

Supporting Information

Cryogenic Scanning Electron Microscopy

Figures 1a and 1b show cryo-SEM images of 1.1 wt% hm-chitosan without carbon microspheres and 1.1wt% unmodified, native chitosan respectively.

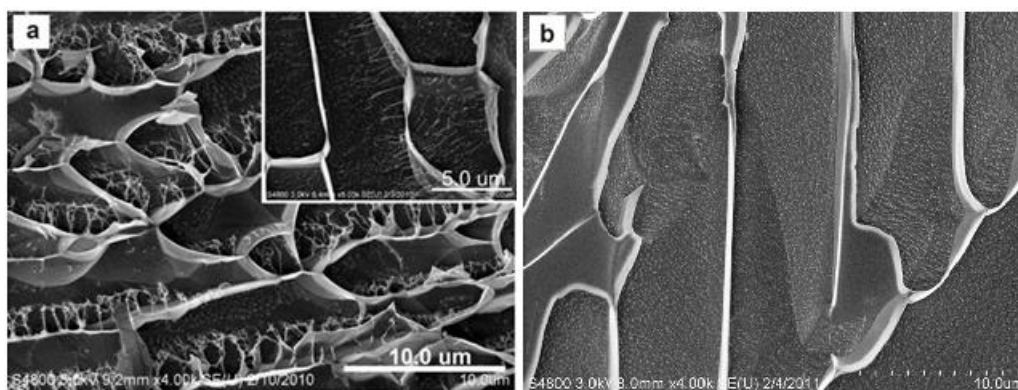


Figure 1: Cryo-SEMs of (a) 1.1wt% hm-chitosan; (b) 1.1wt% native chitosan.

At these concentrations neither of these systems forms a gel.¹⁻⁵ Both systems show a cell-like structure, but the distinctive aspect in the hm-chitosan system are the tendrils protruding from the cell walls. It is difficult to attribute the tendrils to the hydrophobic groups, but we have consistently observed these structures in hm-chitosan systems. The cell-like structures are not artifacts but are representative of the fact that chitosan and hm-chitosan form loose aggregates in solution, even without the addition of the gelling agent (carbons, liposomes).

¹H NMR Relaxation Experiments

¹H spin-lattice relaxation measurements were conducted by the usual inversion-recovery method, employing π - τ - $\pi/2$ pulse sequences with ten scans each and with a relaxation delay of at least 5 times the maximum T_1 estimated in the spin set. Samples were not degassed before the experiment, and therefore the T_1 values reported here cannot be taken to be absolute. Instead, they provide information about the relative relaxation times. Table I below lists the T_1 values for the methyl and methylene groups on the alkyl tails together with the corresponding values for water.

<u>Peak Position [ppm]</u>	<u>1.1wt% hm-chitosan (solution)</u>	<u>1.1wt% hm-chitosan with carbon microspheres (gel)</u>
.758 (-CH ₃)	2.064 sec	3.566 sec
1.174 (-CH ₂ -CH ₂ -CH ₂ -)	0.759 sec	1.502 sec
4.8 (H ₂ O in D ₂ O)	6.399 sec	10.52 sec

Table 1: ¹H NMR Relaxation Times.

As intuitively expected, the T_1 values of the alkyl groups increase upon the addition of carbon and the formation of the gel, due to the binding of these groups to the carbon surfaces through hydrophobic interactions. Recent studies have revealed that the chemical interactions of water molecules with surrounding groups of macromolecules in water-based gels lead to a larger T_1 indicating the presence of bound water through interaction with the polymer network⁶⁻⁹. This observation is consistent with the hm-chitosan and carbon system here, where the formation of the gel framework leads to confined volumes for the solvent (water).

The NMR spectra presented in the manuscript indicate subtle but observable changes in the hm-chitosan alkyl group resonances with increasing concentration of the carbon microspheres. A clear line broadening of the CH₂ and CH₃ proton resonances is observed at gel formation conditions. This broadening indicates motional restrictions of the alkyl side chains upon introduction of the particles, and at particle levels beyond the gelation threshold of 3 wt%, the two methyl group ¹H resonance bands indicate two distinct populations of methyl groups. It is possible that the two observably different bands represent two populations of methyl groups: those adsorbed onto the surfaces of the carbon microspheres and those interacting with other dodecyl groups attached to other hm-chitosan backbones. The distinction between these two populations is difficult to separate out.

References

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