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Supporting information

Tuning compatibility and water uptake by protein charge modification in melt-polymerizable protein-based thermosets

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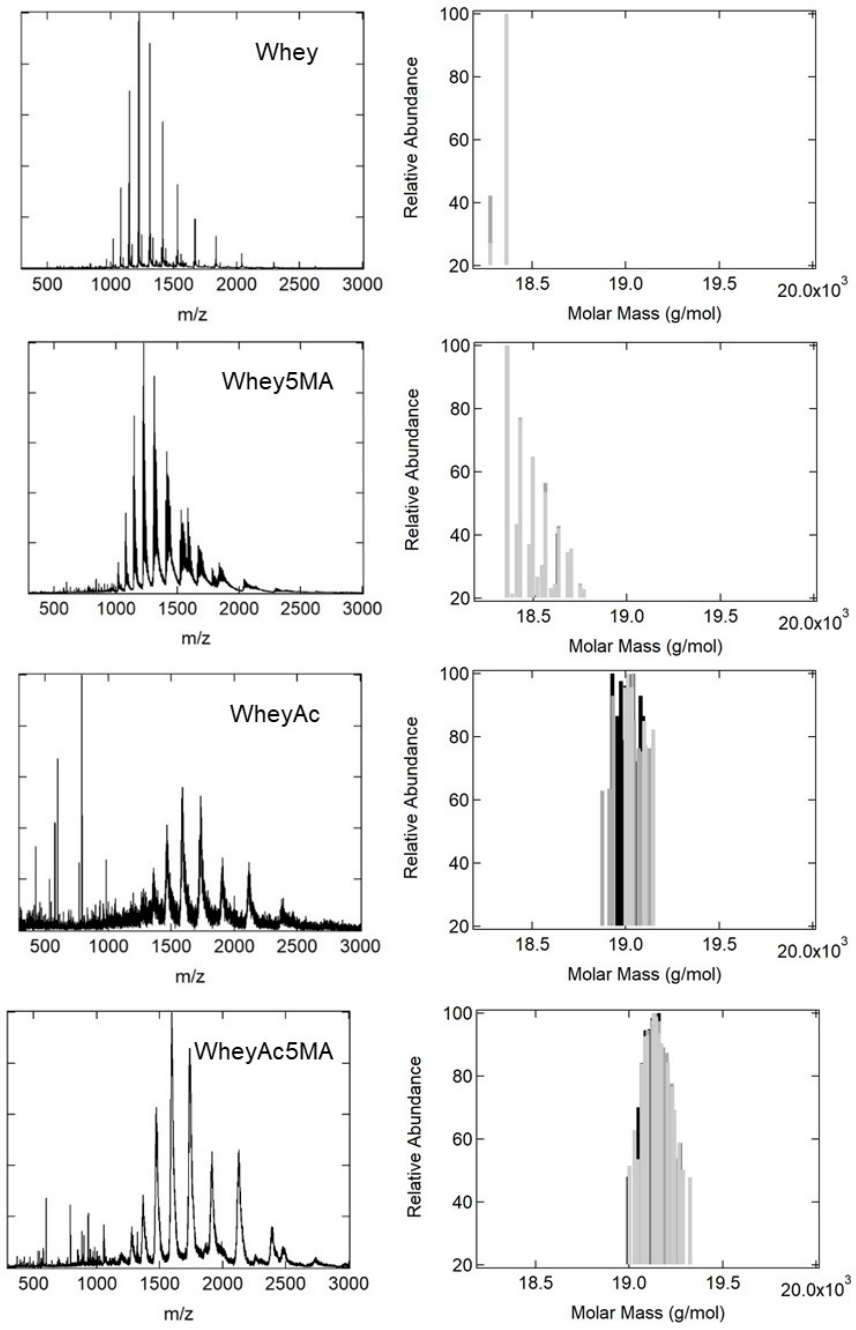

Figure S1. Representative raw mass spectra and deconvoluted molar masses for whey, wheyAc, and their methacrylated counterparts. Deconvoluted molar masses for three LC-MS replicates are shown.

