



## Minireview

# Polysaccharide-based nanocomposites and their applications

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## ABSTRACT

Polysaccharide nanocomposites have become increasingly important materials over the past decade. Polysaccharides offer a green alternative to synthetic polymers in the preparation of soft nanomaterials. They have also been used in composites with hard nanomaterials, such as metal nanoparticles and carbon-based nanomaterials. This mini review describes methods for polysaccharide nanocomposite preparation and reviews the various types and diverse applications for these novel materials.

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## 1. Introduction

This mini review focuses on methods to prepare polysaccharide nanocomposites, the various types of polysaccharide nanocomposites, and their applications. Recent applications of polysaccharides used in preparing nanocomposites for biomedicine, for energy production and storage, for electrical devices, in separation science, and in industrial and materials applications, are reviewed. There are a number of older reviews published on polysaccharide nanocomposites, to which the authors would like to direct the attention of the reader.<sup>1–8</sup>

### 1.1. Polysaccharides

There are three major families of biopolymers, nucleic acids, proteins, and polysaccharides.<sup>9</sup> Polysaccharides are comprised of multiple saccharide units joined to one another through glycosidic linkages and have a number of unique features that differentiate them from the other families of biopolymers. Most polysaccharides are easily and inexpensively recovered natural products produced as energy storage or structural biopolymers by microbes, plants, and animals.<sup>10</sup> Polysaccharides offer a number of advantages over nucleic acids and proteins for applications in materials science. Polysaccharides are generally more stable than nucleic acids and proteins and are usually not irreversibly denatured on heating.<sup>10</sup>

There are a diverse variety of polysaccharides with properties including: low, intermediate, and high molecular weights with differing polydispersities; linear or branched structures; monofunctional, having only hydroxyl groups, or polyfunctional, having hydroxyl, carboxyl, and/or amino groups; a high level of chirality; water soluble or insoluble properties; low toxicity, environmentally safe, and non-immunogenic.<sup>10</sup> The diverse structures and properties of carbohydrates offer molecular and biological advantages for their use in the preparation of nanomaterials and nanocomposites.

### 1.2. What is nanotechnology?

Nanotechnology is a branch of materials science that focuses on the preparation of nanoscale materials of dimensions ranging from 1 to 100 nm.<sup>11</sup> Nanoscale materials often have unique properties due to their small size.<sup>11</sup> Early nanomaterials were generally constructed of 'hard' materials such as metals and carbon-only nanostructures, such as carbon nanotubes (CNTs) or buckyballs.<sup>12</sup> More recently, 'soft' nanomaterials made of synthetic polymers and biopolymers have gained increased interest as part of an effort to avoid nanotoxicity and to ameliorate environmental issues.<sup>13</sup>

### 1.3. Overview of nanocomposites

Nanocomposites are generally comprised of multiple nanoscale materials or a nanoscale material incorporated into a bulk material. Such nanocomposites can correspond to combinations of a 'hard' and a 'soft' nanomaterial, two 'soft' nanomaterials, or

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two 'hard' nanomaterials.<sup>13</sup> Nanocomposites take on the properties of the materials present as well as their size scale. Challenges in preparing nanocomposites include: controlling their fabrication/synthesis; ensuring the compatibility of their different material components; and obtaining desirable/unique properties. Since polysaccharides form a 'soft' nanomaterial, this mini review will focus on combinations of 'hard' and 'soft' nanomaterials and combinations of 'soft' nanomaterials.

## 2. Composite formation

There are a number of ways to prepare or synthesize nanocomposites. These include electrospinning, film casting, dip coating, physically mixing, layer-by-layer assembly, ionotropic gelation, colloidal assembly, co-precipitation, in situ preparation, and covalent coupling. A schematic illustration of the ways in which nanocomposites are made is presented in Figure 1. These methods take advantage of hydrogen-bonding, Coulombic interactions, hydrophobic effects, and electrostatic, and ionic interactions. Examples of polysaccharide nanocomposites, prepared or synthesized by these different methods, are presented in Table 1.

### 2.1. Electrospinning

Electrospinning is a physical method of nanocomposite formulation that involves the extrusion of a solution of polymer in the presence or absence of dispersed nanomaterial through a syringe needle (spinneret) onto a collection plate in the presence of a high voltage field (Fig. 1A). Wet-dry electrospinning utilizes a volatile solvent that evaporates as the nanocomposite is spun, while wet-wet electrospinning can utilize a non-volatile solvent, such as a room temperature ionic liquid, which is spun into a second solvent in a collection dish located between the spinneret and collection plate.<sup>14</sup> Co-axial electrospinning is a newly introduced technology, which can fabricate fibers from two different components simultaneously. The resulting fibers have a core-sheath structure.

Water-soluble polysaccharides, such as starch, are generally wet-dry electrospun. However, few solvents can dissolve crystalline polysaccharides, such as cellulose and chitin, which significantly limits their use in electrospinning. Room temperature ionic liquids (RTILs) are tunable solvents that can be custom designed to dissolve intractable polymers, such as cellulose.<sup>14</sup> RTILs are non-volatile, liquid salt-based, organic solvents with high thermal stability and a large electrochemical window. They are recyclable and, hence, are considered 'green' solvents. Cellulose solutions in RTILs can be electrospun into an ethanol or water coagulation bath to obtain nanofibers (NFs) using simple wet-wet spinning.<sup>15</sup> Once spun, cellulose NFs can be used as a supporting matrix for covalently coupling small molecules<sup>16</sup> or large molecules, such as proteins,<sup>17</sup> to modify the fiber properties.

