Thermally Sensitive and Tunable Water-Soluble Polymer Molds for the Preparation of Porous Hydrogels

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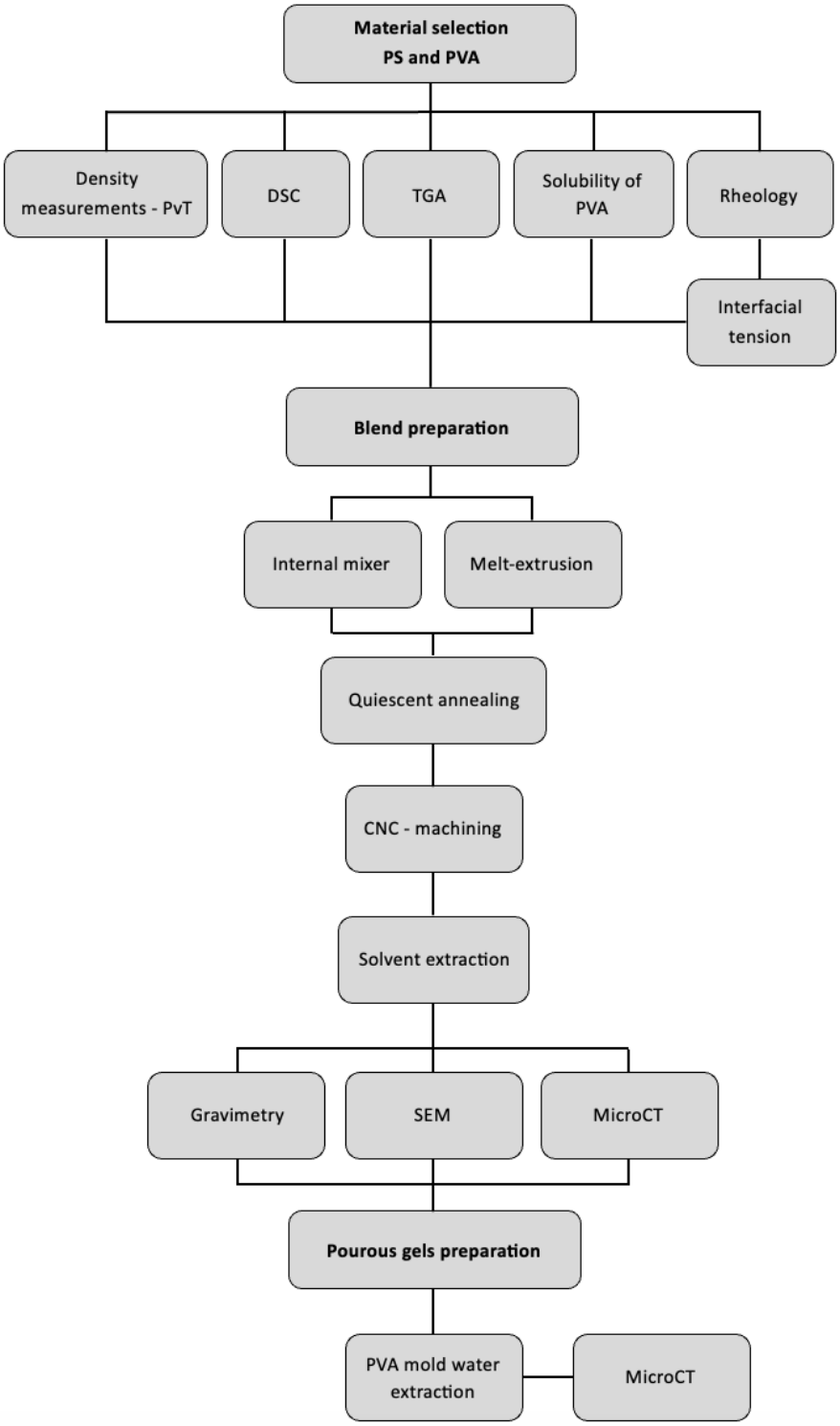
Table S1. Microstructural parameters of polymer blends prepared by extrusion as a function of quiescent annealing time. Domain diameter corresponds to the pore size distribution average ± 1 standard deviation.

