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THE STRUCTURE OF CHITIN AND CHITOSAN

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ABSTRACT

The short range atomic arrangements in crystalline chitin, crystalline chitosan and amorphous chitosan films are shown to be similar in that the fundamental rings and chains are retained in all of these structures. The interchain bonding differs, however, and is weakest in amorphous chitosan and strongest in crystalline chitin.

Introduction

Chitin is the basic structural material in the exoskeletons of arthropods (crab, shrimp, lobster and most insects), and it also occurs in certain fungi. Chemically, the material is a poly-N-acetylglucosamine, and it is related to cellulose, differing from the latter in having an aminoacetyl group, CH_3COHN-, substituted for one of the hydroxyl groups. Chitosan is a partially deacetylated chitin and differs from the latter in being quite soluble in dilute acids; chitin is virtually insoluble and is only decomposed slowly by certain enzymes. Chitosan is a polyelectrolyte and has considerable potential as a chelating agent for minerals, organic materials, and food products. It is also a good film former, and has been shown to impart wet strength to paper. Two pilot plants are now producing chitin and chitosan with the expectation that significant utilization will occur as these materials become available in commercial quantities.

Our research has first attempted to determine whether the structure of chitin and chitosan is dependent on the type of crustacean used as a source of raw material. Thus far, our work has shown that the structure of chitin derived from shrimp and from various kinds of crab (King crab, Chesapeake blue crab, Dungeness and Scarlet Queen) are all very similar.

The chitosans derived from these various chitins also appear to have similar atomic arrangements, but the film-casting and the polymeric properties are apparently affected by the processing procedures. A preliminary look at chitin and chitosan derived from an insect source indicates that there may be some differences, but these early results are tentative. Our work in this area is still in progress and will be reported later. Finally, we are investigating the structure as well as the mechanical and electrical properties of amorphous chitosan films. The properties of these films are critically dependent on the processing techniques and these data will also be presented later. The data given here represent a first step in assessing the basic atomic arrangement in chitin, bulk chitosan, and amorphous chitosan films. We show that the local atomic order in all of these materials is very similar in that the basic glucosamine ring is preserved in each structure. However, the bonding between rings and the formation of and the bonding between chains is quite different in these materials and is apparently very much influenced by the chemical history.

We report here on the structure of chitin derived from King Crab, of flake chitosan prepared from this material and of films cast from the chitosan. The chitin and flake chitosan were prepared at the pilot plant operated by the Food, Chemical and Research Laboratory of Seattle and the films were cast in our laboratory.

Chitin and Chitosan Flake

The chitin and chitosan were received in coarse flake form, and the particle size was reduced by grinding and ball milling. The size of the platelets was reduced by grinding, but the particles retained their plate-like shapes; subsequent data indicated that the basic structure was not changed by the grinding. Compacts were prepared and examined by X-ray diffraction, using monochromatic Cu Kα radiation. All of the compacts exhibited preferred orientation and attempts to eliminate this were not successful.

The principal peaks observed in the chitin patterns exhibited d-spacings of 9.62, 4.61, 4.28, and 3.84A. These values agree quite well with those of Carlstrom,[1] and are consistent with his orthorhombic structure. The relative intensities indicated a strong preferred orientation along the [001] direction, perpendicular to the fiber axis, in agreement with Darmon and Rudall.[2] Our data correspond to an orthorhombic unit cell with a = 4.7, b = 10.5, and c = 10.3 A.

The flake chitosan exhibited patterns which were quite similar to those of chitin, but the peaks were broader and

the smaller peaks were suppressed. There was, however, a pronounced shift of the first peak (002) from d = 9.62 A for chitin to 8.57 A for chitosan. Furthermore, it was found that the position of this peak varied greatly, depending on the water content, as shown in Table 1.

TABLE 1

(002) Spacings of Flake Chitin and Chitosan

chitosan, as received	8.57 A
chitosan, dried, 134°C-2 days	7.45 A
chitin	9.62 A

When thoroughly dried, the d-spacing was considerably smaller; when subsequently soaked in distilled water for a day and then dried at room temperature it returned to the as-received value. Other peaks in the pattern exhibited only slight shifts with this treatment.

The (002) has a spacing which corresponds to the repeat distance between chains in chitin, and presumably in chitosan. We thus postulate that water molecules enter the lattice and are loosely bound between chains along [001] directions. It should be noted that chitin did not take up water and the d-spacings did not vary on drying or soaking. It appears that

the bonding between chains in chitosan is very weak, probably of a van der Waals nature, and this is fundamentally different from the interchain bonding in chitin. Our ESCA (electron scattering) data also indicate that there are significant differences between the carbon bonding in chitin and chitosan.

Chitosan films

Films of chitosan were prepared by dissolving flake chitosan in dilute acetic acid (10 pct), casting onto polished stainless steel plates, and drying at 125°C. The films were stripped and examined by means of X-ray diffraction. Films of varying thickness (.002-.015 in) were prepared. The films were clear and flexible.

All of the films were amorphous and there was no indication of preferred orientation. The broad amorphous diffraction maxima did not correspond to the crystalline peak positions, and we were unable to fit these peaks to a microcrystalline model. The amorphous patterns were analyzed in terms of radial distribution functions. The data were first normalized to modulate the average value of f^2, the atomic scattering factor. Corrections for termination and systematic errors were made, using the procedure outlined by Kaplow, Rowe and Averbach[3] and the radial distribution function was calculated from the corrected scattering data.

