*Supporting Information*

# Reactive 'Cellu-mers' – a Novel Approach to Improved Cellulose/Polymer Composites

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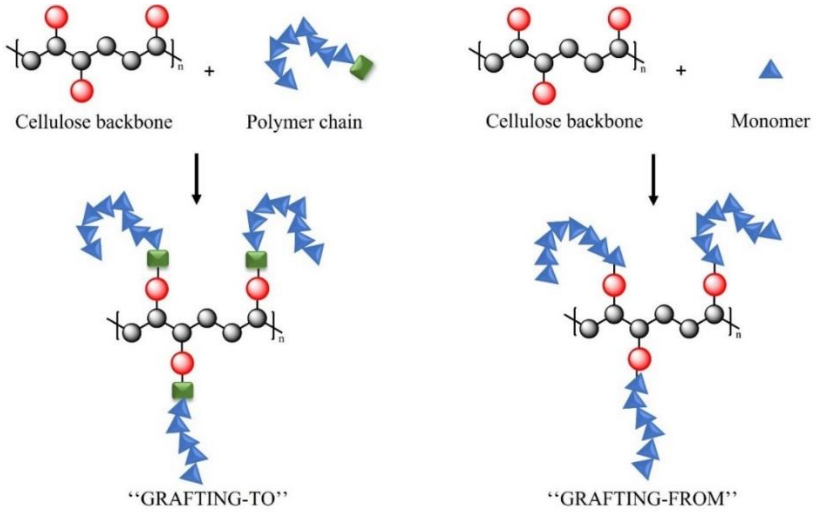


**Figure S1.** Schematic representation of the cellulose grafting approaches: ''grafting-to'' and ''grafting-from''. Red circles represent available reactive groups on cellulose chain, and green squares represent the reactive polymer chain end.

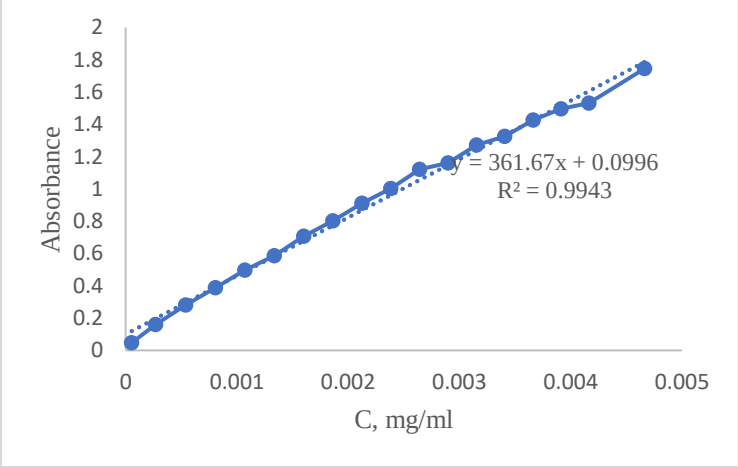


**Figure S2.** Calibration curve used to calculate the degree of substitution of St-modified compounds. 4-vinylbenzyl chloride UV-VIS absorbance at 265 nm was used.