Co-spinning a polysaccharide with a second polysaccharide or a synthetic polymer is also possible. Cellulose can be co-dissolved with other polysaccharides, such as the anticoagulant heparin, in RTILs and electrospun together as composite fibers.<sup>15</sup> Chitosan has been wet-dry electrospun with collagen from hexafluoroisopropanol (HFIP)/trifluoroacetic acid (TFA) to obtain fibers that can mimic the properties of the extracellular matrix. Increasing the chitosan content decreased the average NF diameter, while reduced chitosan content fibers exhibit better mechanical properties and crosslinking with glutaraldehyde vapor can increase fiber stability.<sup>18</sup> Gelatin, a collagen derivative, can be wet-wet electrospun with the acidic polysaccharide hyaluronan from a dimethylformamide (DMF)/water solution.<sup>19</sup> The synthetic biodegradable poly(L-lactide-co-ε-caprolactone) has been electrospun with the anticoagulant polysaccharide heparin (tributyl ammonium salt)

to obtain NFs with heparin as a dispersed phase in the NF matrix.<sup>20</sup> Co-electrospun cellulose acetate and biodegradable poly(*N*-vinylcaprolactam) (PVCL) afford tunable thermal responsive composites.<sup>21</sup>

Nanomaterials have also been incorporated into electrospun cellulose NFs to prepare core-sheath fibers. Conductive cable fibers with an insulating surface were prepared by coaxial electrospinning of multi-walled carbon nanotubes (MWCNTs) and cellulose.<sup>22</sup> Both the nanotubes and the cellulose were dissolved in ionic liquid, and then wet-wet electrospun into a water/ethanol coagulation bath. The nanotube core improved fiber thermal stability and tensile strength and showed electrical conductivity.<sup>23</sup>

### 2.2. Film casting, dip coating, and physical mixing

Film casting and dip coating methods are commonly used to prepare polysaccharide-based nanocomposites (Fig. 1B). Flexible energy storage devices based on nanocomposite cellulosic paper have been prepared from vertically aligned thin-walled MWCNTs grown on silicon substrates by thermal chemical vapor-deposition. Cellulose, dissolved in RTIL and infiltrated into the MWCNT forms a uniform cellulose-MWCNT cast film with excellent electrical properties.<sup>24</sup> Homogeneous dispersions of acid treated single-walled carbon nanotubes (SWCNTs) in a cellulose film can be prepared by film casting from *N*-methylmorpholine-*N*-oxide.<sup>25</sup> Cast films of the pullulan composited with nanofibrillated cellulose show improved thermal and mechanical properties and their malleability and mechanical properties could be further improved by adding glycerol.<sup>26</sup> Transparent nanocomposite films of chitosan and bacterial cellulose can also be film casted from aqueous acetic acid.<sup>27</sup> Film casting cellulose nanofiber/epoxy resin provides excellent thermally conductive, transparent nanocomposites.<sup>28</sup> Powders of pectin, a poly(α-1,4-galacturonic acid), milled with additives, can be cast from water to obtain antimicrobial nanocomposite films.<sup>29</sup>

Heparin-*N*-methylpyrrolidone biocompatible surface dip-coatings with embedded biocidal Ag nanoparticles (NPs) have been explored for use in central venous catheters.<sup>30</sup> Ag-NP-lactose-modified chitosan coatings were tested on the surface of activated thermosets as bactericidal films.<sup>31</sup> Cotton fabrics have been coated with zinc oxide-soluble starch nanocomposites for antibacterial applications.<sup>32</sup>

A novel thermal processing method, involving cycling between 20 °C and -20 °C under controlled tension, can produce nanocomposites of poly(vinyl alcohol) and cellulose.<sup>33</sup> Chitosan, heparin, and hyaluronan can be dissolved in acetate buffer to form polyelectrolyte solutions for the preparation of polysaccharide-based polyelectrolyte complex NPs.<sup>34</sup> Sequential mixing of chitosan and heparin on Au-coated iron oxide nanoseeds affords polysaccharide iron oxide NPs for magnetic resonance imaging of tumors.<sup>35</sup> Microfibrillated cellulose was mixed into a starch solution to prepare biofoams of varying porosity and water content by freezing/freeze-drying.<sup>36</sup>

### 2.3. Layer by layer assembly

Inhibition of bacterial growth has also utilized a layer-by-layer, electrostatically structured polysaccharide film of alginate and chitosan-coated cellulose nanofibrous electrospun mats through the addition of layered silicate<sup>37</sup> (Fig. 1C). Layer-by-layer coating hyaluronic acid dispersed CNTs, followed by an enzyme layer and a final Nafion layer affords electrodes for mediatorless NADH biosensing.<sup>38</sup> After electrospinning chitosan/poly(ethylene oxide) blends, the resulting fibers can be immersed in a hyaluronic acid solution to electrostatically coat the fibers with a layer of hyaluronan.<sup>39</sup> This simple method is effective in forming polyanion/polycation complexes.

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