

PS 2 - Chitin Reactivity During Thermoalkaline Heterogeneous Deacetylation: Comparative Kinetic Study

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α -chitin isolated from blue shrimp (*Litopenaeus stylyrostris*) head waste was prepared under different pre-treatments of the raw material, namely freshly treated, boiled and heat dried (batches Qn-1, Qn-2, Qn-3, respectively). Also a batch of β -chitin from giant squid (*Dosidicus gigas*) pen (sample Qn-4) was studied. All samples reacted with NaOH 50% (w/w) at 60, 65, 70, 75, 80, 90 and 98°C. Deacetylation kinetics was monitored by measuring the degree of deacetylation (DD) using transmission (anhydride KBr pellets) Fourier transformed infrared (FTIR) spectroscopy. The relationship of the absorption bands A1329/A1420 and the calibration curve described by Brugnerotto et al. (Polymer. 42, 3569-3580, 2001) were used to calculate DD. Some values of DD were also determined from C/N ratio measurements by elemental analysis or by solid-state ¹³C CP-MAS NMR. The solubility of the samples during the course of deacetylation was also monitored. The deacetylation procedure took place in two clearly defined stages. At the beginning, the DD increased steadily as function of time and temperature. After a critical point the DD tended to stabilize. This agrees with previous reports (Chang et al. 1997, Carbohydr. Res., 303 (1997) 327-332; Methacanon et al. Carbohydr. Polym. 52 (2003) 119-123). It is remarkable that the first stage did not exceed 30 minutes for any chitin, not even at the lowest temperatures. From the dependence of the apparent velocity constants with temperature (60 – 98 °C) in the chitin samples, it was possible to plot Arrhenius plots. Sample Qn-1 showed two regions of behavior in the Arrhenius plot as confirmed from the various analytical techniques, while the rest of the chitin samples showed only one type of behavior. Activation energies (E_a) values for Qn-1 were 94.4 and 13.7 kJ/mol for temperature ranges [65-71.8] and [71.8-98°C], respectively. While for Qn-2 and Qn-3 α -chitin samples E_a was 33.88 and 70.08, respectively, and for the β -chitin (Qn-4) sample it was 59.62 kJ/mol. The anomalous behavior of sample Qn-1 was attributed to a phase transition that seems to occur in the vicinity of ~73°C. That this transition is observed only in this sample, is possibly due to the swelling of chitin favored by the lower temperature, thus effectively, increasing its reactivity. Thermal pre-treatment applied to the rest of the α -chitin samples and the polymorphic crystalline arrangement of β -chitin itself seems to prevent the appearance of this transition under the temperature range studied. The change in solubility during the reaction for all the chitin samples could be described by a sigmoidal function. Accordingly, at short reaction times the solubility of the samples increase at slow rate, afterwards it raised up to a final stage of moderate solubility increase when the solubility tended to 100%. This was rationalized as the consequence of a modification in the local pattern of deacetylation at the molecular level, that changes during the course of the reaction from homogeneous to heterogeneous.