The Problem

Plastic is light, strong, waterproof, resistant to rot and decay, with high thermal and electrical insulation properties. It can be produced in virtually any color or made clear enough to see through. It can be made it into sheets, rods or just about any shape.

Plastics can be more precisely defined typically as organic polymers or chain molecules, usually synthetic and based on carbon backbones derived from petrochemicals with an almost endless variety of side chains which give various different properties to the material. The carbon chains can be combined with sulfur, oxygen or nitrogen, and in most products the polymer is mixed with additives: fillers, colorants and plasticizers. Plasticity (https://en.wikipedia. org/wiki/Plasticity_(physics)) is the general property of all materials that are able to irreversibly deform without breaking and this has become associated with this class of polymer.

Plastic's high malleability has allowed a great number of manufacturing techniques to occur, making a wide range of products. In addition to knowing a chemical formula, knowing how a plastic object gets produced can offer insights for finding alternate materials. Here are the most common ways that plastic articles are made:

• Injection molding: one of the most common techniques for a wide range of products, this process forces resin pellets into a metal mold and mixes and heats them uniformly for a solid plastic object.

• Extrusion molding: similar to injection molding in that it also heats resin to a plastic state, in this technique the malleable substance is squeezed through a die to create a particular shape. This process lends itself to linear stock such as pipes or door seals and uses multiplesetting thermoplastics or single setting thermoset plastics

• Blow molding: a hot plastic plug called a parison is enclosed by a mold and then blown against the walls of the mold by air pressure, creating a hollow object like a bottle.

• Rotational molding: a dry plastic powder goes into a mold and is heated as the mold is rotated to coat its interior with a thin layer, thus also making a hollow object. Auto parts, toys and furniture are some of the products typically made this way.

• Additive manufacturing: layers of resin are set (polymerized chemically) using various activators such as heat or UV light and an object is built up into its three dimensional shape by adding these precise computer controlled layers one at a time. Fused Deposition Modeling (FDM) where a heated resin sets on contact with the air, and stereolithography (SLA) where light sets a liquid resin into a solid, are two examples among others.

The Model

One of the sources of these newly developed materials is chitin. Chitin is the second most common organic material in the world after cellulose. It is a polysaccharide, or sugar, found in crustacean shells, insect cuticle, fungi walls, the beaks of cephalopods like squid, and the radulae and nacre of molluscs. It is typically combined with other materials in nature to make strong composites. The nacre of the aba-lone shell is a case in point. The chitin scaffolding holds protein gels that are then mineralized to make a composite material tougher than any ceramic.

Arthropod shells or cuticles are another example. These are nanocomposites comprising chitin and protein tissue containing calcium carbonate crystals in a hard microfibrous shell. The parts of this shell, the exocuticle and endocuticle, are designed to resist mechanical loads, being laid in a twisted plywood structure. This tissue illustrates several structural stratagems of nature: composites, building in a hierarchy of linear scales, and using the geometry of structure or array, rather than material, to resist stress.

Chitin is a derivative of glucose, comprising long chains of N-acetylglucosamine units. It is quite similar to its more common relative, the polysaccharide cellulose, but with one hydrox- yl group on each monomer replaced with an acetyl amine group. This allows for increased hydrogen bonding between adjacent polymers giving the chitin-polymer matrix increased strength. While in structure chitin is most like cellulose, the structural component of plant cell walls, in function chitin serves most like the protein keratin, which forms hair, nails and hooves in animals.

Chitin, like cellulose, is used in a wide range of industrial applications: fertilizers, biopesticides, binders for dyes and adhesives, membranes and filters, surgical thread and tissue scaffolding, additives in food processing and in pharmaceuticals.

Chitin is modified typically into chitosan through deacetylation from 75-90%. A common method uses sodium hydroxide in excess as a reagent and water as a solvent. It needs no additive to gel, is heat responsive, and soluble in acidic conditions, but not otherwise. It bonds to metals and proteins, and is the only positively charged polysaccharide.

Chitosan has been researched extensively since the 1980's because of its versatility and promise. In particular, researchers have looked to it as a natural source for hydrogels. Hydro- gels are long, three-dimensional hydrophylic polymer chains that can absorb up to 1,000 times their dry weight in water and can be made from a variety of materials.

The typical hydrogel structure is crosslinked, formed by reactions of the monomers in its base spine or by hydrogen bonding. The material will behave somewhat like a solid and not be dissolved by the water because of the three-dimensional cross-linking within the polymer chain.

