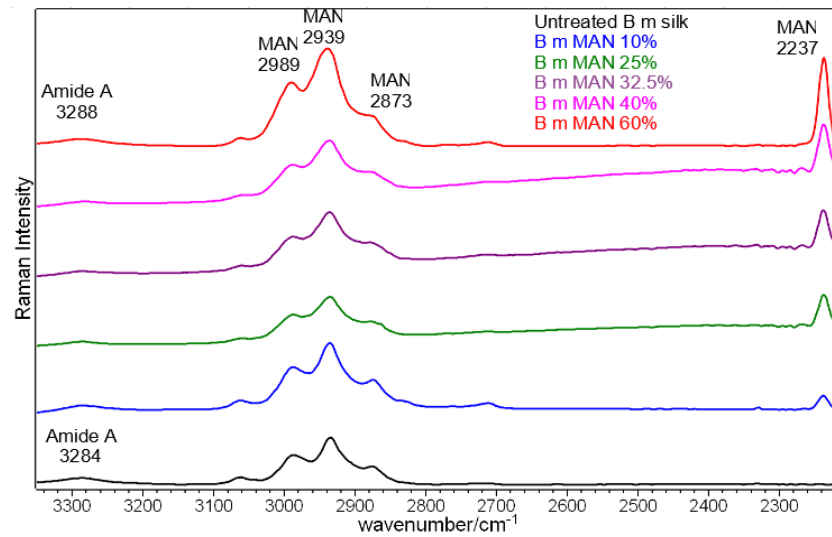


Table S1. Weight gain % of the silk fibers under study after ageing in the Ag⁺-containing solution for 48h.

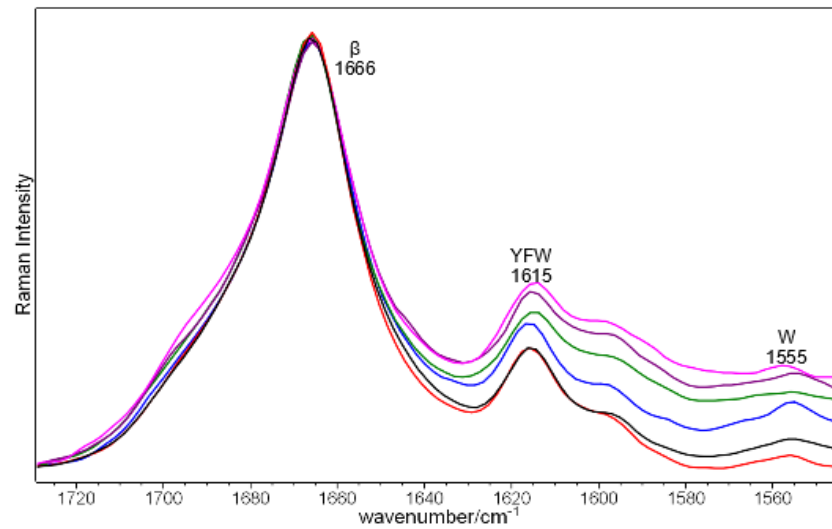
Sample	Weight gain %, t = 48h
control	2.81
MAN 10%	0.01
MAN 25%	0.66
MAN 32.5%	1.06
MAN 40%	1.65
MAN 60%	3.82

Table S2. Weight gain % of the silk fibers under study after 7 and 28 days in the SBF solution.

Sample	Weight gain %, t = 7 days	Weight gain %, t = 28 days
control	-1.53	-5.95
MAN 10%	-1.49	
MAN 25%	-0.97	
MAN 32.5%	0.16	
MAN 40%	0.94	-4.12
MAN 60%	1.08	1.66



(a)



(b)

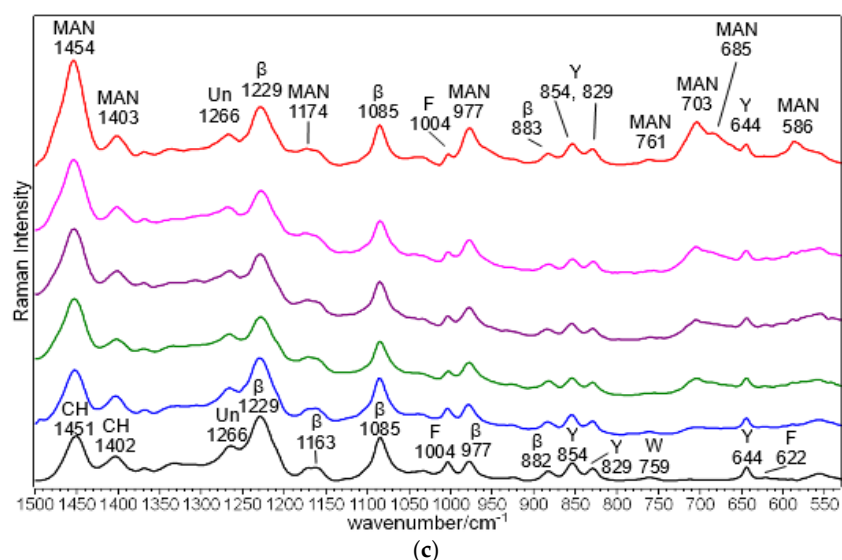
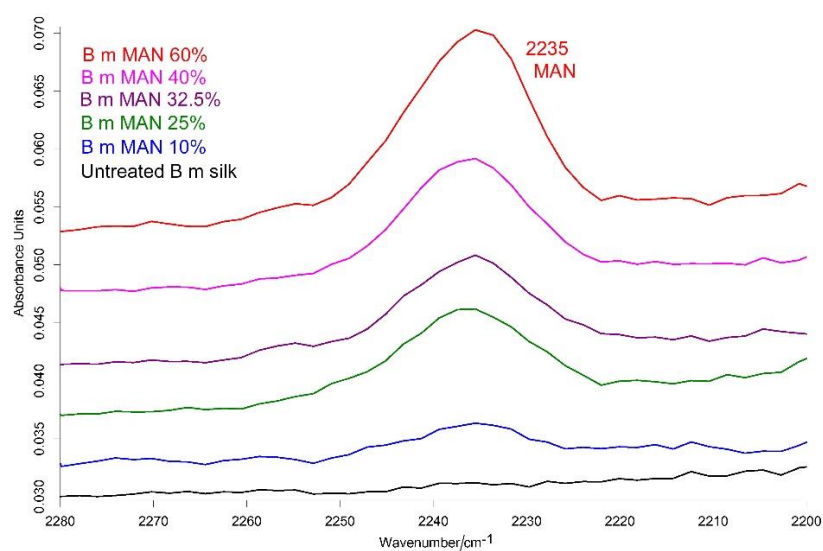
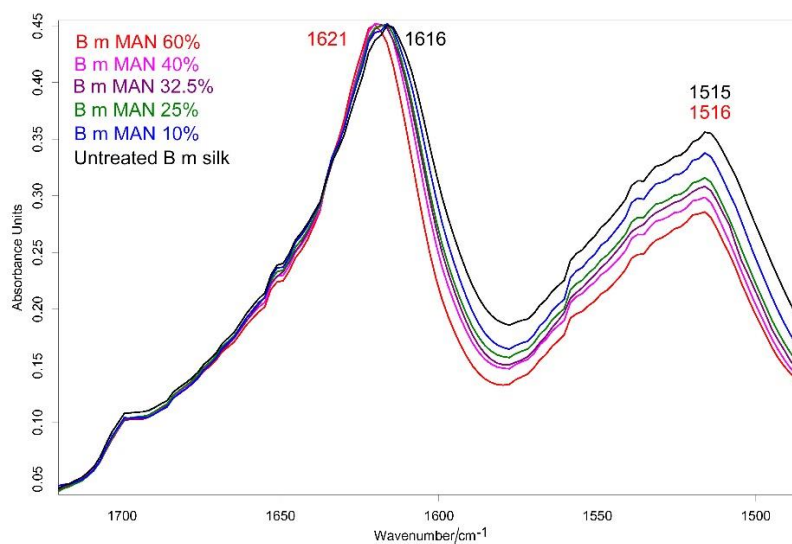
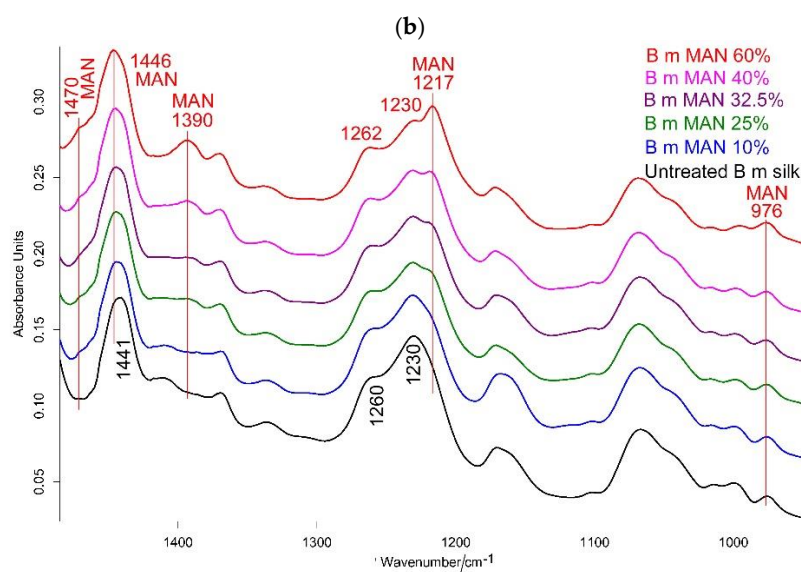