Quiescent annealing time [min]	d_{PVA} $[\mu m]$	d_{pores} $[\mu m]$	S $[cm^{-1}]$	$\emptyset_{PVA}$ $[\%vol]$	$\emptyset_{pores}$ $[\%vol]$
0	47 ± 23	94 ± 24	589	30	70
10	59 ± 19	91 ± 22	503	37	63
20	64 ± 13	67 ± 15	339	42	58
30	96 ± 18	120 ± 30	157	38	62
45	121 ± 33	151 ± 57	111	37	63
60	170 ± 34	204 ± 57	94	41	59

Table S2. Microstructural parameters of polymer blends prepared in an internal mixer as a function of quiescent annealing time. Domain diameter corresponds to the pore size distribution average ± 1 standard deviation

Quiescent annealing time [min]	d_{PVA} $[\mu m]$	d_{pores} $[\mu m]$	S $[cm^{-1}]$	$\emptyset_{PVA}$ $[\%vol]$	$\emptyset_{pores}$ $[\%vol]$
0	28 ± 8	41 ± 23	440	33	67
10	73 ± 12	87 ± 32	275	40	60
20	130 ± 24	162 ± 33	134	39	61
30	181 ± 41	214 ± 75	85	41	59
60	205 ± 43	205 ± 55	84	47	53



Scheme S1. Experimental flowchart describing the preparation process of porous hydrogels using PVA molds, from materials selection and characterization, preparation of PS/PVA polymer blends, preparation and characterization of PVA molds, and resulting hydrogels.

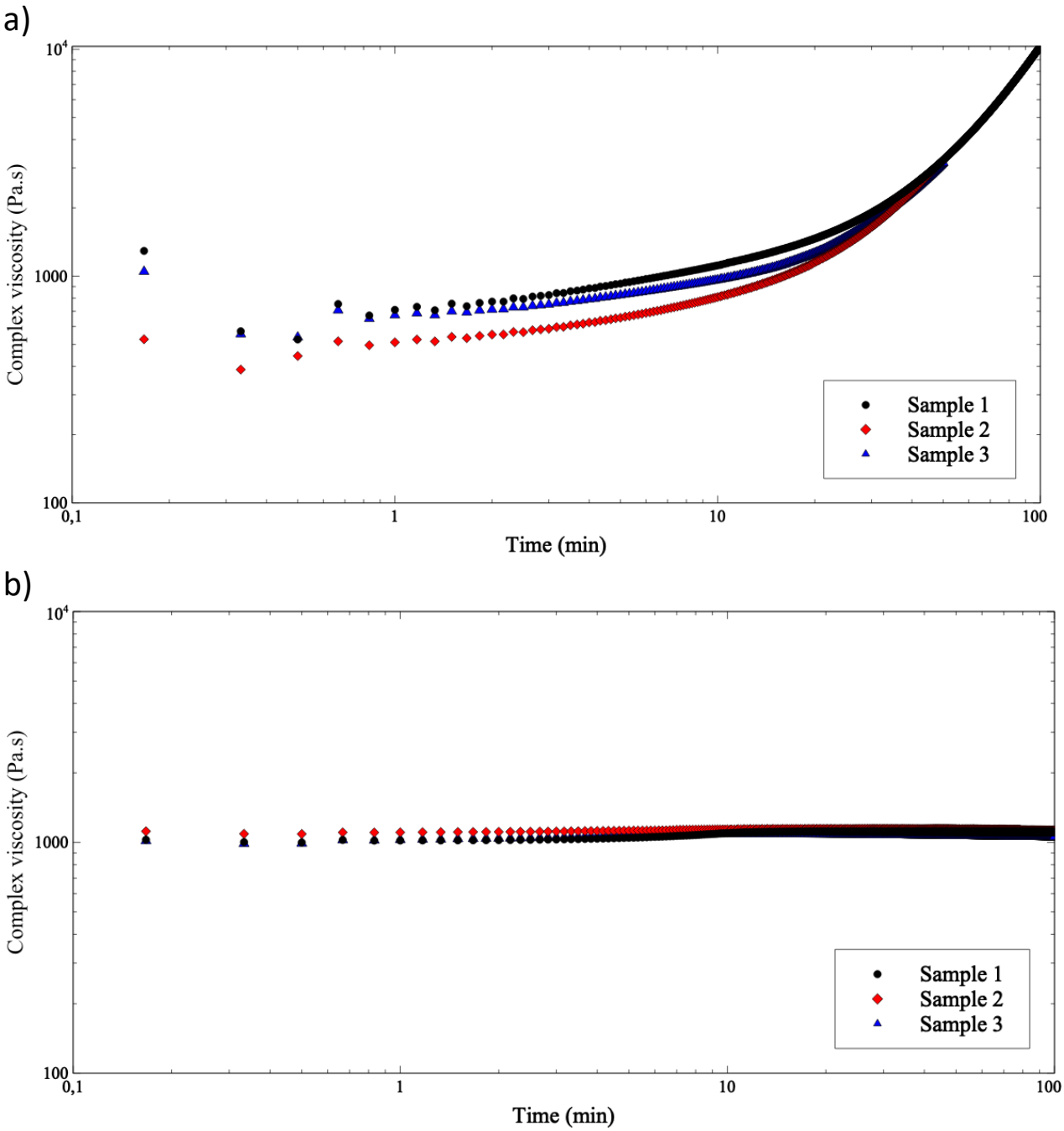


Figure S1. a) Time sweep of PVA at 220 °C, γ_0 = 1% and 1 rad/s; b) Time sweep of PS at 220 °C, γ_0 = 1% and 1 rad/s.

