Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting information:

Casein protein as building-blocks for making ion-conductive bioplastics

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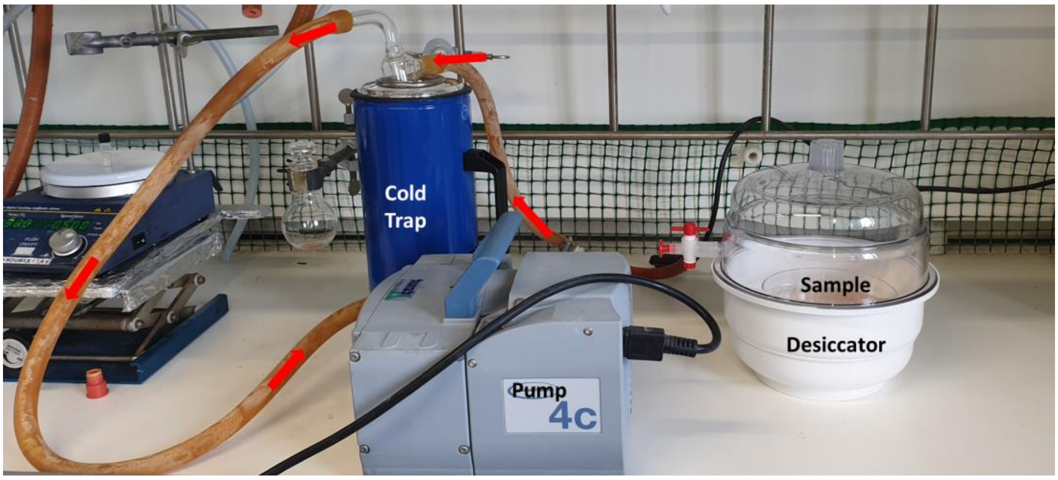

Figure S1. Setup for fluorinated solvent trapping using a cold trap in a closed setup for further recycling.

As mentioned in the main text, the use of the casein protein, which is not solvable in many aqueous and organic solvents has resulted in our use of trifluoroethanol (TFE) and trifluoroacetic acid (TFA) as the main solvents. Although TFE and TFA are being used in many of the polymers industry, they are fluorinated solvents, and accordingly pose a concern. While the bioplastic formation process involves the full evaporation of these solvents, we further show in this Figure S1 the possibility to use a cold trap to capture the solvents while evaporating for any reuse of them later on.

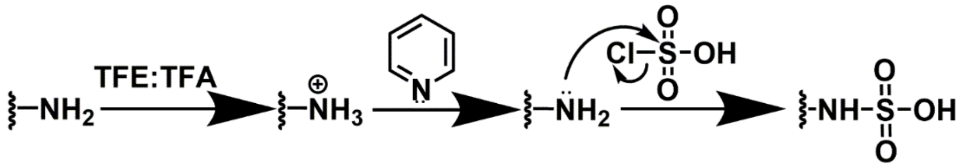

Figure S2. Sulfonation mechanism of the casein protein after adding chlorosulfonic acid: pyridine mixture