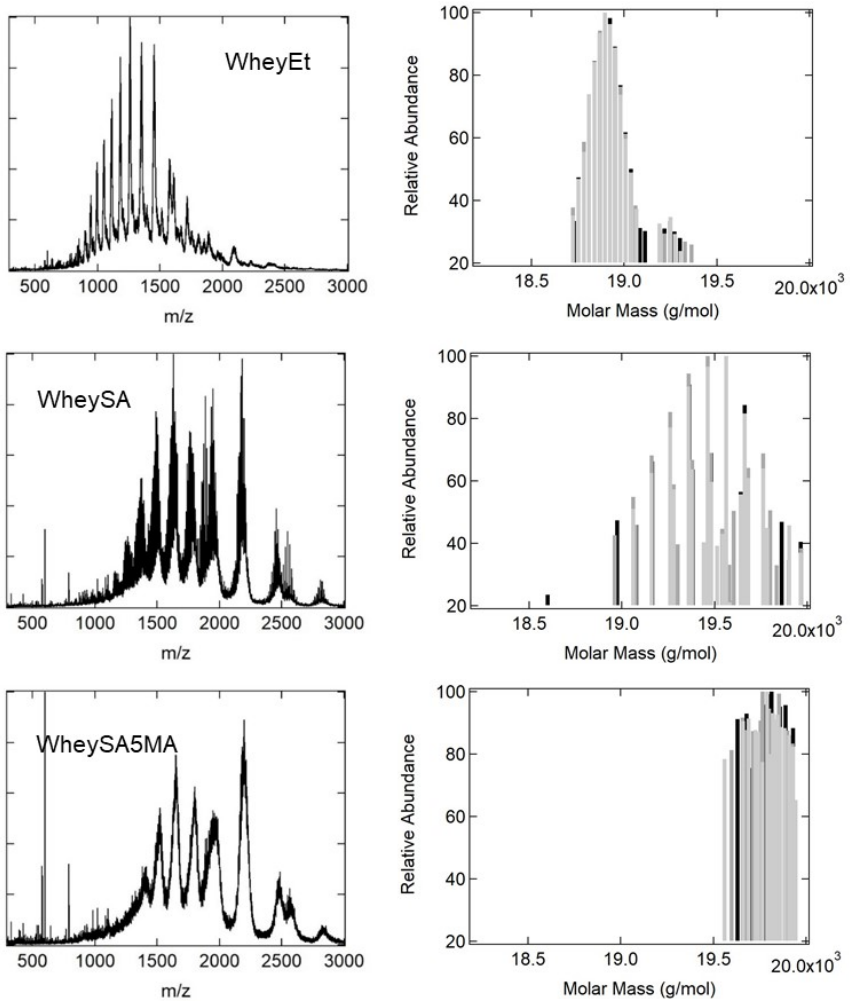

Figure S2. Representative raw mass spectra and deconvoluted molar masses for wheyEt, wheySA, and wheySA5MA. Deconvoluted molar masses for three LC-MS replicates are shown.

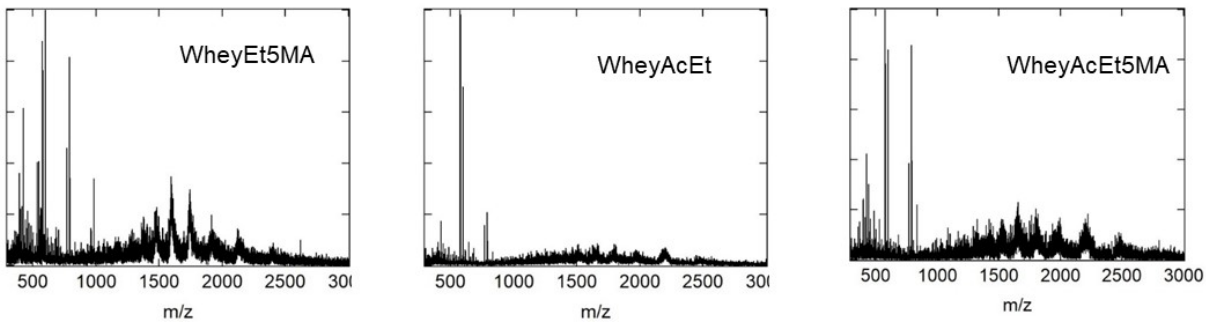

Figure S3. Representative raw mass spectra for wheyEt5MA, wheyAcEt, and wheyAcEt5MA. Deconvolution was not performed due to the low signal to noise ratio

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Table S1. Blending results for whey- non-ionic surfactant- n-BA. Miscible mixtures are noted with a 'Y'.

