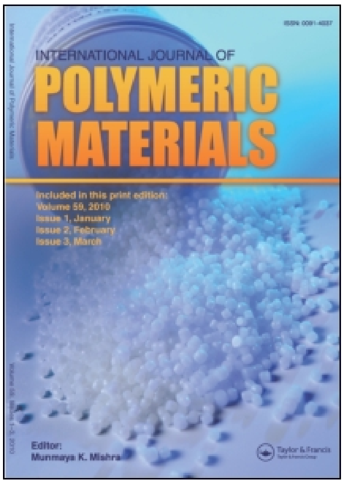

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Effects of sonication on the reactivity of chitin toward its heterogeneous deacetylation

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EFFECTS OF SONICATION ON THE REACTIVITY OF CHITIN TOWARD ITS HETEROGENEOUS DEACETYLATION

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Samples of chitin were submitted to heterogeneous deacetylation in aqueous sodium hydroxide (40%) during 6 hours at 115 ± 2°C. These reactions were carried out with crude chitin and also with samples previously submitted to ultrasound treatment in aqueous suspension for different periods of time. The previous sonication of chitin strongly enhanced its reactivity toward the deacetylation reaction but only slightly favored the depolymerization process. Adding sodium borohydride to the reaction medium reduced the occurrence of depolymerization when untreated chitin was employed but it had no such effect if sonicated chitin was reacted.

Keywords: chitin, deacetylation, ultra-sound, sonication, chitosan

INTRODUCTION

Chitin is one of the most abundant organic materials, being second only to cellulose in the amount produced annually by biosynthesis. It occurs in animals, particularly in crustacea, molluscs and insects where it is an important constituent of their exoskeleta, and in certain fungi where it is the principal fibrilar polymer in the cell wall [1]. Chitin is a linear polysaccharide whose chains are composed of 2-acetamido-2-deoxy-D-glucopyranose residues joined by $\beta(1 \rightarrow 4)$ glucosidic bonds. The principal derivative of chitin is chitosan, generally produced by alkaline deacetylation of chitin. Chitosan also occurs naturally in some fungi but its occurrence is much less widespread than that of chitin and its primary structure corresponds to a linear chain of $\beta(1 \rightarrow 4)$-linked 2-amino-2-deoxy-D-glucopyranose residues [1, 2]. Chitosan and its derivatives have found many practical applications due to their special properties [1, 3], mainly related to their solubility,

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solution viscosity and polyelectrolyte behavior which, in turn, depend on the degree of acetylation and molecular weight of the polymer. The lack of uniformity of the products generated by the alkaline deacetylation of chitin and the simultaneous occurrence of depolymerization, as a result of the high temperature and concentrated sodium hydroxide concentration employed for chitin deacetylation, are problems associated to the obtention of chitosans [1].

Heterogeneous reactions on macromolecular solids, as the deacetylation of chitin, yield uneven products as a consequence of its own nature since the accessibility of reactants to the site reactions on the macromolecules is limited by many factors including the existence of crystalline domains, the size, porosity and swelling capacity of the solid particles. The finely divided solid material, having a larger surface area, affords a better accessibility to the reactive sites and the grinding of the solid to be reacted is a common practice when the heterogeneous reaction on macromolecular solids is concerned [4].

When ultrasound waves are irradiated through a medium, a process referred as sonication, it induces vibrational motion of the molecules which alternately compress and stretch the molecular structure of the medium and, if the intensity of the ultrasound is sufficiently high, cavitation bubbles are generated [5]. As a consequence of the cavitation phenomenon a large amount of energy is locally liberated and the activation of solid particles suspended in the medium may result by size reduction and by a cleaning process in which inert surface layers are removed [6].

In this work, commercial chitin and previously sonicated chitin are submitted to heterogeneous deacetylation in aqueous sodium hydroxide (40%) at $115 \pm 2°C$ during 6 hours to obtain chitosans. The effects of pretreating chitin and the influence of adding sodium borohydride, a reagent usually employed to minimize the occurrence of depolymerization during the deacetylation of chitin [1], to the deacetylation medium are evaluated by determining the average degrees of acetylation, ($\overline{DA}$), and the intrinsic viscosities, $[\eta]$, of the deacetylated products. The first characteristic is an evaluation of the accessibility of the reagents to the reactive sites of chitin chains while the second one allows the evaluation of the extent of depolymerization, which generally occurs during chitin deacetylation in aqueous alkaline suspension.

EXPERIMENTAL

Chitin Deacetylation and Chitosan Purification

The deacetylation reactions were carried out with crude commercial chitin (Sigma, from crab shells) and with samples previously submitted to ultrasound treatment.

For the ultrasound treatment a Branson Sonifier 450 was employed in the intermittent mode and its output power was adjusted to 45 W or to 70 W. The ultrasound horn was immersed in the aqueous suspension of crude chitin (4.6 g chitin/80 mL of water), the assembly was placed inside a soundproof box, and the ultrasound treatment was maintained during 30, 60 or 90 minutes. For the deacetylation of the ultrasound treated chitin, the suspension was filtered, the sample was allowed to dry and then submitted to the desired reaction.

Aiming to minimize the undesired depolymerization process, some deacetylation reactions were carried out in the presence of sodium borohydride (0.1 g $NaBH_4$/1 g chitin).

In a typical deacetylation, a suspension containing 4.6 g of chitin in 220 ml of 40% aqueous sodium hydroxide solution was kept at constant mechanical stirring (350 rpm) in a glass reactor kept at $115° \pm 2°C$. After 6 h the reaction was discontinued, the mixture was cooled to room temperature, filtered and the solid deacetylated product was repeatedly washed with water until the neutrality of washings were attained. Following washing with methanol, the deacetylated product was allowed to dry in ambient conditions.