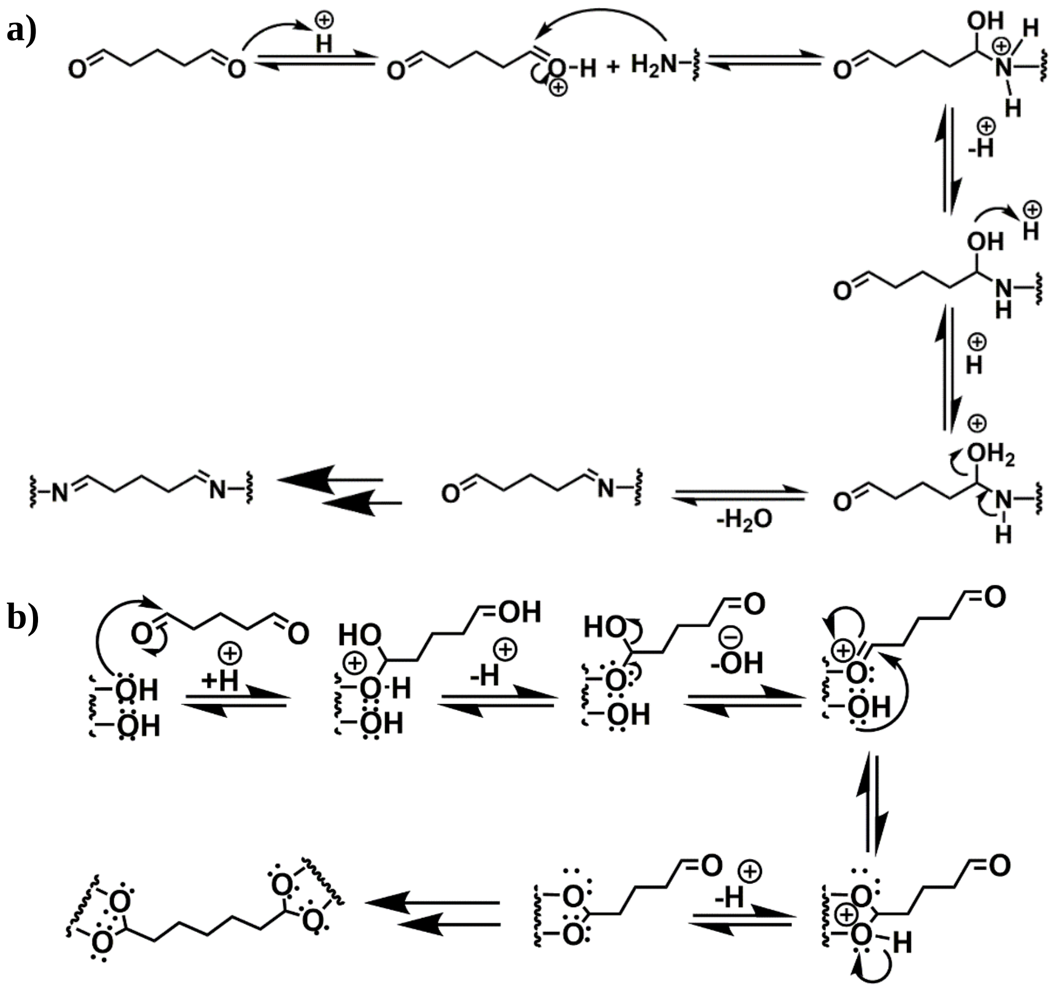

Figure S3. Crosslinking of glutaraldehyde with casein (a) via imine bond formation via -NH_2 containing amino acids and (b) via alcoholic -OH containing amino acid.

