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α-chitin, β-chitin & γ-chitin

There is a growing interest in “different” chitins and chitosans. These differences lie in specific physical and structural arrangements in how chitin (and chitosan) polymers are laid down to form these arrangements within structures. Dr. André Blanchard of Organisan Corporation explains these differences and how they may or may not influence chitosan performance.

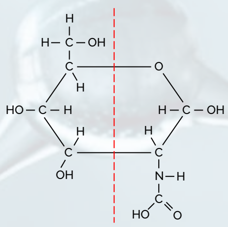
Mark Nichols
678-935-8120
markn@organisancorp.com

Made in U.S.A.
organisancorp.com

Tom Wood
208-317-4580
tomw@organisancorp.com

Chitin is an aminopolysaccharide polymer second in abundance to cellulose. Annual bioproduction is estimated at 10^{11} metric tonnes. Chitosan is derived from chitin through a chemical process known as deacetylation. For now, we will limit our discussion to chitin. Chitin and cellulose are very closely related, one of which is they are both fibrous, linear polymers. Being polymers, both are long molecules. The linearity is because their respective monomers (polymer building blocks) are joined together in exactly the same way via a specific chemical bond that causes the monomers to arrange end to end in a linear fashion. Their respective monomers vary in minor ways. Without getting into a lot of complex chemistry, imagine these polymer chains of chitin as long, straight necklaces. The beads are the monomer constituents joined together end to end forming long, linear chains. The string between the beads is the chemical bond joining the monomers in the polymer chain.

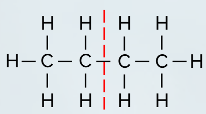
In the native situations, chitin polymer chains are laid down in specific regular arrangements. The regular order of chitin chain deposition infers a crystalline structure. Alpha (α-), beta (β-) and gamma (γ-) are prefixes that refers to the different regular arrangement of chitin chains within the native structures regardless where they are found. Powerful analyses, particularly X-ray diffraction, are able to peer into these structures and the data generated detects differences in the crystal nature of these chitins. With X-ray diffraction, differences in crystal structure as well as other dimensional features can be determined. These forms differ in how the polymer chains are laid down. To explain this, lets look at some chemistry;



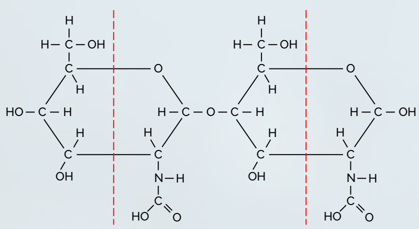
This is the structure of the chitin monomer N-acetylglucosamine. For our purposes, there is no need to be concerned with the details. Note the dotted red line going through the molecule. You will note that the left half is not the same as the right half.

The molecule is not symmetrical.

Conversely, consider Butane below, a simple 4 carbon hydrocarbon gas by comparison:

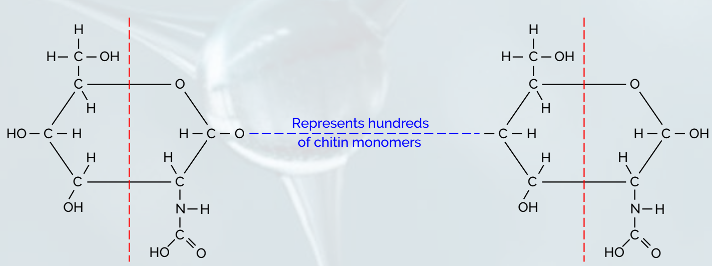


This is an example where the left and right hand sides are symmetrical.

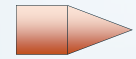


Going back to chitin, if we look at how the mononers are joined together we see that with two or more monomers the symmetry is maintained. In other words, the left and right sides stay the same.

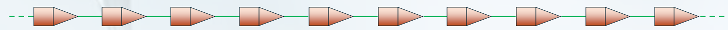
Extrapolating this example from two monomers to hundreds or thousands we can still maintain this difference between the ends of the chitin polymer chain.