Figure S1. Raman spectra of *B. mori* silk fibroin fibers before and after grafting with MAN at different weight gains (i.e., 10%, 25%, 32.5%, 40%, and 60%) in three different spectral ranges: (a) 3350-2180 cm^{-1} , (b) 1730-1530 cm^{-1} , and (c) 1500-530 cm^{-1} . The spectra are normalized to the intensity of the Amide I band. The main bands assignable to β -sheet (β) or unordered (Un) conformation as well as to tyrosine (Y), phenylalanine (F), tryptophan (W), and the grafting agent (MAN) are indicated.



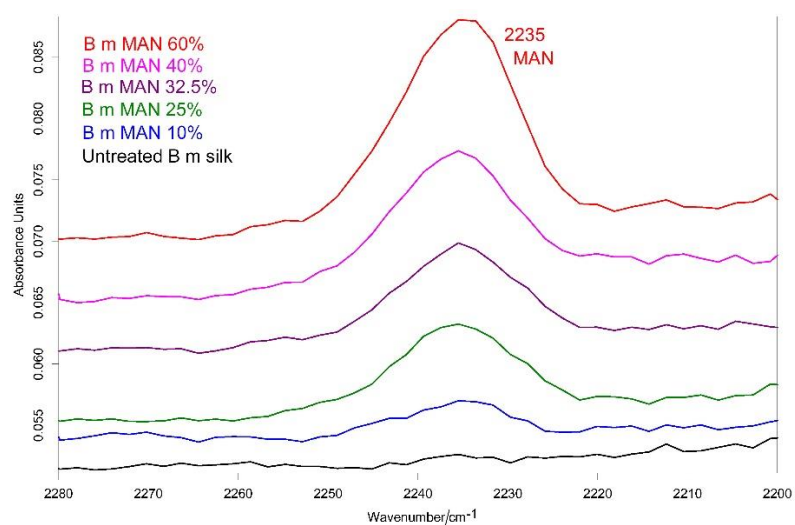
(a)



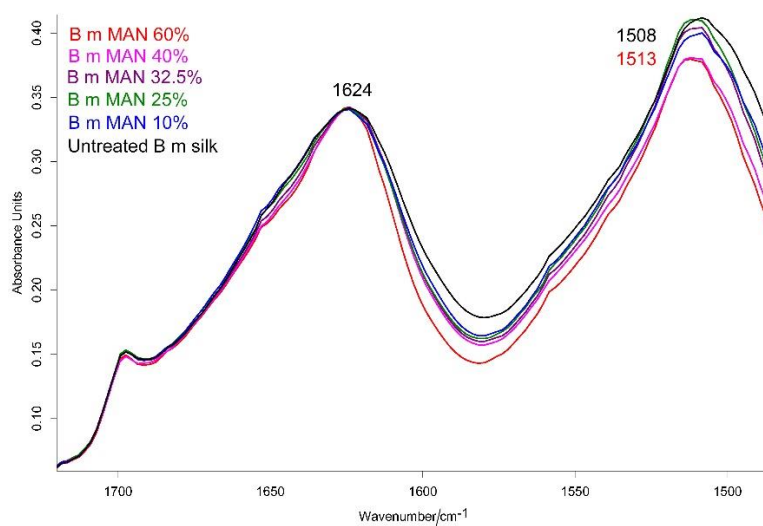


(c)

Figure S2. IR spectra recorded in the parallel orientation on *B. mori* silk fibroin fibers before and after grafting with MAN at different weight gains (i.e., 10%, 25%, 32.5%, 40%, and 60%) in three different spectral ranges: (a) 2280-2200 cm^{-1} , (b) 1720-1485 cm^{-1} , and (c) 1485-950 cm^{-1} . The spectra are normalized to the intensity of the Amide I band. The main bands that underwent changes upon MAN grafting are indicated.



(a)



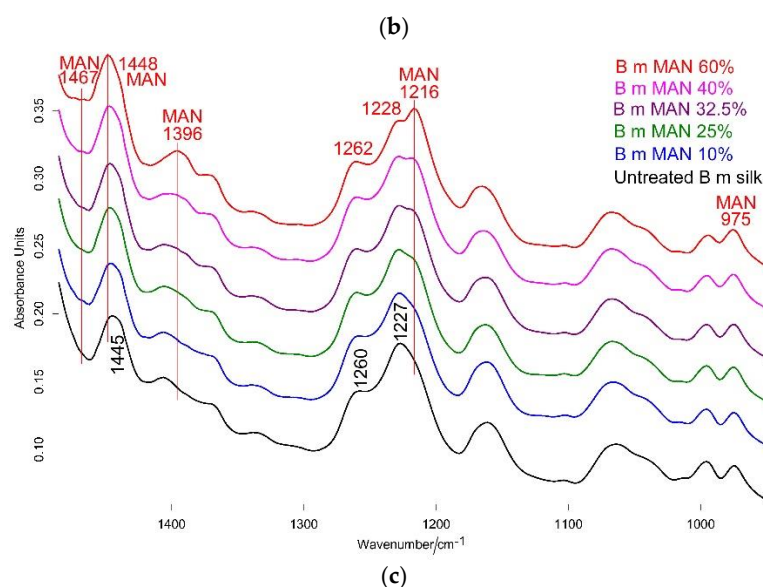


Figure S3. IR spectra recorded in the perpendicular orientation on *B. mori* silk fibroin fibers before and after grafting with MAN at different weight gains (i.e., 10%, 25%, 32.5%, 40%, and 60%) in three different spectral ranges: (a) 2280-2200 cm⁻¹, (b) 1720-1485 cm⁻¹, and (c) 1485-950 cm⁻¹. The spectra are normalized to the intensity of the Amide I band. The main bands that underwent changes upon MAN grafting are indicated.

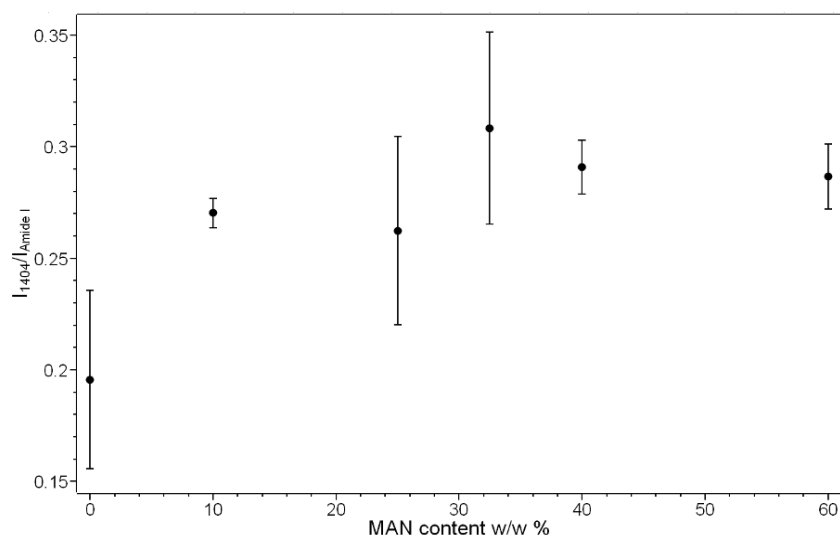


Figure S4. Trend of the $I_{1404}/I_{\text{Amide I}}$ Raman intensity ratio as a function of the weight gain (i.e., MAN content w/w %) for the silk fibroin fibers grafted with MAN.

