



PHYSICOCHEMICAL PROPERTIES OF NITROGENATED DERIVATIVES OF CELLULOSE

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ABSTRACT:

Based on their antibacterial activity, biocompatibility, biodegradability and sorption capability, nitrogenated derivatives of cellulose and chitin and chitosan are of economic interest. Methods like broad-angle X-ray scattering (WAXS), microcalorimetry and sorption have examined the structure and some physical chemistry characteristics of these derivations. To evaluate the degree of crystallinity of the samples, the WAXS enhanced technique has been utilised to determine the connection between the integral intensities of the crystalline and amorphous X-ray diffraction. The computations showed that starting chitin was 0.72, and initial chitosan 0.57 were currently of crystallinity. The decline in the crystallinity degree was noticed after brief duration of ball-grinding, while prolongation of the grinding led to the sample being amorphous completely.

KEYWORDS: cellulose, physicochemical, nitrogenated derivatives, Crystallinity Degree, Wetting Enthalpy, Sorption Ability.

INTRODUCTION:

The most frequent product of the cellulose, 1,4- β -N-acetyl-2-aminodeoxyglucose units, is chitin-nitrogenated polysaccharide. Chitin is found in nature in skeletons of arthropods and insects, mollusc shells, cell walls of fungus, stalks and beaks of cephalopods. It is predicted that 100 billion tonnes of this polymer resource. Commercially, the acid removal of calcium carbonate, followed by alkaline protein and bleaching, may separate chitin from crabs, shrimp and lobster shells. Chitin is the source for the synthesis, by alkaline deacetylation, of another common nitrogenated cellulose derivative – chitosan. Certain fungal cell walls, such as Mucoraceae [1-3], contain natural chitosan.

Due to unique features including low toxicity, antibacterial activity, biocompatibility, biodegradability, and sorption capacity Chitin and especially Chitosan is of economic importance. These derivatives currently provide a wide range of uses including medicine, cosmetics, biotechnology, biocomposites, papermaking, agriculture, and others. Chitin and chitosan thus need to be structurally detailed. Different techniques are employed to determine molecular weight, acetyl and amino groups, humidity and residual protein and mineral content [4-7].

The α -chitin crystalline unit cell is orthorhombic with the P212121 space group, whereas β -chitin has a single-clinical crystalline unit cell with the P21 unit. Chitin's β -form is unstable and can be swelled internally. In addition, chitin's β form is permanently converted into stabler α -polymorph following certain treatments. Chitin X-ray diffractograms reveal 2 strong peaks in 2θ of about 9-9.5°.

from (020) planes and 19-19.5° from (110) crystalline unit planes, plus several little peaks. Crystalline chitosan unit cell is likewise orthorhombic in the space cell group of P212121 and this polymer's X-ray diffractogram contains two peaks of 2θ of about 10 - 10.5° of the planes and 20 - 20.5° of (110), from (020) the planes. Thus, the crystalline peaks are shifted up to a 2θ angle as a result of deacetylation of chitin [8].

A quantitative X-ray phase study that needs compliance with specific requirements, and namely: should be done to ascertain the real degree of crystallinity

- The sample should be in a powder form that is not textured.
- The backdrop of the parasite X-ray should be undermined.
- The test diffractogram should be fixed.
- Diffractograms must be isolated from the adjusted scatter regions relating to crystalline and non-crystalline domain.
- To calculate the degree of crystallinity, the integrated (area) intensity of crystalline and non-crystalline dispersions should be utilised.

The hydrophilicity analysis of the polymer samples may be an indirect approach for estimating the crystallinity. Since water vapour sorption happens inside hydrophilic polymer (amorphous) areas, more crystalline sample sorbs less water. Research of the sorption of water vapour from chitosan samples showed that the sorption capacity of the samples reduces when the deacetylation degree (DD) is increased[9]. The effect of samples' crystallinity on the sorption capacity was described. In addition, a relationship was discovered between the crystallinity of cellulose nitrogen derivatives and wetting enthalpy. The main purpose of this research was to determine a real degree of chitin-chitosan crystallinity to create a quantitative link between the degree of the samples' crystallinity and their physicochemical property.

RESEARCH METHODOLOGY:

- 1) Materials
- 2) Chitin purified powders extracted from the shell of crab and chitosan were purchased from Sigma-Aldrich (MW=400 kDa; DD=85 percent). In the laboratory ball-mill, the first samples were ground with ceramic balls at 250 rpm for 5 and 24 hours to decrease the crystallinity.
- 3) Wide-Angle X-Ray Scattering(WAXS)

