1. INTRODUCTION

Chitin is a natural, non-toxic, biodegradable polymer (1,4-β)-2-acetamido-2-deoxy-D-glucopyranose with a highly ordered structure [1]. This characteristic feature has a decisive impact on the properties of this polymer. Chitin is not highly susceptible to chemical substances. This is indicated by the high molecular weight of chitin obtained on both laboratory and industrial scales [2, 3]. This polymer is not soluble in water or in most solvents. These properties are usually modified by chemical deacetylation. The product of this reaction is chitosan, which, thanks to its biological activity and functional characteristics, has applications in many fields [4 - 8]. The biological and functional properties of this polymer are influenced by its chemical structure and the degree of polymerization [9 - 14]. By describing the dependencies between them, the optimum quality parameters of chitosan for the studied application can be determined. Thus, studies should be conducted on polymers with widely ranging degrees of deacetylation and molecular weights. Chitosans with these properties can be obtained from chitin which is degraded prior to the deacetylation process with chemical, enzymatic, and physical methods [1, 15 - 17]. Studies conducted according to Wojtasz-Pająk and Szumilewicz [17] indicated that thermal degradation may be a simple method for lowering the molecular weight of chitin. The thermal processing of chitin at temperatures ranging from 100 to 160 °C for several to several tens of hours caused significant changes in its degree of polymerization. The conditions applied did not cause significant changes in the chemical structure of the chitin.

Degradation could have had an impact on the degree of order of the polymer structure. This type of changes in chitin structure may cause that the conditions for obtaining chitosan with specified properties will significantly differ from those applied in the stan-
standard method of obtaining polymers. There is a lack of data in the literature regarding how the thermal processing of chitin impacts the kinetics of the deacetylation reaction.

The aim of the studies presented in the current paper was to determine the susceptibility of thermally degraded chitin amide and glycoside bonds to alkaline hydrolysis.

2. MATERIALS AND METHODS

2.1. Raw materials
The raw material for the study was shells obtained from common shrimp (*Crangon crangon* L.) caught at various periods and stored under various conditions. This material was homogenized and cleaned of tissue residue with a diversified procedure for initial processing [3].

The material was stored at a temperature of -25 °C until the study.

2.2. Chitin
2.2.1. Chitin obtained under standard conditions
Following initial preparations, the shells were demineralized according to Wojtasz-Pająk [18] for 20 hours at a temperature of 22 ± 1 °C. After demineralization, the raw chitin was rinsed several times in tap water (1 : 10 w/v) and deproteinized in 5% NaOH (1 : 5 w/w) for 20 hours at a temperature of 22 ± 1 °C. Next, the polymer was rinsed several times in tap and distilled water (1 : 10 w/v). The chitin was dried at a temperature of 80 °C for 10.5 hours. Next, it was ground in a Cyclotec 1093 Sample Mill (Tecator) and dried for 7.5 hours at a temperature of 80 °C. Until the analyses, the polymer was stored in a desiccator. The Roberts method [19] was used to determine the deacetylation degree (DDCHA) of the chitin, while the limiting viscosity number ([ηCHA]) was determined according to Terbojevich and Cosani [20]. Viscosity measurements were conducted at a temperature of 25 ± 0.01 °C with an AVS-350 (Schott Geräte) using a Ubbelohde 53213/lc viscometer with a constant of K = 0.02912 mm²/s². The chitin concentration in N,N-dimetyloacetamide with 5% LiCl ranged from 0.0001 to 0.0003 g/ml of solvent.

2.2.2. Chemically degraded chitin
Following deproteinization, the shells were treated with 5% HCl (1 : 4 w/v) for 25 hours at a temperature of 23 ± 1 °C. After degradation, the chitin was rinsed, dried, and analyzed as described in point 2.2.1.

2.2.3. Thermally degraded chitin
Chitin obtained under standard conditions was degraded at temperatures of 140 and 160 °C for 12 and 2.75 hours, correspondingly. The thermal processing was done in a SUP-4M drying oven. The temperature was measured in the samples, and variation was ±1 °C. After degradation, the samples were cooled in a desiccator and analyzed as described in point 2.2.1.
The impact of the thermal degradation of chitin on the deacetylation process

2.3. Chitosan

Chitosan was obtained from chitin with the properties described in Table 1.

Table 1. Chemical and physical properties of chitin.

