Chitin has been extracted from Philippine blue swimming crab. The extracted chitin was subjected to thermo gravimetric analysis (TGA), Fourier transform infrared (FTIR) spectroscopy and X-ray diffraction (XRD) analysis. The degree of acetylation of the extracted chitin, derived from the X-ray diffraction intensity values of chitin characteristic peaks, revealed that the extracted chitin is purer than the commercially acquired high purity chitin. The extracted chitin was used to form polymer films at different formation conditions. Polymer films were also formed from commercially acquired chitin for comparison. It was shown that films prepared from the extracted chitin at different conditions have greater ultimate tensile strengths as compared to the commercially-available plastic film. Morphologies of the material surface and the fracture surface were investigated using the scanning electron microscope to identify stress concentration sites that contributed to the weakening of material under tensile loading.

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Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: Chitin, Blue swimming crab, Polymer films

1. Introduction

Chitin, also known as poly(β-1→4)-N-acetyl-D-glucosamine, is the second most abundant biopolymer in nature, next to cellulose. It is described as colorless, crystalline or amorphous powder, which is insoluble in water, organic solvents and diluted acid and alkali.
It exists in nature in the exoskeleton of crustaceans and arthropods or in the cell walls of fungi and yeast. But the primary source of chitin is the marine crustacean shell waste from shrimp, prawns and crabs. These crustaceans are estimated to have maximum chitin content of 15 to 20 percent, along with proteins and calcium carbonate. Large amount of chitin is being synthesized worldwide. The total annual production of chitin by arthropods had been estimated at 1,328,000,000 MT from marine ecosystem, 28,000,000 MT from freshwater ecosystem, and 6,000,000 MT from athalassohaline ecosystem. In the end, the major concern in chitin production is not the source but the final product’s quality which depends on the extraction process.

In the Philippines, significant amount of marine and agricultural shells become waste by-products from the food industry, among them is the blue swimming crab (*Portunus pelagicus*) shells. For the year 2011, 29,000 MT of blue swimming crab was captured. The figure corresponds to 1.34% or fourth from the largest of the total fishery capture of the Philippines. In terms of global production, 185,000 MT of blue swimming crab was processed based on the Food and Agriculture Organization of the United Nations.

Several processes have been employed in the extraction of chitin from arthropods. Shimahara & Takiguchi classified the isolation of chitin into two different procedures, the biological extraction and the chemical extraction of chitin. But both of these procedures follow the same stages in chitin isolation; the demineralization stage and the deproteinization stage of chitin extraction. The chemical extraction method, however, yields into higher percent purity chitin as compared to biological extraction.

Both chitin and the chitin-derived chitosan have wide ranging applications in the field of biomedicine, materials science, microbiology, tissue engineering, food technology, agriculture, electrochemical technology, environmental technology, textile, energy and bio-nanotechnology. Chitin’s purity is taken into account to suit the different needs of various applications, e.g. chitin for biomedical application requires higher percent purity to avoid contamination. Recently, the Wyss Institute was able to form bioplastic from chitosan derived from shrimp shells.

It is, therefore, the objective of this study to extract chitin from Philippine blue swimming crab shells. Moreover, the extracted chitin was formed into polymer films. Both the extracted chitin and synthesized film had been subjected to various characterization tests.

### 2. Methodology

#### 2.1. Chitin Extraction

The general procedure established by Shimahara & Takiguchi and the acid concentration, particle size, reaction time, temperature and stirring rate from the results of Chang et al. have been used in the extraction of chitin. The product from the extraction process was subjected to various characterizations to determine composition, degree of acetylation (DA), and thermal stability while comparing with the commercially acquired chitin. Particularly, the DA is indicative of the purity of chitin wherein high values would correspond to a high purity material. The extracted chitin has a computed DA of 68.16% and the commercially available chitin with only 30.99%.

\[
I_{CR} = \frac{I_{020} - I_{am}}{I_{020}} \times 100
\]

\[
DA = 100 - \left( \frac{103.97 - I_{CR}}{0.7529} \right)
\]

Where:

- \( I_{CR} \) - crystalline index
- \( I_{020} \) - intensity of the peak at (020) at 20 < 13°
- \( I_{am} \) - intensity of peak at 20 = 28°
2.2. Polymer Film Synthesis

For the polymer film formation, 5% (w/v) lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) solvent for chitin dissolution was prepared. The covered mixture was stirred at room temperature until all LiCl dissolved. Then, 0.5% (w/v) of extracted chitin was added to the solution, and the solution was agitated until the mixture became homogenous. The solution was then poured into a glass mould, covered with pin-holed aluminum foil, and allowed to set for 24 and 96 hours. The formed gels were soaked in isopropanol and methanol. These were then cold pressed between filter papers, glass plates, and binder clips, then oven-dried overnight. The dried films were again soaked in isopropanol and methanol, then cold-pressed for another 48 hours.