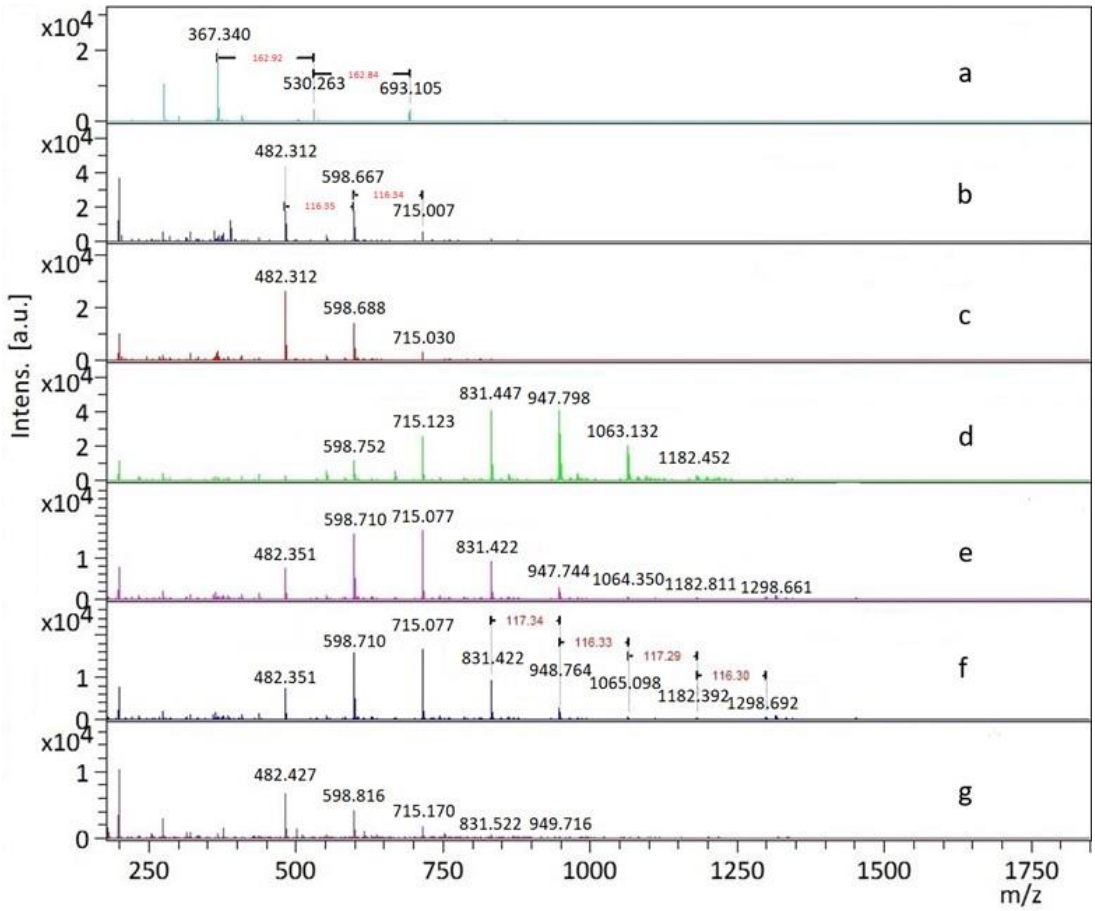


**Figure S3.** MALDI-TOF spectra of cellobiose-m obtained with various molar equivalents of 4-VBC at 25°C for 22 h. a) starting cellobiose; b-g) with added 1, 2, 4, 6, 8 and 30 equivalents of 4-VBC, respectively. DHB was used as a matrix.

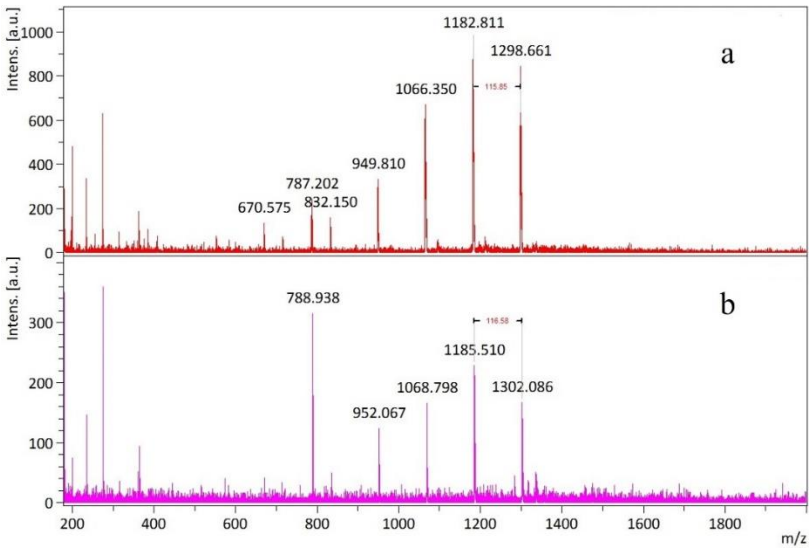


**Figure S4.** MALDI-TOF spectra of cellobiose-m with 4-VBC added at a) room temperature; b) 100°C. Reaction time 22 h, DHB used as a matrix.

