CHITIN AND NANO-CHITIN IN 3D PRINTING: ECO-FRIENDLY INNOVATIONS & APPLICATIONS

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INTRODUCTION

Chitin, ranked as the world's second-most abundant natural polysaccharide, is surpassed in mass solely by cellulose.[1] This natural biopolymer consists of β-1,4-linked N-acetyl-D-glucosamine units and exists in three distinct polymorphic forms determined by the arrangement of its polymer chains: α-chitin, characterized by antiparallel chains; β-chitin, featuring parallel chains; and γ-chitin, which is a blend of both chain orientations. In nature, chitin is found within the cell walls of fungi, shells of crustaceans such as shrimp and crab and the exoskeletons of arthropods,insects and some mollusks. Notably, α-chitin prevails as the most prevalent form and is frequently sourced from crustacean shells.

Henri Braconnot, a renowned French chemist, professor, and pharmacist, is credited with the initial discovery of chitin in 1811. He identified chitin as an alkali-insoluble component extracted from mushrooms and named it "fungine," drawing from the ancient term for chitin. Antoine Odier furthered the study in 1823 by isolating similar alkaline-insoluble fractions from insects. After treating these fractions with sodium hydroxide solution, he designated them as "chitine," derived from the Greek word "Chiton," referring to the protective shells of marine mollusks. Subsequently, the English term "chitin" emerged from these early discoveries. Its unique properties such as biocompatibility and high surface area make it a valuable resource in various industries, including medicine, agriculture, and food production. However, the inherent high crystallinity and robust hydrogen bonding between chitin chains contribute to its insolubility in water and many organic solvents. Despite these properties, chitin has gained extensive application across various domains, including textiles, paper manufacturing, medicinal purposes, 3D printing and wastewater treatment.

"Nano Chitin " refers to nanostructures of chitin, which exhibit varying morphologies depending on their source and extraction method. The synthesis of nano chitin traces back to Revol and Marchessault's work in 1993, where they first produced chitin nanocrystals by subjecting chitin to 3M HCl for up to 6 hours. This pioneering method laid the foundation for the acid hydrolysis technique, which has since become one of the most prevalent methods for synthesizing nano chitin. Typically categorized as nanofibers, nanocrystals, and nanoparticles, these structures differ in their morphology. Nanofibers and nanocrystals share similar characteristics as long, crystalline rods with high aspect ratios. However, nanofibers distinguish themselves by their extended length, often reaching micrometer dimensions, whereas nanocrystals are generally hundreds of nanometers long. On the other hand, nanoparticles lack the crystalline structure and aspect ratios observed in other morphologies due to differences in their synthetic methods.

The unique properties of nano chitin, including its high surface area, biocompatibility, nanostructure engineering, and multiscale properties, have been highlighted in the context of its applications in biomedical and environmental fields. In the biomedical sector, chitin and chitosan nanofibers, derived from chitin, have shown promise in various applications such as tissue engineering scaffolds and drug delivery systems . These nanofibers possess excellent mechanical properties, biodegradability, and biocompatibility, making them suitable for constructing scaffolds that mimic the natural extracellular matrix. In the environmental field, nano chitin has been explored as a sustainable alternative for wastewater treatment, owing to its adsorption capabilities and ability to remove heavy metal ions and dyes from contaminated water sources. . Recently, the application of Nano chitin in 3D printing has also gained attention.

EXTRACTION OF CHITIN

Researchers have recognized marine organisms, particularly arthropod exoskeletons, as pivotal sources of chitin. Furthermore, chitin is procured from the tendons and linings across various biological systems in creatures such as crustaceans, cephalopods, mushrooms, fungal mycelia, among others [Table 1].[3] Significant chitin extraction occurs in shrimp and crab canning industries, leveraging waste materials for this purpose. Shrimp shells, encompassing roughly 30% chitin, feature a complex framework of proteins and calcium carbonate arranged in multiple layers.

The chitin extraction process involves crucial stages, notably the removal of proteins and inorganic calcium carbonate from shells through deproteinization and demineralization processes, respectively]. However, these methods also eliminate certain pigments and lipids during the course. Subsequently, the extracted chitins undergo biosynthesis and are categorized into polymorphic forms: α-chitin, β-chitin, and γ-chitin. Isolated chitin constitutes a copolymer of 2-acetamido-2-deoxy-β-D-glucose and 2-amino-2-deoxy-β-D-glucose. A distinguishing feature of chitin among polysaccharides is its nitrogen content.

