



Virus adsorption of water-stable quaternized chitosan nanofibers



Xue Mi, K. Saagar Vijayaragavan, Caryn L. Heldt*

Department of Chemical Engineering, Michigan Technological University, 1400 Townsend Dr., Houghton, MI, USA

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ABSTRACT

The burden of unsafe drinking water is responsible for millions of deaths each year. To relieve this burden, we are in search of an inexpensive material that can adsorb pathogens from drinking water. In this pursuit, we have studied the natural carbohydrate, chitosan. To impart virus removal features, chitosan has been functionalized with a quaternary amine to form quaternized chitosan *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan (HTCC). HTCC can be electrospun into nanofibers with the non-ionic polyvinyl alcohol (PVA), creating a high surface area mat. High surface area is a major requirement for effective adsorption processes. HTCC is antiviral and antimicrobial, making it a good material for water purification. However, HTCC dissolves in water. We have explored the parameters to crosslink the nanofibers with glutaraldehyde. We have imparted water stability so there is a maximum of 30% swelling of the fibers after 6 h in water. The water stable fibers retain their ability to adsorb virus, as shown for an enveloped and nonenveloped virus. HTCC now has the potential to be incorporated into a microfiltration membrane that can remove viruses. This could create an inexpensive, low pressure filtration membrane for drinking water purification.

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1. Introduction

Drinking water contaminated with pathogens kills millions of people every year.¹ The most common method to remove or inactivate pathogens is the use of chemical disinfectants.^{2,3} However, the most common chemical disinfectant, chlorine, is suspected to create carcinogenic byproducts when natural organic matter is present.⁴ Newer methods include the use of ultrafiltration for bacteria and nanofiltration for viruses.⁵ However, small pore-sized nanofilters require high back pressures to function and are not commonly used in under developed countries. To help relieve the burden of unsafe drinking water, we are in search of an adsorption material that can remove pathogens from water. This material would ideally form a microfiltration membrane that would require low back pressures, but have the ability to clean non-potable water.

In our search for an inexpensive material that has the potential to adsorb pathogens, we have selected chitosan. Chitosan (chemical structure shown in Figure 1) is a polycationic polymer and the *N*-deacetylated derivative of the natural polymer chitin, the second most abundant polysaccharide found on earth next to cellulose.^{6,7} Chitosan is insoluble in water and common organic solvents

because of its rigid crystalline structure. It is soluble in acidic, aqueous solution if the pH value is less than 6.5.⁸

Chitosan is well known to be non-toxic, biocompatible, biodegradable, biofunctional, and hydrophilic.^{9–12} Chitosan has been used as an antimicrobial and antiviral material in the fields of biotechnology, pharmaceuticals, wastewater treatment, cosmetics, agriculture, food science, and textiles because of its advantageous biological properties.^{12–14} However, this activity of chitosan against pathogens is limited to acidic conditions due to its poor solubility above pH value of 6.5, where chitosan starts to lose its polycationic nature.^{7,12} The polycationic nature is what imparts most of chitosan's antimicrobial and antiviral properties. Therefore, the preparation of chitosan derivatives with an improved cationic properties over a wide pH range was studied for their antimicrobial and antiviral activity.^{6,7,10}

Among the various chitosan derivatives, the derivatives with quaternary ammonium groups have shown higher efficient activity against bacteria as compared to those of chitosan.^{6,10,12} Quaternized chitosan *N*-[(2-hydroxyl-3-trimethylammonium) propyl] chitosan (HTCC)^{7,11,14} (chemical structure shown in Figure 1), *N*-*N*-propyl-*N*, *N*-dimethyl chitosan¹⁵ and *N*-butyl-*N*,*N*-dimethyl chitosan iodide^{6,10} showed enhanced antimicrobial activity compared with chitosan.^{14,16} This may be due to the positively-charged quaternary amine group, known to target the negatively charged cytoplasmic membrane of microbes, altering membrane properties and impeding nutrients entering the cells.^{12,16} HTCC and

* Corresponding author. Tel.: +1 906 487 1134; fax: +1 906 487 3213.

E-mail address: heldt@mtu.edu (C.L. Heldt).

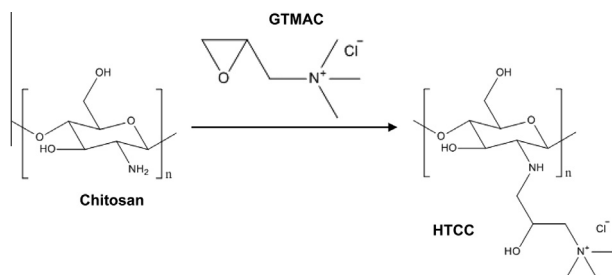


Figure 1. Formation of HTCC from chitosan.

hydrophobically-modified HTCC compounds were shown to inhibit the human coronavirus NL63 and murine hepatitis virus.¹⁷ Double-stranded RNA formulated with quaternized chitosan derivative was shown to inhibit yellow head virus.¹⁸ HTCC blended with graphene can also reduce infectious porcine parvovirus (PPV) concentrations in high salt environments.¹⁹

To form HTCC fibers, we use the technique of electrospinning.^{19,20} This method creates fibers that have a submicron diameter. An electric potential is applied to a polymer solution. When the electric potential overcomes the viscosity and surface tension, a jet is created from the polymer solution. The jet whips as the solvent dries, prior to the resting of polymer nanofibers on the collector. The use of a rotating drum collector helps to create more even surface coverage for filtration media. The high surface to volume ratio of nanofibers is sought to increase the adsorptive capacity and accessible surface area of the membrane.

