

Polymer-free Cyclodextrin Nanofibers via Electrospinning

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STATEMENT OF PURPOSE/OBJECTIVE

The aim of this study is to produce electrospun cyclodextrin (CD) nanofibers without using a carrier polymer matrix.

INTRODUCTION

Cyclodextrins (CDs) are cyclic oligosaccharides having a truncated cone-shaped structure which are produced by the enzymatic conversion of starch. CD molecules have relatively hydrophobic interior part and owing to this property they can form non-covalent host-guest inclusion complexes with various molecules. There are three native cyclodextrin types; α -CD, β -CD and γ -CD having six, seven and eight glucopyranose units respectively [1,2]. These three main CDs have limited solubility; however, by the chemical modification (methyl-CD and hydroxypropyl-CD), CD molecules gain higher solubility compared to native CDs (α -CD, β -CD and γ -CD) [3]. Due to their intriguing properties, CD molecules are applicable in many areas such as pharmaceuticals, functional foods, filters, cosmetics, textiles as well as advanced functional systems [4,5].

Electrospinning is a versatile and simple technique to produce nanofibers from a variety of materials such as polymers, polymer blends, sol-gels, composites, etc. In electrospinning method, a very high electrical field is applied to the polymer solution/melt, then continuous polymer jet is occurred and resulted in ultrafine fibers ranging from tens of nanometers to a few microns in diameter [6,7]. The high surface-to-volume ratio and highly porous structure of nanofibers make them applicable in biotechnology, membranes/filters, textiles, sensors, electronics, energy areas [8,9].

In principle, electrospinning requires high molecular weight polymers and high polymer concentration for ensuring the entanglements and overlapping between the polymer chains that is necessary to produce uniform nanofibers. Therefore the electrospinning of non-polymeric system may be a quite challenge [10,11]. On the other hand, CD molecules are capable of self-assembly and forming aggregation with intermolecular hydrogen bonding so they can create the entanglement and overlapping effect in their solution by the help of aggregation that is required for electrospinning process [12,13].

In our previous study, we have firstly reported the electrospinning of polymer-free nanofibers from methyl- β -cyclodextrin (M β CD) and inclusion complex of hydroxypropyl- β -cyclodextrin (HP β CD) with triclosan [14, 15]. In this study, we have achieved to produce nanofibers by using three different chemically modified CDs (HP β CD, HP γ CD and M β CD) in three different solvent systems (water, DMF and DMAc) without using any carrier polymer matrix [16].

APPROACH

The electrospinning of HP β CD, HP γ CD and M β CD were performed by preparing water, DMF and DMAc solutions in different concentrations (100% (w/v) to 160% (w/v)). In order to observe the effect of the urea on the fiber formation, 20% (w/w, with respect to CD) urea was added into the CD solutions in water and DMF at the optimized CD concentrations. The electrospinning parameters were determined as: applied voltage 10-20 kV, tip-to-collector distance 10-20 cm and the solution flow rate 0.5-2 ml/h. The viscosity and conductivity measurements of the CD solutions were performed to observe their effect on the fiber formation. Moreover, the particle size of the aggregates in CD solutions was measured by using dynamic light scattering (DLS) system. The scanning electron microscope (SEM) was used to determine the morphological property and the diameter of the CD nanofibers. While the crystalline structure was investigated by using X-ray diffractometer (XRD), the thermal property studies were carried out by using thermogravimetric analyzer (TGA).

RESULTS AND DISCUSSION

The optimizations of modified CDs were achieved at different concentrations for water, DMF and DMAc. The bead-free ultrafine HP β CD fibers were obtained at 160% (w/v) concentration in water and 120% (w/v) in DMF and DMAc. For HP γ CD, the bead-free fibers were produced at 160% (w/v) concentration in water and at 125% (w/v) in DMF and DMAc. On the other hand, the optimization of M β CD was attained at 160% (w/v) concentration for all solvent types (Figure 1). The morphology and the diameter of CD nanofibers were affected by the used CD derivate, its concentration and the type of the solvent system. The uniform fibers were only obtained at the required level of concentration/viscosity and conductivity values. Because of the lower viscosity and higher conductivity, much thinner fibers were produced in

water compared to fibers electrospun from DMF and DMAc solvent systems.

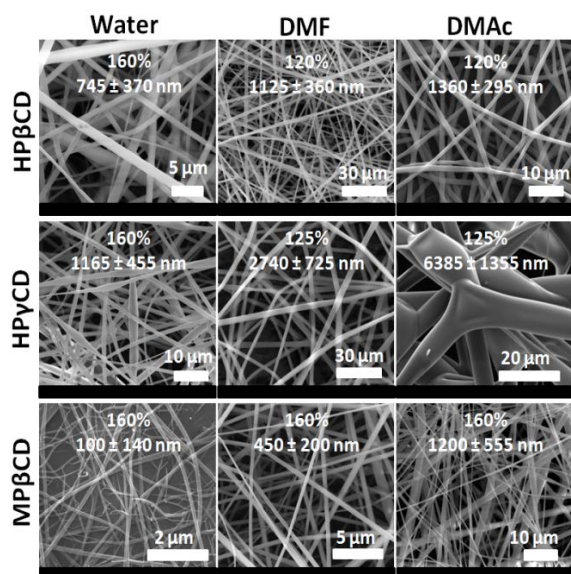


Figure 1. Representative SEM images of modified CDs (HPβCD, HPγCD and MβCD) nanofibers produced at optimized concentration in water, DMF and DMAc.

By adding urea to the concentrated CD solutions, the hydrogen bond between CD aggregates were broken so only splashed areas and bead structures were yielded (Figure 2).

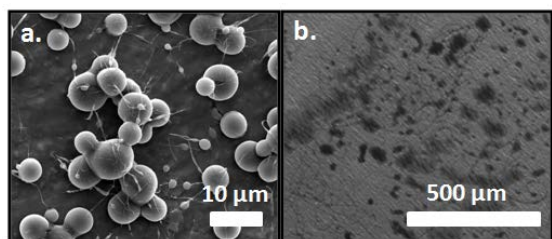


Figure 2. The SEM images of the bead structure and splashed area that were obtained as a result of adding %20 urea (w/w) to (a) 160% (w/v) HPβCD in water, (b) 120% (w/v) HPβCD in DMF.

Figure 3 indicates that CD nanofibers have some mechanical integrity and can be easily handled and folded.

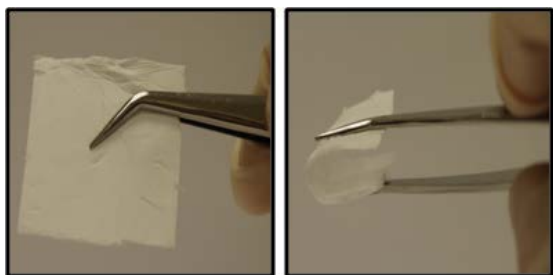


Figure 3. Photographs of HPβCD nanofibers showing the mechanical integrity of nanowebs.

CONCLUSION

The CD nanofibers formation originates from the presence of considerable aggregates and intermolecular interactions between the CD molecules in their concentrated solutions. They are mainly attractive structure having very large surface area of nanofibers with specific functionality of the CDs so the CD nanofibers might extend the use of these molecules in the fields of biotechnology, food, textiles, and filtration or in other functional systems.

FUTURE WORK

The integration of cyclodextrin unique properties with nanofibers makes them more intriguing and applicable for specific purposes. As a future work; we will investigate the molecular encapsulation capability of CD nanowebs for filtration applications.

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