		Whey		
		1:1	1:2	1:3
Ecosurf	Nonionic, fatty acid based	y	y	y
BG-10	Nonionic, alkyl polyglucoside	y	y	y
Triton X-100	Nonionic, octiylphenol ethoxylate	y	y	y
Glycerol	Nonionic polyol	y	y	

Table S2. Theoretical bovine β-lactoglobulin net charge at pH = 7, based on amino acid sequence and number of modification from LCMS results. Insoluble wheyEt5MA had 2 estimated methacrylations per bolvine β-lactoglobulin while wheyAcEt5MA was assumed to have same degree of acetylation and esterification as wheyAc and wheyEt, respectively, and 2 methacrylate groups.

	Whey5MA	WheyAc5MA	WheyEt5MA	WheySA5MA	WheyAcEt5MA
Theoretical net charge	-8.8	-14.8	14.2	-24.7	6.2

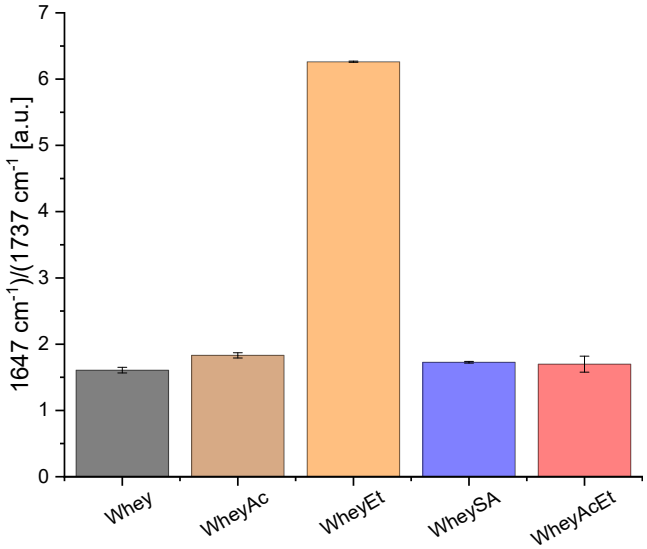

Figure S4. ATR-FTIR performed on protein-surfactant-poly(n-butyl acrylate) blends prepared using non-methacrylated proteins. Differences in compatibility highlighted using the peak area ratio of the protein amide I (centered at 1647 cm^{-1}) to the poly(n-butyl acrylate) carbonyl (centered at 1737 cm^{-1}).

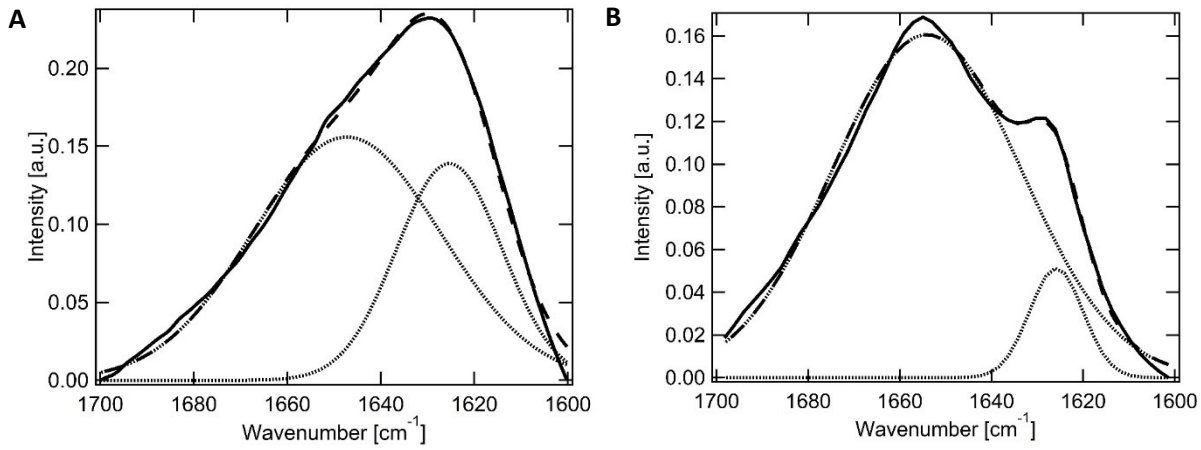

Figure S5. Representative FTIR plot showing the amide I baseline corrected peak (solid line), deconvoluted peaks (dotted line), and the fit (dash line). This measurement was taken on wheySA5MA protein powder (a) and copolymer (b).

