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# Regenerated silk fibroin using protic ionic liquids solvents: Towards an all ionic liquid process for producing silk with tunable properties.

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## Experimental procedure

### Silk foam formation

Silk foams were produced by injecting the 5wt% dissolved silk (silk is dissolved in either HFIP or BMIMAc) into the coagulation solvent. The coagulation solvent is the named protic ionic liquid at some ratio of water. The foams were left in the coagulation solvent for 1 hour and then rinsed several times in water. Each sample was repeated 3 times

### Fourier transform infrared , FTIR

Infrared spectra were recorded with an attenuated total reflectance Fourier transform infrared (FTIR) spectrophotometer (Vertex 70) (Bruker Biosciences Pty, Australia). Each spectrum was obtained in absorbance mode in the range of 4000–600 cm-1. To measure different conformations, average of 3 spectrum in the amide I mode (1595–1705 cm_1) was deconvoluted, and curve was fitted using OPUS 5.5 software adapting the procedure used by Hu et al.[1] with some modifications. Deconvolution was carried out adapting a Lorentzian model using a bandwidth of 25 cm_1 and a noise reduction factor of 0.3. A straight base line correction of FSD spectrum was performed followed by curve fitting using a Gaussian model. Band positions were determined based on fixed number bands, determined according to the second derivatives of the original spectra, were automatically adjusted by the autofit program using a Levenberg–Marquardt algorithm. Finally, each individual spectrum was area normalized to obtain percentage conformations within the amide I region. The procedure was repeated 3 times for each spectrum.

Table 1 Deconvolution of amide I region of RSF using different pILs as the coagulation solvent.

| | Native fiber | $TeaH_2PO_4$(20 %water) contents (%) | TEALa (20%water) contents (%) | TeaTf (20%water) contents (%) | TeaMs (20%water) contents (%) |
|---|---|---|---|---|---|
| Side chain Tyr (1605-1620) | 0 | 2.35 | 2.30 | 2.30 | 2.22 |
| β-Sheet (1621-1630) | 48.61 | 55.45 | 52.31 | 50.04 | 53.44 |
| Silk I (1647-1655) | 33.36 | 38.43 | 8.24 | 0 | 0 |

| | | | | | |
|---|---|---|---|---|---|
| α-helix (1655-1662) | 0 | 0 | 34.61 | 45.23 | 42.23 |
| β-Turns (1678-1692) | 18.03 | 3.77 | 2.54 | 2.11 | 2.43 |

Table 2: Deconvolution of amide I region of RSF using TMGLa:water as the coagulation solvent at various TMGLa : water concentrations.

| | Native fiber | TMGLa (0%water) contents (%) | TMGLa (20%water) contents (%) | TMGLa (40%water) contents (%) | TMGLa (60%water) contents (%) | TMGLa (80%water) contents (%) | TMGLa (90%water) contents (%) |
|---|---|---|---|---|---|---|---|
| Side chain Tyr (1605-1620) | 0 | 24.45 | 10.66 | 6.14 | 30.43 | 20.43 | 33.56 |
| β-Sheet (1621-1630) | 48.61 | 39.6 | 54.54 | 62.16 | 27.31 | 28.45 | 37.49 |
| Silk I (1647-1655) | 33.36 | 0 | 14.31 | 10.64 | 24.1 | 0 | 11.60 |
| α-helix (1655-1662) | 0 | 31.66 | 11.59 | 0.00 | 1.39 | 31.39 | 2.35 |
| β-Turns (1678-1692) | 18.03 | 4.29 | 8.89 | 21.05 | 10.49 | 3.16 | 9.89 |

Table 3: Deconvolution of amide I region of RSF using all ionic liquid processing

| | Native fiber | *All ionic liquid* silk |
|---|---|---|
| Side chain Tyr (1605-1620) | 0 | 0.8 |
| β-Sheet (1621-1630) | 48.61 | 63.60 |
| Silk I (1647-1655) | 33.36 | 6.32 |
| α-helix (1655- | 0 | 26.82 |

| | | |
|---|---|---|
| 1662) | | |
| β-Turns (1678-1692) | 18.03 | 2.45 |

X-ray Diffraction, XRD

Wide angle X-ray scattering (WAXS) of films was performed on a diffractometer (X'Pert PRO from PANalytical) with Cu Ka radiation (ג= 0.154 nm), operated at 40 kV and 30mA. Scanning rate was 0.02°/min. Background scattering was removed using Spectra Xpert High Score plus software

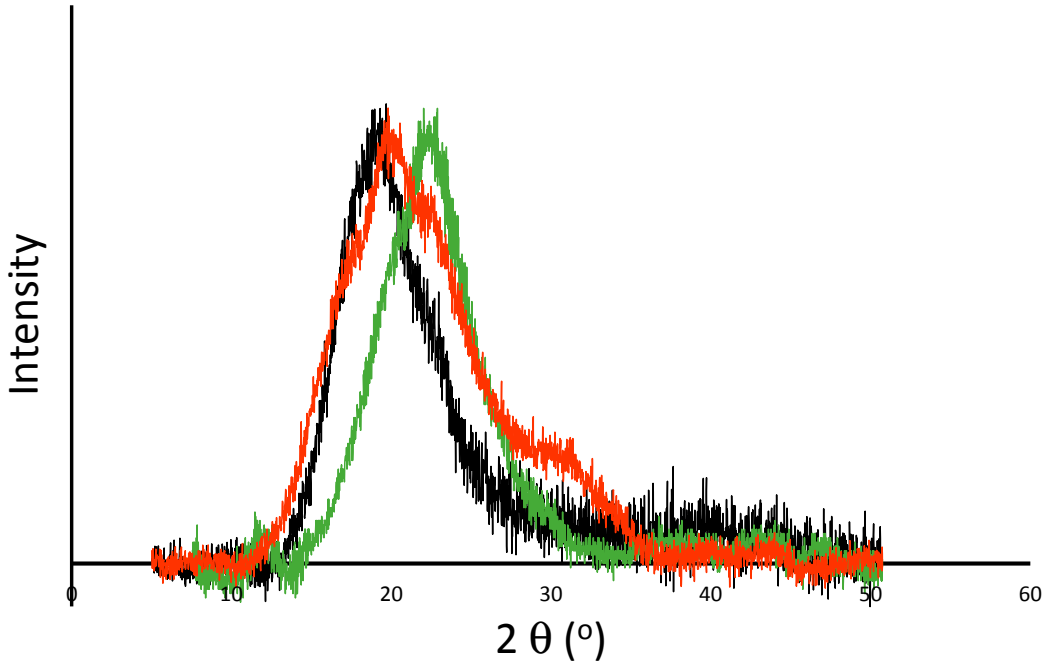


Figure 1: X-ray diffractograms of regenerated silk foams using pIL solutions at 20wt% water; black $TeaH_2PO_4$ , red TeaLa and green TeaMs.