Examples of hydrogels in nature are cartilage, the vitreous humor of the eye, tendons, mucus and blood clots. Typically these are made from proteins like collagen. Other natural hydrogel materials being investigated for tissue engineering include agarose, methylcellulose, and hyaluron.

Hydrogels exhibit some useful properties because of this 3D chemical structure: their swelling can be controlled and activated by environmental conditions like changes in pH, temperature, ionic strength, solvent composition, pressure, and electrical potential. They can be biodegradable, bioerodible and bioabsorbable, and in many situations these processes are tunable. They are therefore used in biomedical applications such as transdermal drug delivery and implant coatings, soft contact lenses, pills and capsules, bioadhesives, wound healing, tissue engineering, cell culture and in electrophoresis, and chromatographic packaging.

Natural polymers like chitosan are attractive to biomedical researchers because they generally have high biocompatibility, intrinsically interact with cells, are biodegradable, and produce low toxicity byproducts. Researchers have mitigated some of their disadvantages, such as low mechanical strength and relative inconsistency of batch compared to synthetic formulations. Often they have combined relatively benign natural products with the least offensive synthetic ones, such as blending chitosan with methacrylates.

<u>The Translation</u>

Shrilk ("one of the materials that will change the future of manufacturing"): a conflation of the words "shrimp" and "silk," the two sources of material for the plastic. The shrimp provides chitin, the sugar from which the more useful chitosan is made, and insect silk provides fibroin, a protein. These two substances are laid in a composite that takes advantage of the properties of each to make a product that is both strong and durable.

Researchers had observed the crosslaid nature of abalone and arthropod shells and mimicked it, plywood fashion, at the micro scale. This is a helical structure, in which rafts of chitin microfibrils in a protein matrix form a sheet or lamina. Each sheet is rotated with respect to the one below, in a manner like plywood. Like logs in a raft the microfibrils crosslay the layers above and below, thus making a very strong structure that can resist stress from all angles.

The resultant material was not only bio-based, but also biodegradable and biocompatible.

Working exclusively with chitosan, they had been able to demonstrate a scalable production process for a chitosan-based plastic that could be either injection molded or cast like any current plastic.

"This chitosan fabrication method offers a new pathway for large-scale production of fully compostable engineered components with complex forms, and establishes chitosan as a viable bioplastic that could potentially be used in place of existing non-degradable plastics for commercial manufacturing."

the three dimensional mechanical properties of the chitosan: despite the remarkable strength of structures like insect cuticle and mollusc nacre, most applications of the material destroyed one of its best attributes. Heretofore, ground shrimp shells had been used widely for fertilizer, cosmetics and food additives, but the crude processing had removed chitin's structure. Almost all of the then current processes failed to produce 3D materials with the organization, ecological integration, or structural properties of natural chitinous systems. Some of the few uses of the material that retained its integral structure were found in the biomedical field as thin films or scaffolds in microfluidic devices and surgical wound dressings.

Rather than freeze drying, chemically changing the polymer or blending it with thermoplastic polymers, the researchers concentrated a dilute solution in acetic acid to form a pliable liquid crystal.

"An initial solution of 3% chitosan is concentrated until it reaches the viscosity necessary to be molded. To cast the solution, it is warmed up to decrease the viscosity and poured over the mold. The viscosity increase at room temperature helps to keep the polymer on the walls of the mold; the final crystallized form of chitosan is separated from the mold after the remaining solvent evaporates. In the case of injection molding, the polymer (by its own or mixed with a filler) is concentrated to a plastic state and warmed up at 80 degrees C before being injected in the mold. Just after the injection, the mold is open and the fabricated objects removed".

They were able to demonstrate its utility as a stock for injection molding and casting while still retaining its natural microscale crystalline organization. The reconstituted chitosan uses the structure found in the original substance, rather than more material, to create strength, a basic principle of nature.

Production costs are currently above that of petroleum-based plastics, but the adding of wood flour to the chitosan formula makes the cost comparable. Researchers believe that economies of scale will further reduce unit costs. Chitin, sourced by grinding up shrimp shells or growing fungi, does not impact land-based food production.

The material also gets high marks for recyclability and biodegradability. For one thing, dyes used within the polymer are recoverable, and therefore the plastic does not have to be sorted before being recycled. Chitosan can capture and retain small molecules, a property that had been used in the biomedical field to develop novel controlled-release molecular delivery systems. Water soluble dyes held within the chitosan could be released under a more acid regime and the uncolored chitosan recycled. Additionally, the material will not only break down in a matter of weeks, but will add nitrogen to any soil that it is in, encouraging plant growth.