Table S3. Deconvoluted ATR-FTIR peak positions (in cm^{-1}) for modified protein powder and protein-surfactant-poly(n-butyl acrylate) copolymer. Peak fitting was performed on amide I peaks, with peak positions, heights, and widths as fitting parameters. The two peaks at 1618-1628 cm^{-1} and 1647-1657 cm^{-1} were assigned to β-sheet, and α-helix and unordered structures respectively.[1] N=1 for protein powder, N=5 for copolymer.

Unmodified whey protein					
	Whey				
Peak 1 (cm^{-1})	1628				
Peak 2 (cm^{-1})	1653				
Methacrylated protein powder					
	Whey5MA	WheyAc5MA	WheyEt5MA	WheySA5MA	WheyAcEt5MA
Peak 1 (cm^{-1})	1626	1624	1623	1625	1623
Peak 2 (cm^{-1})	1650	1648	1647	1647	1647
Copolymer					
	Whey5MA	WheyAc5MA	WheyEt5MA	WheySA5MA	WheyAcEt5MA
Peak 1 (cm^{-1})	1624	1626	1619	1626	1626
Peak 2 (cm^{-1})	1657	1655	1657	1655	1657

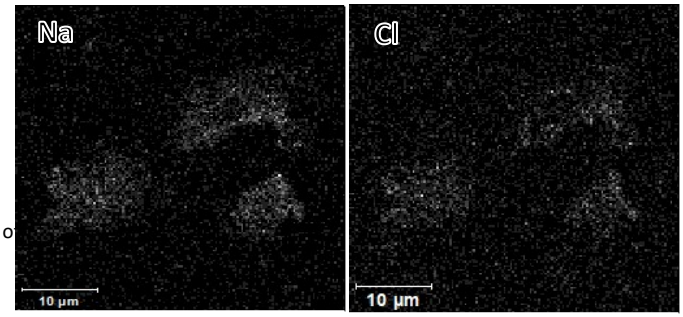

Figure S6. SEM-EDX of WheySA5MA with Na) sodium and Cl) chloride mapping, brighter is higher count rate.

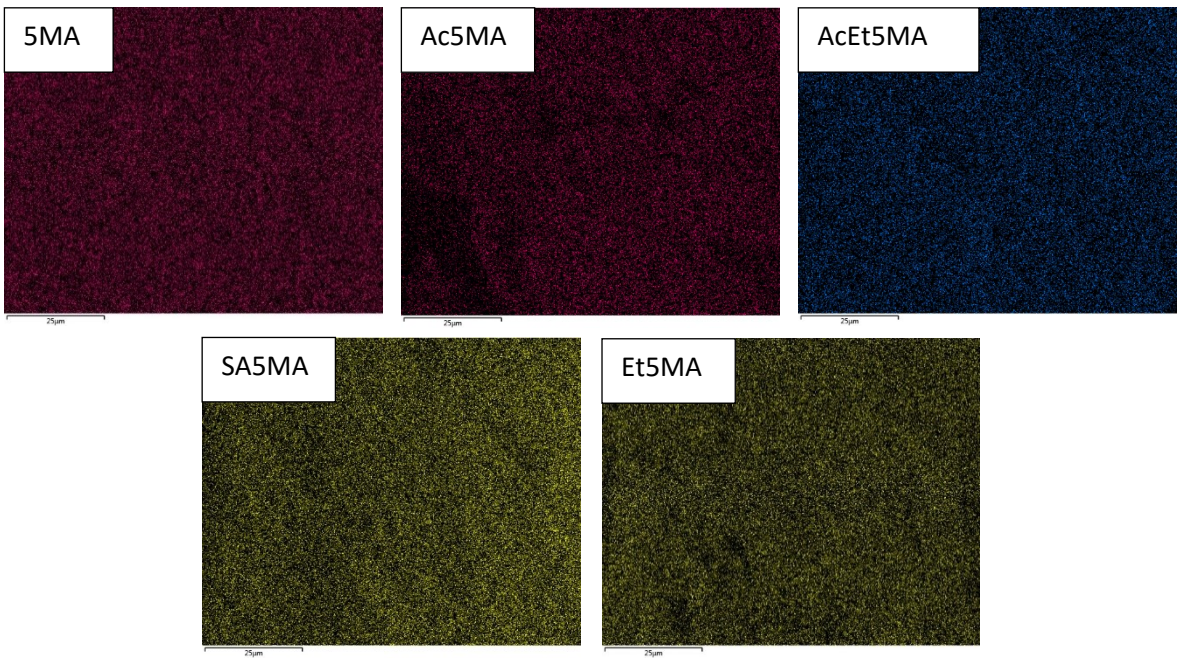

Figure S7. SEM-EDX mapping of nitrogen (N) of protein copolymers at 3000x magnification.