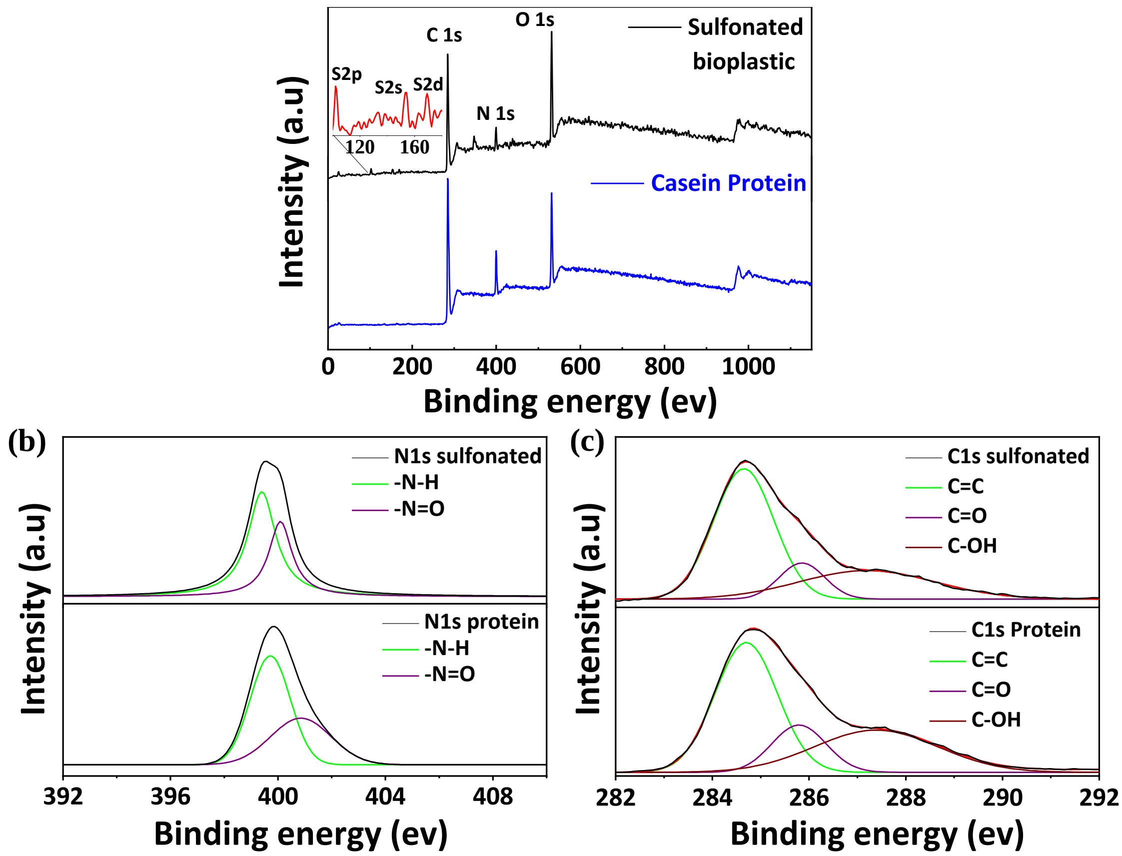

Figure S4. (a) X-ray photoelectron spectroscopy survey spectrum and zoom-ins on (b) the N1s and (c) the C1s bands of the casein-based sulfonated bioplastic in comparison to the powdered casein protein used for making the bioplastic.

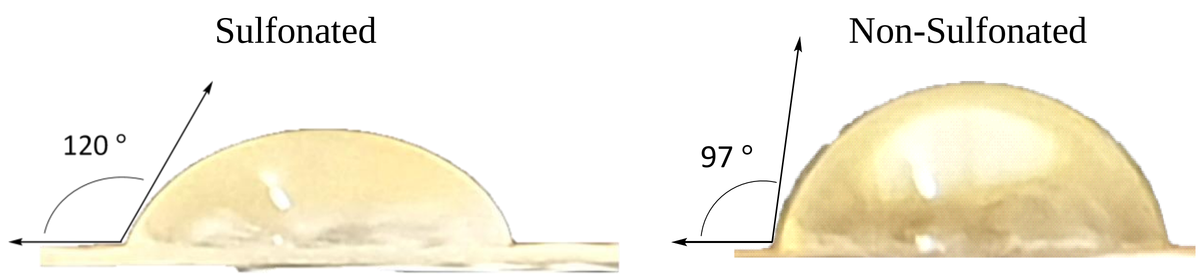

Figure S5. Contact angle measurements of the sulfonated and non-sulfonated bioplastics upon placing a 50 μL water droplet.