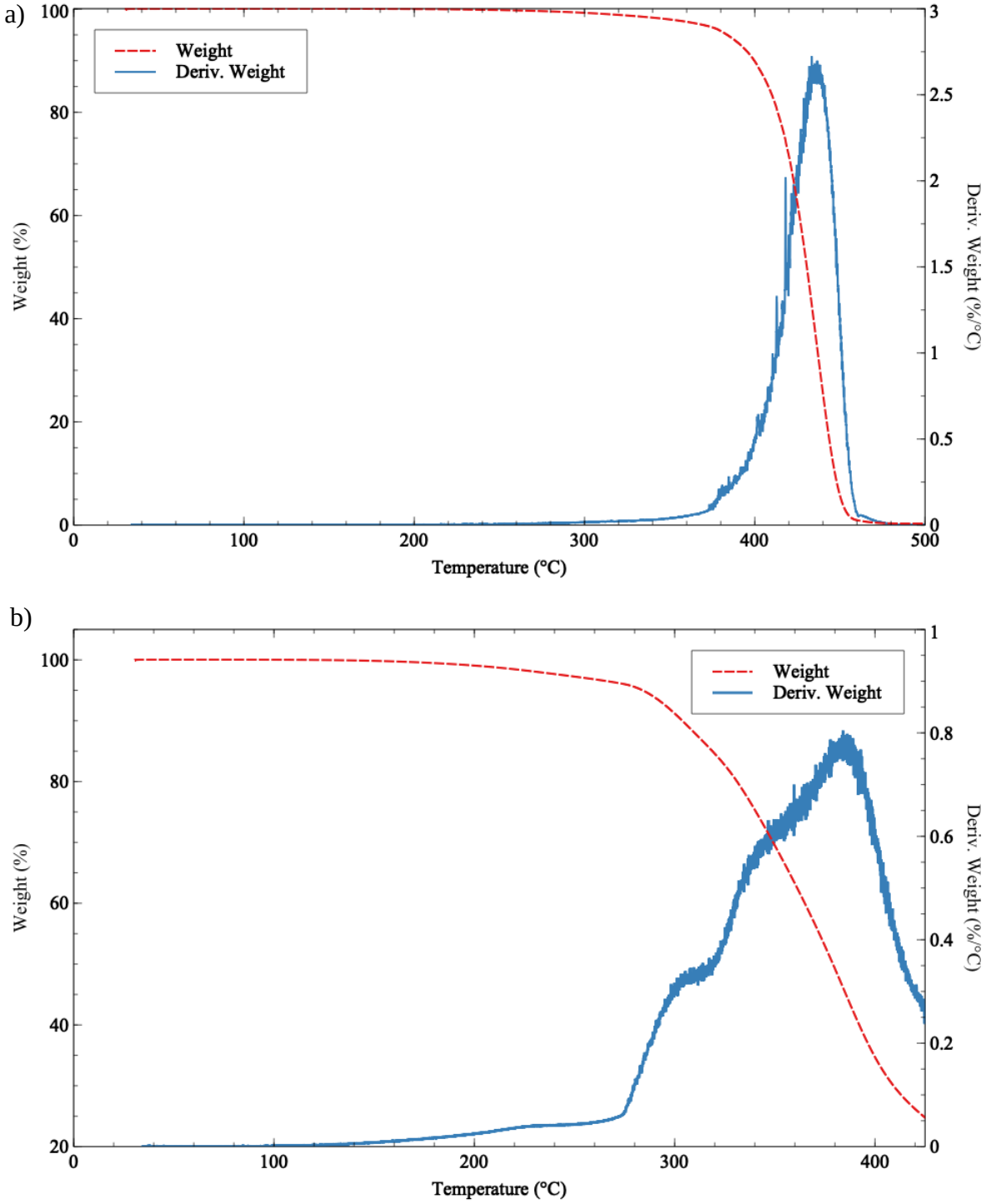


Figure S2. Thermogravimetric analysis of (a) PS and (b) PVA. Blue curve: sample weight (%) as a function of temperature T; Red curve: derivative of sample weight with respect to T (%/°C) as a function of T.

