

**Supplemental Material for “In situ microscopic studies on the structures and phase behaviors of SF/PEG film with solid-state NMR and Raman imaging”**

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Table. S1 FTIR band positions and vibrational assignments for PEG and silk fibroin.<sup>a</sup> After Ling et al.<sup>1</sup> and references therein.

|      | Peak (cm <sup>-1</sup> ) | Assignment  |                                   |
|------|--------------------------|---|-----------------------------------|
| PEG  | 2887                     | CH <sub>2</sub> stretching                          |                                   |
|      | 1469                     | CH <sub>2</sub> stretching                          |                                   |
|      | 1342                     | CH <sub>2</sub> wagging                             |                                   |
|      | 1280                     | CH <sub>2</sub> twisting                            |                                   |
|      | 1242                     | CH <sub>2</sub> twisting                            |                                   |
|      | 1148                     | C-O stretching                                      |                                   |
|      | 1113                     | C-O stretching                                      |                                   |
|      | 1103                     | C-O stretching                                      |                                   |
|      | 1062                     | C-O stretching, CH <sub>2</sub> rocking             |                                   |
|      | 963                      | CH <sub>2</sub> rocking, CH <sub>2</sub> stretching |                                   |
|      | 843                      | CH <sub>2</sub> rocking, C-O stretching             |                                   |
|      | SF                       | 1698  | Amide I, $\beta$ turns            |
|      |                          | 1640  | Amide I, random coil and/or helix |
| 1620 |                          | Amide I, $\beta$ sheet                              |                                   |
| 1540 |                          | Amide II, random coil and/or helix                  |                                   |
| 1530 |                          | Amide II, $\beta$ sheet                             |                                   |

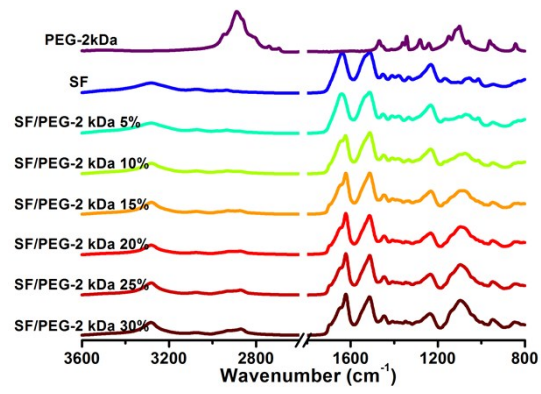


Figure S1. ATR-FTIR spectra of PEG-2 kDa and SF/PEG-2 kDa blend films with various PEG contents.

Table. S2 Raman band positions and vibrational assignments for PEG and silk fibroin<sup>a</sup>

|     | Peak (cm <sup>-1</sup> ) |         | Assignment <sup>2-5</sup>                                      |
|-----|--------------------------|---------|--|
| PEG | 1480 m                   |         | CH <sub>2</sub> stretching                                     |
|     | 1395 w                   |         | CH <sub>2</sub> wagging ,CH <sub>2</sub> twisting              |
|     | 1280 m                   |         | CH <sub>2</sub> twisting                                       |
|     | 1234 w                   |         | CH <sub>2</sub> twisting                                       |
|     | 1148 s                   |         | C-C stretching, CH <sub>2</sub> rocking                        |
|     | 1060 m                   |         | C-O stretching, CH <sub>2</sub> rocking                        |
|     | 932 m                    |         | C-O stretching, CH <sub>2</sub> rocking                        |
|     | 846 s                    |         | CH <sub>2</sub> rocking, C-O stretching                        |
|     | Silk I                   | Silk II |  |
| SF  | 1659 vs                  | 1663 vs | Amide I, C=O stretching  |
|     | 1456 m                   | 1448 m  | CH <sub>3</sub> antisymmetric bending, CH <sub>2</sub> bending |
|     | 1276 s                   | 1264 w  | Amide III  |
|     | 1245 m                   | 1229 m  |  |
|     | 1104 m                   | 1084 m  | C <sup>α</sup> -C <sup>β</sup> stretching, ρCH <sub>3</sub>    |
|     | 855 s                    | 857 w   | Fermi resonance Tyr  |
|     | 830 m                    | 828 w   |  |