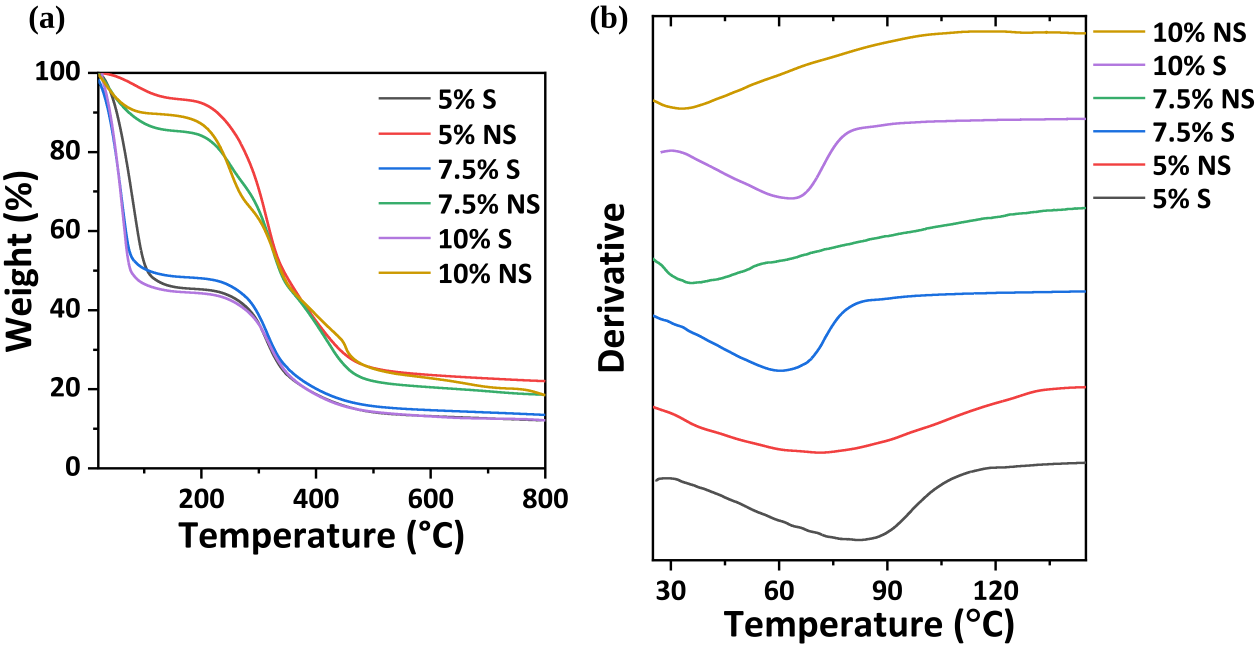

Figure S6. (a) TGA measurements for all of the sulfonated and non-sulfonated casein bioplastics at different cross-linker concentrations. (b) The normalized derivatives of the graphs in (a) for the temperature range <140°C.

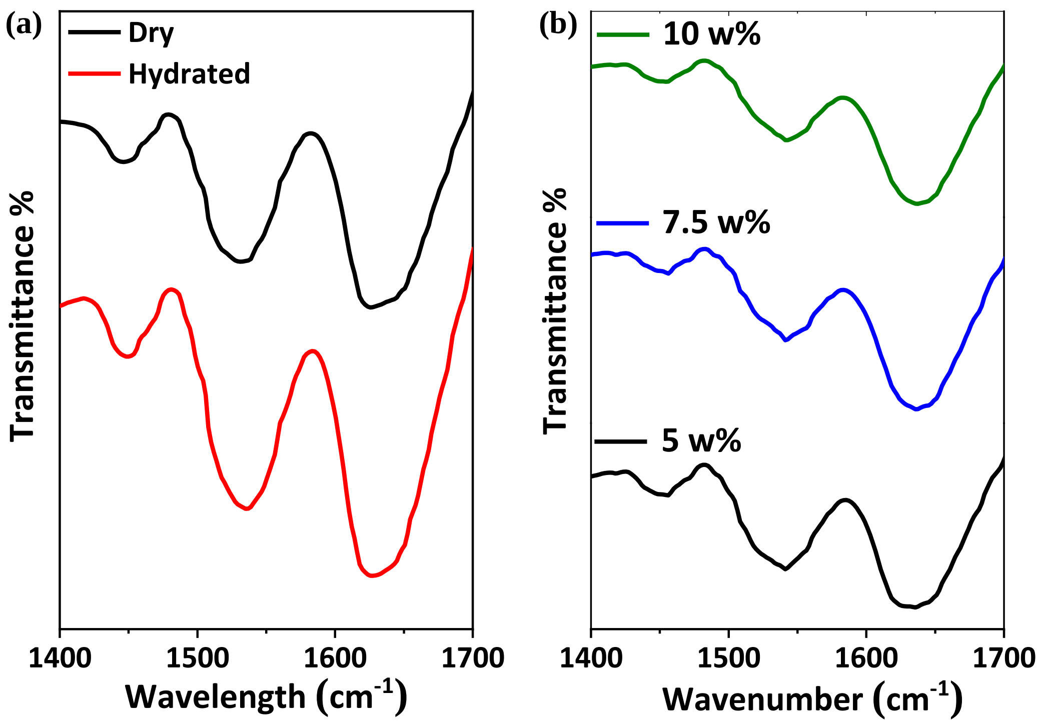

Figure S7. (a) FTIR measurements of the hydrated and dehydrated casein sulfonated bioplastic. (b) FTIR measurements of the sulfonated casein bioplastics at different cross-linker concentrations.

