The role of water mobility in water-responsive actuation of regenerated silk fibroin films.

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Abstract: Water-responsive (WR) materials hold great promise as evaporation energy harvesting actuators, opening the doors to a novel category of green energy production. As is often the case, the bio-derived materials present best in the class performance, with unprecedented water-responsive energy densities. However, a lack of understanding of the fundamental mechanisms involved in WR actuation has limited the engineer and upscaling of these materials thus far. In our work we use a humidity-controlled transmission FTIR to probe the hydrogen bonding networks formed by the absorbed water in the regenerated silk fibroin films. These films demonstrate varying energy densities as a function of their post-treatment, which changes the secondary structures for the biopolymer. We identified the presence of bulk-like mobile and ice-like bound water populations in the material and more importantly, we find that there is a common threshold of bound-to-mobile water ratio above which the material becomes water responsive and is able to induce tensional stress during dehydration. The trend was shown for three samples with significantly differing secondary structures and WR properties, yet all exhibited a common value for the threshold bound-to-mobile water ratio. Moreover, we also used the inherent silk luminescence to evaluate the localized hydration at the molecular scale for the amorphous phase of the biopolymer, which follows a similar trend as the dehydration induced tension. However, the molecular scale tension indicated by the FTIR amide II and III peak shifts, shows deviations from the trend, as it does not present a clear inception point at a fixed relative humidity value, as is the case for the macroscale induced tension, but rather increases linearly throughout the humidity range for all the tested samples.

Besides the better fundamental understanding of WR actuation and the potential towards evaporation energy harvesting, the importance of water population ratios in materials might be extended to general biopolymer material hydration and active biological matter research.