Supplementary Information

Mechanical Testing

Tensile tests of the electrospun mats[1,2] (n=5) were performed with an Instron (Model 5943) using a 10N load cell at a constant strain rate of 10 mm min^{-1}. Mat dimensions were measured using a digital caliper. The tensile stress and strain (Figure S1) was defined at the maximum load applied. Both properties increased with increasing HPCD content, indicating blending has improved the mechanical properties. This trend is consistent with previously published work on chitosan blended electrospun nanofibers.[3]

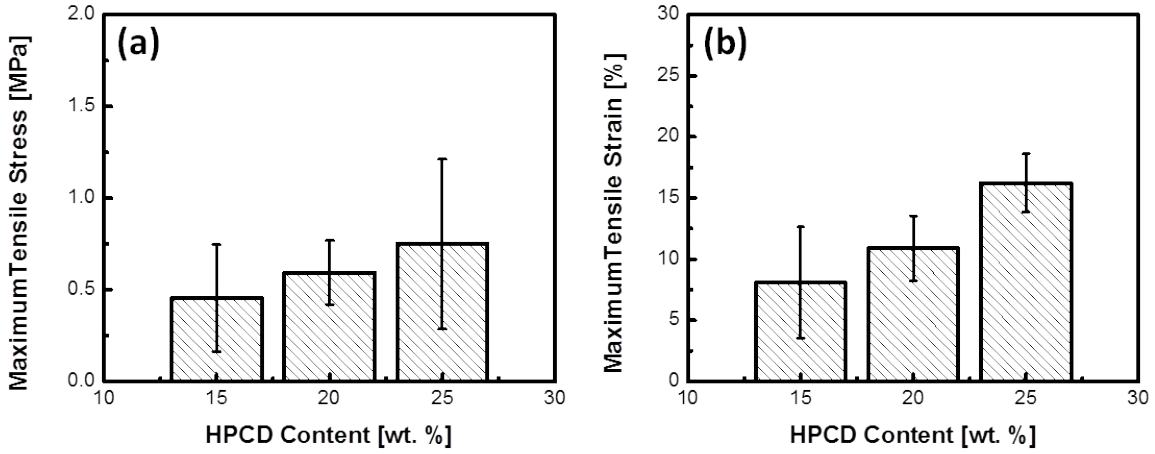

Fig. S1 Tensile stress (a) and strain (b) measurements of 2 wt.% chitosan in TFA with increasing HPCD content.

Mat Dissolution

These dissolution studies were conducted by soaking approximately 5 mg of pealed electrospun mat (n=6) in DI water. Figure S2 shows the qualitative features that each mat underwent during dissolution, including slowly degrading while becoming transparent, to breaking up, and finally dissolving fully. Final dissolution times were reported to be the times (average ± standard deviation) where no discernible material was apparent. Increasing the HPCD content was found to increase the rate of mat degradation, most likely due to HPCD's high solubility in water (Table. S1).

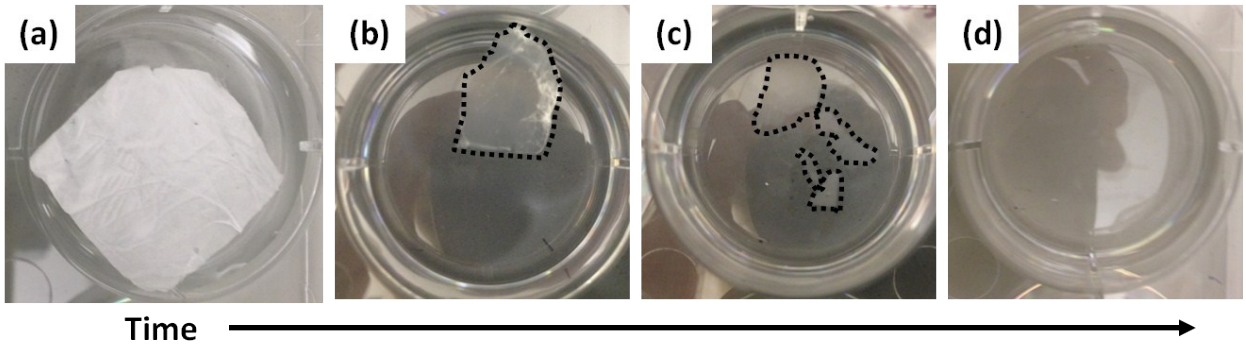

Fig. S2 The evolution of the dissolution of chitosan/HPCD/TFA mat fibers with increasing time.