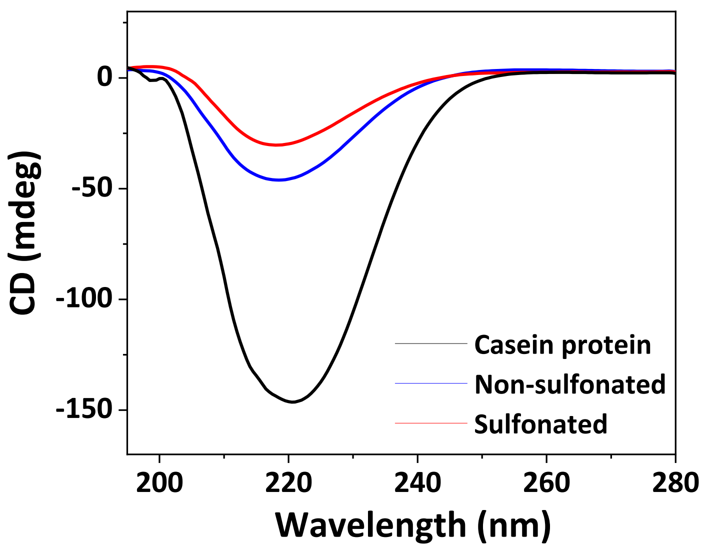

Figure S8. CD spectrum of the non-sulfonated and sulfonated casein plastics compared to the native casein protein.

Table S1. Summary of the young's modulus, elongation, and maximum stress values of the casein bioplastics of different cross-linker concentrations in the hydrated and dehydrated state.

Cross linker w%	**Sulfonated film** -Hydrated	**Sulfonated film -** Dehydrated	**Non-sulfonated film -** Hydrated	**Non-sulfonated film -** Dehydrated
	Tensile Young's modulus (MPa)			
5	2.8 ± 0.5	10 ± 5.2	22.8 ± 2	24 ± 9
7.5	6.9 ± 2.5	21.6 ± 8	109.5 ± 22.7	175.3 ± 40.5
10	4.5 ± 1.4	16.3 ± 6.9	127.5 ± 49	197.4 ± 78.8
	Elongation (%)			
5	100 ± 10.5	60 ± 23.6	41.7 ± 10.5	28 ± 2.5
7.5	66 ± 3.7	27 ± 8.2	18.8 ± 6.6	26.5 ± 16.5
10	79 ± 10.1	58 ± 23.9	15 ± 3.5	24.2 ± 4.5
	Maximum stress (MPa)			
5	0.4 ± 0.2	1.5 ± 0.5	2.5 ± 1	4.2 ± 1.1
7.5	0.6 ± 0.2	1.7 ± 0.2	9.4 ± 2.8	11.6 ± 3.3
10	0.8 ± 0.2	2.5 ± 0.5	5.3 ± 1	19.2 ± 1.5

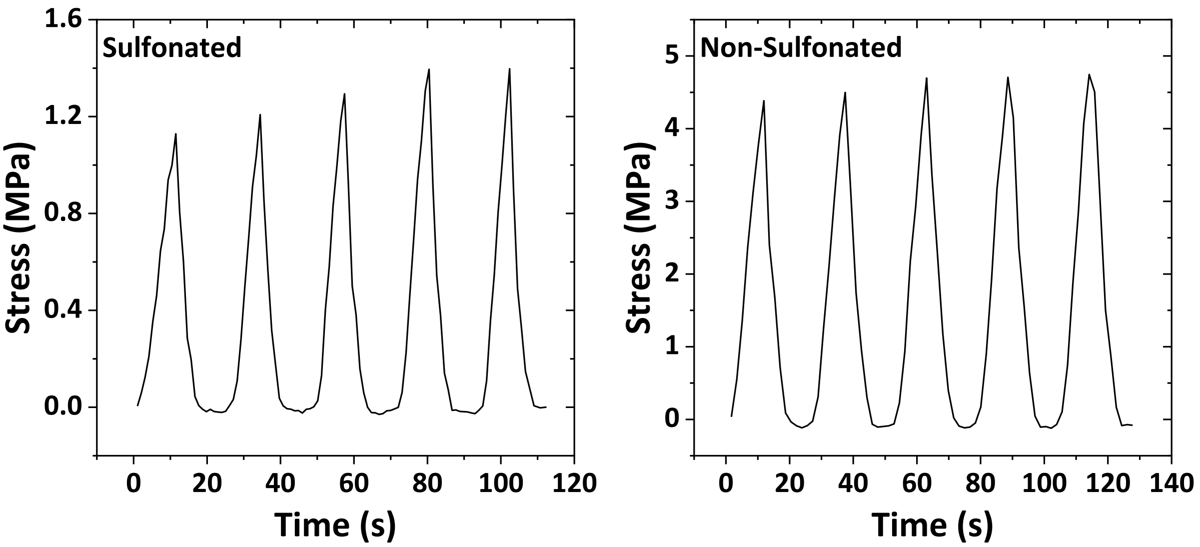

Figure S9. Mechanical fatigue test of the sulfonated and the non-sulfonated bioplastics, measured for the bioplastics made with 7.5 wt.% GA and measured at 5% strain.