Source		% Chitin
Crustacean Sources	Shrimp shells	36.43
	Shrimp shells (P. longirostris)	26.98
	Crabs shells	23.72
	Mussel shells	16.73
	Squid gladius (L. vulgaris)	31.2
Insect	Silk worm	NA
	Flour moth	9.5–10.5
	Argynnis pandora	22
	Hawk mouth	NA
	Mealworm (Tenebrio molitor)	NA
	Comb-clawed beetle (Omohlus sp)	NA
	White-grub cockchafer (Melolontha melolontha)	13–14
	Water scavenger beetle (Hydrophilus piceus)	19–20
	Colorado potato beetle (Leptinotar decemlineata)	7
	Dung beetle (Catharsius molossus)	17
	Large ground beetle (Colosoma rugosa)	NA

	Dark black chafer beetle (Holotricia parallela)	15
	Mealworm beetle (Zophobas)	4.6
	Lucanus cervus	10.9
	Polyphylla fullo	11.3
	Grasshopper	NA
	Mexican katydid (Pterophylla betrani)	11.8
	Moroccan locust (Dociostaurus maroccanus)	14
	House cricket (Brachytrupes potentosus)	7.15
	Celes variabilis	11.8
	Calliptamus Barbarus	20.5
	Ailopus simulatrix	5.3
	Two spotted field cricket (Gryllus bimaculatus)	NA
	Desert locust (Schistocerca gregaria)	22.5
	Blattella germania	4.4
	Periplaneta americana	3.4
	Cicada lodosi	NA
	Musca domestica	9

	Hermetia illucens	7
	Apsis melifera	8.8
	Vespa crabro	2.2
Fungal Sources	Aspergillus niger	42.0
	Penicillium notatum	18.5
	Penicillium chrysogenum	19.5 - 42.0
	Saccharomyces gutulata	2.3
	Mucorrouxii	9.4
	Siboglinidae	33.0
	Cnidaria	3.0 - 30.0
	Brachiopod	4.0 - 29.0

Table 1 : Chitin Sources

3D PRINTING EVOLUTION AND MATERIAL INNOVATION

3D printing or, Additive manufacturing,[2] involves creating three-dimensional objects layer by layer using computer-aided design (CAD). This technique has rapidly evolved, showing significant potential in part manufacturing. It minimizes material wastage by adding material precisely where needed, contributing to sustainable production. Recent data from Wohler's report highlights substantial growth in global 3D printing revenue: $3.07 billion in 2013, $5.02 billion in 2015, rising to $12 billion within three years, and an anticipated increase to $21 billion by 2020. The economic significance of 3D printing stems from its flexibility and capacity to create intricate part configurations and designs. It grants complete control over design and manufacturability, ensuring precision modeling and minimal errors in the printed part. While stereolithography, the first 3D printing technology, was invented in 1987 by Charles Hull, it gained widespread traction only in the late 2000s due to obstacles like manufacturing costs, surface finish, and limited materials. Eventually, recognized as a revolutionary manufacturing method, 3D printing saw a surge in manufacturers and became renowned for its potential to diversify part production methods.

Its impact on society is profound, as it empowers amateur users to create prototypes with basic engineering knowledge. Desktop 3D printers, user-friendly and automated, require minimal skill and no post-processing, allowing immediate utilization of printed parts. This technological democratization accelerates the discovery of new techniques and processes, benefiting both industrial and research domains. In these contexts, 3D printing offers geometric freedom, enabling the creation of intricate tooling and molds for various processing chains, like the automated fiber placement process on 3D printed molds.

CHITIN'S PROPERTIES AND ADVANTAGES FOR 3D PRINTING

Chitin, a naturally occurring biomaterial, exhibits a hierarchical structure and manifests in three crystal variations: α-chitin, β-chitin, and γ-chitin. α-Chitin originates from crustaceans such as shrimp and crab shells, insects like spiders, and fungi like aspergillus niger. In contrast, β-chitin is acquired from squid rings and cuttlefish bone, while γ-chitin is mainly found in organisms like Orgyia dubia and Ptinus. γ-Chitin's unstable structure, attributed to three glycoside chains, tends to undergo transformations into other crystalline forms.

Chitin displays varying densities in animals, resulting in different physical appearances. Inspired by this, Neri Oxman, an innovative MIT researcher, aimed to utilize chitin's properties to create multifunctional structures. Their experiment involved extracting chitin from shrimp shells and employing 3D printing methods. This led to a remarkable achievement—a recyclable, eco-friendly 3D printing material. They crafted a continuous 12-foot-long structure with varying densities, showcasing seamless transitions from beams to meshes. These results hint at the material's potential to scale up for larger applications, even window-sized structures. The immense potential of this biodegradable 3D printing substance is clear. Its ready availability as a natural material, sourced abundantly from crustacean waste, ensures its exceptional cost-effectiveness in raw form. Moreover, the chemical procedures for its modification or deacetylation are straightforward. This recyclable material exhibits remarkable properties ideal for 3D printing at any scale, while also maintaining an environmentally friendly profile.

