (%)
Water content	8,05 ± 0,30
Ash content	60,27 ± 0,47
Fat	0,291 ± 0,0049
Protein	2,773 ± 0,0049

Table 4 shows that the water content of chitosan is higher than before going through the isolation process; this can be caused by the drying process at the deacetylation stage. The resulting water content value still meets BSN's

standards of ≤ 10%. The ash content in chitosan is still high, indicating that there are still minerals believed to be in the form of CaCO3, the main content of oyster pearl shells. However, the presence of CaCO3 can also be utilized as an ingredient in the synthesis of conductive particles, as in the research conducted by Gärtner et al. (2022). CaCO3 yang synthesized from oyster pearl shells by Gärtner et al. (2022) is used as a template and produces conductivity that can be applied to conductive inks [22]. Oyster shell powder successfully isolated is then synthesized into nano chitosan to reduce size. Chitosan and nano chitosan powders that have been produced are characterized to determine their electrical properties through particle size analysis, PDI, and zeta potential of the two samples.

The chitosan and nano chitosan samples were tested using a Particle Size Analyzer (PSA) to obtain the particle size distribution and PDI (Polydispersity Index) values. The test results can be seen in Figure 2 and Figure 3.

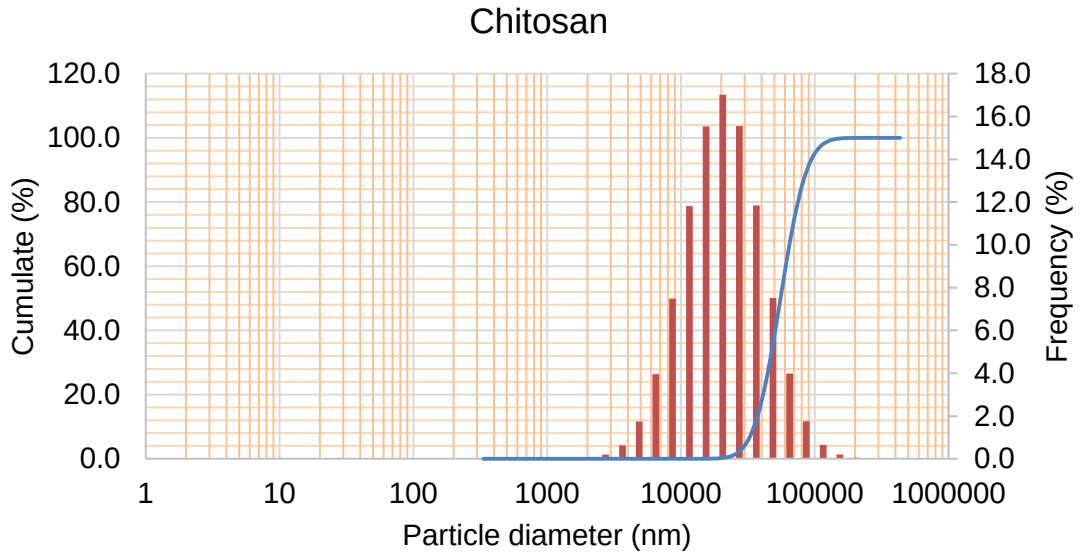


Figure 2 Chitosan particle size distribution chart

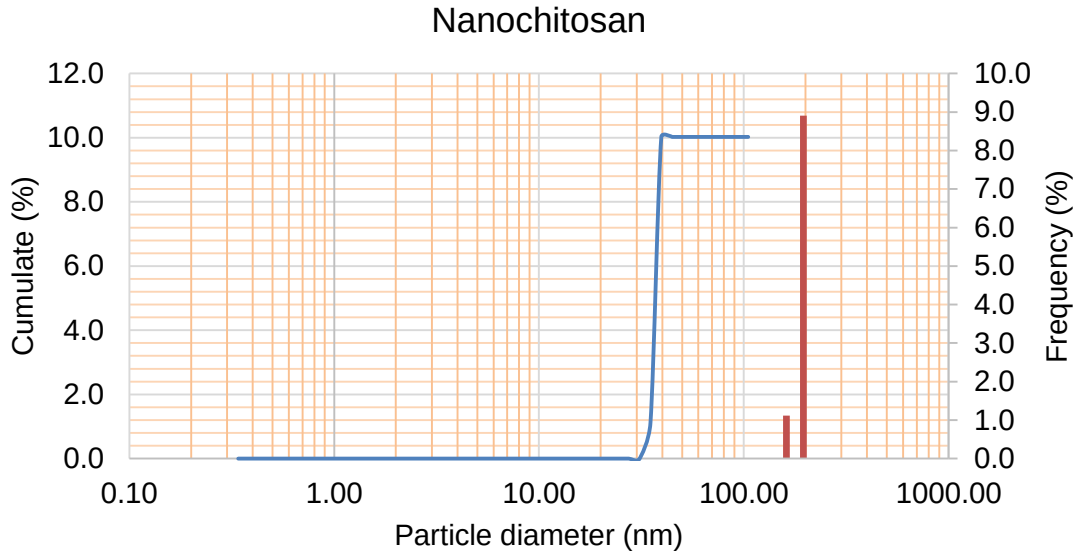
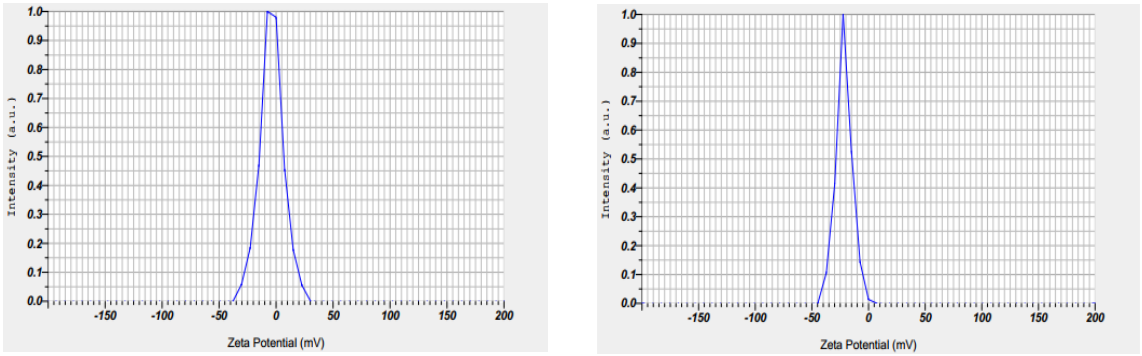


Figure 3 Nanochitosan particle size distribution chart

Based on the test results using PSA, the average value of chitosan particle distribution is 52.043 µm, which starts to be distributed from the size of 13.012 µm to 275.177 µm. In nanochitosan, the average particle size distribution is 2175.6 nm, which starts to be distributed from 39.58 nm to 3621,48 nm. Based on Table 1, the particle size formed in the nano chitosan phase can be categorized as fine particles of fine powder particles. In addition to particle size distribution data, PDI data was also obtained. The PDI value obtained for chitosan was 1.291, and nanochitosan was 1.110. The PDI value obtained is greater than 0.7, meaning the particles formed are highly polydispersed and have a very wide particle size distribution.