<table>
<thead>
<tr>
<th>Sample symbol</th>
<th>DD&lt;sub&gt;CHA&lt;/sub&gt;, %</th>
<th>[η]&lt;sub&gt;CHA&lt;/sub&gt;, ml/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CHA&lt;sub&gt;S1&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>3.2</td>
<td>2947</td>
</tr>
<tr>
<td>CHA&lt;sub&gt;S1.1&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</td>
<td>3.1</td>
<td>1879</td>
</tr>
<tr>
<td>CHA&lt;sub&gt;S1.2&lt;/sub&gt;&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.7</td>
<td>1855</td>
</tr>
<tr>
<td>CHA&lt;sub&gt;S2&lt;/sub&gt;</td>
<td>3.4</td>
<td>3403</td>
</tr>
<tr>
<td>CHA&lt;sub&gt;S3&lt;/sub&gt;</td>
<td>3.4</td>
<td>3264</td>
</tr>
<tr>
<td>CHA&lt;sub&gt;S4&lt;/sub&gt;</td>
<td>3.1</td>
<td>2494</td>
</tr>
<tr>
<td>CHA&lt;sub&gt;Ch&lt;/sub&gt;&lt;sup&gt;d&lt;/sup&gt;</td>
<td>3.4</td>
<td>1640</td>
</tr>
</tbody>
</table>

<sup>a</sup>CHA<sub>S</sub> – chitin obtained under standard conditions

<sup>b</sup>CHA<sub>S1.1</sub> – chitin degraded at a temperature of 140 °C for 12 hours

<sup>c</sup>CHA<sub>S1.2</sub> – chitin degraded at a temperature of 160 °C for 2.75 hours

<sup>d</sup>CHA<sub>Ch</sub> – chemically degraded chitin

The chitin was treated with 50% NaOH (1 : 30 w/w) at temperatures of 100 to 120 ± 1 °C for 30 to 120 minutes. After deacetylation the product was rinsed several times with hot distilled water (1 : 10 w/v) and dried at a temperature of 80 °C for 3.5 hours.

The deacetylation degree (DD<sub>CHN</sub>) of the chitosan was determined with potentiometric titration [16], while the limiting viscosity number ([η<sub>CHN</sub>]) was determined according to Terbojevich and Cosani [20].

Viscosity measurements were performed according to point 2.2.1 using a Ubbelohde 53210/I viscometer with a constant of K = 0.009852 mm<sup>2</sup>/s. The concentration of chitosan in 0.5 M acetic acid with 0.2 M sodium acetate ranged from 0.00021 to 0.00095 g/ml solvent.

The results were compared with previous data for chitosan from chitin obtained using the standard procedure (CHA<sub>S5</sub>) with a [η<sub>CHA</sub>] = 2895 ml/g DD<sub>CHA</sub> = 3.5 [21].

3. RESULTS AND DISCUSSION

3.1. Studies of the susceptibility of thermally degraded chitin amide bonds to alkaline hydrolysis

Studies of the impact of thermal degradation on the susceptibility of chitin to deacetylation were conducted by subjecting polymers obtained from the standard method (CHA<sub>S1,2,3,4</sub>), thermal degradation (CHA<sub>S1.1</sub>, CHA<sub>S1.2</sub>), and chemical degradation (CHA<sub>Ch</sub>) to alkaline processing as described in point 2.3 (Table 1). The deacetylation degrees of the chitins were similar (approximately 3%), but the degrees of polymerization varied. The limiting viscosity numbers ranged from 1640 to 3403 ml/g.
Changes in the deacetylation degree of thermally and chemically degraded chitins and these obtained using the standard procedure were similar when the process was conducted at a given temperature (Figure 1).

![Figure 1. Kinetics of the deacetylation reaction of chitins degraded thermally (CHA$_{S1.1}$, CHA$_{S1.2}$), chemically (CHA$_{Ch}$), and undegraded (CHA$_{S1.5}$).](image)

The rate of the reaction was the highest in the first thirty minutes and then it decreased. The deacetylation degrees of chitosans obtained under the same conditions from the studied chitins changed within the limits presented in Table 2. The differences between the maximum and minimum levels did not exceed 1.5%.

**Table 2. Range of changes in the deacetylation degrees of chitosans obtained from chitins that had been degraded thermally, chemically, or undegraded.**

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>Time, min</th>
<th>Minimum DD$_{CHN}$, %</th>
<th>Maximum DD$_{CHN}$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>30</td>
<td>69.5</td>
<td>70.5</td>
</tr>
<tr>
<td>100</td>
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<td>78.7</td>
</tr>
<tr>
<td>120</td>
<td>30</td>
<td>76.8</td>
<td>77.5</td>
</tr>
<tr>
<td>120</td>
<td>60</td>
<td>80.7</td>
<td>81.6</td>
</tr>
<tr>
<td>120</td>
<td>90</td>
<td>82.8</td>
<td>83.5</td>
</tr>
<tr>
<td>120</td>
<td>120</td>
<td>84.1</td>
<td>84.8</td>
</tr>
</tbody>
</table>