Chitin, despite its widespread availability and compatibility with biological systems, faces limitations due to its limited solubility and unique structure, characterized by the linear (1,4)-β-N-acetyl glycosaminoglycan configuration. These structural aspects lead to its high crystallinity and robust hydrogen bonding, limiting its application versatility. To overcome these challenges, scientists are delving into nano-chitin as a potential solution. Nano-chitin preserves the core attributes of chitin while offering an expanded surface area and heightened functionality. This enhanced form holds significant promise, especially in the realm of biomedicine.

APPLICATION AND CASE STUDIES

Nano-chitin presents notable potential as a rheological modifier, enabling its utilization in various 3D printing processes. The conventional printing of pre-poly(1,8-octanediol-co-Pluronic F127 citrate) (POFC) emulsion has been historically challenging due to the insolubility and unmeltable characteristics of citrate-based thermoset bioelastomers. However, experiments conducted by Gu[4] showcased a significant breakthrough by incorporating chitin nano-crystals (ChiNC) as a rheological modifier. This addition effectively regulated the flow behavior of pre-POFC emulsion, facilitating the direct ink writing printing of POFC frames. Moreover, ChiNC played a pivotal role as a supporting agent during thermal hardening processes, preventing filament collapse. The resulting pre-POFC/ChiNC inks exhibited favorable mechanical performance and demonstrated low swelling, rendering them suitable for direct ink writing printing applications.

Noiva and Fernandes[5] created a hydrogels from alginate and nanochitin particles, assessing their suitability as bioinks for 3D printing. The study also involved producing cellulose nanocrystals (CNC) and chitin nanowhiskers (CTNW) through acid hydrolysis. The CNC:alginate hydrogel displayed notable water absorption capabilities, with CNC enhancing mechanical properties. Similarly, CTNW:alginate bioinks showed promising hydrogel properties, indicating water retention abilities and structural integrity. Rheological analyses revealed increased viscosity in both bioinks, surpassing that of pure alginate. CTNW:alginate bioink with a high CTNW concentration enabled the successful 3D printing of structures, marking the initial utilization of nanochitin particles in alginate solution for such prints. However, further enhancements in the printing process are necessary

Reymark D. Maalihan's[6] research focused on enhancing mechanical and thermal properties in stereolithography and 3D printing. The study utilized chitin nano-whiskers (CNWs) extracted from crab chitin to create nano-composites. By integrating 1.0wt% CNWs into NEAT MA (methacrylate), the research demonstrated improvements in the mechanical properties and maximum thermal degradation temperatures of the resulting nano-composites. This incorporation effectively boosted both mechanical strength and thermal resistance while maintaining the favorable characteristics of the 3D-printed MA/CNWs nano-composites.

Balaji Sadhasivam's[7] investigation showcased the potential of Poly(butylene adipate-co-terephthalate) (PBAT) infused with different proportions of raw nano-chitin for 3D printing biodegradable fillers. Through rigorous testing of thermal and mechanical properties, the research demonstrated increased rigidity in correlation with higher nano-chitin mass fractions. While the impact on thermal stability was relatively moderate, the inclusion of nano-chitin notably enhanced the overall thermal stability of PBAT. The resulting PBAT-NC nano-composite exhibited capabilities for fabrication into practical items like plastic supports, utilizing processing conditions similar to those employed in LDPE (Low-Density Polyethylene) manufacturing.

Fijoł et al[8] engineered PLA-based filters reinforced with TCNF or ChNF via 3D printing, revealing exceptional surface quality and a consistent pore structure. These filters displayed remarkable strength, high permeability, and demonstrated efficient adsorption of copper ions while effectively removing microplastics from water. An additional advantage lies in their reusability, allowing for recycling across multiple applications. The simplicity of production through 3D printing hints at the prospect of affordable and adaptable filtration systems. Future investigations could concentrate on refining surface functionalities to cater to specific application requirements.

CONCLUSION

In conclusion, the integration of chitin and nano-chitin into the realm of 3D printing has initiated a wave of eco-friendly innovations across various industries. Chitin's versatility, found abundantly in nature and available in various forms, has revolutionized 3D printing by enabling the creation of recyclable materials with diverse densities, even for large structures. Nano-chitin, with its enhanced properties, shows promise in biomedicine and materials science. Several studies have highlighted the utilization of chitin and nano-chitin in 3D printing. These materials act as modifiers in bioinks, improving mechanical properties and enabling direct ink writing of bioelastomers.

Nano-chitin-infused materials also exhibit improved rigidity and thermal stability, paving the way for applications in biodegradable fillers and water filtration systems. In essence, the integration of chitin and nano-chitin into 3D printing processes has opened new avenues for sustainable material innovation. Their versatility, coupled with advancements in 3D printing technologies, holds immense promise for revolutionizing industries, ranging from biomedicine to environmental conservation. Further exploration and refinement in the application of chitin-based materials in 3D printing processes will continue to drive innovation, offering solutions for diverse challenges across various domains.

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