Going back to the bead on a necklace analogy, we can represent the monomer left and right halves as different shapes to simplify the above with a much simpler model using an asymmetric shape to represent the monomers.

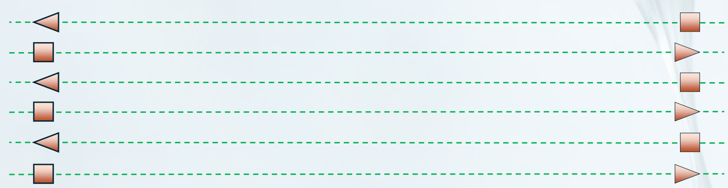


Because of this asymmetrical shape, we can identify left and right "ends" of the monomers involved in the chemical bonds joining them together. Looking at the polymer model as a whole, the right hand "end" also has a different shape than the left "end".

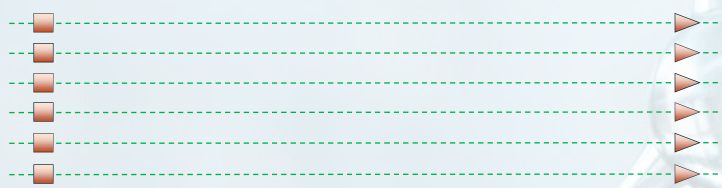


This introduces the concept of directionality, which is the basis in differentiating α-chitin from β-chitin from γ-chitin. In other words, it is how these chains are laid down relative to one another in the native structures that characterizes crystallinity and defines them as α, β or γ-chitin. We can simplify the model further by removing the internals and just leaving the left and right ends. A section of the polymer would look something like this

With this model, we can better illustrate the structural differences between α, β and γ-chitin. Beginning with α-chitin, each strand runs in an opposite (or antiparallel) direction to the adjacent strand. There are chemical bonds called hydrogen bonds that hold these chains together. Alone, hydrogen bonds are quite weak but innumerable ones create a strong bonding force. This is analogous to Velcro. Each hook and loop is easy to pull apart but it is more difficult to separate a large piece with multiple thousands of these hook and loop structures. Alpha chitin has the most hydrogen bonds per unit length and is the most stable.

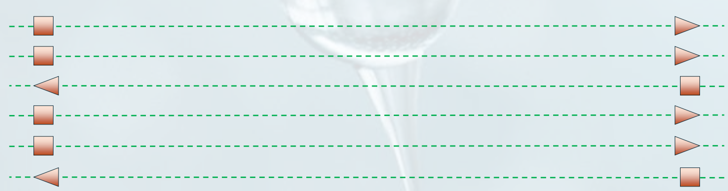


Beta chitin is a looser structure where all the chains run in the same (parallel) direction



With β-chitin there are less hydrogen bonds per unit length (half as much as α-chitin). Beta chitin is primarily sourced from squid pens though there are other known sources where this crystalline form can be found.

With γ-chitin, the polymer strand arrangement is a sort of hybrid between α-chitin and β -chitin. With this form, two polymer strands run parallel and the third runs antiparallel. Hydrogen bonding per unit length is somewhere between the α and β forms.



Though γ-chitin is not seen as being as common as alpha and beta forms, it has reportedly been found in some fungi (including yeasts) and beetle cocoon fibers.

Alpha chitin is mostly found in crustacean shells such as prawns, crabs and lobsters, as well as beetle shells and fungi cell walls and is recognized as the most abundant crystalline form.

Alpha, β and γ-chitin are more associated with biological structures as opposed to being solely correlated with particular organisms. For example, insect cuticles are α-chitin whereas the peritrophic membrane features β-chitin. Regardless of the source, the manner in which chitin is arranged in various biological structures is quite complex. It is largely the crystalline form and arrangement that contribute to the corresponding major functional attributes. For example arthropod exoskeletons are quite hard, rigid and quite inflexible, with squid pens, there is some rigidity, but greater flexibility.