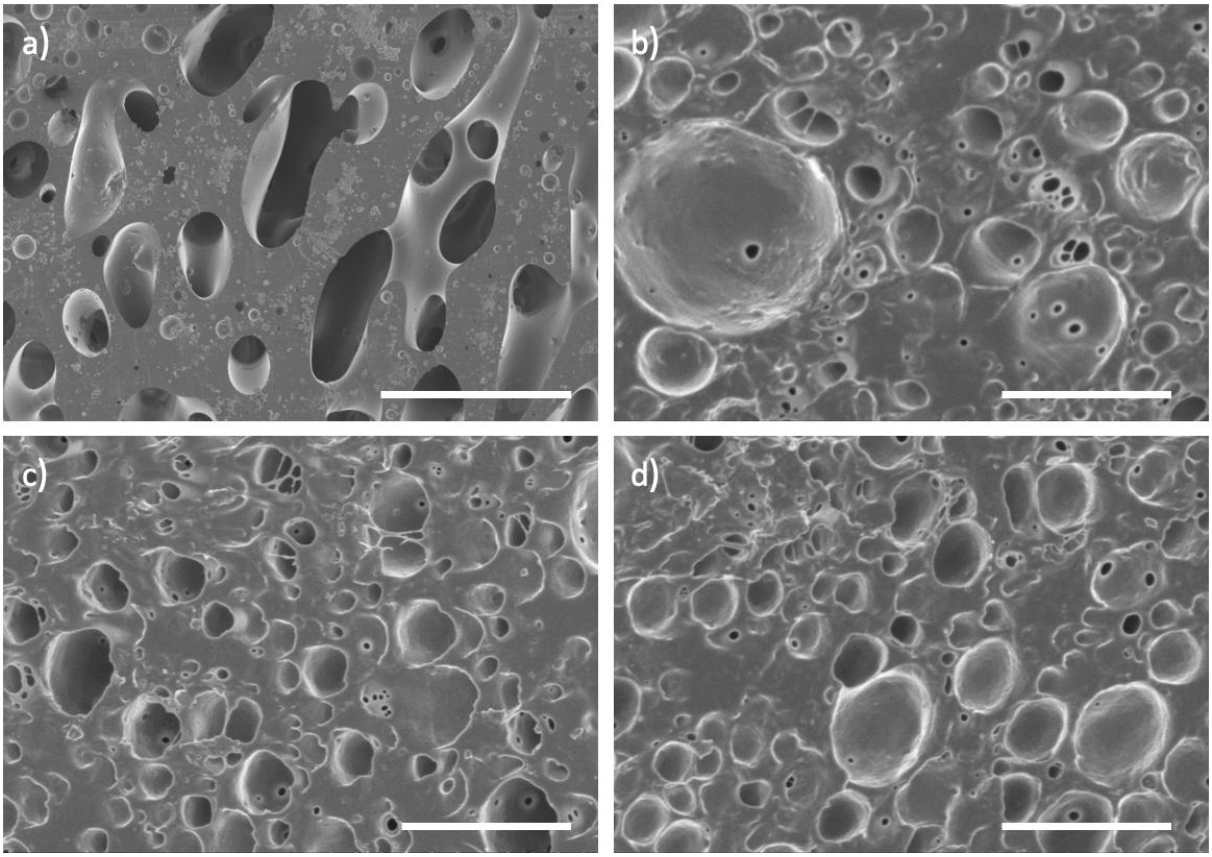
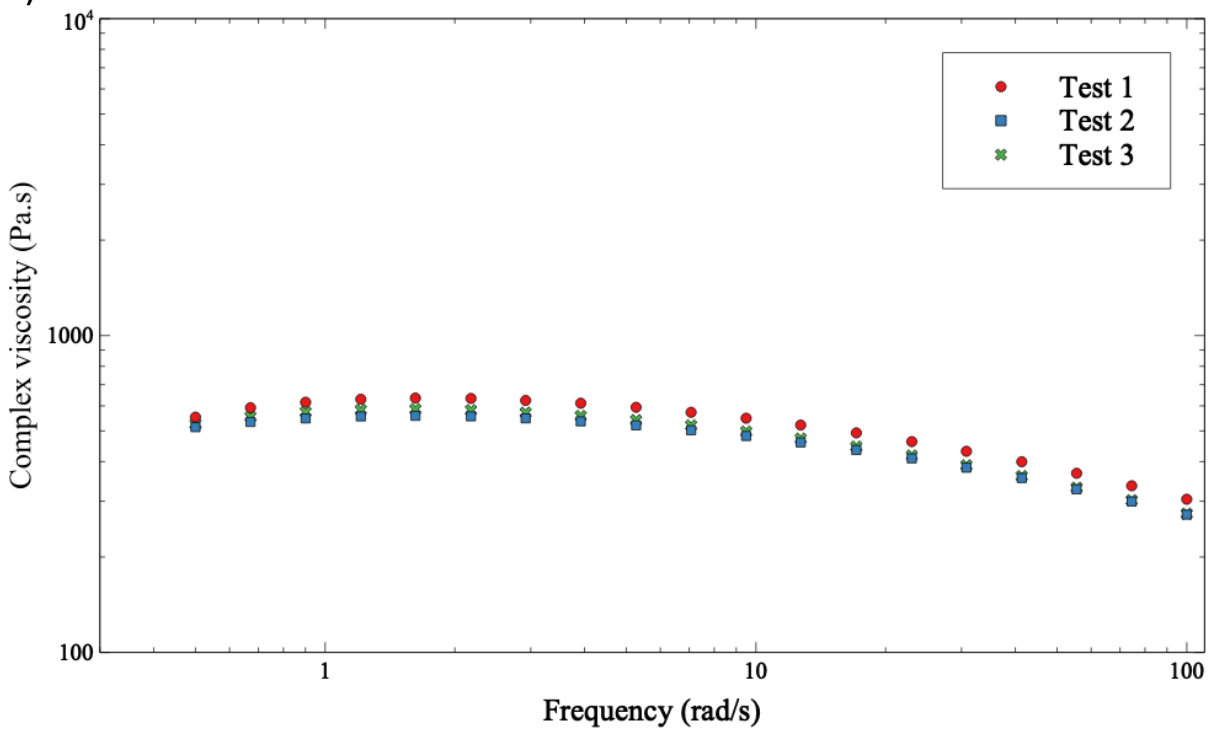