Chitosan was purified by dissolving the deacetylated product in dilute acetic acid solution, filtering the resulting solution and carefully adding concentrated alkali to it until the precipitation of the polymer. The polysaccharide was filtered and exhaustively washed with water until neutrality of washings, and then with methanol. The purified chitosan was a white powder completely soluble in dilute aqueous solutions of acetic acid and hydrochloric acid but insoluble in pure water.

Characterizations

The average degrees of acetylation of chitosans were determined by ^1H NMR spectroscopy of the purified samples dissolved in D_2O/HCl (100 : 1 v/v) at 80°C, by using a Bruker 200 MHz spectrometer, as described in more detail elsewhere [7, 8].

The intrinsic viscosities were determined by capillary viscometry of chitosan dissolved in 0.3 mol/L acetic acid/0.2 mol/L sodium acetate buffer ($pH \cong 4.5$). The pure solvent and the chitosan solutions were previously filtered through 0.22 μm membranes and the measurements were carried out at $25°C \pm 0.01°C$. The AVS-350 viscometer coupled to the AVS-20 automatic burette, both from Schott-Gerate, were used in these determinations allowing the sequential dilution of the chitosan solution directly into the glass capillary ($\phi = 0.53$ mm), by adding the previously programmed volumes of the solvent. Intrinsic viscosities resulted by extrapolation of the Huggins equation [9] to infinite dilution and the corresponding viscosity average molecular weights (M_V) were calculated by applying the values of K and a determined in the same solvent and temperature [10].

RESULTS AND DISCUSSION

The commercial chitin used in this work is a heterogeneous powder with respect to the average diameter of its constituent particles but more than 70% of the original sample is constituted by finely divided materials ($\phi < 1.0\,\mathrm{mm}$). This fraction of particles, the more abundant one, seems to dominate the chemical behavior of chitin toward its heterogeneous deacetylation since very similar chitosans were produced if crude or fractionated chitin was reacted but the deacetylation yield was higher in the latter case [11]. Also, excessively ground chitin, which is rich in smaller particles ($\phi < 0.25\,\mathrm{mm}$), could not be as efficiently deacetylated because a major part of the powder adhered to the reactor walls and to the stirring bladers, yielding uneven results and poor reproducibility.

If crude chitin or previously sonicated and dried chitin were employed for deacetylation, different chitosans were obtained (Tab. 1) but the reaction yields, based on the weight of deacetylated product recovered in each case, were very similar (≅55%).

In fact, these results showed that chitin previously sonicated in suspension of pure water, filtered, dried and then added to the reaction medium, was much more reactive toward deacetylation than crude chitin, but the depolymerization process was only slightly favored when pre-treated chitin was submitted to deacetylation (Tab. 1). The experimental data showed that the deacetylation of untreated chitin resulted in chitosan with $\overline{DA} = 15\%$ while the chitosan samples which were generated from previously sonicated chitin were much more deacetylated ($\overline{DA} < 9\%$). On the other hand, the intrinsic viscosities and the corresponding viscosity average molecular weights of all chitosans, independently of being produced from crude or pre-treated chitin, were similar and within a narrow range of values.

These results also showed that sonication effects are not increased by prolonging the treatment. Also, independently of the output power (45 W or

TABLE 1 Average degrees of acetylation ($\overline{DA}$), intrinsic viscosities ($[\eta]$) and viscosity average molecular weight ($\bar{M}_v$) of deacetylated chitin*

Sample[†]	*Sonication time (min.)*	$\%(\overline{DA})$	$[\eta]$ *(mL/g)*	$\bar{M}_v \times 10^4$
C0	0	15 ± 3	616 ± 63	14
C30	30	7.3 ± 0.1	586 ± 6	12
C60	60	8.4 ± 1	540 ± 30	11
C90	90	8 ± 3	573 ± 6	11
$[\mathrm{C0}]_{\mathrm{SB}}$	0	12 ± 1	940 ± 27	24
$[\mathrm{C60}]_{\mathrm{SB}}$	60	10 ± 2	962 ± 66	25

* Values correspond to the average of at least two independent deacetylations.

[†] Numbers stand for the time to which chitin was submitted to sonication before deacetylation and subscript SB identifies the reactions carried out in the presence of sodium borohydride (0.1 g $NaBH_4$/1 g chitin).

70 W) employed for the ultrasound treatment, very similar chitosans resulted when chitins previously sonicated for 30 min were deacetylated. The execution of three consecutive steps of sonication (20 min/step) intercalated with the filtering and drying of the treated chitin did not result in increased activation for deacetylation, as evaluated by the intrinsic viscosity ($[\eta] = 603\,\mathrm{mL/g}$) and average degree of acetylation ($\overline{DA} = 9\%$) of the chitosan obtained in a single experiment.

Adding sodium borohydride to the reaction medium slightly affects the deacetylation efficiency but it promoted a considerable reduction in the depolymerization rate, independently of reacting crude or pre-treated chitin.

A study on the morphological characterization of untreated and sonicated chitin by using scanning electronic microscopy is being developed and recent results indicate that sonication enhances the sample homogeneity and the surface area of the particles, effects which may be responsible for the enhanced reactivity of sonicated chitin toward the deacetylation reaction.

CONCLUSIONS

Previously sonicated chitin is much more reactive than crude chitin toward the deacetylation reaction, probably due to the enhanced accessibility caused by this treatment. The occurrence of the morphological changes provoked by sonication is the most probable cause for the enhanced reactivity of sonicated chitin. The addition of sodium borohydride to the deacetylation medium was an efficient measure to reduce the occurrence of severe depolymerization.

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