Are these crystal forms modified or disrupted during the extraction of chitin and conversion to chitosan? The α, β and γ-chitin crystal forms are found in native structures. The plethora of hydrogen bonds effectively keeps the polymer chains in rigid linear arrays. Chitin is the most intransigent material in the arthropod cuticle, fungal cell walls and squid pens. Chitin extraction strategies vary from different sources. With arthropods like shellfish, generally there is a demineralization step followed by a protein removal step. Other sources like squid pen and insects are not mineralized like shellfish so there is less reliance on a demineralization step. With fungi, the chitin is embedded in a polysaccharide based matrix. Being a polysaccharide derivative in its own right, the chemistry of chitin extraction here is different from the other sources but there is still a protein removal step.

Regardless, the parent crystalline structure survives the process to obtain chitin as X-ray diffraction can differentiate the three crystal types. Deacetylation of chitin to chitosan is a more rigorous chemical procedure but the crystal structure of anhydrous chitosan has been made indicating preservation of the parent arrangement. Additionally, if one were to process a crab carapace all the way to chitosan, the original structure remains– it still looks like a crab carapace. So, the α, β or γ descriptors relating to crystal structure can still be valid.

However, when chitosan is solubilized, the solvents penetrate the crystal matrix, completely dissociating the polymer strands from one another destroying the ordered array of polymer strands, liberating them from one another. Solubilizing basically means all the individual chitosan strands are dissociated from one another yielding a collection of free, individual strands suspended in an aqueous medium. Complete dissolution means the parent crystal structure is completely lost and any reference to that structure at this point is somewhat irrelevant. Therefore solid chitosans can be referred to α, β or γ forms. With liquid, solubilized chitosan, use of α, β or γ prefix can only be associated with their respective parent chitin origins. In solution, the individual polymer strands are more free to move and exhibit relatively greater flexibility than when they are in their respective crystal states. The chitosan molecules are free to interact with the solvent molecules.

Once the crystal structure is lost by dissolving chitosan, reassociation to the parent ordered state is not possible. The parent crystal arrangement does not dictate the properties of the derived chitosan in solution. Consider a mixture of chitosans from α, β and γ sources solubilized together. The chitosans would exist in solution as free polymer chains without any resemblance or signature to associate them to their respective parent arrangements. Chitosan is a copolymer (heteropolymer) of glucosamine and N-acetylglucosamine. If we imagine these three parent chitosans are the same percent deacetylation and same chain lengths then these chitosans, once in solution and regardless of source, are indistinguishable from one another. Any qualifying measurement like viscosity or percent deactylation of such a solution would represent an average of all the chitosans present. Additionally, the different sourced chitosans would not segregate from the other forms or reassociate in solution to their parent types.

The next question is whether the parent crystal structure has any bearing on quality of chitosan or its functionality.

It is understood that chitin and chitosan are both copolymers of glucosamine and N-acetylglucosamine. What differentiates them is the relative proportions of each monomer in the polymer molecules. Chitin is predominantly N-Acetyl glucosamine (usually greater than 95%). Chitosan, being partly defined by its solubility in dilute organic acids is majority glucosamine but there is a wider range of proportions of glucosamine to N-Acetylglucosamine. Chitin is not soluble in these solvents. When chitin is deacetylated, there is a progressive removal of acetyl groups. The degree or extent of this deacetylation (acetyl removal) is expressed as percent deacetylation (%DA) or degree of deacetylation (DDA). The %DA reported for chitosans have ranged from around 55% to over 95%. Higher quality chitosans have a %DA greater than 80%.