In addition to particle size testing, zeta potential testing was carried out to determine the amount of electrostatic charge of particles in the dispersion and the stability of the particle suspension. The zeta potential of chitosan and nano chitosan can be seen in Figure 4.



(a) **(b)**

Figure 4 Zeta Potensial graph (a) Chitosan (b) Nanochitosan

The zeta potential value of chitosan was found to be -3,9 mV, while that of nanosize was found to be -21,6 mV. The negative zeta potential value indicates the accumulation of positive charges near the particle surface and the negative electrical properties of chitosan and nano chitosan particles. The negative nature is that the repulsive force between particles is more stable [23]. The zeta potential value of nano chitosan, which is greater than its micro size, can be caused by the effect of the addition of negatively charged tripolyphosphate, thus increasing the negative ions formed [15]. The zeta potential value of chitosan and nano chitosan has not exceeded ± 30 mV, which means that the chitosan and nano chitosan solutions are unstable [24]. However, the nono chitosan solution has a value close to -30 mV, so it can be concluded that the nano-sized chitosan solution is more stable than the micro-sized one.

CONCLUSION

Based on the research results presented, chitosan and nanochitosan sourced from oyster pearl shells (*Pinctada maxima*) can be used as an alternative to electrolyte polymers. The zeta potential value of nano-sized chitosan is greater, which causes a greater repulsive force. So that nano-sized chitosan has more stable conditions. Conductivity testing needs to be done, varying the chitosan composition. Other materials also need to be added to increase potential and conductivity.

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