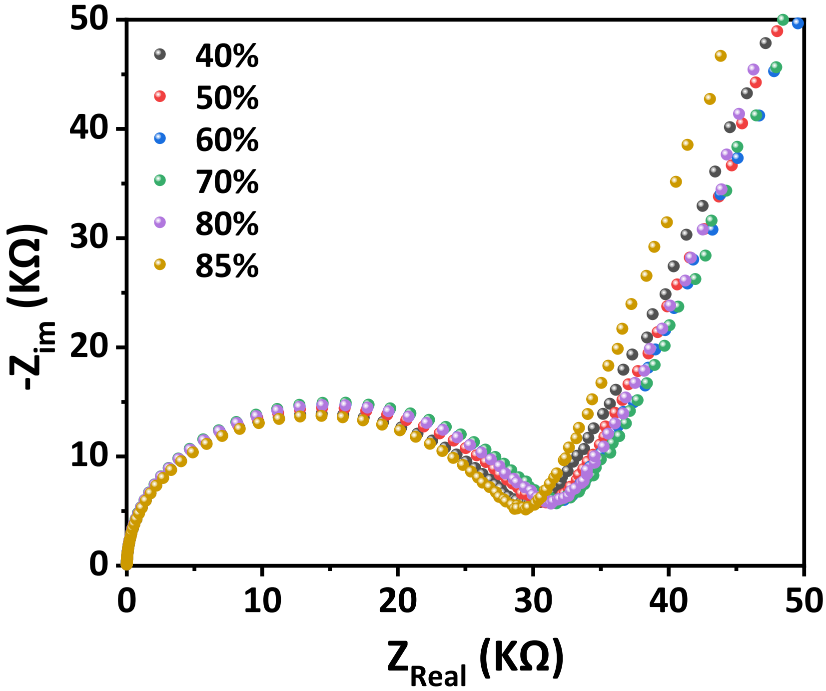

Figure S10. EIS measurements as a function of RH percentage for the hydrated sulfonated bioplastic.

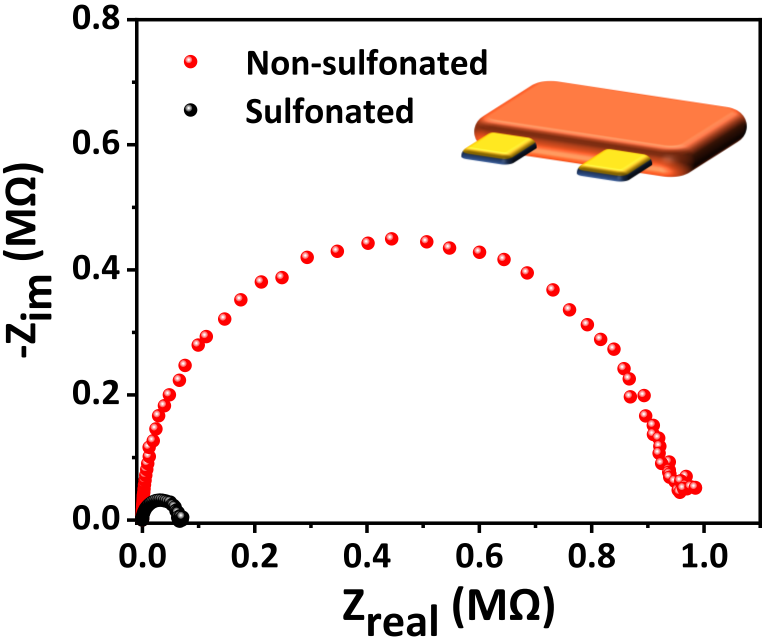

Figure S11. EIS measurements of the sulfonated and non-sulfonated bioplastics in the bulk electrodes configuration.