HPCD Content [wt.%]	Dissolution Time [hr]
10	*95 ± 24*
15	*71 ± 13*
20	*37 ± 7*
25	*24 ± 6*
30	*8 ± 2*

Table S1 Mat dissolution times of 2 wt.% chitosan/TFA mats with increasing HPCD content.

Mat Porosity

Mat porosity (Figure S3) was analyzed using SEM micrographs and ImageJ binary processing. Mat porosity was determined to be the percent of void space area to the total surface area.[1] Data is expressed as mean ± standard deviation (n = 5) with the statistical significance determined using one-way analysis of variance. A value of $p < 0.1$ was considered statistically significant.

The mat porosity was found to be independent of HPCD content as long as uniform nanofibers were present. However, mat porosity did statistically increase with increasing chitosan content, from approximately 60% to 68%. This increase suggested that chitosan plays a significant role in the 3D phenomena.

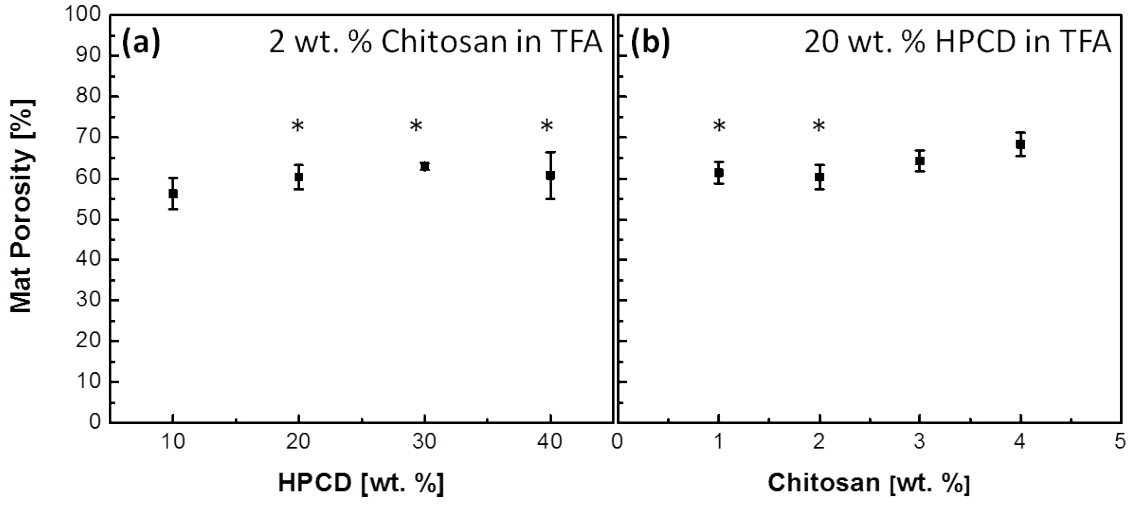

Fig. S3 Mat porosity measurements of 2 wt.% chitosan/ TFA mats with increasing HPCD content (a) and 20 wt.% HPCD/TFA mats with increasing chitosan content. The asterisks indicate data that is statistically different ($p < 0.1$) from all other conditions, except for other asterisks.

Solution Conductivity

Solution conductivity of 2 wt.% chitosan in 1 vol.% acetic acid with HPCD content increasing from 1 to 50 wt.% were measured using a Mettler Toledo meter. The addition of HPCD to chitosan solutions decreased the solution conductivity, as shown in Fig. S4. Decreases in solution conductivity typically have an adverse effect on fiber formation,[4] however, we see no evidence of this indicating some other effect is assisting chitosan electrospinning.