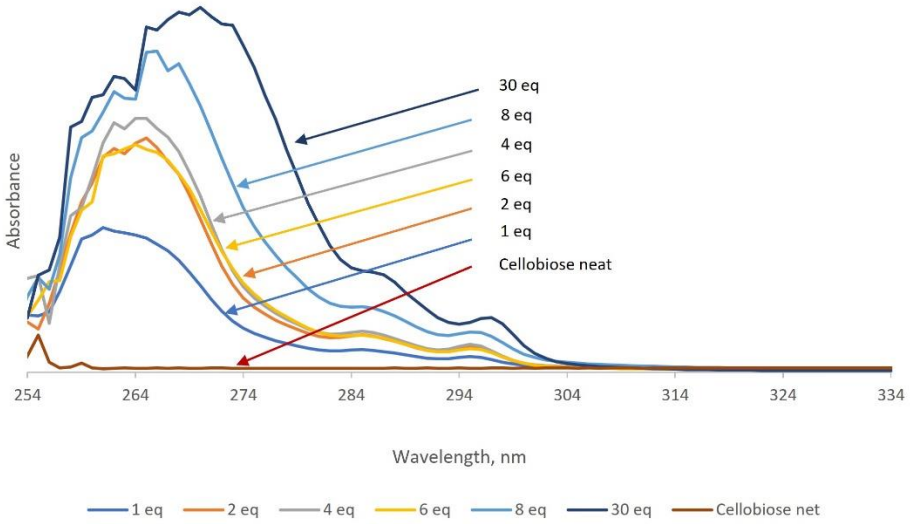


**Figure S5.** UV-Vis absorption spectra of cellobiose-m. Absorbance is increasing with the increase in number of molar equivalents of the 4-vinylbenzyl chloride used for modification:1-6) 1, 2, 4, 6, 8 and 30 equivalents of 4-VBC, respectively; spectrum of pure cellobiose (0 equivalents) is also included.

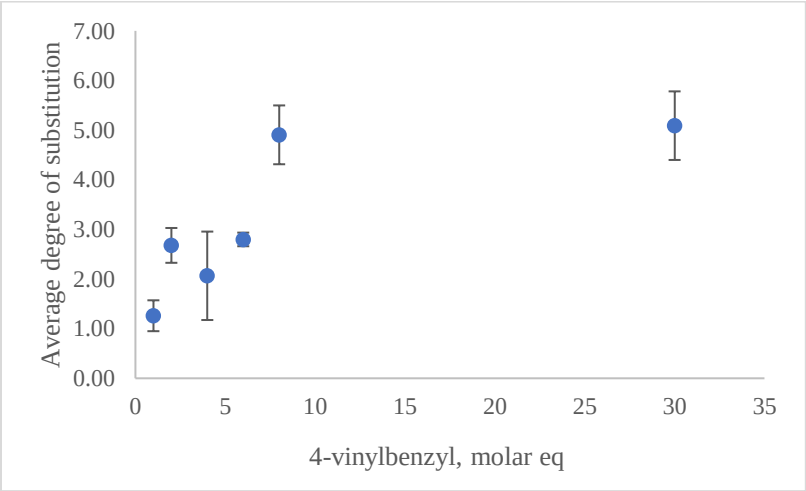


**Figure S6.** Degree of substitution of cellobiose-m at various 4-VBC molar equivalents. Calculated using the UV calibration curve at 265 nm (Figure S2).

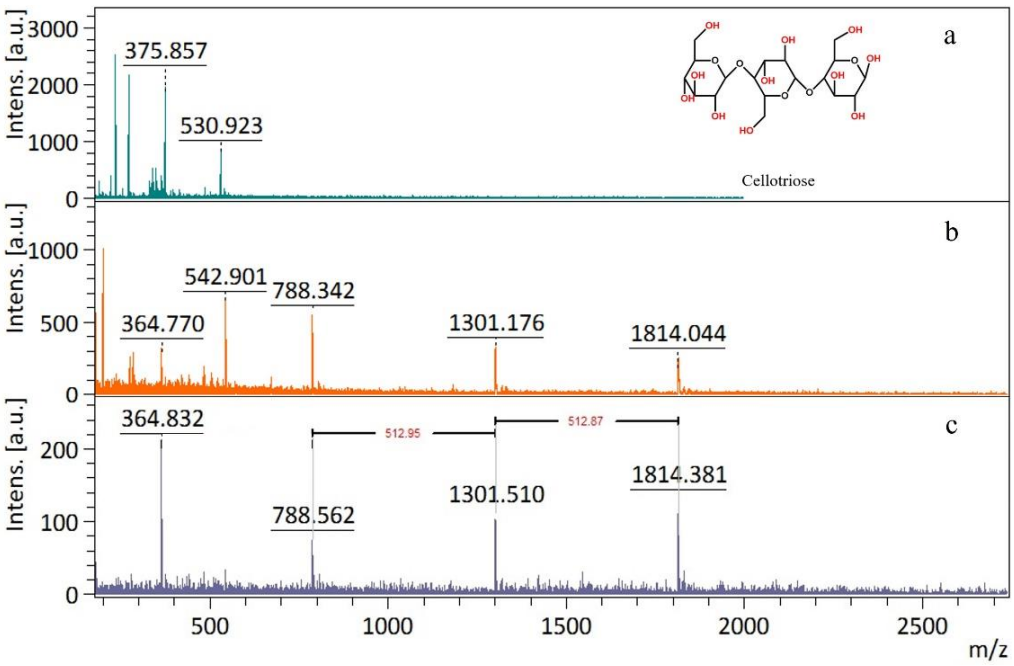


**Figure S7.** MALDI-TOF spectra of cellotriose modification. a) net cellotriose; b) cellotriose reaction mixture after 16 h of the reaction; c) modified cellotriose after 24 h of the reaction. DHB was used as the matrix.