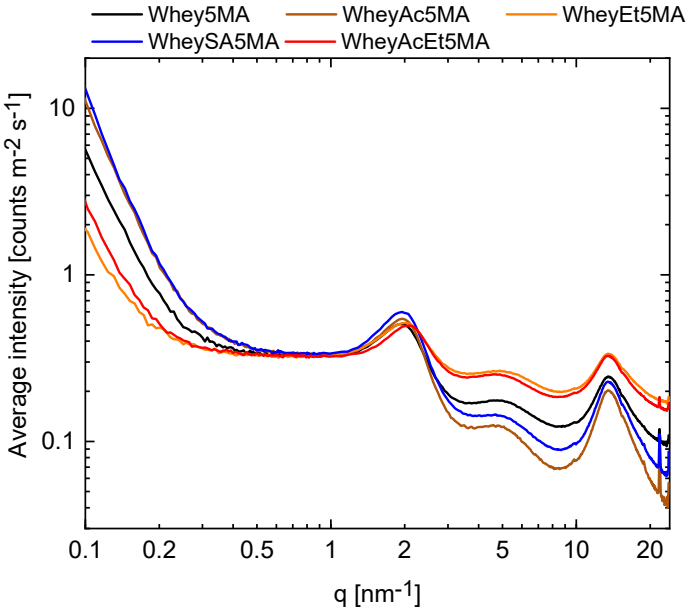

Figure S8. Representative SAXS and WAXS curves for whey5MA copolymer, with and without charge modification. WAXS curve offset to match the overlapping region with SAXS.

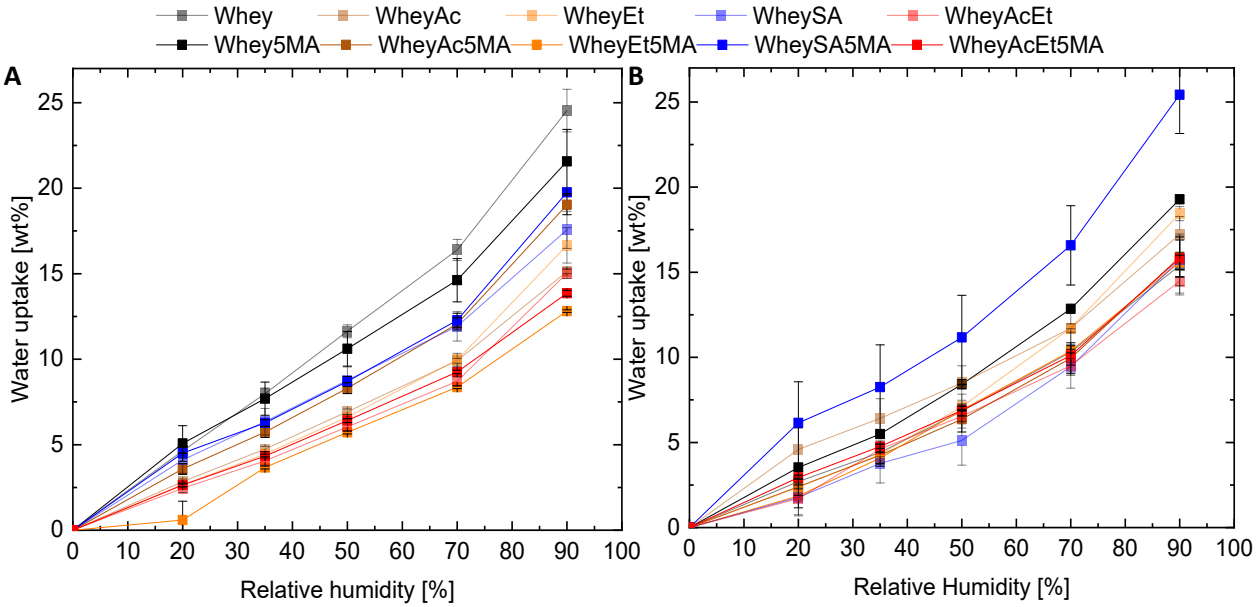

Figure S9. Relative-humidity water uptake of A) protein and B) protein:surfactant 1:1 complex.