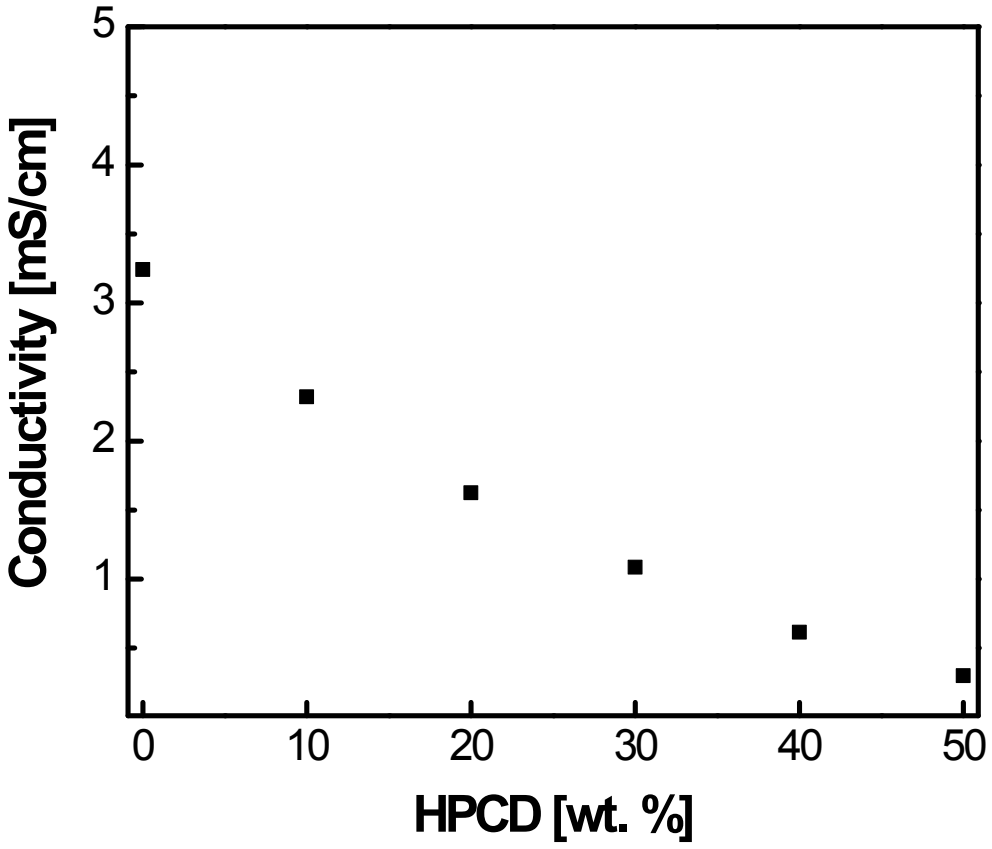

Fig. S4 Solution conductivity of 2 wt.% chitosan solutions in 1 vol.% AA with increasing HPCD content.

Solution Surface Tension

Solution surface tension measurements were conducted for chitosan and HPCD blends in 1 vol.% AA using the Wilhelmy plate method. The addition of chitosan and/or HPCD created no appreciable change in the surface tension (Table S2) and remained near that of water (58.85 mN/m).

CS	HPCD	Surface Tension	Standard Deviation
wt.%	wt.%	mN/m	mN/m
0	50	53.75	0.274
1	10	55.38	0.064
1	20	55.36	0.096
1	30	54.98	0.100
1	40	54.69	0.229
1	50	54.41	0.098
1	60	53.69	0.035
2	0	59.22	0.076
2	10	55.03	0.069
2	30	55.41	0.090
2	40	54.46	0.293
2	50	54.33	0.130
3	0	57.33	0.108
3	30	54.40	0.033
3	40	54.38	0.162
4	0	52.74	0.175
4	30	54.63	0.194
4	40	54.76	0.145

Table S2 Solution surface tension of 1 vol.% AA solutions with increasing chitosan (CS) and HPCD contents.