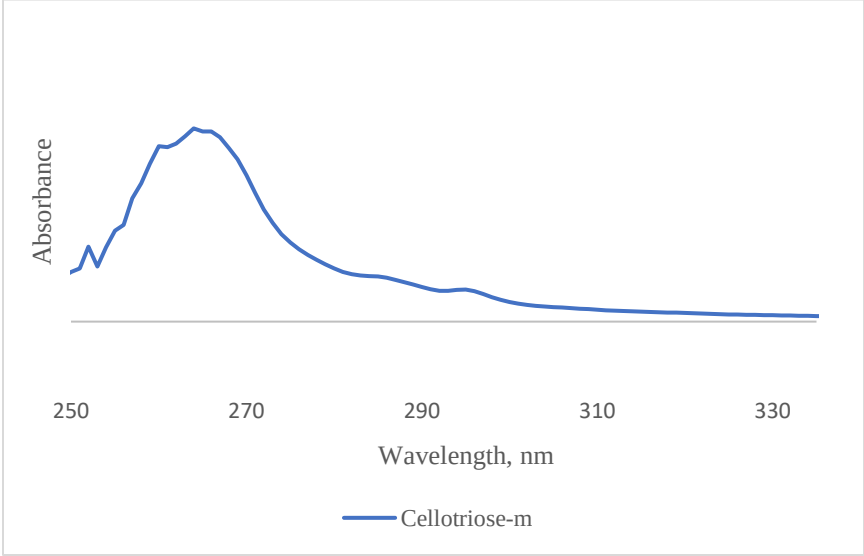


**Figure S8.** UV-Vis absorption spectrum of modified cellotriose. DS was calculated using the UV calibration curve at 265 nm (Figure S2).

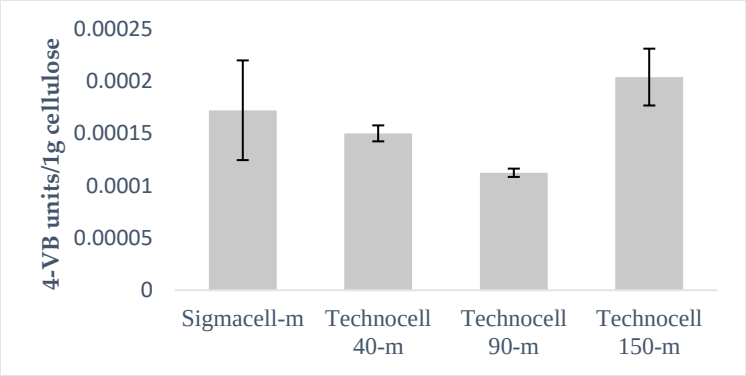


**Figure S9.** Calculated amount of the number of 4-VBC groups attached to 1g of cellulose using four different types of cellulose. Values were calculated using the calibrated UV-Vis absorbance at 265 nm.