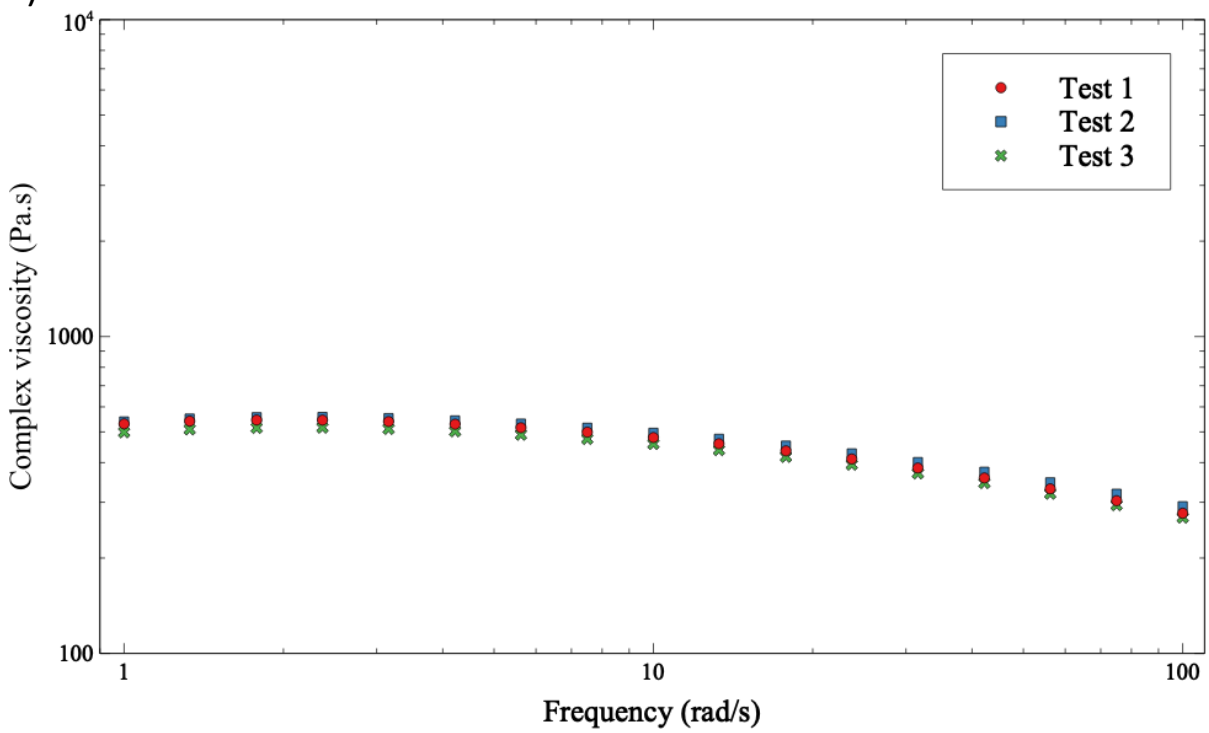


