

Supporting Information

Vegetable oil hybrid films cross-linked at air-water interface: Formation kinetics and physical characterization

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Figure S1 shows the ²⁹Si solid state NMR spectra measured for the final cross-linked hybrid films to investigate the presence of the siloxane bonds. The signal found at -65.966 ppm corresponds to T3 which is related to three siloxane bonds structure. Also the T1 and T2 structures were found at -49.220 ppm and -57.977 pmm, respectively. The percentage of the condensation reaction is CD=78.56 %, calculated according to the following relation:

$$CD = \frac{1T1 + 2T2 + 3T3}{3} * 100$$

where T refers to the integrated area of each peak.

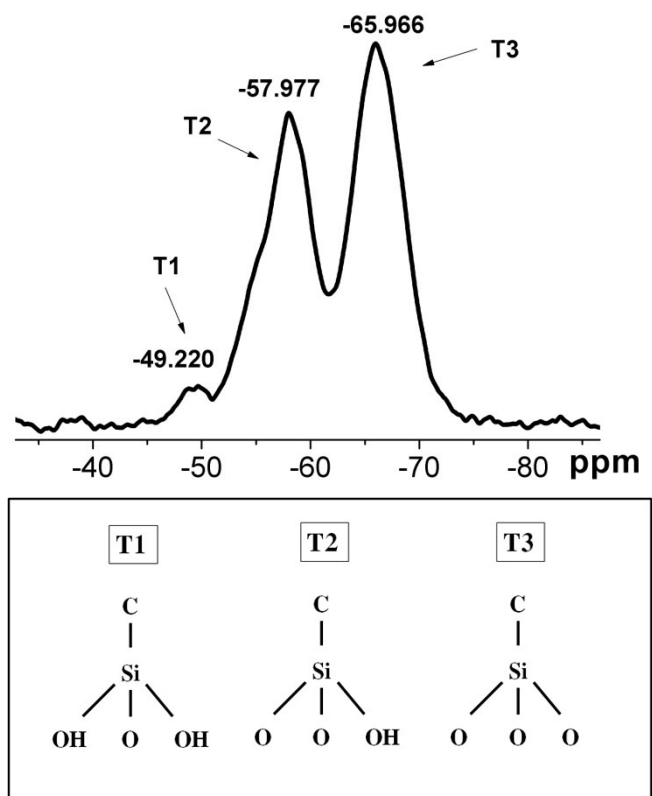


Figure S1: ^{29}Si solid state NMR spectra of the final cross-linked film.

Figure S2-a depicts the dynamic frequency sweep (DFS) data taken for different times after the oil deposition on the water surface. All measurements have been performed at a strain amplitude $\gamma_0=1\%$, well within the linear viscoelastic regime. After a time of 24 hours G' value reaches a steady value. In Figure S2-b DFS measurements of the films are presented after the film formation at controlled temperature.

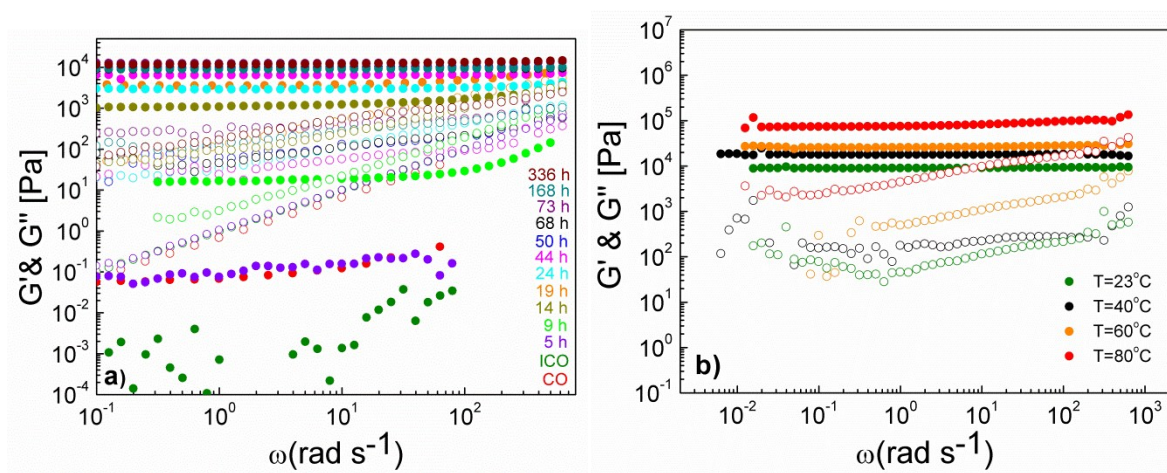


Figure S2: Dynamic frequency sweep measurements of ICO at strain amplitude of $\gamma_0=1\%$ a) at different times and b) at different temperatures after 24 hours. G' is denoted with filled symbols and G'' with open symbols.