Urea Addition

The addition of urea, a chaotropic agent, to a solution can disrupt hydrogen bonding and reduce the ability to electrospin nanofibers if hydrogen bonding plays a significant role in fiber formation.[5] We found that urea addition does not improve neat chitosan electrospinning, nor does it disrupt fiber formation of chitosan/HPCD blends, (Fig S5). This lack of change indicates that hydrogen bonding is not the primary parameter of chitosan fiber formation.

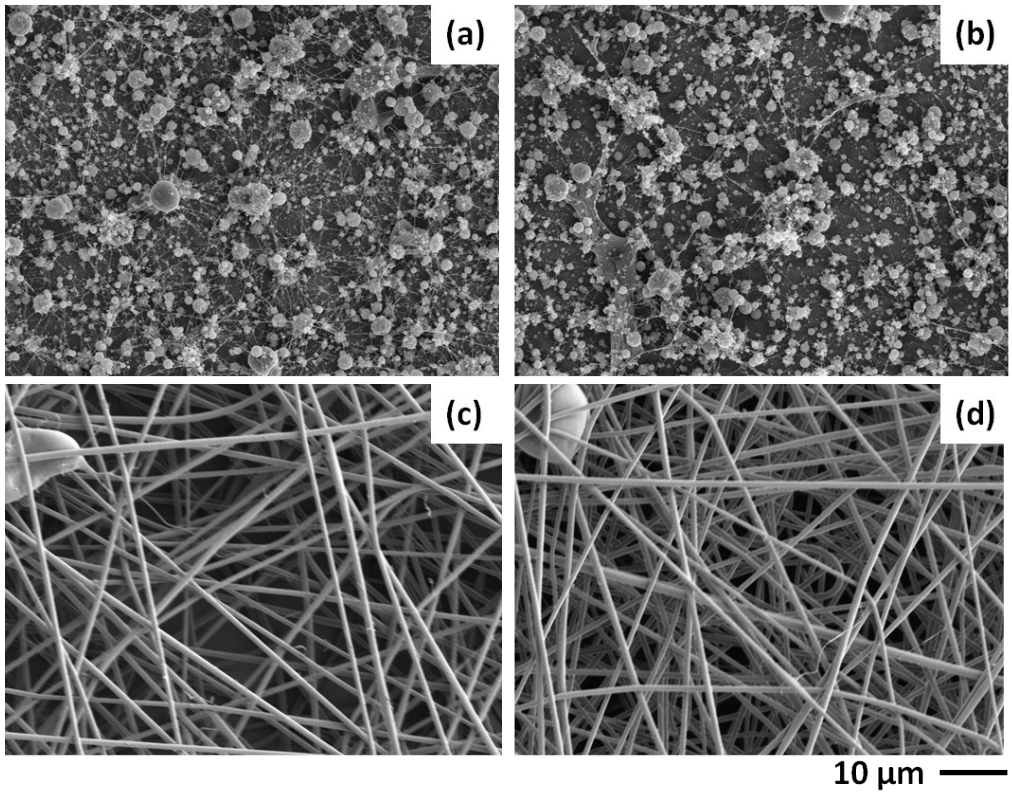

Fig. S5 SEM micrographs of 2 wt.% chitosan in TFA with different mole ratios of chitosan to urea. Top: neat chitosan with (a) 1:10 and (b) 1:100 mole ratios. Bottom: blended with 20 wt.% HPCD with (c) 1:10 and (d) 1:100 mole ratios.

References

1. J. Rnjak-Kovacina, S. Wise, Z. Li, P. Maitz, C. Young, Y. Wang, A. Weiss, Biomaterials, 2011, **32**, 6729-6736.
2. S. Ramswamy, L. Clarke, R. E. Gorga, Polymer, 2011, **52**, 3183-3189.
3. H. Zhang, S. Li, C. Branford White, X. Ning, H. Nie, L. Zhu, *Electrochimica Acta*, 2009, **54**, 5739-5745.
4. D. Li and Y. N. Xia, *Advanced Materials*, 2004, **16**, 1151-1170.
5. J. Manasco, C. Saquing, C. Tang, S. A. Khan, *RSC Adv*., 2012, **2**, 3778-3784.