Figure S3. Microstructure of PS/PVA blends prepared in an internal mixer, after the selective extraction of PVA with water for micrograph (a), and selective extraction of PS using chloroform for micrographs (b) to (d). PS/PVOH compositions in vol%: a) 61/39 ; b) 60/40 ; c) 55/45 ; d) 50/50. Notice first in (a) the PVA sub-inclusions in the PS phase following PVA extraction with water, and then the small openings in the extracted dispersed PS phase linking the extracted droplets together, creating a percolated network, in (b) to (d). The white scale bars represent 100 µm for micrograph (a) and 2 µm for micrographs (b) to (d).

a)


10^4
1000
100
Complex viscosity (Pa.s)
1
10
100
Frequency (rad/s)
Test 1
Test 2
Test 3

b)


10^4
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Complex viscosity (Pa.s)
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Frequency (rad/s)
Test 1
Test 2
Test 3

c)

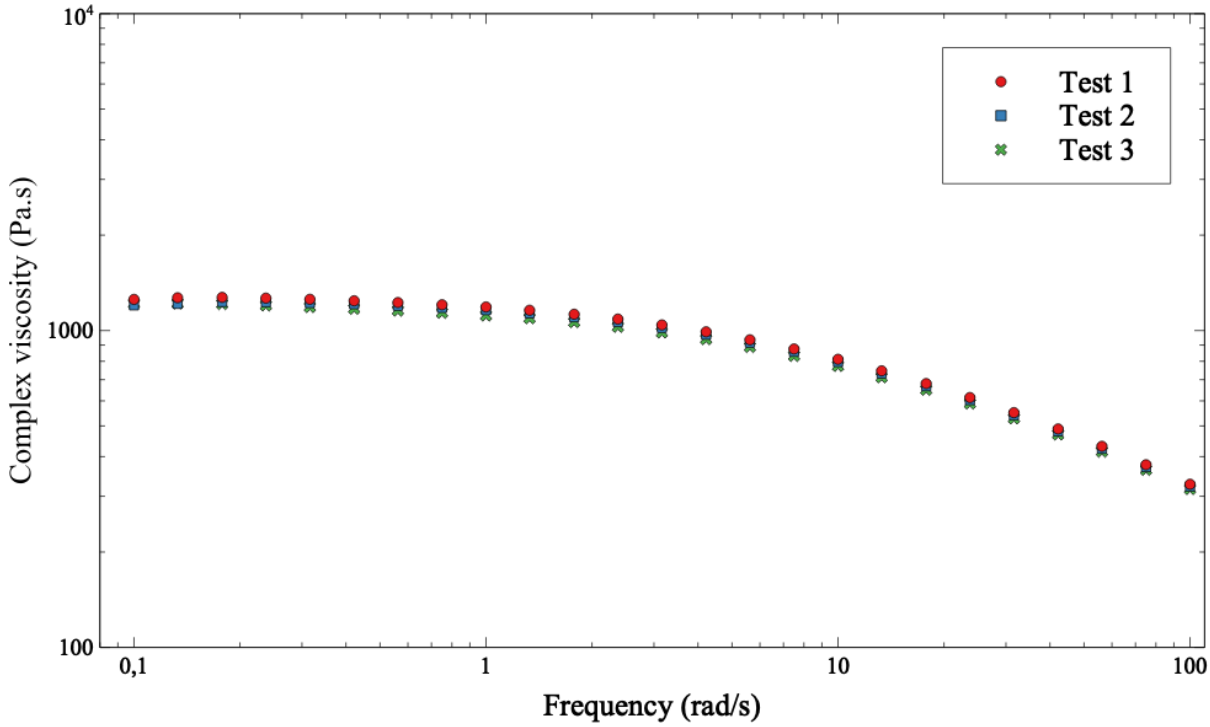

Figure S4. a) Frequency sweep of PVA at 220 °C, γ_0 = 1%, frequency from 0.5 rad/s to 100 rad/s; b) Frequency sweep of PVA at 220 °C, γ_0 = 1%, frequency from 1 rad/s to 100 rad/s; c) Frequency sweep of PS at 220 °C, γ_0 = 1%, frequency from 0.1 rad/s to 100 rad/s.