The final films were characterized and compared with commercially available plastic film using UTM testing for tensile strength tests. SEM imaging was also conducted to evaluate the weak polymer film’s surface morphology.

3. Results and Discussions

3.1. Extracted chitin

Fig.1 shows the extracted chitin from the Philippine blue swimming crab shells. It can be seen that the powder exhibits a light red to orange color. The weight change of the extracted material with increase in temperature of the extracted chitin is shown in Fig. 2. There are two observable shoulders that can be associated to significant weight losses from the material. The first shoulder, between 95-99°C, can be accounted by the loss of water, while the second peak, which appears at around 390°C, can be associated to chitin similar to the one produced by Abdou et al. with chitin degradation at 372°C.
Fig. 2. Thermogravimetric profile of extracted chitin.

The FTIR spectrum of extracted chitin, shown in Fig. 3, can be observed to have a series of narrow absorption bands which are typical of crystalline polysaccharide samples. Amide I band, which is responsible for the splitting of wavenumbers between 1600 to 1500 cm$^{-1}$, corresponds to the inter-sheet hydrogen bonding due to the hydroxymethyl group that can be associated to the band peak at 1630 cm$^{-1}$ and the intra-sheet hydrogen bonding at the C=O stretching region with wavenumber 1660 cm$^{-1}$. This inter- and intra-sheet hydrogen bonding is characteristic of chitin which gives chitin’s highly insoluble property.

Fig. 3. FTIR spectra of extracted chitin and commercially acquired chitin.

Intensities of characteristic XRD peaks of chitin (Fig. 4) were used to determine the degree of acetylation (DA) of the extracted chitin using Eq. 1 and 2 by Zhang et al. The values of crystalline index of the chitin samples are shown in Table 1. It can be seen that the extracted chitin has a higher index of crystallinity and degree of acetylation compared to that of the commercially acquired chitin material.
Fig. 4. XRD profiles of extracted chitin and commercially acquired chitin.

Table 1. Crystalline index of chitin samples at (020).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(020)</th>
<th>Amorphous</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2θ (°)</td>
<td>d-spacing (Å)</td>
</tr>
<tr>
<td>Extracted Chitin</td>
<td>9.07</td>
<td>9.75</td>
</tr>
<tr>
<td>Commercially Available</td>
<td>10.03</td>
<td>8.81</td>
</tr>
</tbody>
</table>

3.2. Chitin-based polymer films

The polymer films formed from the extracted chitin is shown in Fig. 5. These films were subjected to tensile loading and compared to the commercially available plastic film. It can be observed from Fig. 6 that both extracted chitin-based films have higher tensile strengths than the film prepared from commercially acquired plastic film with only 18.90 MPa. It can also be observed that a longer forming time increased the tensile strength of the film to 44.22 MPa. Observing the sample under the SEM revealed that the surface of the weak film is rough. These irregularities could have served as stress concentration sites, which, under continuous application of tensile load, eventually formed into cracks and propagated across the film to failure.
Fig. 5. Photograph of chitin-based polymer film.

Fig. 6. Ultimate tensile strength of films formed from extracted and commercially acquired plastic film.

Fig. 7. SEM micrograph of chitin polymer film formed that exhibits a rough surface finish.
4. Conclusion

In this study, chitin was successfully extracted from the Philippine blue swimming crab. Characterizations showed that the degradation temperatures of the extracted material correspond to the characteristic degradation temperatures of chitin. Further spectroscopy analysis using FTIR revealed the characteristic signals of hydrogen bonding in chitin, thereby confirming identity of the material. It was also found that the extracted chitin has purity better than that of commercially acquired chitin wherein much lesser XRD peak intensity from associated soluble protein was observed. The extracted chitin also has a high degree of acetylation. After the formation of polymer films from the extracted chitin, it was found that the chitin polymer films have higher tensile strength up to 44.20 MPa as compared to commercially available plastic film. It was also found that shorter forming times favor the formation of surface roughness which lowered the tensile strength of the film.

It is recommended that thorough study on the parameters for extracting chitin be conducted. Optimizing the conditions in both the extraction of chitin and synthesis of film will in the long run be a factor considering the processes commercial viability.

Acknowledgements

The authors would like to thank DOST-ERDT and AUN/SEED-Net for the financial support provided at various stages of this study. The authors would also like to thank Ms. Jill Manapat for her assistance in the UTM testing.

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