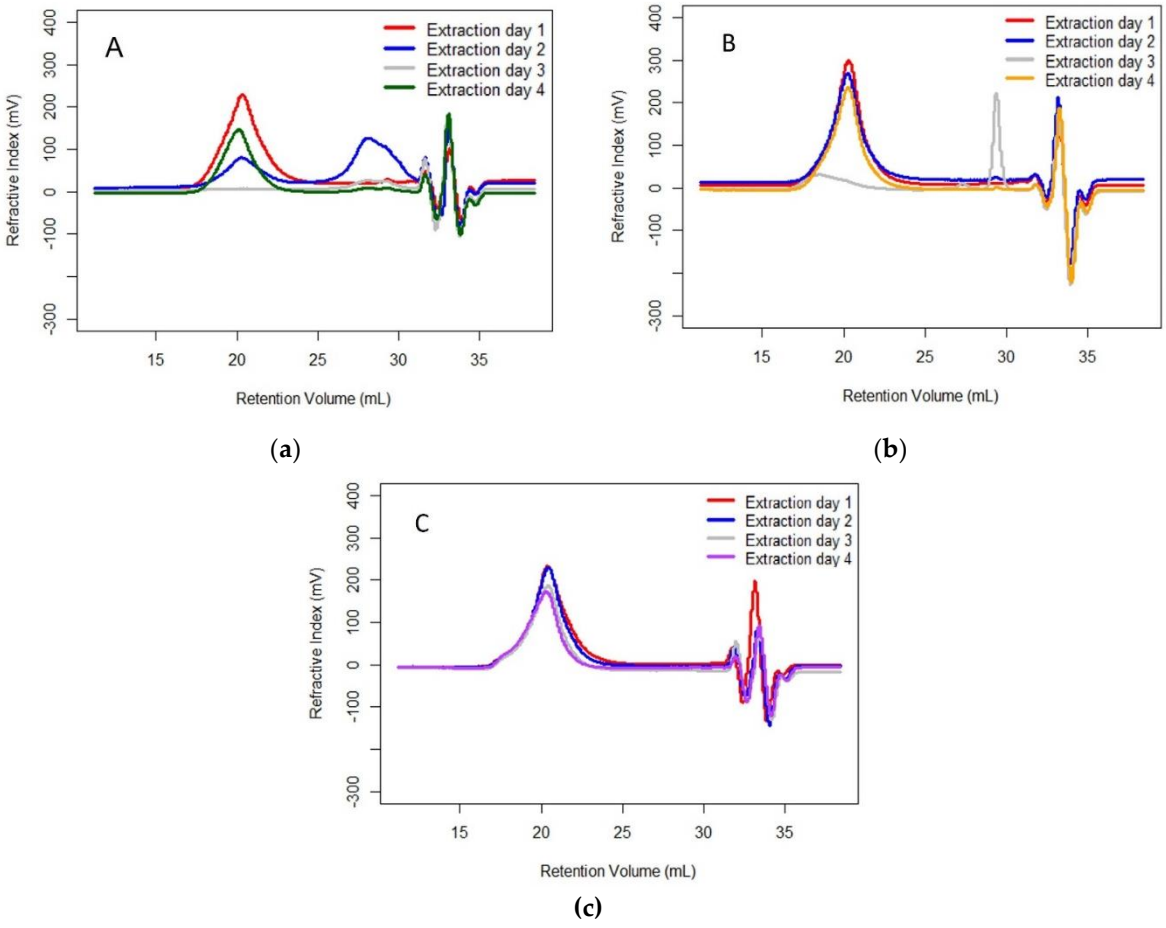


**Figure S10.** SEC chromatograms of PSt samples extracted from cellobiose-m (A), cellotriose-m (B) and Sigmacell-m (C) based semi-IPNs.

**Table S1.** Molecular mass and dispersity index (Đ) of non-crosslinked PSt extracted from cellobiose-m (CB-PSt), cellotriose-m (CTR-PSt), Sigmacell-m (CELL-PSt) gels and of PSt polymerized in a presence of a non-modified carbohydrate filler.

| **PSt network** | **Mn, kDa** | **Đ** |
|---|---|---|
| CB-PSt | | |
| Day 1 | 70,500 | 3.04 |
| Day 2 | 65,000 | 3.17 |
| Day 3 | 155,000 | 5.58 |
| | 1,800 | 1.04 |
| | 360 | 1.07 |
| Day 4 | 76,000 | 2.99 |
| CTR-PSt | | |
| Day 1 | 55,500 | 3.55 |
| | 386 | 1.07 |
| Day 2 | 60,000 | 3.03 |
| | 460 | 2.56 |
| Day 3 | 570 | 1.87 |
| Day 4 | 81,000 | 2.65 |
| CELL-PSt, 1w% | | |
| Day 1 | 50,000 | 5.01 |
| Day 2 | 64,000 | 3.99 |
| Day 3 | 79,000 | 3.77 |
| Day 4 | 98,000 | 3.49 |
| CELL-PSt, 5w% | | |
| Day 1 | 47,800 | 6.1 |
| CELL-PSt, 10w% | | |
| Day 1 | 32,500 | 4.24 |
| Mixtures | | |
| PSt/CB | 60,300 | 2.10 |
| PSt/CTR | 76,000 | 1.60 |
| PSt/CELL | 51,500 | 2.10 |

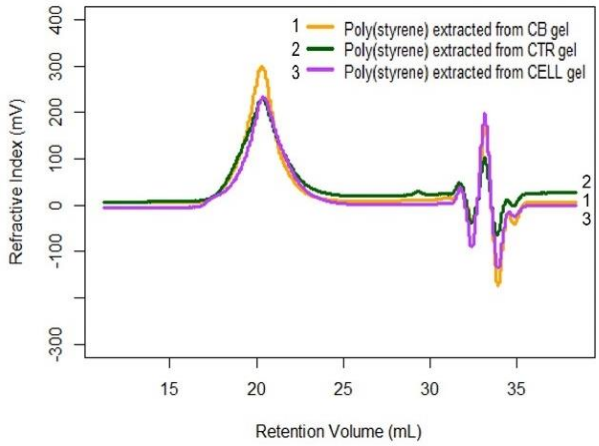


**Figure S11.** SEC chromatograms of poly(styrene) samples extracted after 24 h from (1) cellobiose-m (CB- gel), (2) cellotriose-m (CTR- gel), and (3) Sigmacell-m (CELL- gel) based networks.