For HTCC nanofibers to become an adsorptive membrane material, the fibers must not dissolve in water. Crosslinking of polymer structures is a common method to impart membrane stability in water soluble polymers.²¹ PVA fibers were crosslinked with maleic anhydride to create a filtration membrane.²² HTCC blended with polyvinyl alcohol (PVA) was photo-crosslinked to impart antimicrobial resistance to the fibers.¹⁰ Glutaraldehyde vapor was used to crosslink HTCC–PVA fibers to create an antimicrobial surface.⁷

Here, we demonstrate that HTCC nanofibers can be crosslinked while retaining their nonwoven structure and their ability to bind to negatively-charged viruses. We have explored the crosslinking conditions that give the greatest water stability. These conditions allowed for high virus removal. Our model viruses include the non-enveloped porcine parvovirus (PPV), one of the smallest known mammalian viruses and the enveloped virus, Sindbis virus. This nanofiber material has the potential to become an inexpensive defense against water-borne diseases.

2. Results and discussion

2.1. Characterization of HTCC

HTCC, was prepared by the reaction of chitosan with GTMAC in an aqueous solution, as shown in Figure 1. To confirm the successful synthesis of HTCC, FTIR spectra and NMR spectra of chitosan

and HTCC are shown in Figure S1. Both the results of FTIR and NMR spectra are in agreement with previous reports.^{11,14,19,23}

The degree of quaternization (DQ) of HTCC was determined to be $76.4 \pm 4.3\%$. This DQ value demonstrates that the amino groups on chitosan were substituted by quaternary ammonium salt groups. The remaining groups were likely acetylated since the chitosan used in this work was 75–85% deacetylated.

2.2. Electrospinning of HTCC blends

PVA has been shown to be a non-ionogenic partner for the formation of HTCC nanofibers.⁷ We explored how the ratio of HTCC to PVA affected the fiber formation. This has been explored in a wide range of values,⁷ and we chose a more narrow range. In Table 1, it shows that the conductivity and absolute viscosity increase with an increase in HTCC content. Fiber diameter decreases with increasing HTCC content. Our results are consistent for conductivity and fiber diameter to those of Alipour et al.⁷ however, our increase in viscosity is not consistent with the reported decrease in viscosity.⁷ This may be due to the different molecular weights of chitosan and PVA used in each work. From SEM images, shown in Figure S2, the density of fibers formed from a 10 w/v% polymer blend greatly decreased once the HTCC content reached 50% of the total polymer content. This is consistent with other's findings for 12 w/v% HTCC–PVA solutions.⁷ We desired the highest amount of HTCC as could be electrospun for water purification applications.

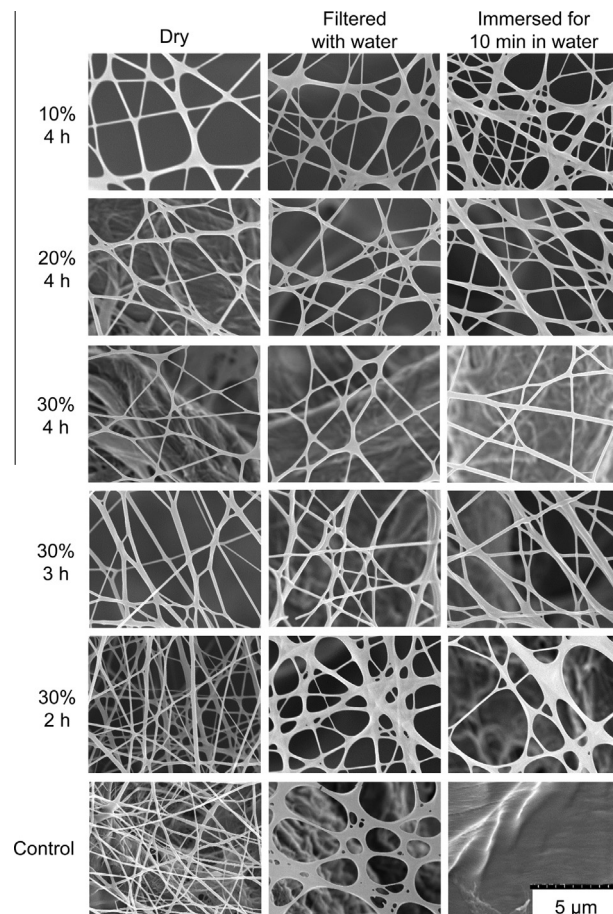


Figure 2. Images of glutaraldehyde crosslinked HTCC–PVA nanofibers. Electrospun nanofibers were crosslinked with different percentage of glutaraldehyde and for different times, as shown on the left. They were then tested for water stability by filtering with water or immersing in water for 10 min, as shown on the top.

Table 1
Viscosity, conductivity, and fiber diameter of electrospun HTCC–PVA

HTCC–PVA	Absolute viscosity (mPa s)	Conductivity (mS/cm)	Nanofiber diameter (nm)
3:7	2000 ± 244	4.4 ± 0.7	119 ± 8
4:6	2409 ± 141	6.1 ± 0.5	102 ± 1
5:5	3023 ± 289	7.3 ± 0.8	97 ± 1
6:4	3536 ± 257	9.1 ± 0.8	84 ± 1
7:3	3805 ± 71	10.0 ± 0.5	na

na–not available.

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