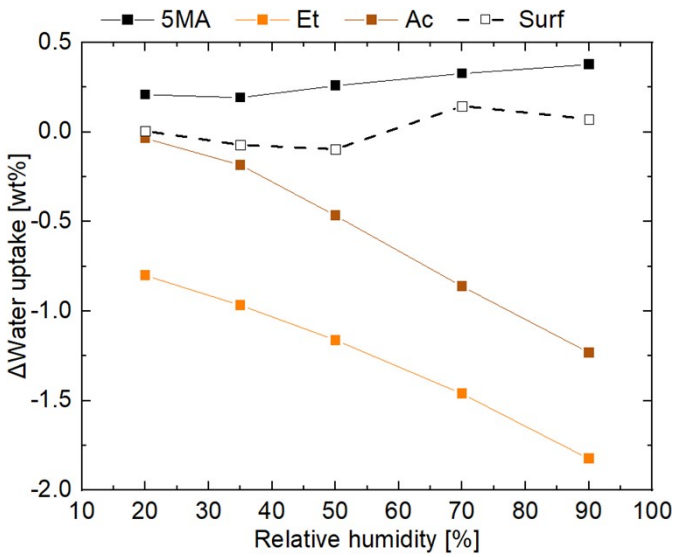

Figure S10. Main effect estimates of protein modification and complexation on water uptake of proteins. The 2^4 factorial analysis was performed with methacrylation (5MA), esterification (Et), acetylation (Ac) and surfactant complexation (surf) as factors.

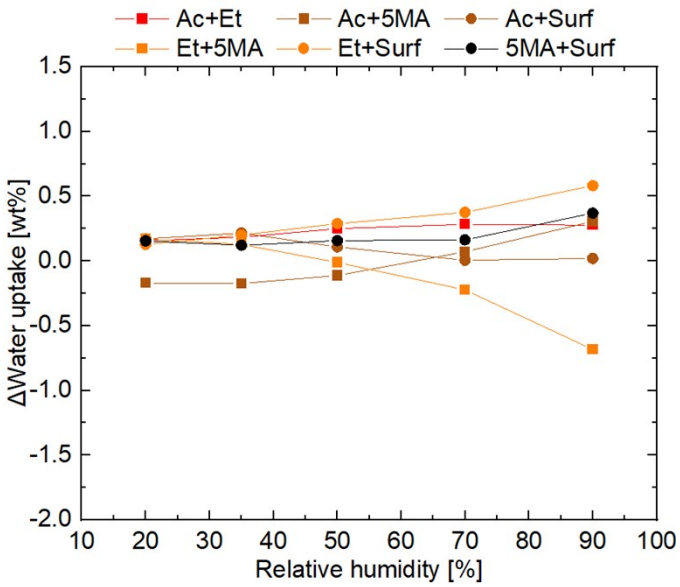

Figure S11. Two-way interaction estimates of protein modification and complexation on water uptake of proteins. The 2^4 factorial analysis was performed with methacrylation (5MA), esterification (Et), acetylation (Ac) and surfactant complexation (surf) as factors.

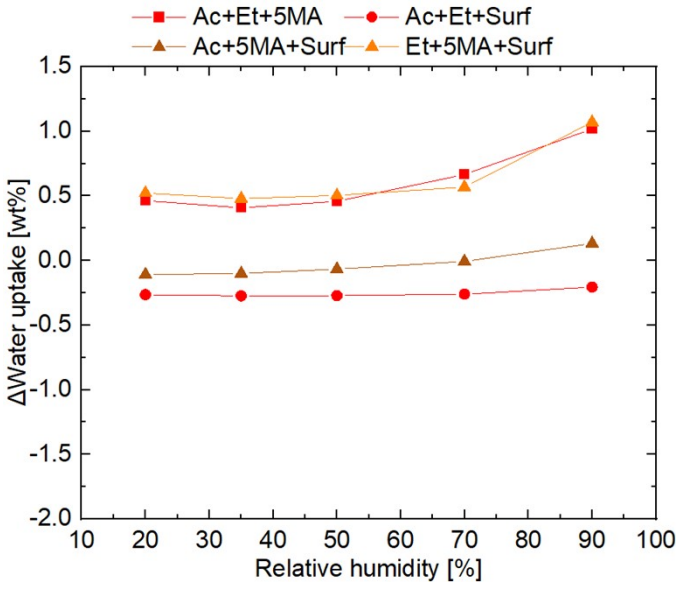

Figure S12. Three-way interaction estimates of protein modification and complexation on water uptake of proteins. The 2^4 factorial analysis was performed with methacrylation (5MA), esterification (Et), acetylation (Ac) and surfactant complexation (surf) as factors.