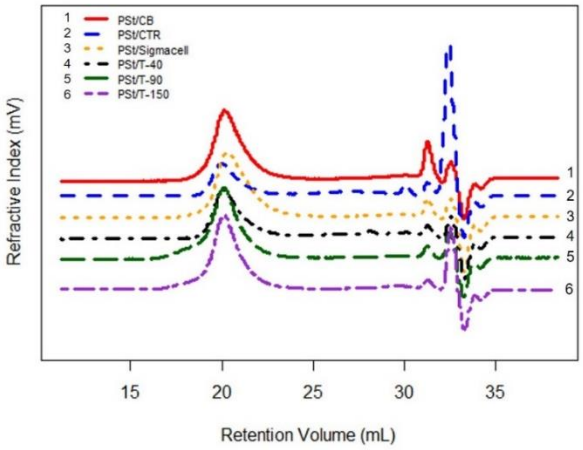


**Figure S12.** SEC chromatorgrams of PSt formed in the presence of non-modified fillers. 1) PSt formed in the presence of cellobiose; 2) PSt formed in the presence of cellotriose; 3) PSt formed in the presence of Sigmacell cellulose; 4) PSt formed in the presence of T-40 cellulose; 5) PSt formed in the presence of T-90 cellulose; 6) PSt formed in the presence of T-150 cellulose.

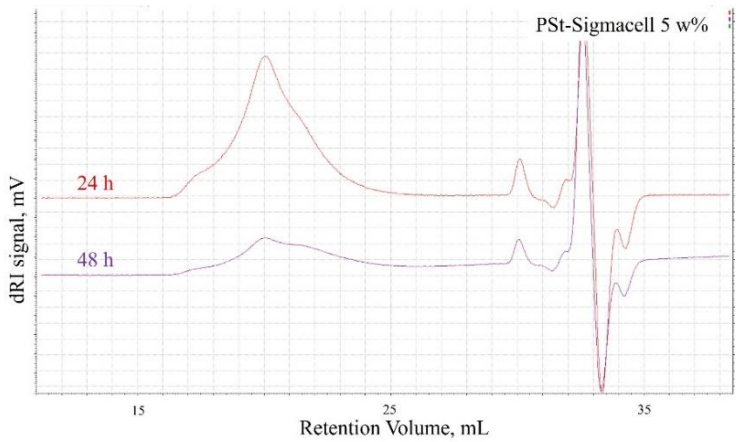


**Figure S13.** SEC chromatograms of PSt samples extracted from Sigmacell-m based semi-IPN with 5 w% of a filler. Extracted for 24 and 48 hours.

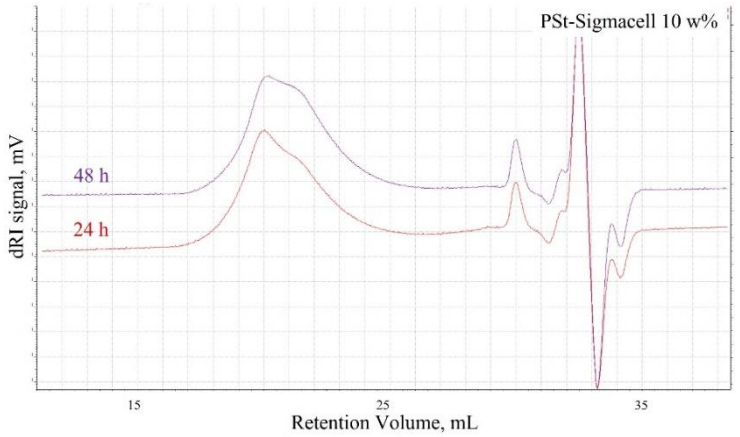


**Figure S14.** SEC chromatograms of PSt samples extracted from Sigmacell-m based semi-IPN with 10 w% of a filler. Extracted for 24 and 48 hours.