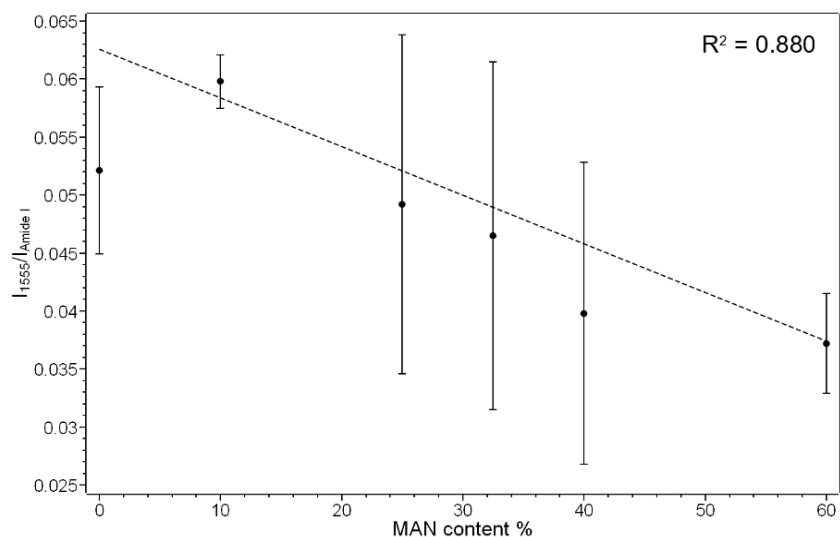


Figure S5. Trend of the $I_{1555}/I_{\text{Amide I}}$ Raman intensity ratio as a function of the weight gain (i.e., MAN content w/w %) for the silk fibroin fibers grafted with MAN.

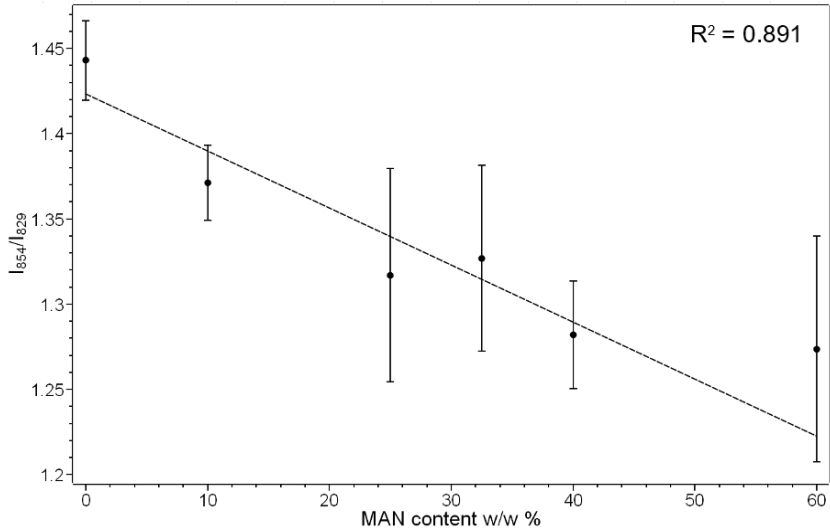


Figure S6. Trend of the I_{854}/I_{829} Raman intensity ratio as a function of the weight gain (i.e., MAN content w/w %) for the silk fibroin fibers grafted with MAN.

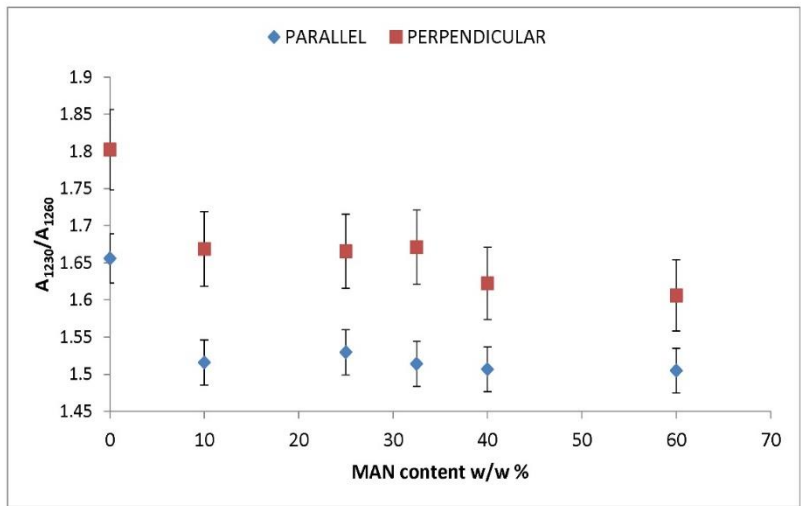


Figure S7. Trend of the A_{1230}/A_{1260} absorbance ratio as a function of the weight gain (i.e., MAN content w/w %).

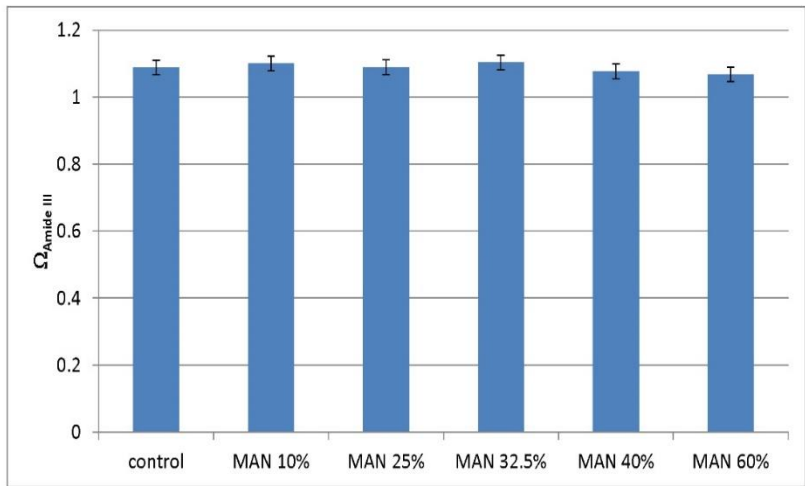


Figure S8. Values of the $\Omega_{\text{Amide III}}$ marker as obtained from the IR spectra recorded in the parallel and perpendicular orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN).

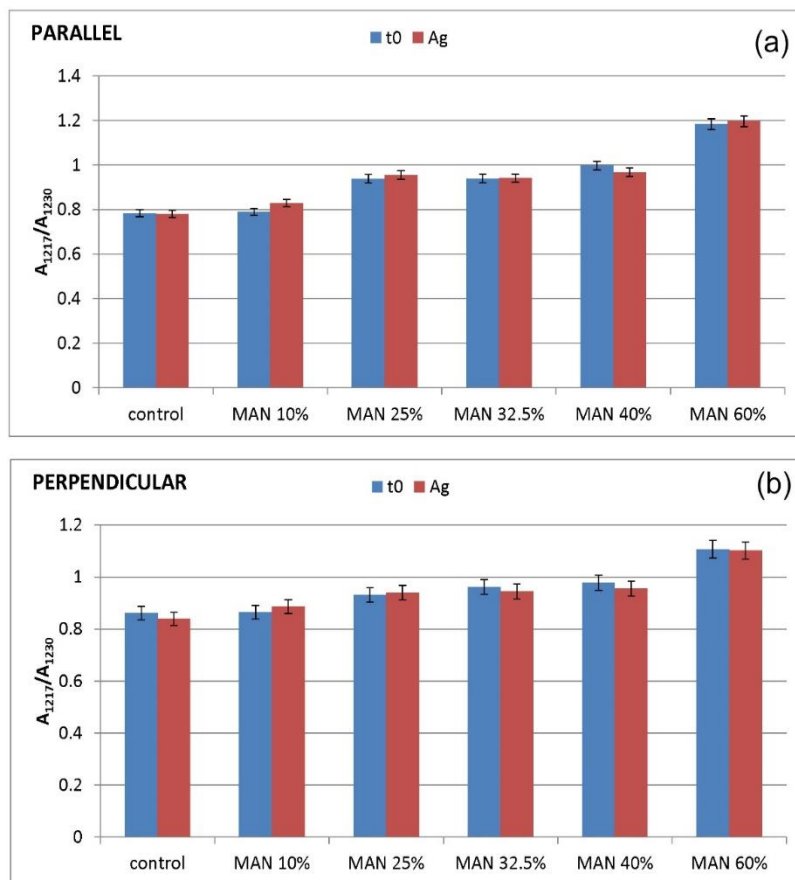


Figure S9. Values of the A_{1217}/A_{1230} absorbance ratio as obtained from the IR spectra recorded in the parallel (a) and perpendicular (b) orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t_0) and after ageing of the fibers in the Ag^+ containing solution for 48h.