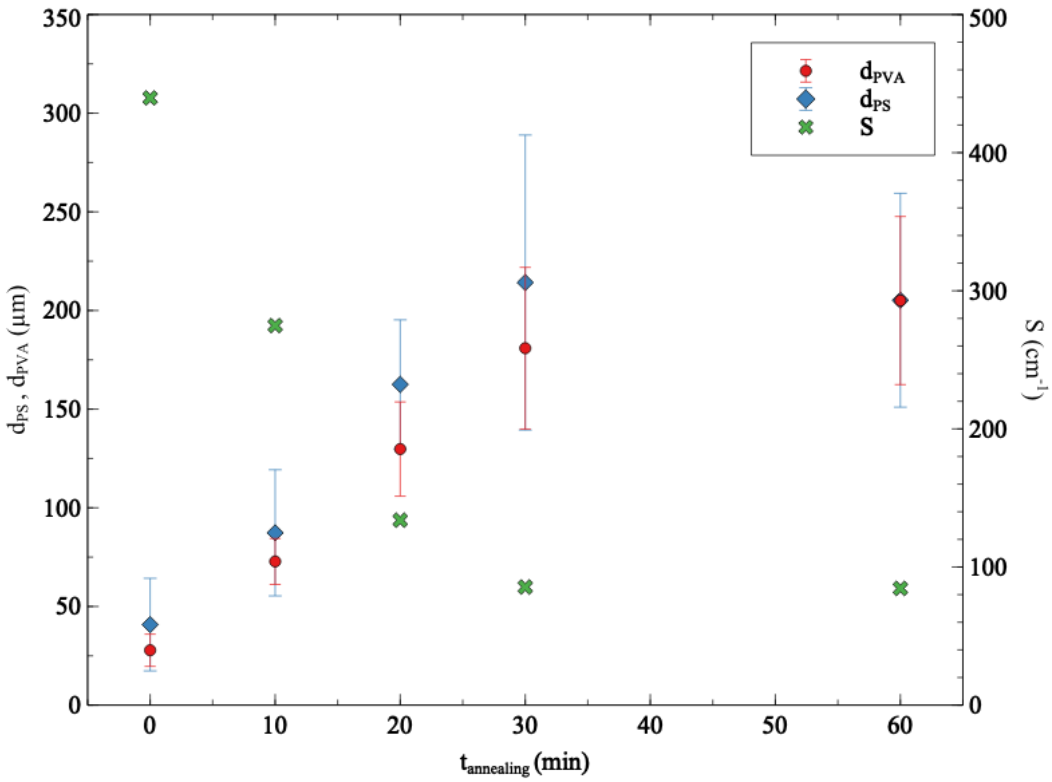

Figure S5. Average diameter (thickness) of the PS (d_{PS}) and PVA (d_{PVA}) domains, and specific interfacial area *S*, as a function of quiescent annealing time $t_{annealing,}$ for the PS/PVA 61/39 blend prepared with the internal mixer. The data points for the diameters correspond to the average pore size of the distribution ± one standard deviation.

