Preparation and property of surface deacetylated chitin nanofiber

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Chitin in the crustacean shells such as crabs and prawns exists in the form of crystalline chitin microfibril of about 2-5 nm in width. Recently, it has been reported that the chitin nanofiber can be isolated by mechanical treatment under acidic condition. This is because cationization of amino groups on the surface of chitin microfibril promotes nanofibrilation. The chitin nanofiber is expected as a reinforcement to give optically transparent and the low thermal expansion composites. As chitosan, that is deacetylated chitin, has antimicrobial property, the surface deacetylated chitin nanofiber is expected to exhibit antimicrobial property. The present study clarified the property of the surface deacetylated chitin nanofiber.

Materials and methods

α-chitin from crab shell (Nacalai Tesque) was purified with 4wt% NaOH solution. The purified chitin was deacetylated with 20-40wt% NaOH solution at 90°C for six hours under the stirring, and the obtained sample was analyzed by the ATR-IR and X-ray diffraction. The deacetylated chitin was dispersed in water at 1 wt %, and acetic acid was added to adjust the pH value to 3-4 to facilitate fibrillation. The slurry of 1 wt % deacetylated chitin was passed once through a grinder (MKCA6-3; Masuko Sangyo Co., Ltd.) at 1500 rpm. The obtained nanofiber was observed by FE-SEM (JSM-6700F; JEOL). The deacetylated chitin nanofiber slurries were converted to thin sheet by suction filtration, and dried at 110°C. The mechanical properties of the obtained thin sheets were evaluated by tensile test.

Results and discussion

Table 1 shows degree of deacetylation of the chitin prepared by NaOH solution at 90°C for six hours. When the chitin was treated with 40wt% NaOH, α-chitin crystal structure changed, indicating that deacetylation occurred inside of α-chitin crystal. However, when 20-35wt% NaOH was used, the α-chitin crystal structure and crystal size did not change. These results demonstrate that deacetylation by 20-35wt% NaOH mostly takes place on the surfaces of α-chitin crystal.

The nanofibers obtained from untreated chitin were found to have a width of about 10-50 nm. On the other hand, the nanofibers obtained from 35wt% NaOH treated chitin demonstrated a uniform width of about 10 nm.

Figure 1 shows the results of tensile test. Young’s modulus and tensile strength of sheet increased with the degree of deacetylation. Since the number of amino groups on the surface of chitin nanofibers increased due to deacetylation, it is suggested that the number of hydrogen bonds between nanofibers increased.

Table 1. Degree of deacetylation (DDA) of the chitin prepared with different NaOH concentration at 90°C for six hours.

<table>
<thead>
<tr>
<th>NaOH concentration</th>
<th>chitin 20%</th>
<th>35%</th>
<th>40%</th>
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<tbody>
<tr>
<td>DDA</td>
<td>0.06</td>
<td>0.24</td>
<td>0.54</td>
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Figure 1. Stress-strain curves of surface deacetylated chitin nanofiber sheet.