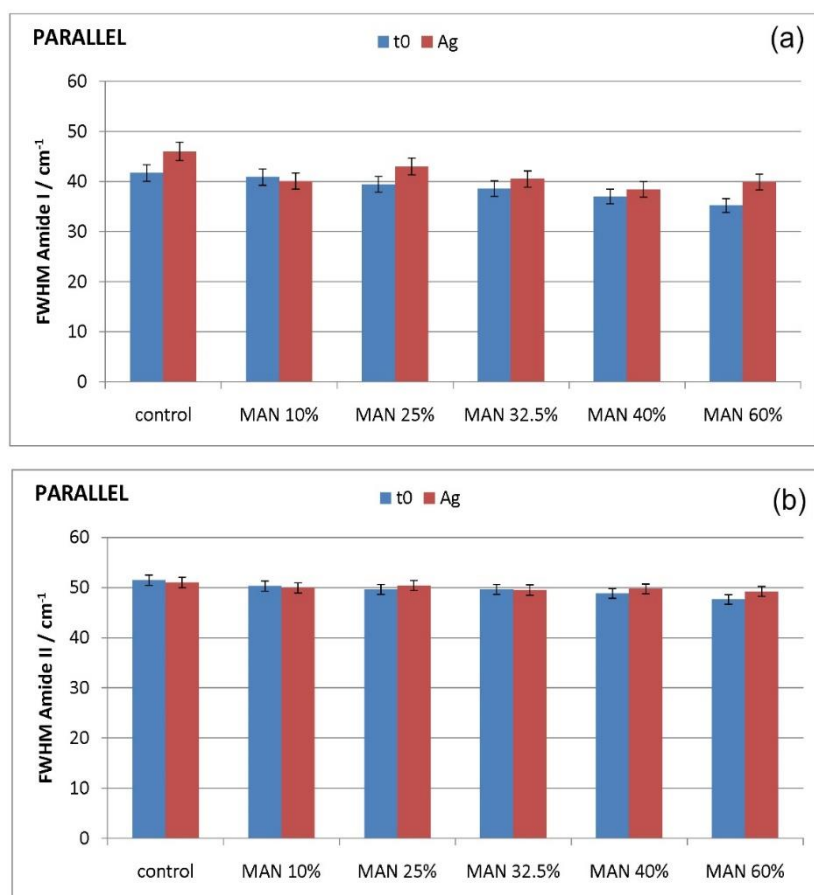


Figure S10. Values of the FWHM of Amide I (a) and Amide II (b) as obtained from the IR spectra recorded in the parallel orientation on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in the Ag⁺ containing solution for 48h.

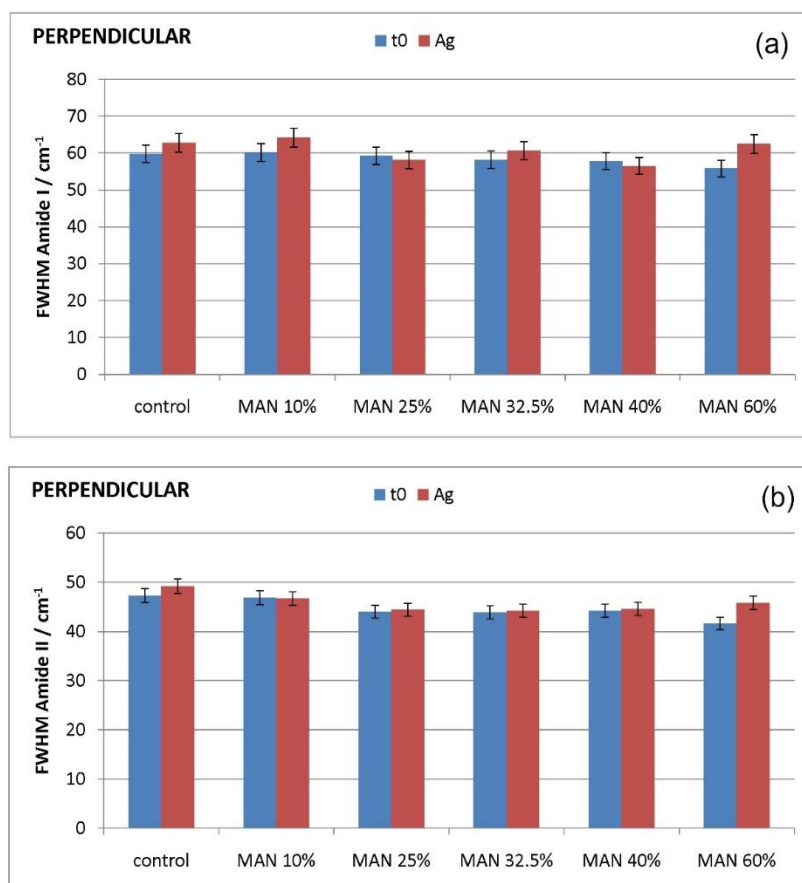


Figure S11. Values of the FWHM of Amide I (a) and Amide II (b) as obtained from the IR spectra recorded in the perpendicular orientation on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in the Ag⁺ containing solution for 48h.

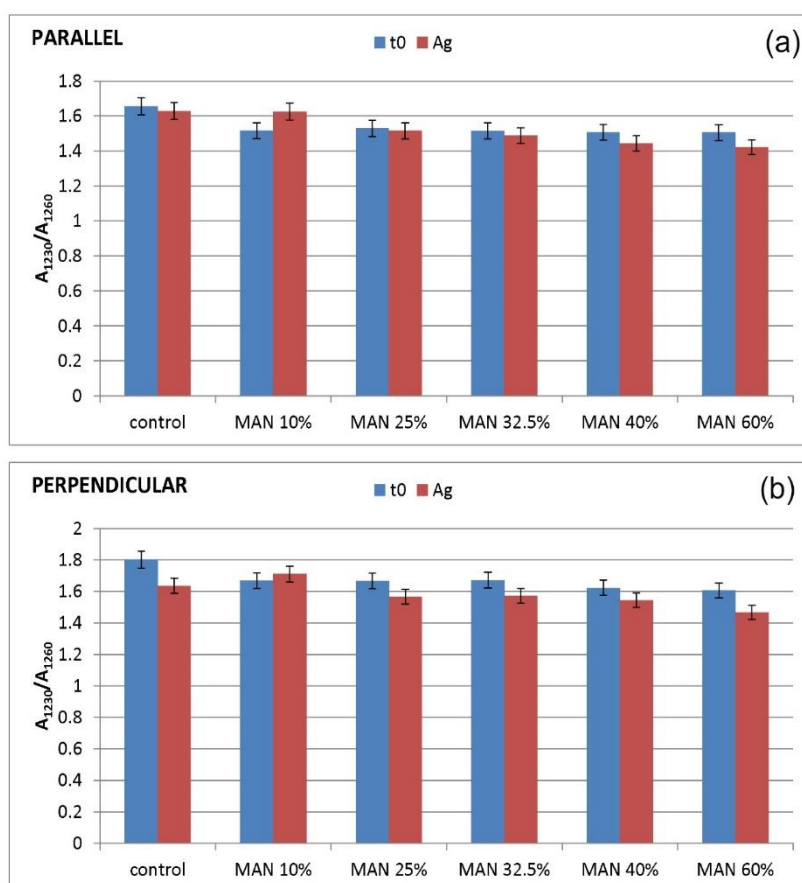


Figure S12. Values of the A_{1230}/A_{1260} absorbance ratio as obtained from the IR spectra recorded in the parallel (a) and perpendicular (b) orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in the Ag^+ containing solution for 48h.