Molecular weight is another quality parameter. While molecular weight is important, it is critical to understand what this means. Molecular weight is an indication of polymer chain length. It is important to understand that in any chitosan sample, polymer chain length is not uniform across the sample. Far from it. The sample will represent a population of molecular weights (polymer lengths). The distribution may be tight and it could be less so. The molecular weight figure is an average measure. Usually, molecular weight is determined indirectly by measuring viscosity and performing some calculations. It is simply not practical to screen chitosans at the molecular level to generate products of "exact" molecular weights. From a lab perspective, individual molecular weights and their relative quantities in a sample can be determined via chromatographic or other separation/ detection methodologies. Commercially this is impractical. Generally the processing conditions, treatment/ age of the raw shell and other factors can influence the resultant molecular weight.

Viscosity is the resistance to flow. Chitosan solutions do exhibit viscosity. The measured viscosity will be a function of concentration, %DA and molecular weight. There are even ideas that patterns of deacetylation (eg random deacetylation along the chain, blocks of polymer deacetylated/ acetylated regions) may influence viscosity. Generally with polymeric chitosans, solutions above 2-3% become viscous to a point of being difficult to process, mix and subsequently pour. The viscosity generated by chitosan in solution is due to these large polymer chains sliding over each other. Concentration and chain length accentuate this effect.

Recently, chitosan oligomers have entered the market. Oligomers (or oligos) are short chain fragments of chitosan. Oligo is a Greek prefix meaning "few". There is no exact number that defines "few". There are a couple of formulation advantages to oligos. The shorter chain ones are water soluble (approximately less than 10-12 glucosamines in the oligo chain). These shorter chains allow for a greater amount to be added to formulations without incurring the viscosity penalty. As such, solutions of 50% and higher can be achieved.

As a natural material, nature has a way of processing the material so chitosan is biodegradable, unlike synthetics that persists in nature. As natural carbohydrate polymers go, chitosan is a highly functional polymer. A cursory internet search reveals a plethora of activities and applications in a number of industries. The literature is rich with research on chitosan applications and development of novel derivatives with characteristically unique functionality and properties. Most of this is based on chitosan's cationic nature (a rare feature in carbohydrate biopolymers). It is this cationic property that allows chitosan to be soluble in various liquids that are bio friendly and biocompatible. Chitin can be solubilized as well but those solvents are much harsher and not biocompatible. It is the facile solubility and biocompatibility that greatly increases the value of chitosan over chitin.

There are a lot of things to understand about our company and its products. First, we are a market leader. We innovate. We are not a "me too" company which seems to be the trend with our competitors. Numerous aspects separate us from others in the market. Since chitosan is such an important raw material for us, we don't source from the cheapest vendor. Our chitosans are manufactured from shellfish exoskeletons that are sustainably harvested. Our chitosans are top quality food grade material. In addition, our chitosans enjoy a "Generally Recognized As Safe" (GRAS) status from the US FDA. Our chitosans are also compliant with California Proposition 65, that state's Safe Drinking Water and Toxic Enforcement Act of 1986. Chitosan quality has a significant impact on performance.

Unlike others, we do not view chitosan as just a name or the latest trend or buzzword we have encountered. We have been in this industry since 2012 actively pioneering the way forward with our chitosan agricultural technology. We are not at the cutting edge, our competitors may claim to be there. We are out in front of that edge with a file, honing it, defining it with our collective technology, experience and expertise. Chitosan is a science and a technology with a history. Chitosan is not a monolithic, one size fits all material. Far from it. Organisan Corporation has understood this from the beginning and is at the forefront developing specific chitosan-based products for a number of agricultural applications. We pioneered chitosan agricultural technology. Chitosan is known to be active in many areas. For example, chitosan is recognized as a plant growth regulator, a plant defense booster, an elicitor, has fungicidal and antimicrobial properties and is also employed as a sticker agent in adjuvant formulations. Chitosan works well with the natural biology of the soil and has been employed with much success with several commercial beneficial biological agents such as *Beauveria bassiana* in combatting the deleterious effects of many plant pathogens.

