MINI REVIEW Functional biocomposites

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ABSTRACT

The most essential features of the two polysaccharides are discussed, as well as the reasons for their interest in being combined. We exhibit several composite material structures and shapes that have lately been produced. Aerogels, hydrogels, films, foams, membranes, fibres, and nanofibres are covered, as well as the primary manufacturing processes, such as coextrusion, co-casting, electrospinning, coating, and adsorption. It has been demonstrated that the combination of bacterial cellulose and chitosan has lately attracted increased interest. This is especially appealing because both are examples of a biopolymer that is biodegradable and safe for humans and the environment. Rising living standards and increased environmental consciousness are driving drivers behind the development of these materials. This minireview will give you a detailed view about functional biocomposite.

Key Words: Biocomposites; Functional materials; Cellulose-chitosan; Fibres

INTRODUCTION

ellulose and chitin are the most common biopolymers on the planet. , Both are structural polysaccharides because they help plants and anim--al form hierarchical systems [1]. The unexpected discovery of cellulose nitrate synthesis in 1845 and the first effective conversion of insoluble chitin to its soluble counterpart in 1859 opened the door to myriad cellulose and chitosan uses [2]. Both polymers have become enormously important in the development of materials and products relevant to virtually all aspects of human life, such as food, clothing, health and medical devices, pharmaceuticals, filtering and purification materials, and construction materials, thanks to the development of extraction, derivatisation, and solubilisation processes. The frequency of reports on the effective combination of the two biopolymers rose in the 1990s. The papers in this section discussed the creation of films from cellulose and chitosan blends [3]. The idea of merging the two polymers came from the fact that they have a similar molecular structure, i.e., a highly functionalised, stiff-chain, linear molecular structure, but have different qualities that might be combined productively. Because of the amino group present, cellulose possesses hydrophilicity, structure, and mechanical capabilities, whereas chitosan has an electron donor function and antibacterial properties [4]. Understanding the molecular interactions of cellulose and chitosan has been critical in the creation of composite materials. Holmberg and Laine research groups gave some critical information on such interactions. To far, many architectures and shapes of cellulose-chitosan composites have been created based on these theoretical research.

Films, aerogels, hydrogels, membranes, fibres, and other materials have been developed and thoroughly explored in order to use all of the important functionalities of cellulose and chitosan. Biodegradable polymers or biopolymers are very essential since they offer a great alternative to petroleum-based goods. Biopolymer composites are desperately needed to supply ecologically friendly materials and hence lower the carbon footprint. Furthermore, the important qualities of the two biopolymers chitosan and cellulose, such as renewability, sustainability, non-toxicity, biodegradability, and specialised functionality, will lead to the development of a new generation of multifunctional composites employed in a variety of applications [5].

The purpose of this article is to describe the extent and complexity of the combination of two remarkable biopolymers, cellulose and chitosan, as well as their significance in the production of unusual materials and products [6]. The numerous composite structures and forms that have recently been produced and analysed are described, including porous structures such as aerogels, hydrogels, membranes, and foams, as well as films and, of course, fibres, with specific emphasis on nanofibers. The coating and manufacturing of thin films on diverse substrates is highlighted as a significant approach for composite material fabrication.

Cellulose

Soft and hard woods are the most abundant sources, but there are

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also annual plants, weeds, and bamboo, as well as animal sources such as the sea organism Tunicat, which produces animal cellulose tunicin; microorganisms that produce bacterial cellulose, such as Gluconacetobacter Xylinum strains, and so on [7]. In nature, cellulose often forms a composite with hemicelluloses and lignin in woody plants. As a natural substance, cellulose has been used by humans for thousands of years in the form of wood, paper, and textile fibres such as cotton, flax, or ramie, among others.

Cellulose is the most essential structural component of the plant cell wall, accounting for its mechanical strength [6], and it has a complex supramolecular structure that has been studied by many scientists, leading to the development of several structural models. Amorphous crystalline fibrils, or crystalline fibrils with an amorphous surface layer, were among the models used. However, when compared to the attributes of real systems, both models have flaws. As a result, the "mesomorphous-crystalline paracrystalline" model of elementary fibrils was presented, which allows for the description of both native and modified celluloses and predicts mechanical, thermal, sorption, solubilit This model also describes how different types of nanocellulose, such as nanocrystalline cellulose, nano whiskers, and nanofibrils, may be produced chemically or mechanically. These forms are all elongated, needle-shaped, elliptical, or rod-shaped and have been demonstrated to be virtually ideal reinforcing components in biocomposites, particularly when paired with chitosan.y, and other characteristics [6].