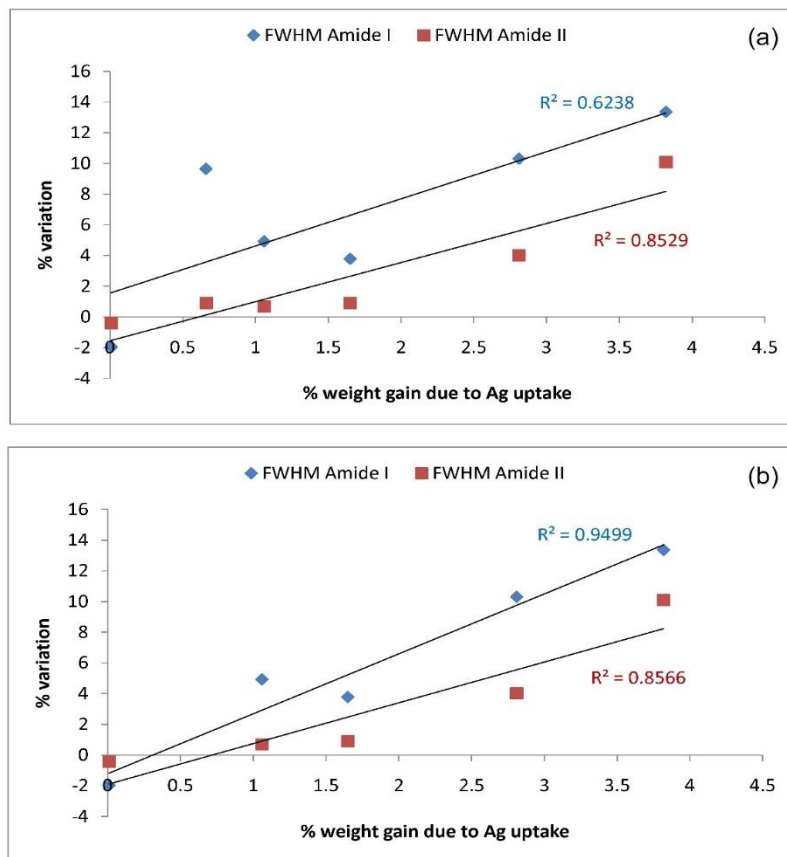


Figure S13. Trend of the % variation of the FWHM of Amide I (in the parallel spectra) and Amide II (in the perpendicular spectra) upon ageing in the Ag^+ solution for 48h, as a function of the % weight gain due to silver uptake. Graph (a) reports data from all the samples, while (b) reports trends calculated excluding the 25% MAN-grafted sample (outlier).

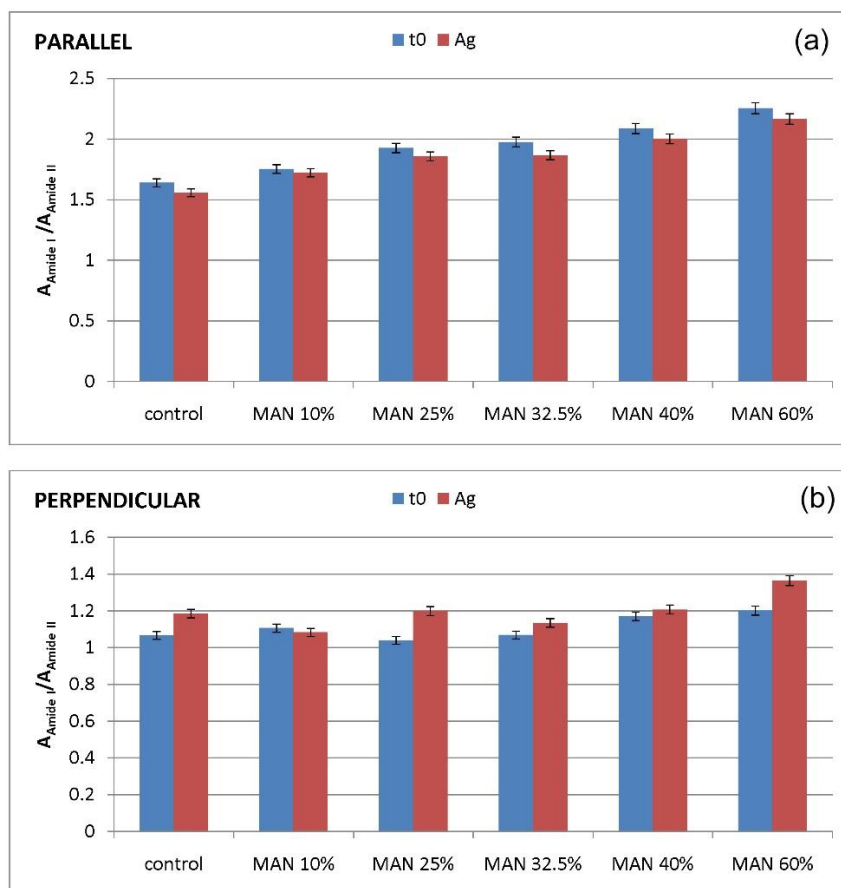


Figure S14. Values of the $A_{\text{Amide I}}/A_{\text{Amide II}}$ absorbance ratio as obtained from the IR spectra recorded in the parallel (a) and perpendicular (b) orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in the Ag^+ -containing solution for 48h.

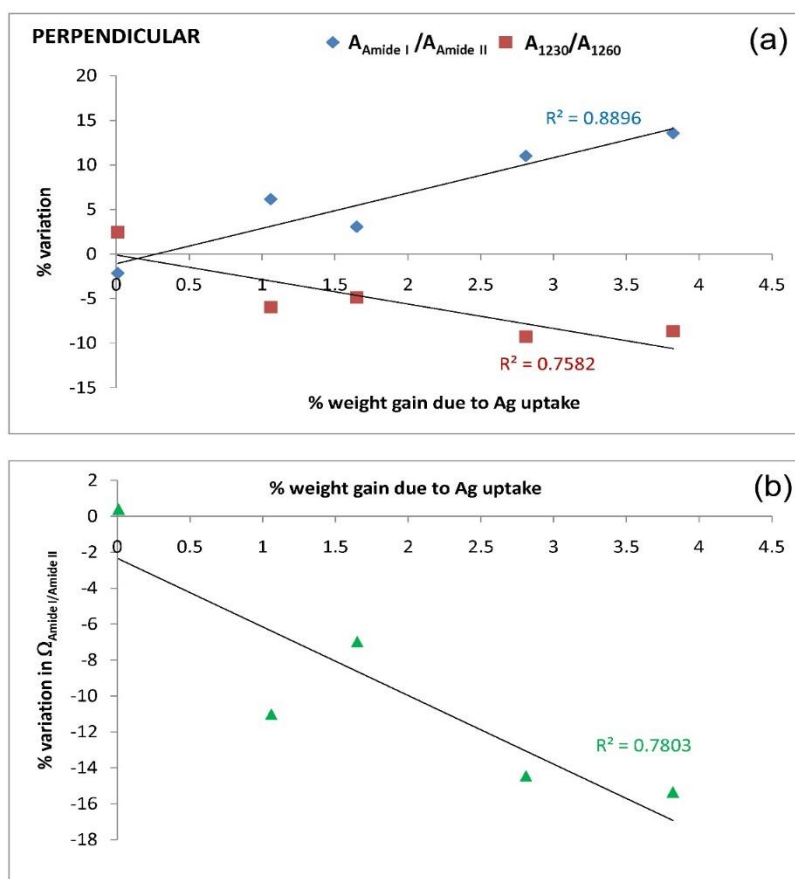


Figure S15. (a) Trend of the % variation of the $A_{\text{Amide I}} / A_{\text{Amide II}}$ and A_{1230} / A_{1260} absorbance ratios (in the perpendicular spectra) and (b) $\Omega_{\text{Amide I}} / A_{\text{Amide II}}$ upon ageing in the Ag^+ solution for 48h, as a function of the % weight gain due to silver uptake.

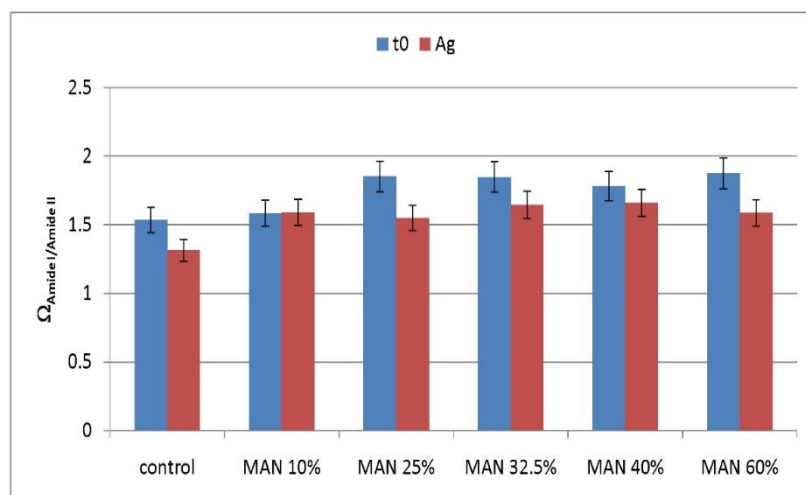


Figure S16. Values of $\Omega_{\text{Amide I}} / A_{\text{Amide II}}$ as obtained from the IR spectra recorded in the parallel and perpendicular orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t_0) and after ageing of the fibers in the Ag^+ containing solution for 48h.