We don't stop there. We constantly refine our manufacturing processes to give you top quality, functional product, tailored to your needs. We leverage our proprietary manufacturing, technical expertise and technology to modify our manufacturing processes to create specifically crafted products with tailored chitosan properties. We constantly support and improve our manufacturing with lab work testing formulas, seeking efficiencies, testing new inerts and actives. All this builds on the already impressive experience we have with chitosan. Unlike our competitors, our products are not just chitosan solutions of various claimed concentrations. chitosan is a functional foundational raw material for us. Our products are specifically formulated and feature chitosan as a main active component along with other actives and proprietary inerts. Our products feature chitosan incorporated in a formulation that maximizes its bioavailability, its penetration in the soil and plant tissues. Our products include proprietary inerts that maximally enhance chitosan effectiveness that is not seen with chitosan alone. Our chitosan based products work in concert with many soil beneficials. Together, this combined synergy creates a far more rhizosphere friendly environment, keeping pathogens and pests at bay. Our chitosan products are the result of extensive research, product refinement and field testing. This means, all chitosan products ARE NOT the same, especially products we manufacture. All of our products are manufactured at our Broussard, Louisiana facility and shipped to you from there. We take the time and effort to consult and listen to our customers and formulate chitosan based products that suits their needs. And we don't walk away. We are committed to you, our customers, we work closely through all aspects of your crop's growing cycle. We listen to you, advise and recommend tailored strategies with tailored products to deliver the results you want.

By working with us, this is what you can expect and we will deliver. We are your chitosan experts. This is not a groundless claim. We are not newcomers. The Organisan team has over 80 combined years experience under one roof that comprehensively covers chitosan from raw material acquisition, manufacturing, processing, product development, R&D, sales, marketing, agronomy, and application. We have sales support 24/7. We back that sales team with technical sales support. We have invested the last 12 years developing products and applying them with success all over the country and internationally, on various crop types, environments and geographies. Years of consistent results from the field attest to this. We know chitosan, we know how to manufacture it, formulate products with it, sell in the markets we service and we know how to apply it. We maintain an in-house library of over 6000 publications gathered from the literature. This resource is available to our personnel and we are constantly searching the literature for applications, technology and other aspects of chitosan that apply to our business. So when you do business with us, you are not just buying another chitosan product, you are getting that specifically formulated product along with accessing our experiences and expertise. We are on your side and want nothing more than to see your success. That is our commitment to you.

So, if you've tried "chitosan" products and did not see the outcome you wanted, there's a good chance your product was not made specifically for your use or made by a company that knows what it is doing. That's why you should invest your hard earned dollars with a team of 80+ years experience backing the right product to maximize your results. And you'll only get that knowledge and experience with the Organisan team and/or our authorized representatives.

The Pioneer in Agricultural Chitosan Technology

Dr. André Blanchard, Ph.D., Plant Molecular Biology
Vice President, Technology and Operations, Organisan Corporation
Extensive Chitosan research and application for 30 years.

Our proprietary manufacturing operations are located in Broussard, LA close to where our scientist lives. The "science" behind the formula was created, developed and is manufactured under the supervision of Dr. André Blanchard. Originally from south Louisiana, André spent most of his young life growing up in Inverness, Scotland (you'll be treated to both accents). He attended the University of the West of Scotland getting his bachelors in Applied Biology. André went on to gain his Ph.D. in Plant Molecular Biology at the University of Exeter in southwest England. From there, he returned home in 1992.

André brings a combined 25 years experience in academia and the private sector. André has worked with industrial scale recycling technologies and specialty chemicals manufacture. Within these industries, he has gained experience in directing product and process research and development. These efforts led in the technical development of a process (now a US Patent) for manufacturing a key raw material. André is also experienced in small business management, consulting, technology transfer, commercializing technologies, project management, process design and manufacturing strategies. He also initiated several collaborative projects with leading universities involving several external grant funded efforts from Federal agencies.

André's association with chitosan over the past 18 years has involved researching and formulating new products, designing manufacturing processes, marketing and commercialization.

André is leveraging his experiences to leading future innovations of a variety of products, and constantly improving the manufacturing process.