The N-succinil-chitosan is a chemically modified derivative of the biopolymer chitosan. The succinic anhydride attached to the free amino groups presented along the chitosan’s polymer chain imparts to the molecule different physicochemical properties not exhibited before the modification. These chemical modifications enhance chitosan’s solubility in slightly acid, neutral and alkaline media. These properties are related to the long alkyllic chains attached to hydrophilic parts. In this case the hydrophilic part of D-glucosamine promotes stronger interactions with the water molecules, and consequently, enhances the solubility of the chitosan polymer. It is worthy mentioning that non-modified free chitosan is soluble only in acidic medium (pH 5.5).

INTRODUCTION
Chitin is a biopolymer similar to cellulose and quite abundant in nature. It is extracted mainly from crustaceous skin or shells. (SINGLA, 2001; KHAN, 2002; TANGPASUTHADOL, 2003). Due to the natural origin of chitin, different variants are found in environment. In addition, when chitin is submitted to different chemical processes, a series of polymers varying in the degree of deacetylation (DD), molecular weight (MW), viscosity, pKa, etc, may be generated (CHATELET, 2000; CANELLA, 2001; SINGLA, 2001).

Chitosan is a natural polysaccharide composed of (1-4)-D-glucosamine units originated from the total or partial deacetylation of chitin in alkaline solutions (SINGLA, 2001; DEE, 2004). Chitosan is soluble in acid medium (pH 5.5) due to the presence of free amino groups along the polymer chain. The presence of these amino groups allows the synthesis of different chitosan derivatives (KHAN, 2002; FRANCO, 2004). The purpose of this study was to synthesize a N-succinil-chitosan derivative based on a methodology proposed by Yamagushi et al, 1981 with some modifications (YAMAGUSHI,1981).

MATERIAL AND METHODS
Chitosan samples were obtained from shrimp’s shells and purchased from Farma Service Bioextract (São Paulo, Brasil). All chemicals were of analytical grade.

Sample preparation. Two samples of N-succinil-chitosan were prepared by reaction of chitosan (Chit) with succinic anhydride at 1:1 w/w (0.06:0.01, mol/mol) and 1:3 w/w (0.06:0.03 mol/mol) proportions named as CS1:1 and CS1:3, respectively. These molar quantities of chitosan/anhydride are smaller than what it was suggested in the original work of Yamagushi et al. (1981), who used an excess of anhydride (16,4mole/mo groups). In addition, sample. was precipitated with ethanol, not methanol as the authors proposed, without yield losses. Moreover, the previous solubilization of succinic anhydride in acetone was substituted by direct addition of the succinic anhydride to the reactional medium.

Sample characterization. The solubility of chitosan and its synthesized derivative was evaluated in different pHs: acid medium (pH=4.0: 3% CH₃COOH solution), neutral medium (pH=7.0, water) and alkaline medium (pH=10.0; 0.1 mol L⁻¹ NaOH solution) at room temperature (25ºC). Qualitative observations of the samples submitted to the solubilization tests were registered at the 1st, 5th and 10th h period. The deacetylation degree (DD) of chitosan and its derivative was determined by infrared spectroscopy (Bomem MB-100 FTIR, Germany) and ninhydrin titration The substitution degree (SD) was determined using the same techniques. (CUROTTO, 1999; CANELLA, 2001; KHAN, 2002).

The hygroscopic degree was measured under vacuum in 90.70% humidity dessicators containing BaCl₂ salt. Samples were previously liophylized during 24 h, accurately weighted and placed in the dessicator. The measurements were done in 1 h intervals during a five-hour-period, until constant weight for chitosan and its derivative.

RESULTS AND DISCUSSION
The solubility measurements are shown in Table 1 for three different pHs. Chit was perfectly soluble in acetic acid solution but precipitates at neutral and alkaline solutions. This is expected due to the presence of amino groups along the polymer chain which are protonated under low pH. SC1:1 becomes partially solubilized in the entire pH range due to the increasing substitution of the amino groups by carboxylic groups, which become negatively charged above pH 6.0. The highly substituted SC1:3 appears insoluble in pH 4.0 due to the predominance of carboxyl ic groups compared to amino groups but totally solubilized at high pH, where the complete dissociation of carboxylic acid groups occurs.
Table 1. Solubility tests of Chit and modified chitosans CS1:1 and CS1:3 in different solutions and pHs.

<table>
<thead>
<tr>
<th>Solubility</th>
<th>pH=4.0</th>
<th>pH=7.0</th>
<th>pH=10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3% CH₃COOH</td>
<td>Water</td>
<td>0.1 mol L⁻¹ NaOH</td>
</tr>
<tr>
<td>Chit</td>
<td>++++</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SC1:1</td>
<td>++</td>
<td>++</td>
<td>+++</td>
</tr>
<tr>
<td>SC1:3</td>
<td>-</td>
<td>++</td>
<td>++++</td>
</tr>
</tbody>
</table>

Deacetylation degree (DD) of original chitosan sample was determined to verify how many amino groups were available to react with succinic anhydride. Substitution degree (SD) was determined for the modified samples. In Figure 1 both results of DD for Chit and SD for SC1:1 and SC1:3 are shown.

It’s possible to verify that the initial Chit presented a DD of 45% while the substituted samples, SC1:1 and SC1:3, presented a SD of 10 and 20%, respectively. The increased substitution of amino groups by carboxylic groups is directly related to the increase in solubility related previously.

In Figure 2 the capacity of the samples to absorb humidity at room temperature are shown. It is possible to verify that the modified samples absorbed more humidity than Chit. All samples absorb more humidity in the first hour followed by shorter increase in the next 5 hours when the weight becomes constant. Among all samples, SC1:3, which is the most substituted sample, presented a larger hygroscopic degree as a function of time and temperature.

CONCLUSION

The different physicochemical properties determined in this study indicate that N-succinic-chitosan can be applied in many biotechnological fields increasing the use in cosmetics, pharmaceutical and toiletries.

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REFERENCES