TGA measurements were performed to hybrid films in order to study the pyrolysis kinetics of cross-linking and confirm the formation of inorganic/organic hybrid formation. Figure S3-a presents the weight loss as a function of temperature up to 600°C (and 5°C/min) for a final film, showing degradation between 241 to 550 °C and the presence of about 12% in mass of inorganic material. The maximum first degradation step temperature occurs at 350 °C which is attributed to the dissociation of urethane bonds. The second degradation step (up to 450 °C) is related with the scission of the triglyceride chains. Figure S3-b shows the temperature as a function of time for a fixed point of weight loss which corresponds to 0.01% where after 7 days the temperature reaches a steady value.

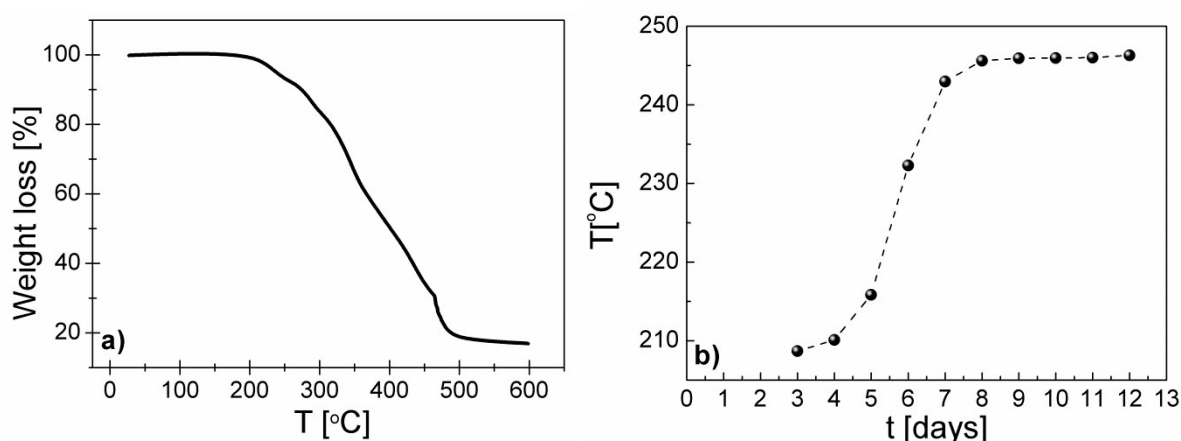


Figure S3: a) TGA measurement of the final film plotted as weight loss versus temperature up to 600°C (heating rate: 5 °C/min) and b) evolution of the temperature corresponding to 0.01% weight loss versus time.

Figure S4 depicts ATR-IR spectra of the films at different times between 4000 and 650 cm^{-1} , showing the characteristic peaks for triglycerides and silica formation. For urethane groups (NHCOO) a characteristic peak has been detected at 3346 cm^{-1} for N-H stretching. At 2925 cm^{-1} and 2855 cm^{-1} the asymmetric and symmetric C-H stretching bonds for methylene groups have been observed. The peak at 1718 cm^{-1} that corresponds to C=O stretching mode has also been observed. Finally, the bond at 1460 cm^{-1} for asymmetric C-H bending mode and 1390 cm^{-1} for symmetric C-H bending mode has been also detected. In Figure S4-B and S4-C the ATR-IR spectra at 1195 cm^{-1} (Si-O-Si) and at 957 cm^{-1} (Si-OH), respectively are presented.

