

SUPPORTING INFORMATION

Molecular simulations of the interfacial properties in silk-hydroxyapatite composites

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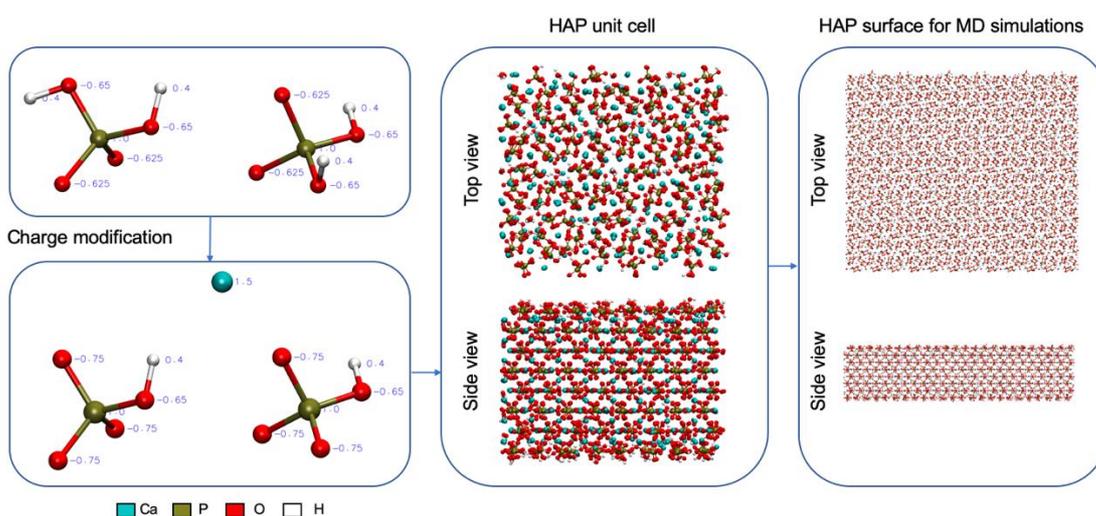


Figure S1 – Procedure used in this manuscript to modify surface charges and atomic composition in hydroxyapatite surfaces resolved at pH 7.

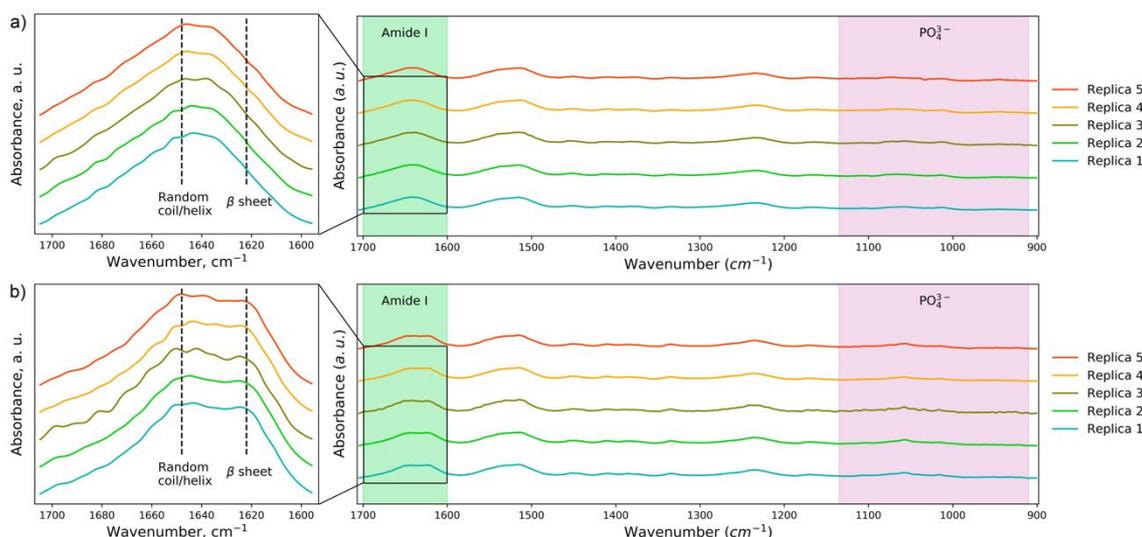


Figure S2 – FTIR spectra for silk + 1 wt% HAP samples ($n=5$) before (a) and after (b) water annealing. The data shows a lack of the PO_4^{3-} peak (associated with the presence of HAP in the sample) in all the replicas. This explains the lack of differences between these spectra and those for samples consisting only of silk.