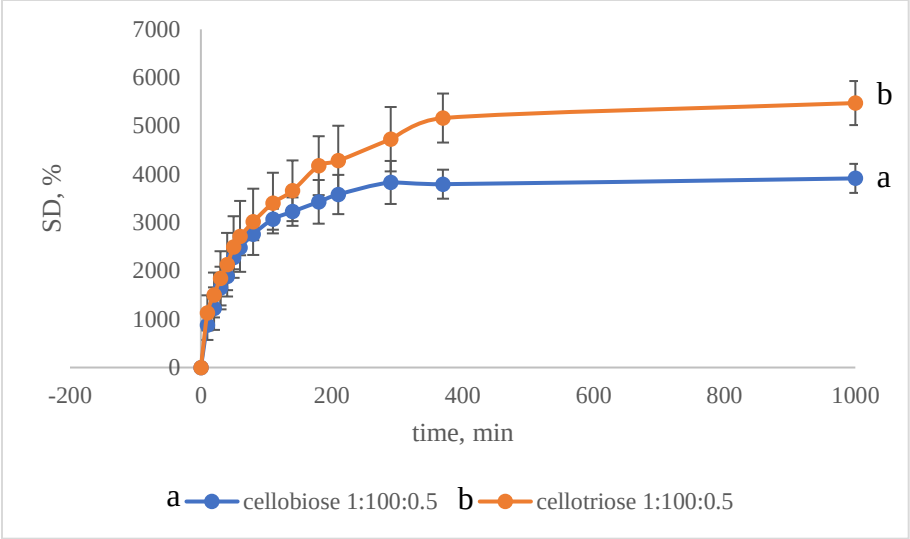


**Figure S15.** Swelling degree (SD, %) of PSt gels containing multi-functional cellobiose-m (a) and cellotriose-m (b) as crosslinks.

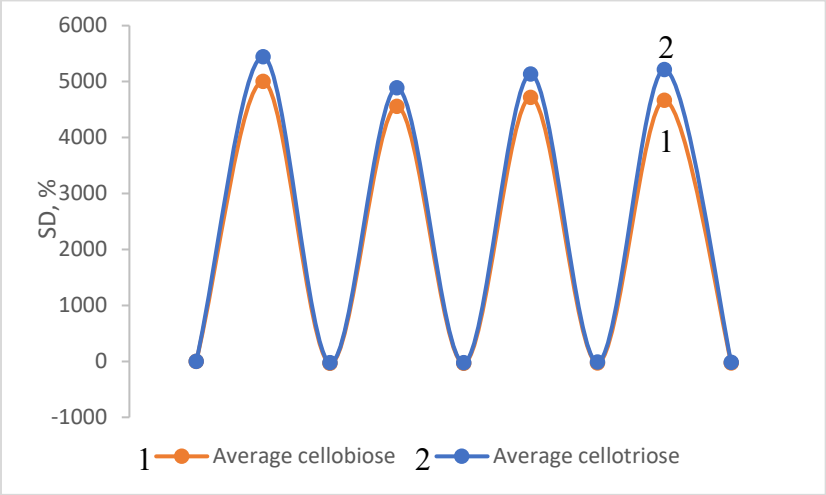


**Figure S16.** Swelling/deswelling capabilities of networks with cellobiose-m (1) and cellotriose-m (2). Four cycles are shown.