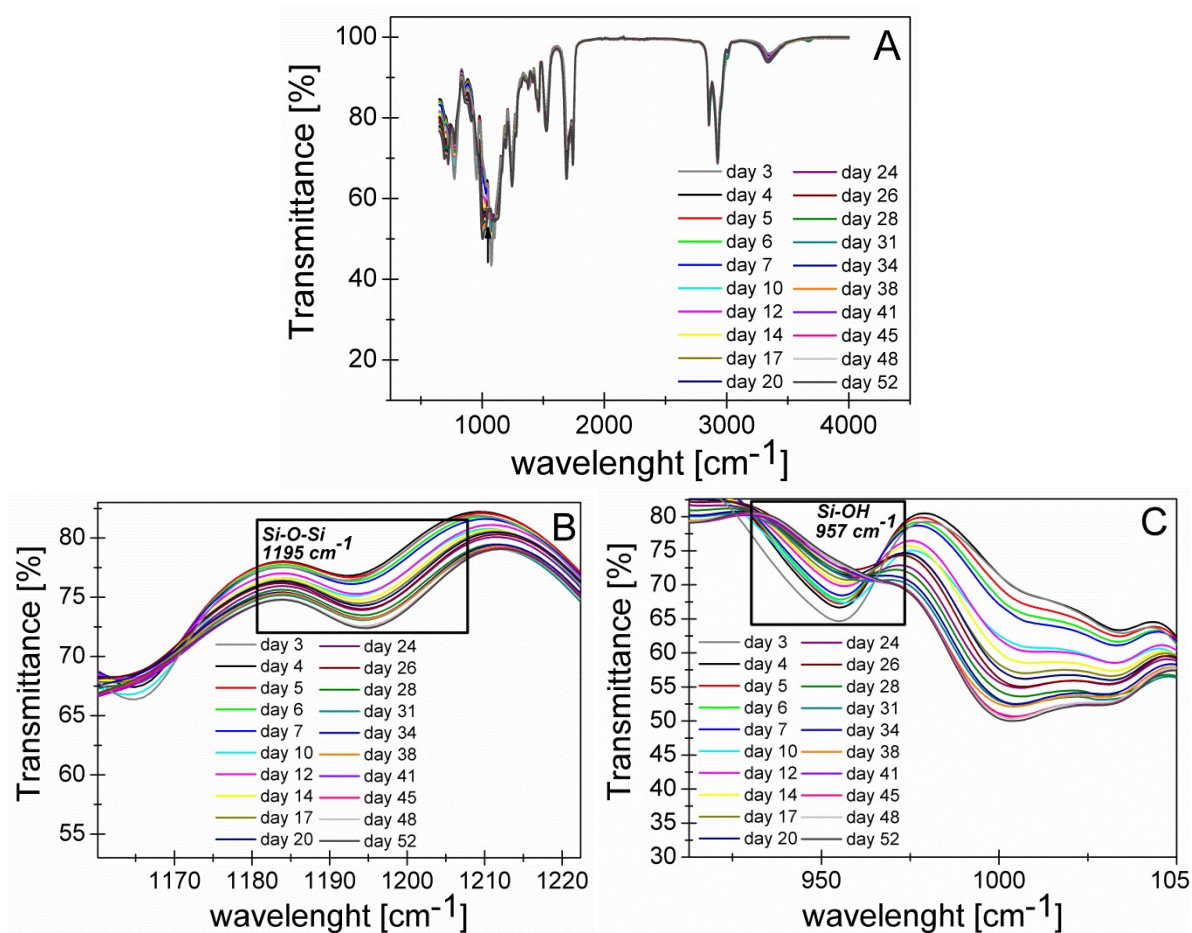


Figure S4: ATR spectra plotted as transmittance versus wavelength. a) full range data, b) zoom at 1195 cm^{-1} (Si-O-Si) and c) at 957 cm^{-1} (Si-OH).

Small angle X-ray scattering and small angle neutron scattering were performed in order to obtain information about the structure of the final films at low- q range. The results with both methods did not show any Bragg peak, suggesting no ordering on the nanometer and tens of nanometer scale.

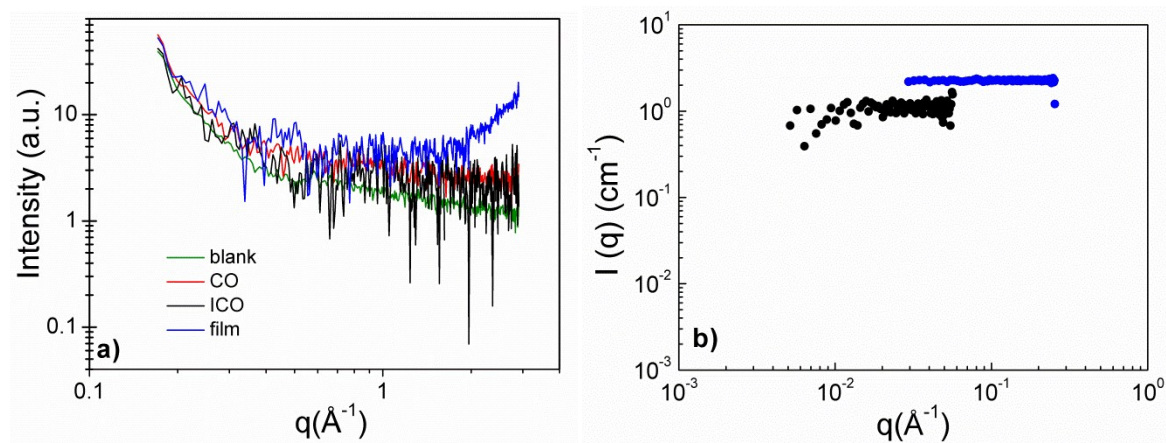


Figure S5: a) Small angle X-ray scattering and b) Small angle neutron scattering of the final cross-linked films plotted as intensity versus q -vector.