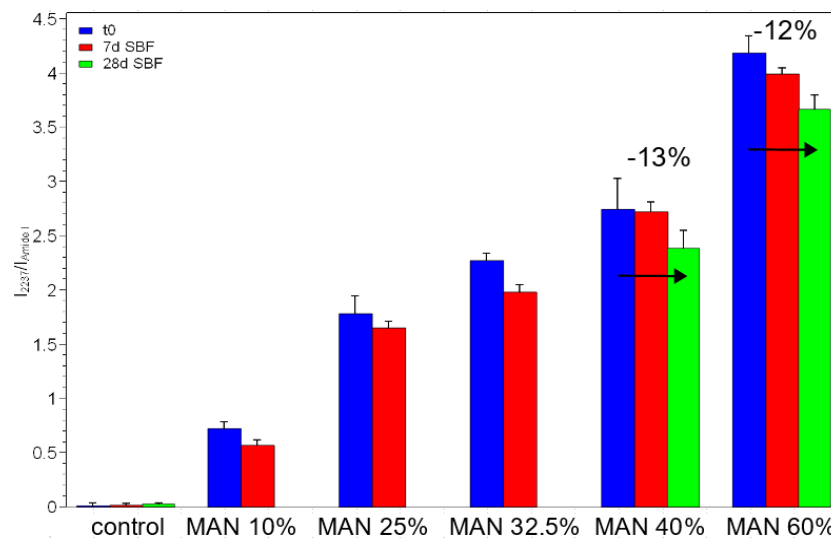


Figure S17. Trend of the $I_{2237}/I_{amide\ I}$ Raman intensity ratio before and after 7 and 28 days of immersion in the SBF solution.

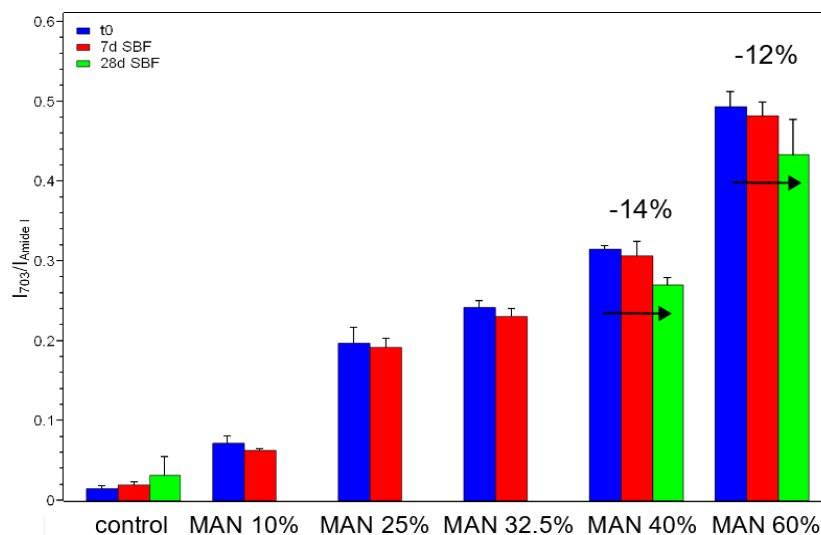


Figure S18. Trend of the $I_{703}/I_{amide\ I}$ Raman intensity ratio before and after 7 and 28 days of immersion in the SBF solution.

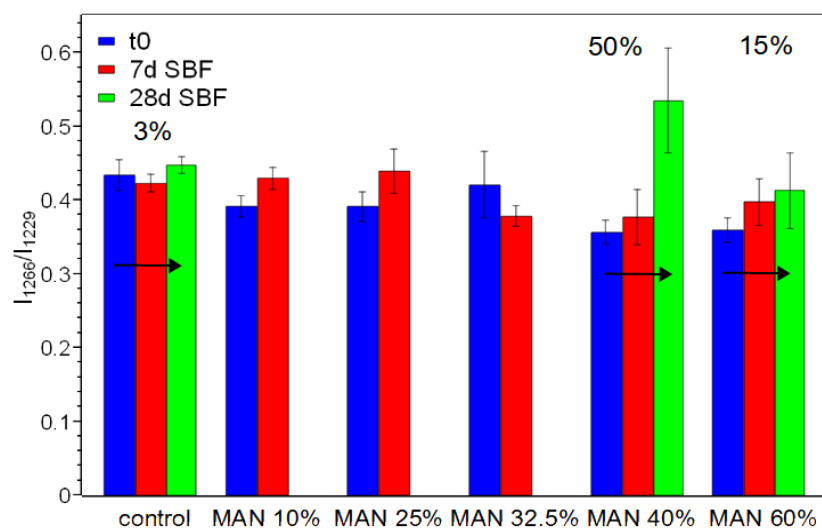


Figure S19. Trend of the I_{1266}/I_{1229} Raman intensity ratio before and after 7 and 28 days of immersion in the SBF solution.

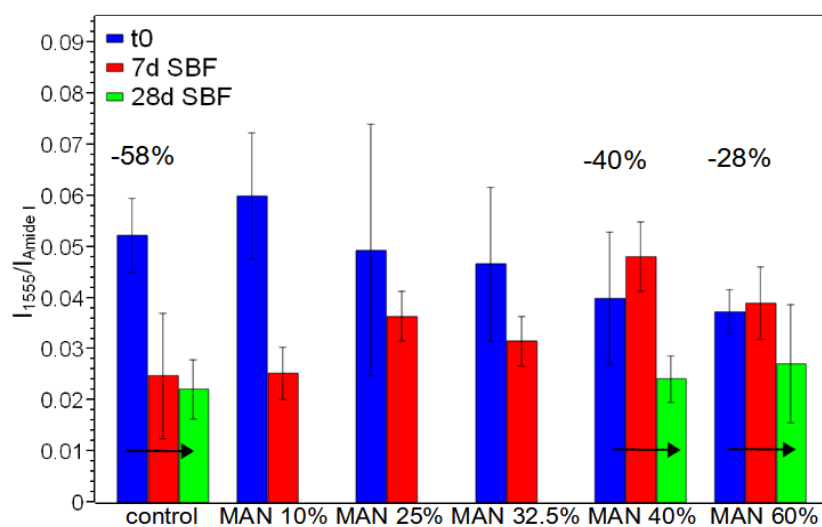


Figure S20. Trend of the $I_{1555}/I_{amide\ I}$ Raman intensity ratio before and after 7 and 28 days of immersion in the SBF solution.

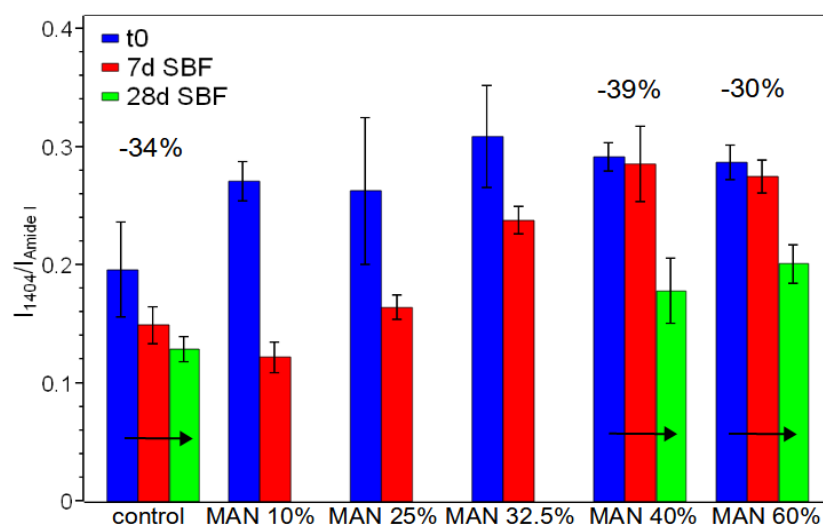


Figure S21. Trend of the $I_{1404}/I_{amide\ I}$ Raman intensity ratio before and after 7 and 28 days of immersion in the SBF solution.