The dry powders with the same mass (250 mg) are pressed into tablets, which are employed in WAXS-experiments (diameter 15 mm, thickness 1.5 mm). A Rigaku-Ultima Plus diffractometer ($\text{CuK}\alpha$ – radiation, $\lambda = 0.15418$ nm) is used to record diffractogram samples of 2θ of angle ranging from 5 to 50°. The parasite background (bg) of the air, appliances, Compton scattering, thermal agitations of atoms and molecules and crystalline lattice distortions were removed after the diffractograms were recorded. The X-ray-intensity is divided into the corrective coefficient of diffractogram to correct, $K(\theta)$, that contains the latent-polarization factor(LP) and the starting intensity of the X-ray beam(J): $K(\theta) = JLP$ [10]. In addition, the overall intensity of the rectified diffractogram was split in sections of amorphous(Cr) and crystalline(Am) dispersion (Fig. 1, 2). A comparable transfer of the profile of the amorphous sample's X-ray dispersion was performed (Fig.3). Finally, the actual degree of crystallinity (X) was determined according to the following:

$$X = I_{cr} d\theta / I_o d\theta = F_{cr} / (F_{cr} + F_{am}) \quad (1)$$

where the corrected diffractogram is total intensity after parasite background removal; (bg) I_{cr} is intensity of the crystalline dispersal; F_{cr} is the region of crystalline scattering;



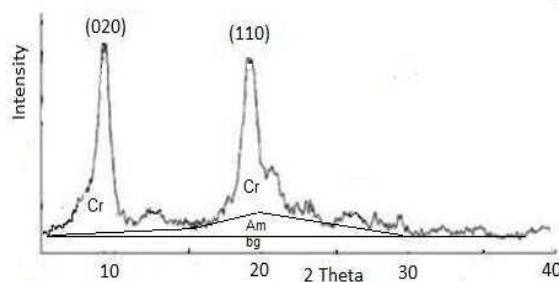


Figure 1. Illustration of the method for determination of crystallinity degree of chitin

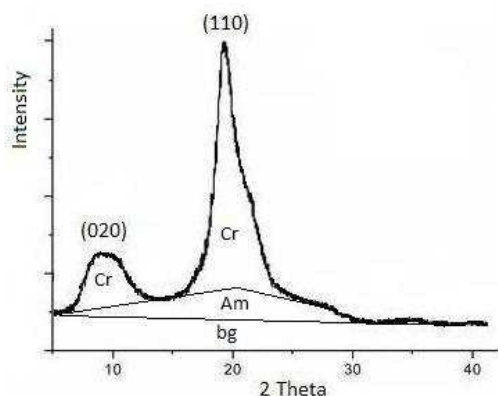


Figure 2. Illustration of the method for determination of crystallinity degree of chitosan

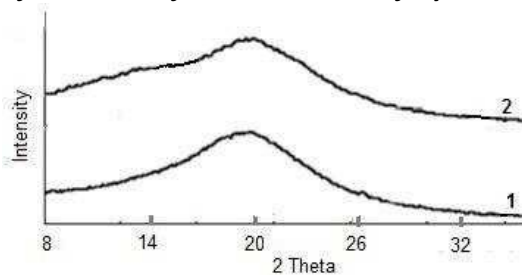


Figure 3. Profiles of X-ray scattering of amorphous chitosan (1) and chitin (2)

4) Water Vapor Sorption

Mac-Ben vacuum appliance with a spring helical quartz scale [12] the sorption experiment was performed at 25°C using a vacuum. Before the experiments started, the samples were dried at 105°C and further degassed in the sorption device to consistent weight.

II. RESULTS AND DISCUSSION

X-ray diffractogram was characteristic of α -polymorphics, with two 2θ of 9.2° and 19.0° expressed peaks (Fig. 1, 4). These peaks are similarly produced by X-ray diffraction from crystalline cell (020) and (110) planes with interplane distances of 0.96 nm and 0.47 nm. Initial chitosane samples showed that diffract from (020) and (110) crystalline cell plans with a background distance of 0.88 nm and 0.45 nm, respectively, the diffractor was 2θ of 10° and more intensive in 2θ of 20° (Fig. 2,5). After a very short time of ball-grinding (for 5 h), the intensity of the diffraction pits reduced which was shown when the samples were partially decrystallized (Fig.4,5). Prolonged slurring (for 24h) resulted in full decrystallization of the specimens and development of broad diffractograms with one maximum at $2\theta \approx 20^\circ$ (Fig.3).



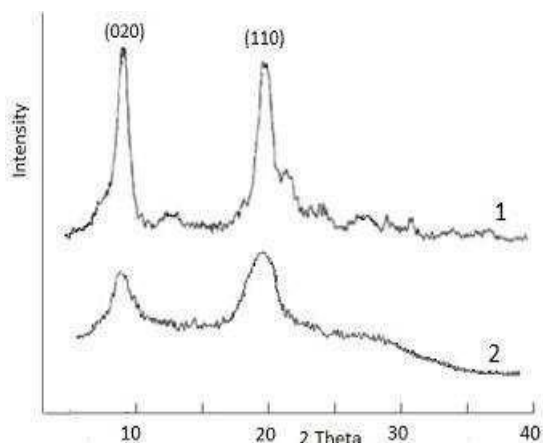


Figure 4. X-ray diffractograms of chitin samples: initial (1) and ground for 5 h (2)

