

DEACETYLATION OF CHITIN AT LOW TEMPERATURE: EFFECT OF THE CHITIN POLYMORPH

B. R. MOREIRA^{1*}, J. A. de M. DELEZUK¹, M. S. MARIANO¹, W. G. BIROLI¹, S. P. CAMPANA-FILHO¹.

¹ Instituto de Química de São Carlos, Universidade de São Paulo, São Carlos-SP, Brazil. e-mail: brunarm@iqsc.usp.br

Chitin is a polysaccharide abundantly present in the matrix of the skeletal structure of invertebrates such as arthropods, annelids and mollusks. It is a linear polymer composed predominantly of 2-acetamido-2-deoxy- β -D-glucose units linked by β -(1 \rightarrow 4) bonds [1]. The main polymorphs of chitin, alpha- and beta-chitin, differ in the arrangement of its chains in the crystalline domains. In alpha-chitin, the chains are arranged in an antiparallel disposition, which allows the formation of numerous inter- and intra-chain associations by hydrogen bonding, ensuring a dense packing. In beta-chitin, the chains adopt a parallel arrangement, preventing the occurrence of hydrogen bonds and resulting in a less densely packed material [2]. Chitosans, copolymers containing 2-acetamido-2-deoxy- β -D-glucose and 2-amido-2-deoxy- β -D-glucose units in which the latter predominate, are usually obtained by treating chitin in concentrated alkaline medium at moderate to high temperature. In this work, alpha- and beta-chitin are submitted to an alkaline treatment at low temperature aiming the obtention of chitosan.

Alpha-chitin (DA=71%) and beta-chitin (DA=81%) were extracted from cephalotorax of *Macrobrachium rosenbergii* and pens of *Loligo sampauiensis*, respectively. For carrying out the deacetylation reactions chitin was dispersed in 40% sodium hydroxide, the resulting suspension (0.044 g/mL) was poured in a Petri dish and then kept at 30°C for 48h. The resulting products were soluble in dilute acid medium and they were named according to the parent chitin polymorph as alpha-chitosan (DA=34%) and beta-chitosan (DA=24%). The different arrangements of alpha- and beta-chitin give rise to different X-rays diffraction patterns. Thus, alpha-chitin shows several crystalline peaks while beta-chitin shows only two peaks. The lack of reflections and the presence of broader and less intense peaks indicate that beta-chitin adopts a less ordered arrangement as compared to alpha-chitin. It was also observed that the chitosan samples resulting from the

deacetylation of alpha- and beta-chitin adopted less ordered arrangements (Fig. 1).

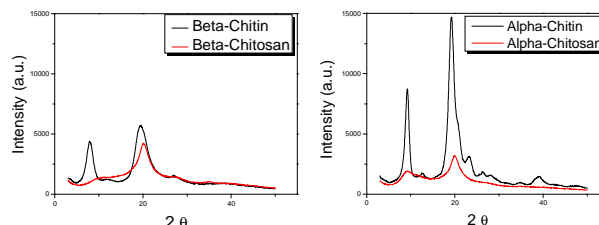


Fig. 1. X-ray diffraction of chitin and chitosan.

Indeed, the crystallinity indexes (I_{CR}) of beta-chitosan and alpha-chitosan are 22.7% and 35.5% lower than those of beta- and alpha-chitin, respectively. However, it is evident from Fig.1 that some characteristic features of the parent chitin are still found in the X-rays diffraction patterns of the corresponding chitosan.

Table 1. Thermogravimetric analyses of chitin and chitosan.

Sample	DA(%)	Mass loss (%)	$T_{max}(^{\circ}C)^a$
β -Chitin	81,0	54,19	347,0
β -Chitosan	24,0	41,04	291,0
α -Chitin	71,0	66,31	349,0
α -Chitosan	34,0	41,55	296,0

^a Temperature at which the rate of degradation of samples is maximum.

The lower crystallinity of chitosan can partially explain the results from the thermogravimetric analyses, as the chitosan samples exhibited lower temperatures of maximum degradation (T_{max}) as compared to the parent chitins (Table 1). In addition, regardless of the chitin polymorph, both chitosan exhibited similar weight losses at T_{max} , suggesting a common pathway for the thermal degradation.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the funding agencies CAPES, CNPq and FAPESP for financial support.

REFERENCES

1. Rinaudo, M., *Progress in Polymer Science*, 31 (2006) 603
2. Campana-Filho, S. P., Britto, D., Curti, E., Abreu, F. R., Cardoso, M. B., Battisti, M. V. Sim, P. C., Goy, R. C., Signini, R., Lavall, R. L. *Química Nova*, 30 (2007) 664