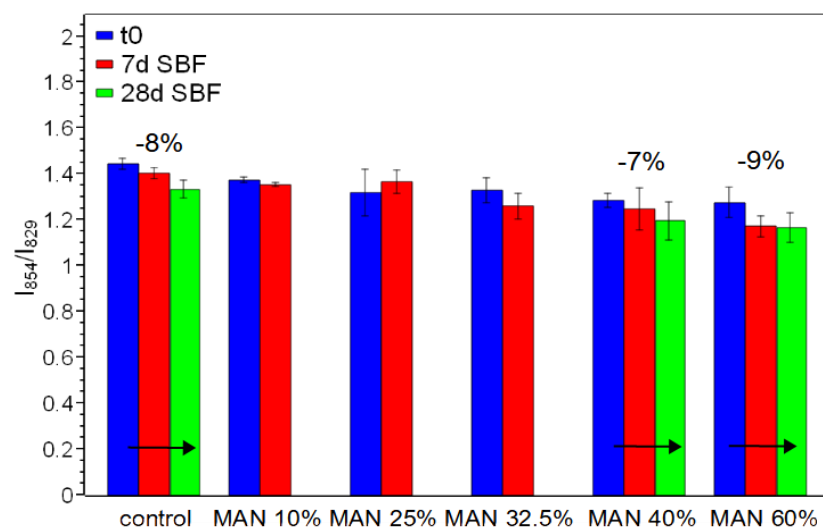


Figure S22. Trend of the I_{854}/I_{829} Raman intensity ratio before and after 7 and 28 days of immersion in the SBF solution.

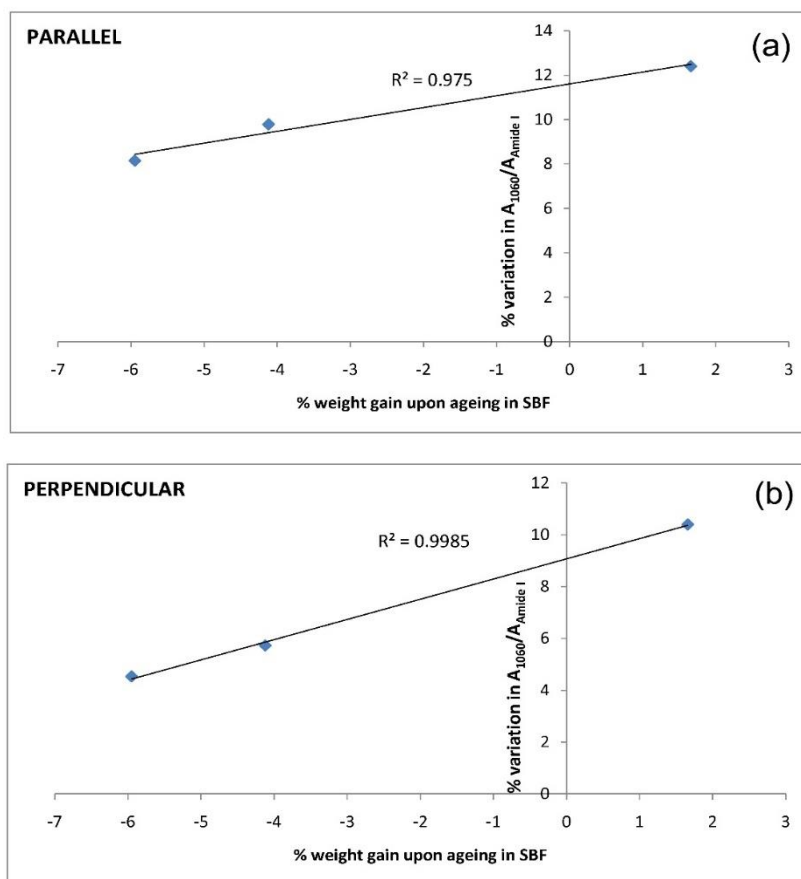


Figure S23. Trend of the % variation of the $A_{1060}/A_{\text{amide I}}$ absorbance ratio ((a) parallel spectra; (b) perpendicular spectra) upon ageing in SBF for 28 days, as a function of the % weight gain.

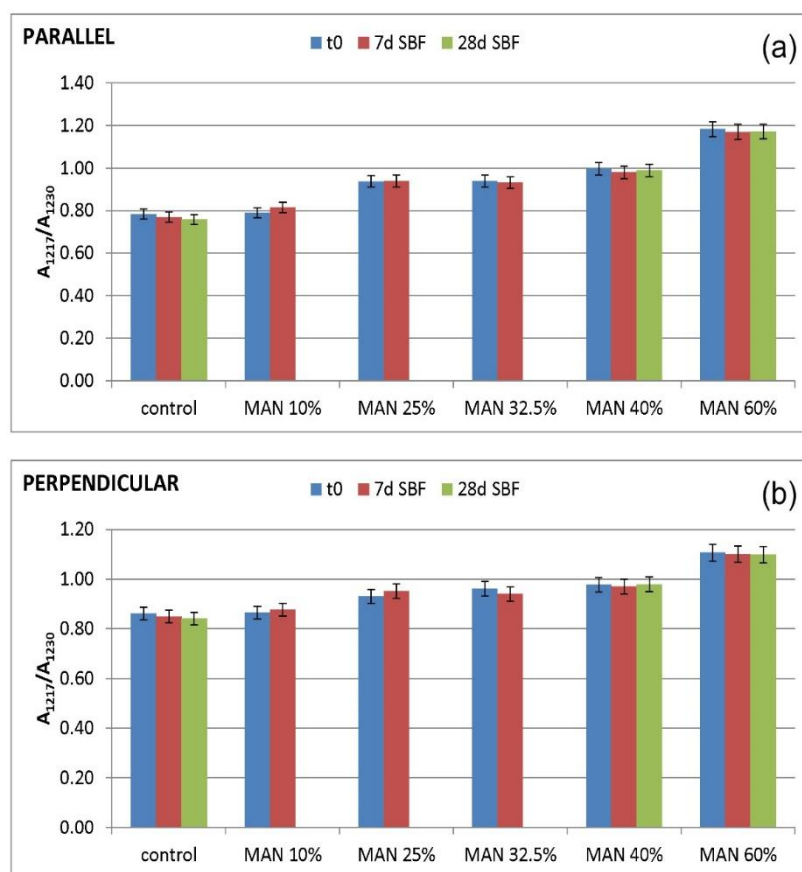


Figure S24. Values of the A_{1217}/A_{1230} absorbance ratio as obtained from the IR spectra recorded in the parallel (a) and perpendicular (b) orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in SBF.

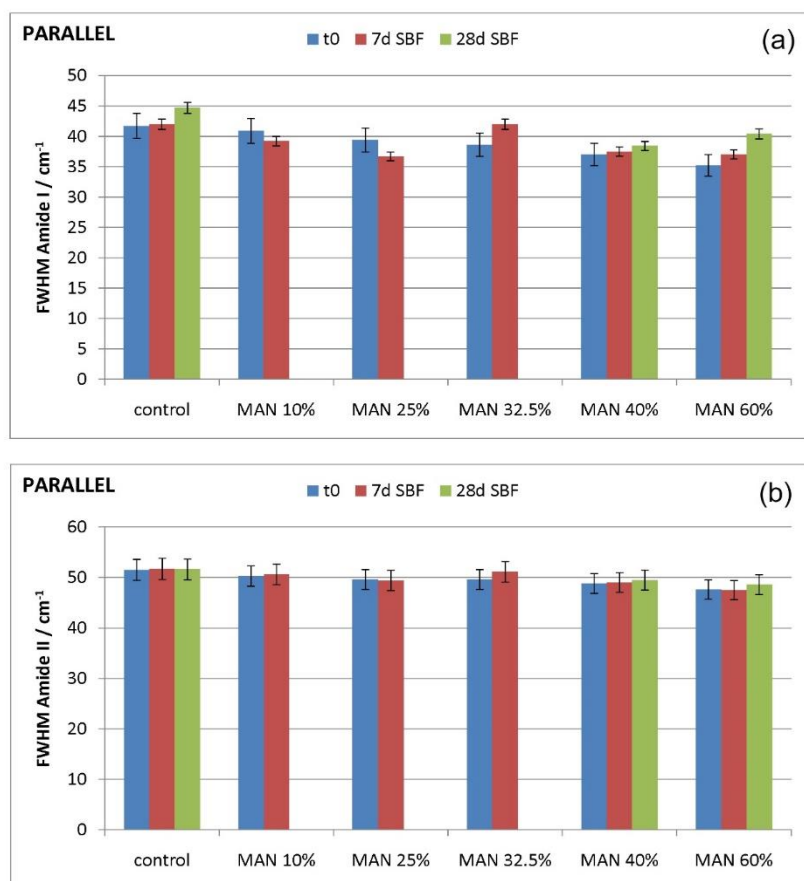


Figure S25. Values of the FWHM of Amide I (a) and Amide II (b) bands as obtained from the IR spectra recorded in the parallel orientation on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in SBF.

