S.1 Circular Dichroism (CD) Spectroscopy

Circular dichroism spectra were acquired using a Chirascan spectrophotometer (Applied Photophysics Ltd, Surrey, UK). The path length of the cuvette (Hellma GmbH & Co. KG, Müllheim, Germany) was 1 mm. Total biopolymer concentration in the cuvette was 0.1 mg/mL for all samples. Far UV CD spectra were recorded from 280 to 190 nm with step size of 1 nm and bandwidth of 1 nm. Near UV CD spectra were recorded from 400 to 250 nm with step size of 1 nm and bandwidth of 1 nm. The measurements were performed at room temperature (22 °C). The presented data are average of two independent measurements, each averaged of five scans.

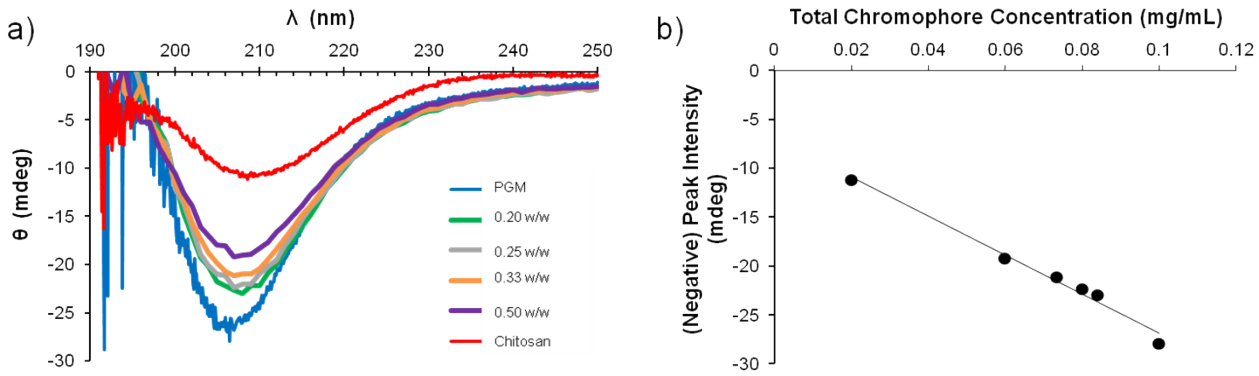

Figure S1. a) Far-UV circular dichroism spectra of PGM, chitosan and their mixtures (denoted according to the [chitosan] / [biopolymer] weight ratio), b) Negative peak intensity of the samples examined versus the total chromophore concentration.

Figure S1a shows the far-UV CD spectra of the samples examined. Near-UV CD spectra were also recorded, however, none of the samples exhibited any signal, indicating the absence of tertiary structure (data not shown).[1] In the far-UV CD spectra, all of the samples exhibit a broad negative band, characteristic of irregular (random coil) secondary structure.[2] PGM has a negative peak

centered at 206 nm, typical of its peptide chromophores.[3] Chitosan has its characteristic negative peak centered at 209 nm due to the n-π* transition of the -NHCO- chromophores.[4, 5] All the mixtures of chitosan / PGM exhibit a broad single peak, centered at 207 nm, irrespectively of the ratio of chitosan / PGM in the mixture. This indicates that PGM and chitosan maintain their random coil conformation in solution even after interacting with each other. The intensity of the negative peak decreases as the ratio of chitosan in the mixture increases. It must be kept in mind that the chromophores of chitosan are only in its acetylated parts (~ 20% in our study).[6] Hence, increasing the chitosan ratio in the mixture results in decreasing the total chromophore concentration in the solution. This is illustrated in Figure S1b, where the negative peak intensity increases in proportion to the total chromophore concentration of the solution. The shift of the peak at 207 nm for all the mixtures may be due to the interaction between chitosan and PGM observed by DLS and ζ-potential measurements. Such shifts have been explained as a consequence of interaction changes involving the chromophores.[4] Hence, the shift in this case is indicative of a change in the interactions of the chromophores resulting from the interaction between chitosan and PGM. Whether this change is due to intermolecular H-bonding formation or due to disruption of intramolecular H-bonds of these groups cannot be concluded from the CD spectra.

S. References

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Graphical Abstract