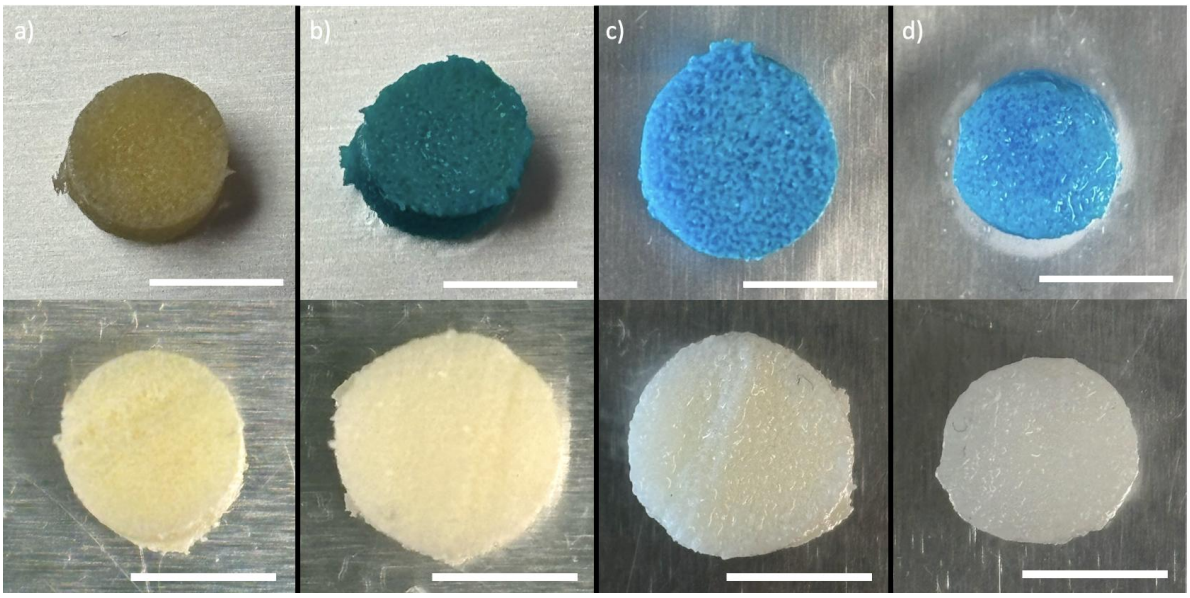

Figure S6. Comparison of experimental steps for the preparation of a porous hydrogel composed of 4% w/v sodium alginate (SA), with a PVA mold prepared from a PS/PVA 61/39 vol% blend annealed for 30 min. The steps are as follows: a) Porous PVA mold before injection of the gelling solution, after blend annealing, CNC machining and PS extraction; b) Porous PVA mold right after solution injection; c) PVA mold after the injection of the SA solution and gelation, having spent 24 h in a 4% w/v aqueous $CaCl_2$ solution at 5 °C; d) 4% w/v SA porous hydrogel after the extraction of the PVA mold with water at 70 °C for 1 day. The top row shows the injection at 1°C, while the bottom row shows the injection at 5 °C – notice the volume difference. For top row, the hydrogel phase is stained with a blue food coloring dye to better distinguish the phases.

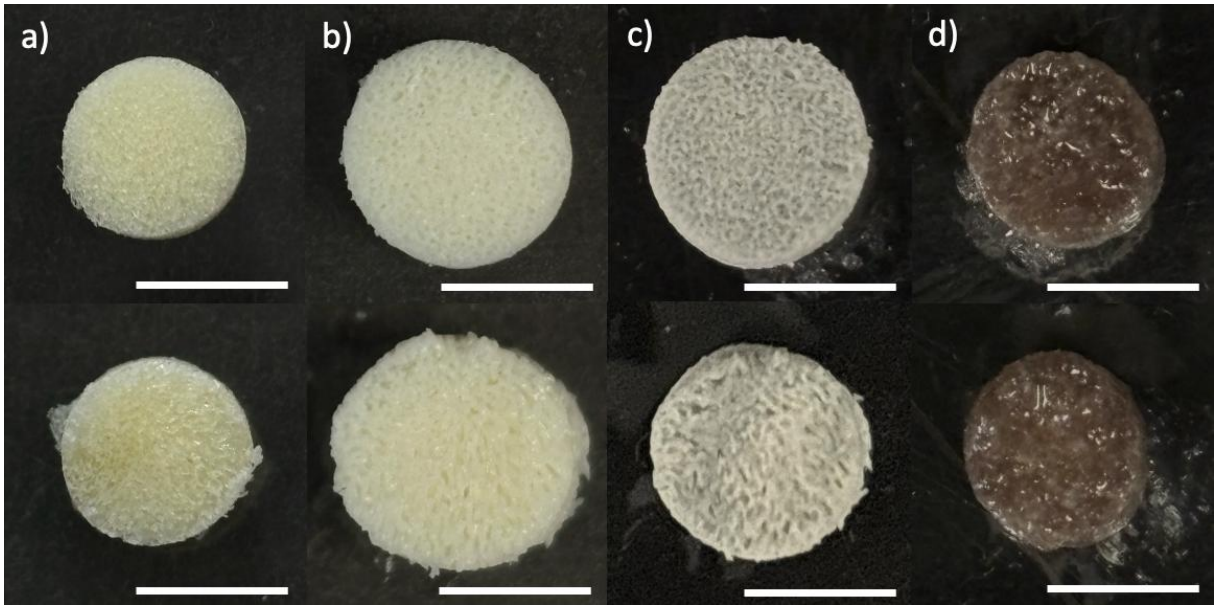

Figure S7. Experimental steps for the preparation of a porous hydrogel composed of 2% w/v sodium alginate (SA), 0.75% w/v chitosan (CHI) and 0.05% w/v genipin (GNP) with a PVA mold prepared from a PS/PVA 61/39 vol% blend annealed for 30 min (top row) and 60 min (bottom row). The hydrogel phase is colored by genipin. The steps are as follows: a) Porous PVA mold before injection of the gelling solution, after blend annealing, CNC machining and PS extraction; b) PVA mold after the injection of the solution at 2 °C; c) PVA mold + hydrogel 24 h after gelation at 37 °C in a humid oven; d) Porous hydrogel after the extraction of the PVA mold with water at 70 °C for 4 days. The white scale bar represents 0.5 cm.