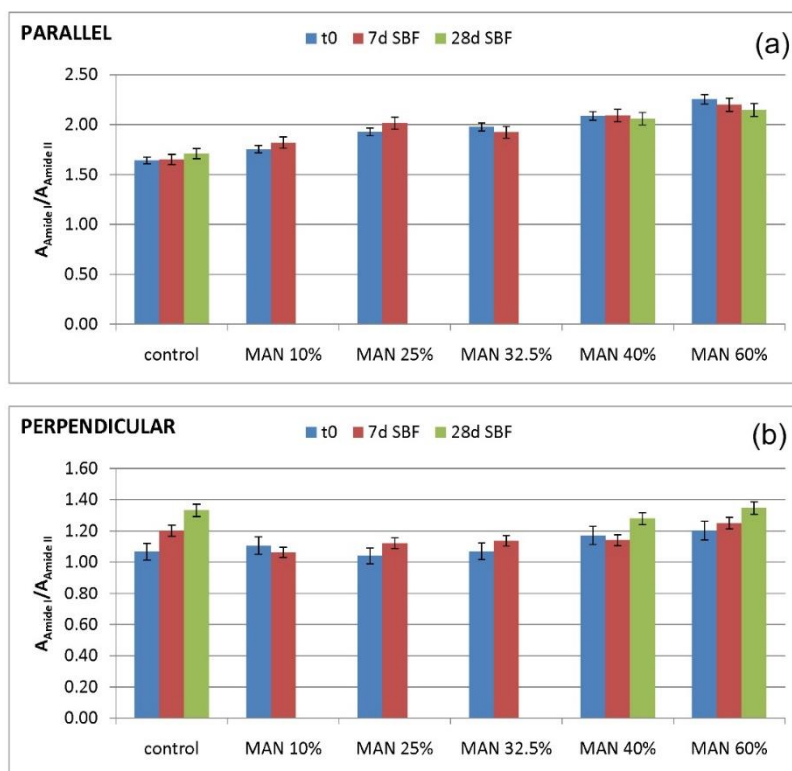


Figure S26. Values of the $A_{\text{Amide I}}/A_{\text{Amide II}}$ absorbance ratio as obtained from the IR spectra recorded in the parallel (a) and perpendicular (b) orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in SBF.

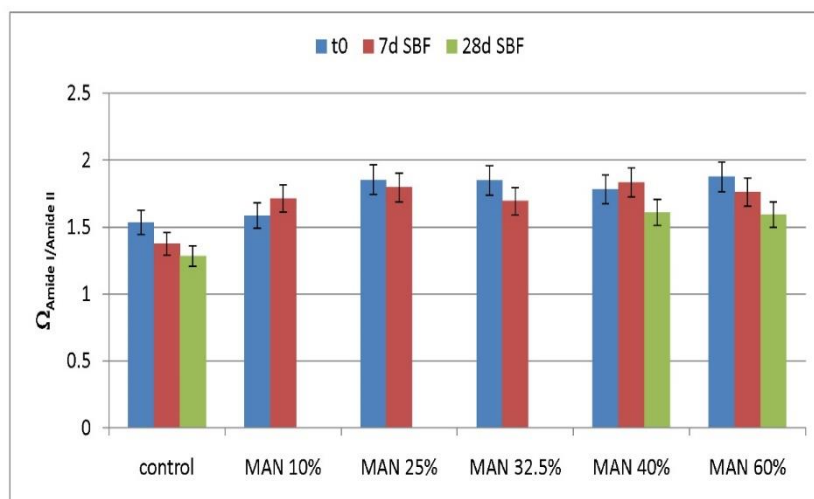


Figure S27. Values of the $\Omega_{\text{Amide I/Amide II}}$ marker as obtained from the IR spectra recorded in the parallel and perpendicular orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in SBF.

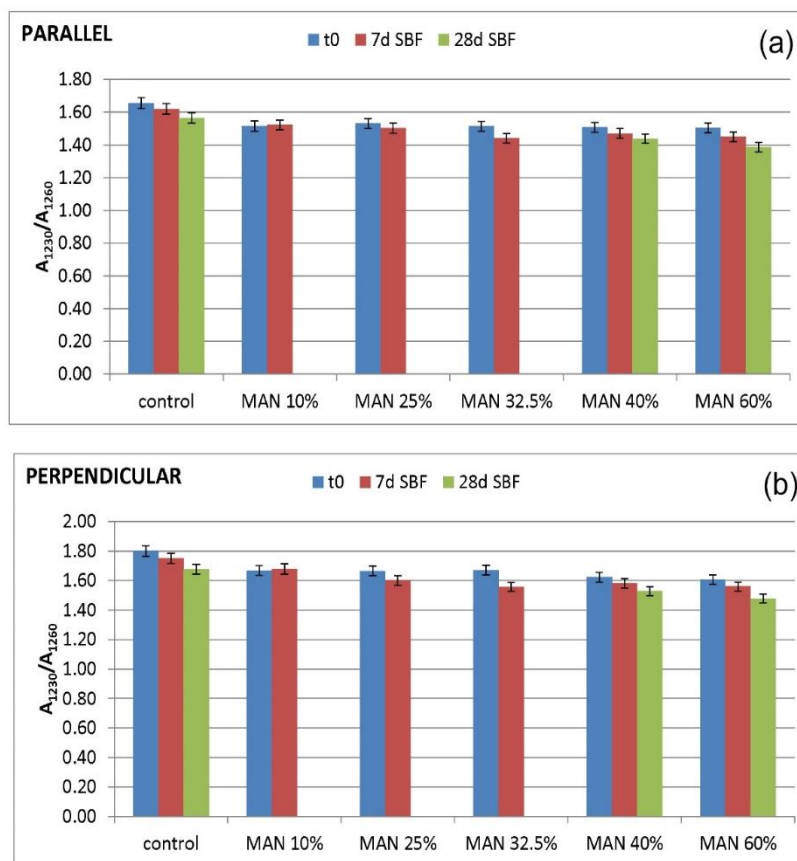


Figure S28. Values of the A_{1230}/A_{1260} absorbance ratio as obtained from the IR spectra recorded in the parallel (a) and perpendicular (b) orientations on the samples under study (control = untreated fibers, and MAN grafted fibers containing different amounts of MAN) before (t0) and after ageing of the fibers in SBF.

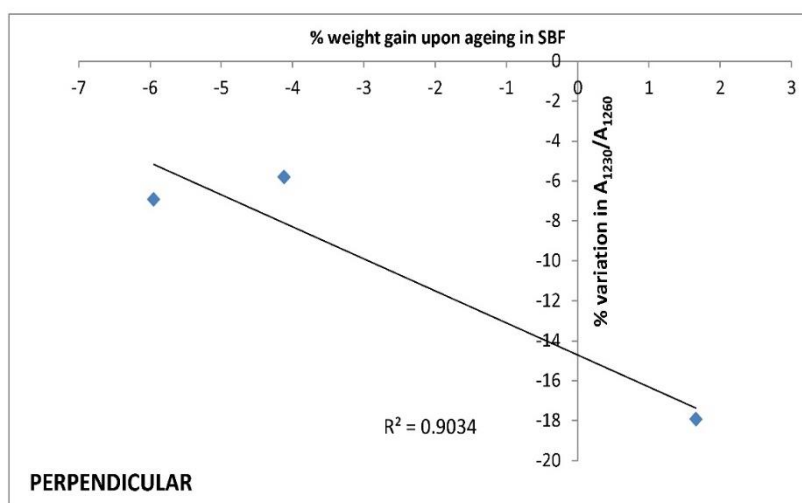


Figure S29. Trend of the % variation of the A_{1230}/A_{1260} absorbance ratio upon ageing in SBF for 28 days as a function of the % weight gain (perpendicular spectra).