Cotton fibres are a good model system for representing natural cellulose structure in plants, and they are also a rich source of acellulose, with mature cotton fibres containing 90% to 95% of it. Cellulose microfibrils in mature cotton have a comparatively high crystalline region concentration (63%-68%) and are made up of 2-3 elementary fibrils with a reasonably wide cross-section (3.6 nm-4.7 nm). Martinez-Sanz et al. [6] demonstrated that mature cotton fibre cellulose microfibrils have a core-shell structure with a densely packed inaccessible I crystalline core with a diameter of about 2 nm surrounded by a hydrated paracrystalline shell that allows moisture to penetrate The discovery and development of appropriate solvents and dissolving techniques resulted in a wide range of regenerated cellulose solid structures, including films (cellophane) and fibres such as viscose, cupro, modal, lyocel, and others. These fibres are 100% cellulose and, as such, differ significantly from natural fibres. They have poorer wet mechanical characteristics and higher hydrophilicity than natural fibres, owing to reduced DP of cellulose and hence lower crystallinity. into the relatively densely packed microfibrils.

With its outstanding qualities, cellulose might be a great substrate for the development of functional biocomposites with hydrophilicity and mechanical properties. As a result, it is widely used in industries like as packaging, medicine, and hygiene.

However, antibacterial qualities are critical in many applications, and it has been demonstrated that chitosan may provide a number of useful solutions in this regard. Combining chitosan with cellulose can provide cellulose additional capabilities such as antibacterial, antioxidant, and antiwrinkle qualities [8]. To increase certain functions while avoiding the drawbacks of cellulose and main chitosan, derivatives of these materials have been produced and mixed to make composites.

Chitosan

In live organisms, chitin (C₈H₁₃O₅N)n is known to form microfibrill-

-ar structures. Fibrils are often embedded in a protein matrix, resulting in the characteristic hierarchical composite skeleton structure.

Odier originally coined the term "chitine" (from the Greek "chiton") in 1823, after discovering it in the elytra of insects. Because chitin and cellulose have similar molecular structures , they serve comparable functions as structural polysaccharides in living organisms: chitin in the cuticles of invertebrates and insects, and scaffolds and cellulose in terrestrial plants . The primary function of both biopolymers is support and protection , with the key variation in their molecular structure being the acetamide group on the C-2 position in chitin vs the hydroxyl group in cellulose.

Chitin is a nitrogenous, rigid, and inelastic substance that is white in colour. It is a polymer made up of 2-acetamido-2-deoxy–D glucopyranose units. Chitin is deacetylated to varying degrees depending on its source and isolation conditions [9]. The degree of deacetylation in chitin is typically 0.9, indicating that it includes 5 to 15% of any amino groups that may occur during the extraction operation. It is comparable to the average length of macromolecules in chitin, which is likewise affected by its source.

Chitosan is typically synthesised from chitin by alkaline hydrolysis of acetamido groups. Chitosan becomes soluble in aqueous acidic solutions when the Deacetylation Degree (DDA) reaches around 50% Muzzarelli described the procedures for deacetylation of chitin in detail in 1973. Several techniques for deacetylation of chitin have been proposed, the majority of which include alkali treatment with various combinations of strong sodium and potassium hydroxide solutions (from 30% to 60%), temperatures (from 70°C to 140°C), and treatment periods (up to 10 h).

Alternative approaches to increasing the DDA and molecular weight of chitosan while lowering the process alkali concentration and energy consumption included enzymatic treatments, steam explosion, low-frequency ultrasound, microwave assistance, multi stage procedures, and so on.

The DDA is critical for chitosans' activities and uses, including as antibacterial capabilities, immunological boosting, cholesterol reduction, and so on.

In general, low (DDA) chitosan has a DDA between 55% and 70%, medium chitosan has a DDA between 70% and 85%, high chitosan has a DDA between 85% and 95%, and ultra-high chitosan has a DDA between 95% and 100%. Some specific solvents, such as n-butylalcohol-sodium hydroxide, amyl alcohol, or dimethyl sulfoxide, were proposed to create chitosan with ultra-high DDA; however, such techniques raise expenses and the environmental load.

The proportion of deacetylated glucosamine units and their location in the macromolecules substantially impact chitosan's molecular activity, solubility, and shape in aqueous conditions. As the only semi-natural cationic polymer, it is of great interest in a variety of applications such as adsorption, flocculation, depollution, bioactivity, and so on. Chitosan is soluble in acidic solutions due to -NH2 functional group protonation and the conversion of chitosan to polyelectrolyte. The ideal solvent for chitosan is formic acid; nevertheless, acidic acid, at around 1% and pH 4, is the most usually utilised [10].

CELLULOSE-CHITOSAN FUNCTIONAL BIOCOMPOSITES

The structure-forming ability, mechanical capabilities, hydrophilicity, and water stability of cellulose have been combined with the electron donors and, of course, antibacterial properties of chitosan. They might be made by bulk processing, such as homogenous mixing in dissolved or solid form, or through adsorption or coating techniques, which typically use chitosan as the adsorbate and cellulose as the substrate.

In general, increasing the cellulose content enhanced the mechanical strength of the composites, whereas increasing the chitosan content improved the antibacterial and biocompatible qualities.

The chemical structures of cellulose and chitosan are similar, which predicts their compatibility and the potential of combining. Holmberg and colleagues comprehensively explored the intermolecular interactions between cellulose and chitosan 25 years ago [6].