<sup>a</sup>Abbreviations: vs, very strong; s, strong; m, medium; w, weak;

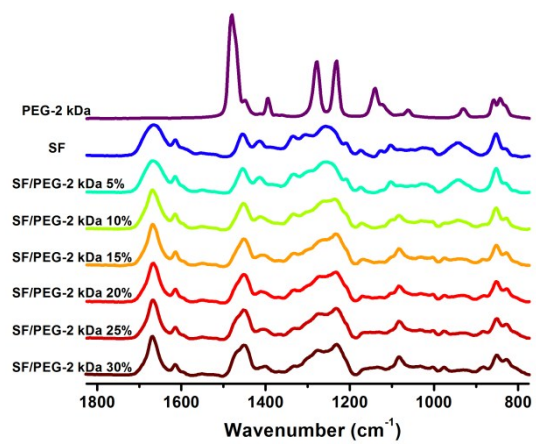


Figure S2. Raman spectra of PEG-2 kDa and SF/PEG-2 kDa blend films with various PEG contents.

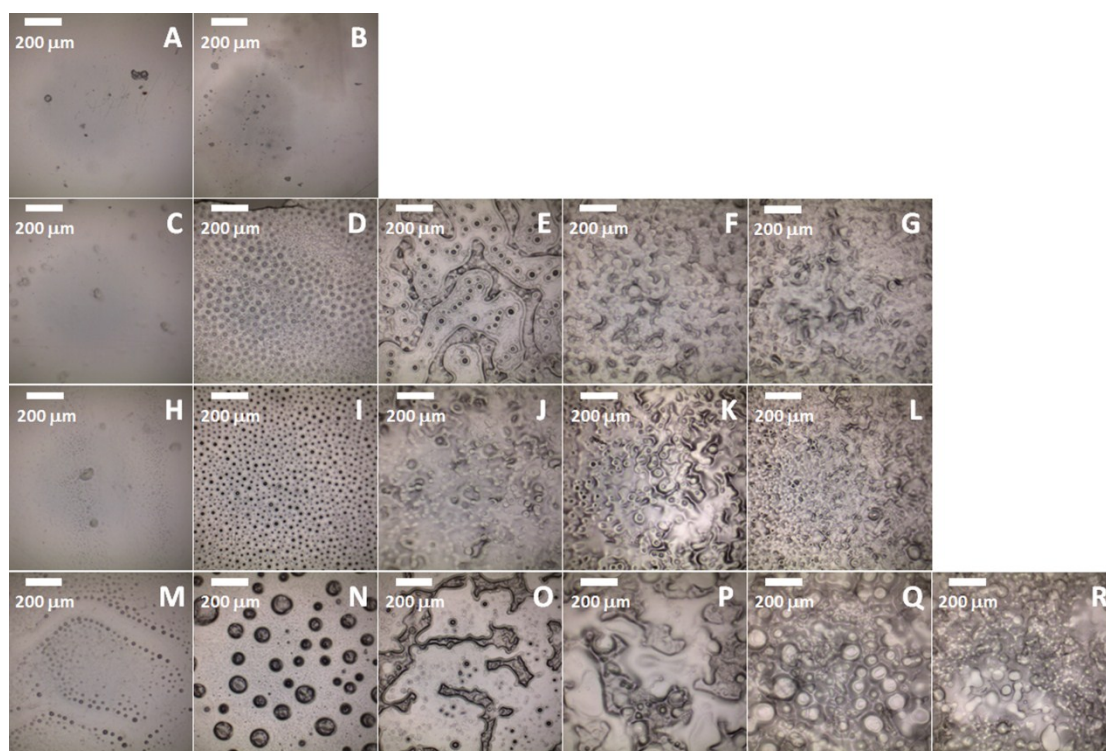


Figure S3. Optical images of phase separation of silk film blend with PEG-2 kDa of 30% (A); PEG-4 kDa of 30% (B); PEG-6 kDa of 10% (C), 15% (D), 20% (E), 25% (F), 30% (G); PEG-10 kDa of 10% (H), 15% (I), 20% (J), 25% (K), 30% (L); PEG-20 kDa of 5% (M), 10% (N), 15% (O), 20% (P), 25% (Q), 30% (R).

## References

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