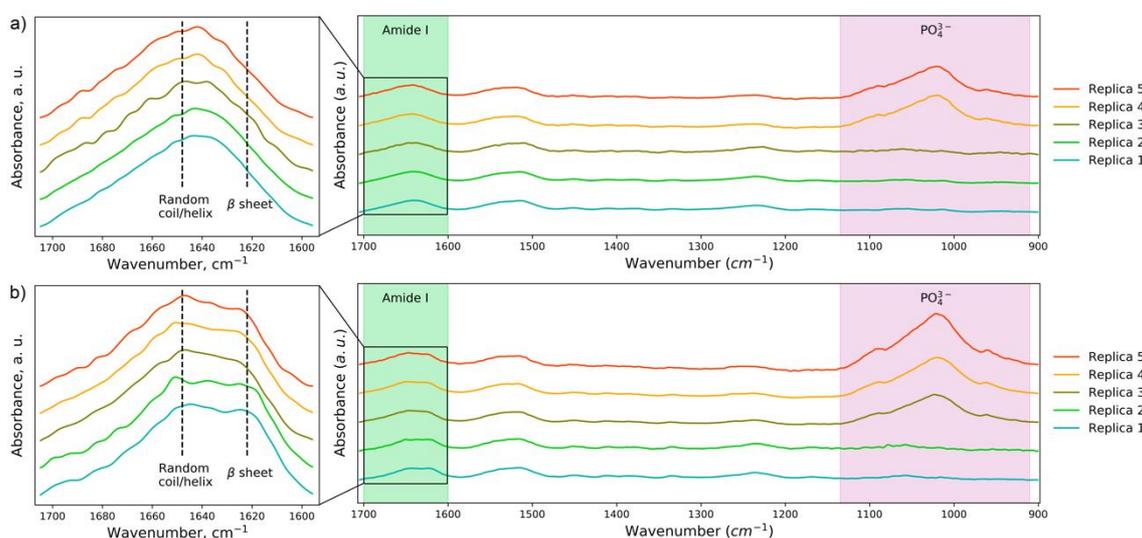


Figure S3 – FTIR spectra for silk + 5 wt% HAP samples ($n=5$) before (a) and after (b) water annealing. The data shows that the presence of the PO_4^{3-} peak (associated with the presence of HAP in the sample) was not present in all the replicas, indicating a non-uniform distribution of HAP in these samples. The samples in which the HAP-related peak was present were associated with a lower content of β -sheet structures, as shown in the inset on the left.

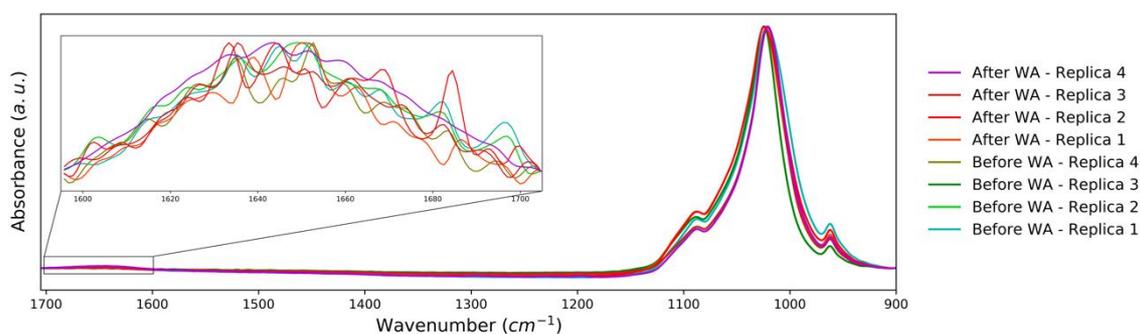


Figure S4 – FTIR spectra of HAP ($n=4$) before and after water annealing (WA). The inset represents the amide I region, where no differences can be observed in the spectra before and after water annealing. This indicates that any changes detected in this region in silk-HAP material are caused by conformational changes in the silk protein.

Table S1 – Secondary structure of silk as obtained by deconvoluting the amide I peak ($n=5$) at different HAP contents, before and after water annealing.

HAP Content (wt %)	Before water annealing				After water annealing			
	0	1	5	10	0	1	5	10
Beta Sheet (%)	22.6 ± 0.9	22.6 ± 1.2	21.8 ± 1.9	15.7 ± 0.9	40.0 ± 0.3	40.2 ± 0.5	36.9 ± 3.5	33.1 ± 2.9
Random Coil/Helix (%)	74.4 ± 1.0	74.2 ± 1.0	74.7 ± 1.7	79.8 ± 1.2	57.0 ± 0.5	56.5 ± 0.5	59.6 ± 3.4	63.1 ± 2.5
Beta Turn (%)	3.0 ± 0.1	3.3 ± 0.3	3.5 ± 0.7	4.5 ± 0.4	3.0 ± 0.2	3.8 ± 0.2	3.5 ± 0.6	3.8 ± 0.5