They validated the intermolecular interactions between the molecules of the two polymers and discovered long-range attractive forces between the cellulose surface and the chitosan-coated surface in a dilute electrolyte solution, most likely owing to bridging if oppositely charged. Coulomb interactions are at the heart of their interactions. Blended cellulose-chitosan composites may be made from solutions in two ways: independently dissolving each biopolymer in common solvents and then blending the two solutions, or mixing the solid polymers and dissolving both in the same solvent. The second technique is more rational, but finding the correct common solvent for both biopolymers is difficult. Common solvents for cellulose and chitosan that have recently been researched include N METHYLMORPHOLINE-N-OXIDE (NMMO), ionic liquids, and ethylene diamine/potassium thiocyanate, which are often costly and difficult to remove from the material. However, using green solvents to dissolve cellulose and chitosan directly remains a challenge.

Structures

To fully exploit all of the distinguished chitosan and cellulose functions, such as appropriate mechanical properties, large accessible surface area and well-defined porosity, high functionality, and so on, research focuses on the development and application of a variety of cellulose-chitosan composite structures and forms, primarily aerogels , foams or sponges, membranes , hydrogels and films , nanoparticles fibres and nano Many alternative approaches and procedures have been used and explored, including various solubilisation processes and drying techniques for the creation of aerogels, such as freezedrying, supercritical conditions, vacuum, ambient pressure, microwaves, and so on.

Extrusion, injection, and moulding of polymer blends or coextrusion of two or more distinct polymers are the most generally used or socalled traditional methods for the manufacturing of polymer composites, which comprise a range of procedures for the creation of films, fibres, and membranes. These procedures are especially well adapted to thermoplastic polymers, as long as the processing temperatures are high enough to obtain the required form after cooling. Some of these approaches are ineffective when biodegradable polymers are utilised owing to polymer breakdown. In these circumstances, more frequent processes include solvent casting, phase separation such as gelation, freezing, or drying, and so on.

Cellulose solutions have been spun via the viscose method for millennia to make regenerated cellulose fibres, and the first attempts

to produce cellulose-chitosan composite fibres were also made in this manner. However, in recent decades, there has been a growing interest in using electrospinning technologies to create nanofiber composite structures from cellulose and chitosan.

Another efficient method for combining cellulose with chitosan is to generate thin layers and/or coatings, which are typically formed on cellulose as a solid macroscopic substrate. Coating procedures are designed to transfer liquid onto a solid substance to form a surface layer, assuring maximum availability at the surface. The temperature, viscosity, pH, concentration, and ionic strength of the liquid are used to regulate the thickness and homogeneity of the coating, as well as its stability.

The coating may be modified using all of these physicochemical factors and potential pretreatments (e.g., plasma) to generate a permanent bond or an uncontrolled or controlled release. Coating can be done using a variety of technical approaches, each with its own set of economic and environmental implications.

Electrospraying is a technology for producing micro/nanospheres as coatings that has been effectively employed in the manufacture of chitosan-based micro and nanospheres. Aside from being a highyielding approach, electrospraying has the benefit of not requiring an external dispersion/emulsion phase, which frequently contains components that are undesirable in biomedical applications. It can also be used to make thin, homogenous coating films.

Hydrogels, aerogels, sponges, and membranes

These are all examples of porous and cellular networks. One of the most significant uses of these structures is the removal of various sorts of contaminants from water, such as dyes, heavy metals, proteins, oil, and so on. According to Shen et al review's article, much fundamental research on the preparation of cellulose and chitin hydrogels has been conducted, including the development of solvent systems for native cellulose or chitin, hydrogel formation techniques, physical or chemical cross-linkers, and drying methods combining both polymers, among other things.

Weng et al. synthesised a cellulose-chitosan composite nanofiltration membrane through interfacial polymerisation of piperazine and trymesoil chloride. The modified membrane demonstrated a high rejection rate in aqueous dye-salt solutions as well as acceptable performance under a variety of pressure situations.

CONCLUSION

Cellulose and chitosan have developed as renewable materials with a wide range of possible uses. The new age of replacing nonrenewable elements with renewable materials is permeating every area of human life. Furthermore, the use of multifunctional materials has facilitated fast scientific innovation in most sectors, particularly when they come into touch with other materials and/or tissues (the human body or food via packaging) and must adapt to unexpected conditions.

Despite the fact that the number of research papers and publications on generating novel materials by combining cellulose and chitosan has expanded significantly since 2011, numerous problems remain. The first involves creating intimate mixes of the two biopolymers, while the second involves creating chitosan coatings, thin films, nanoparticles, or nanofibres on cellulose substrates such as films, membranes, textiles, paper, and so on. Both techniques have benefits and drawbacks.

The key issues with the first technique are the selection of an

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appropriate, environmentally friendly solvent and the regulation of the degree of interactions between the two polymers, both of which have a significant influence on the functionality (bioactivity) of the resulting composite.

In the second strategy, where chitosan is often placed in the form of nanoparticles, nanofibers, or thin films over a cellulose substrate, greater surface area usually results in more effective functioning. However, the fundamental issue in many applications is that these coatings have inadequate mechanical or chemical resistance.

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