We define an atomic density function $\rho(r)$ such that

$$c_i = \int_{r_i-\delta}^{r_i+\delta} 4\pi r^2 \rho(r) \qquad (1)$$

where C_i is the number of atoms between $r_i-\delta$ and $r_i+\delta$, and r_i is the radius of a spherical shell about any given atom. We further define the radial density function

$$J(r) = 4\pi r^2 \{\rho(r)-\rho_o\} \qquad (2)$$

where ρ_o is the average atomic density and $J(r)$ is a function which describes the average density of atoms about an average atom in the material. For convenience we define,

$$G(r) = 4\pi r \{\rho(r)-\rho_o\} \qquad (3)$$

and it is easily shown that

$$G(r) = \frac{2}{\pi} \int_o^\infty F(k) \sin kr \, dk$$

where $F(k) = k(I/f^2-1)$, $k = 4\pi\sin\theta/\lambda$ and I is the corrected diffracted intensity. We are thus able to obtain the radial distribution function G(r) from the diffraction data.

Figure 1 shows the radial distribution function obtained for a chitosan film. The positions of the principal correlation peaks are given in Table 2 and compared with the relevant distances in crystalline chitin.

Thus, our preliminary picture of the structure of amorphous chitosan films is one in which the rings observed in crystalline flake chitin are retained, along with some of the chains, but with considerable misorientation of the chains. The short range order in crystalline chitin, in crystalline flake chitosan and in amorphous film chitosan are all similar, but the bonding between chains becomes progressively weaker as we progress from chitin to the amorphous films. The acetylamine group apparently plays an important role in the bonding of chitin and the properties of chitosan will thus be very dependent on the degree of deacetylization.

TABLE 2

Correlation Distances in Crystalline Chitin and in Amorphous Chitosan Films

correlations in chitosan films, A	distances in crystalline chitin, A
1.50	1.50*
2.62	2.62*
3.75	3.75°
5.15	5.15°

* intraring

° interring, but in same chain

Acknowledgements

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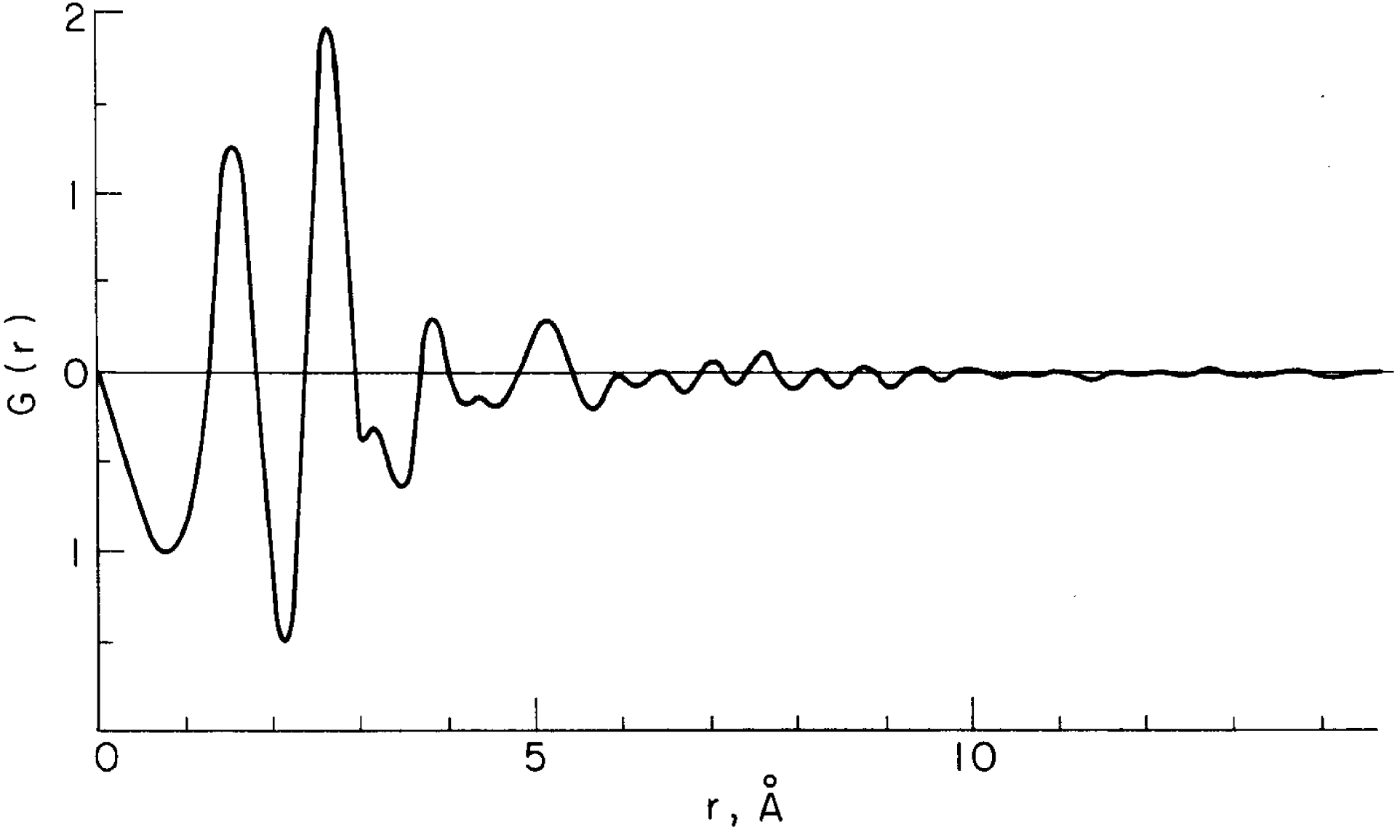

Figure 1. Radial distribution function of amorphous chitosan film