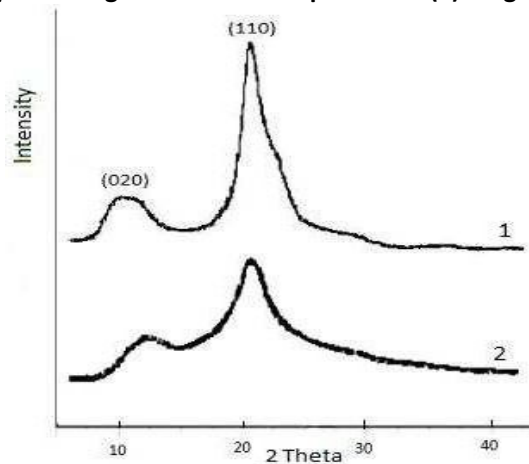


Figure 5. X-ray diffractograms of chitosan samples: initial (1) and ground for 5 h (2)

The real level of crystallination for initial chitin was 0.72, and for the original chitosan sample was 0.57, calculation using equation (1) based on the enhanced X-ray technique (Table 1). A drop in sample crystallinity grades to 0.40-0.45 was induced by short-term grinding (for 5h), whereas prolongation (for 24h) was achieved in the sample amorphication completeness.

Table 1. Crystallinity degree (X) of the samples

Sample	X
Chitin	
Initial	0.72
Ground for 5 h	0.45
Ground for 24 h	0
Chitosan	
Initial	0.57
Ground for 5 h	0.40
Ground for 24 h	0



Microcalorimetric tests demonstrated the reversal of wetting enthalpy in the chitin and chitosan samples to the crystallinity level (Table 2).

Table 2. Wetting enthalpy (H) of the samples having different crystallinity degree (X)

Sample	X	H, kJ/kg
Chitin		
Initial	0.72	38
Ground for 5 h	0.45	75
Ground for 24 h	0	134
Chitosan		
Initial	0.57	76
Ground for 5 h	0.40	101
Ground for 24 h	0	174

The crystallinity level of the samples may be estimated with the findings of wetting enthalpy as follows:

$$X_H = 1 - (H/H_a) \quad (3)$$

For full amorphized sample, where H_a is wetting enthalpy.

CONCLUSION:

In the many characteristics of polymers, the crystallinity is an essential structural trait. It also allows the supramolecular structure of polymers to be understood. Sadly, the crystallinity of chitin and chitosan specimens was not adequately evaluated utilising the ratio of x-ray height. To this aim, heights and heights of amorphous dispersions of 2θ 12o, 12.6o or 16o have been employed in crystalline diffraction pits (110) and (020) planes. The research indicated nevertheless that the highest amorphous ray dispersion is found at $2\theta \approx 20o$, but not 2θ in the 12-16o range. In addition, the assessment of crystallinity from the highest peak ratio is theoretically not warranted, as the peak height is not commensurate with the crystalline or amorphous content. Only if integral intensity (areas) of the X-diffraction were utilised, is the law of phase proportionality seen. In this work, an improved approach was utilised to estimate crystallinity on the basis of the computation of the connection between the integrated intensities of crystalline and amorphous X-ray diffractions. The real levels of crystallinity of the original chitine have been calculated to be 0.72 and of the original chitosan sample 0.57. The decline of the crystallinity of the samples was seen shortly after ball grinding, whereas further grinding resulted in full amorphization of the samples.

REFERENCES:

1. Rinaudo M. "Chitin and chitosan: properties and applications," Progr. Polym. Sci., vol. 31, pp. 603-632, 2006.
2. Aranaz I., Mengibar M., Harris R., Panos I., Miralles B., Acosta N., Galed G., and Heras A. "Functional characterization of chitin and chitosan," Current Chem. Biol., vol. 3, pp. 203-230, 2009.
3. Roberts G. Chitin Chemistry. London: MacMillan, 1998.
4. Struszczyk M.H. "Applications of chitosan," Polymery, vol. 47, pp. 396-403, 2002
5. Muzzarelli R.A.A., and Muzzarelli C. "Chitosan chemistry: relevance to the biomedical sciences," Adv. Polym. Sci., vol. 186, pp.151-209, 2005.



6. Diaz-Rojas E.I., Arguelles-Monal W.M., Higuera-Ciapara I., Hernandez J., Lizardi-Mendoza J., and Goycoolea F.M. "Determination of chitin and protein content during the isolation of chitin from shrimp waste," *Macromol. Biosci.*, vol. 6, pp. 340-347, 2006.
7. Dutta P.K, Dutta J., and. Tripathi V.S. "Chitin and chitosan: chemistry, properties and applications," *J. Sci. Ind. Res.*, vol. 63, pp. 20-31, 2004.
8. Zhang Y., Xue C., Xue Y., Gao R., and Zhang X. "Determination of the degree of deacetylation of chitin and chitosan by X-ray powder diffraction," *Carbohydr Res.*, vol. 340, pp. 1914-1917, 2005.
9. Mucha M., and Balcerzak J. "Thermal effect accompanying water adsorption by chitosan with different deacetylation degrees," *Polish Chitin Soc.*, vol. 12, pp. 49-55, 2007
10. Ioelovich M., and Leykin A. "Study of sorption properties of cellulose and its derivatives," *Bioresources*, vol. 6, pp.178-195, 2011.
11. Ioelovich M. *Cellulose: Nanostructured Natural Polymer*. Saarbrücken: Lambert Academic Publishing.