The similar deacetylation degrees of chitosans obtained under the same conditions from chitins that were degraded chemically or thermally and from polymers obtained in the standard manner indicate that thermally modifying the molecular weight of the polymer...
The impact of the thermal degradation of chitin on the deacetylation process did not alter significantly the susceptibility of amide bonds to alkaline deacetylation. The susceptibility of amide bonds to alkaline hydrolysis is strictly connected with the secondary structure of the chitin [22]. Significant changes in the degree of order of the chitin structure caused by thermal degradation could have impacted the kinetics of the deacetylation reaction. Changes in the deacetylation degree during the process conducted under the applied conditions could have differed from those presented in Figure 1. Increase or decrease in the degree of crystallinity of chitin would cause decrease or increase in the rate of deacetylation.

3.2. Studies of the susceptibility of the glycoside bonds of thermally degraded chitin to alkaline hydrolysis

Degrading chitin at temperatures of 140°C and 160°C for different time periods obtained products with comparable degrees of polymerization. This is indicated by the similar limiting viscosity numbers ([\eta]CHA_S1.1 and CHA_S1.2 that were 1879 and 1855 ml/g, respectively (Table 1).

The deacetylation of chitins CHA_S1.1 and CHA_S1.2 as described in point 2.3 caused a further decrease in molecular weight. Chitosans obtained, under the same conditions, from CHA_S1.1 and CHA_S1.2 had comparable molecular weights. This was indicated by their limiting viscosity numbers (Figures 2, 3).

![Figure 2. Alkaline degradation of chitins degraded thermally (CHA_S1.1, CHA_S1.2), chemically (CHA_Chi) and undegraded (CHA_S2.4) during deacetylation conducted at a temperature of 100 °C.](image-url)
The impact of the thermal degradation of chitin on the deacetylation process

Figure 3. Alkaline degradation of chitins degraded thermally (CHA$_{S1.1}$, CHA$_{S1.2}$), chemically (CHA$_{Ch}$) and undegraded (CHA$_{S2.4}$) during deacetylation conducted at a temperature of 120 °C.

After 30 minutes at temperature of 100 °C or 120 °C, the respective limiting viscosity numbers were 697 and 700 ml/g and 615 and 611 ml/g. After 120 minutes at temperature of 100 °C or 120 °C, they were 663 and 662 and 505 and 493 ml/g, respectively.

These were close to the limiting viscosity numbers of chitosans obtained under the same conditions from chemically degraded chitin (CHA$_{Ch}$). CHA$_{Ch}$ had a lower degree of polymerization than did the thermally degraded chitins. Thus, the limiting viscosity numbers of products of deacetylation chitins CHA$_{S1.1}$ and CHA$_{S1.2}$ should be within the [η]$_{CH}$ of chitosans obtained from CHA$_4$ and CHA$_{Ch}$ and should be closer to the latter. The results indicate that in the alkaline environment chitins CHA$_{S1.1}$ and CHA$_{S1.2}$ were degraded to a greater degree than was the CHA$_{Ch}$.

The secondary structure and polydispersity degree of the chitin impact the alkaline degradation of the polymer [23 - 25]. The fact there is no significant difference in the kinetics of the deacetylation of chitins CHA$_{S1.1}$ and CHA$_{S1.2}$ or CHA$_{Ch}$ (Figure 1) indicates that the larger than anticipated changes in the molecular weights of chitins CHA$_{S1.1}$ and CHA$_{S1.2}$ do not result from the higher susceptibility of the glycoside bonds of these polymers to alkaline hydrolysis. They were probably caused by the increase in the chitin polydispersity degree during thermal degradation.

The limiting viscosity numbers of chitosans from thermally degraded chitins were, depending on the process applied conditions, from 1.4 to 1.7 times lower than the [η]$_{CH}$ of the polymers obtained from chitin of the highest degree of polymerization (CHA$_{S2}$) (Table 1, Figure 2, 3). Their degrees of deacetylation were, however, close to the DD$_{CH}$ of the chitosans obtained from this chitin.
4. CONCLUSIONS

Thermal degradation did not significantly change the susceptibility of chitin amide bonds to alkaline hydrolysis. The degrees of deacetylation of chitosans from thermally degraded chitins were close to the degrees of deacetylation of chitosans obtained under the same conditions from undegraded and chemically degraded chitins.

Modifying the molecular weight of chitin with the thermal method permits to obtain chitosans with low molecular weights and deacetylation degrees that change within the same range as the deacetylation degrees of the polymers derived from chitin that is usually available on the market.

In addition the thermal degradation caused probably increasing of the degree of polydispersity of chitin.

5. REFERENCES