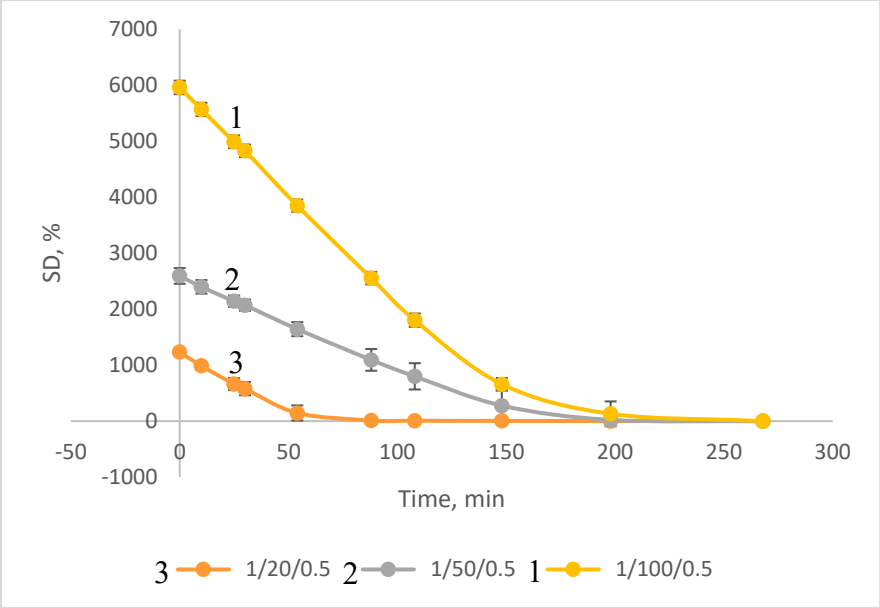


**Figure S17.** Deswelling of the gel with different components ratio. 1) 1/100/0.5; 2) 1/50/0.5; 3) 1/20/0.5

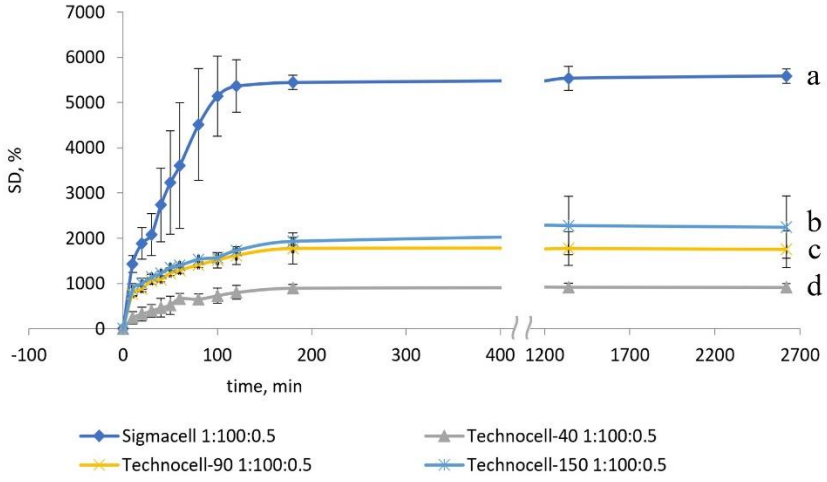


**Figure S18.** SD of the CNF-m gels formed with the same reagents' ratio. a) Sigmacell 1:100:0.5; b) Technocell-150 1:100:0.5; c) Technocell-90 1:100:0.5; d) Technocell-40 1:100:0.5.

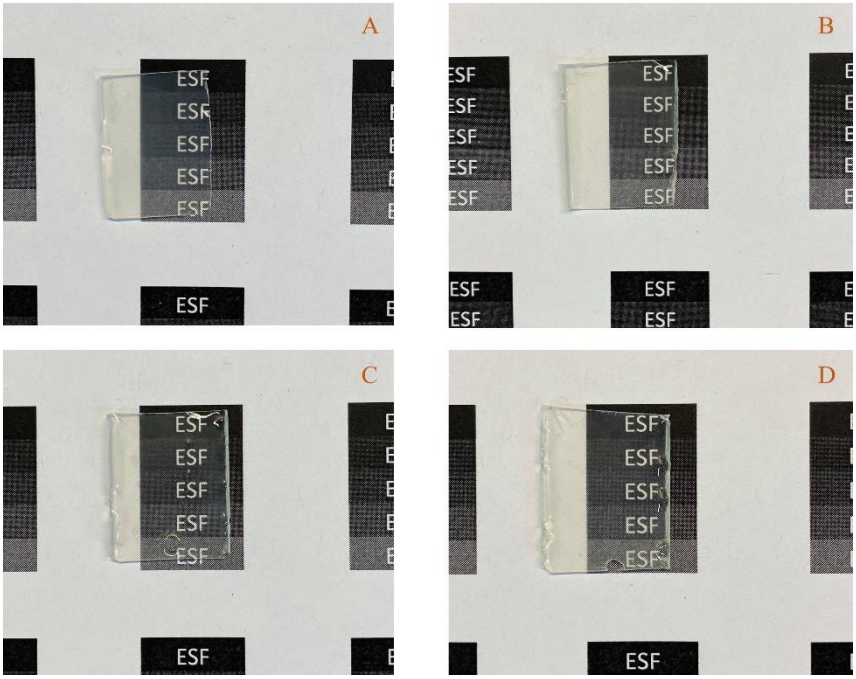


**Figure S19.** Opacity of PSt/cellulose composites. Material thickness -1.5 mm. A) Sigmacell-m composite, B) T-40-m composite, C) T-90-m composite, D) T-150-m composite.

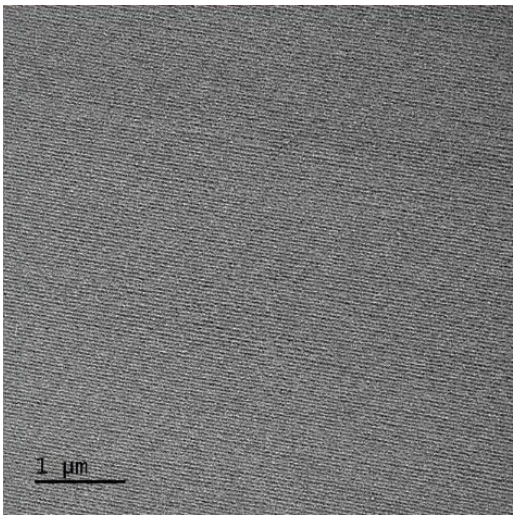


**Figure S20.** Transmission electron micrograph of PSt, stained with 2% uranyl acetate, magnification 8000×.

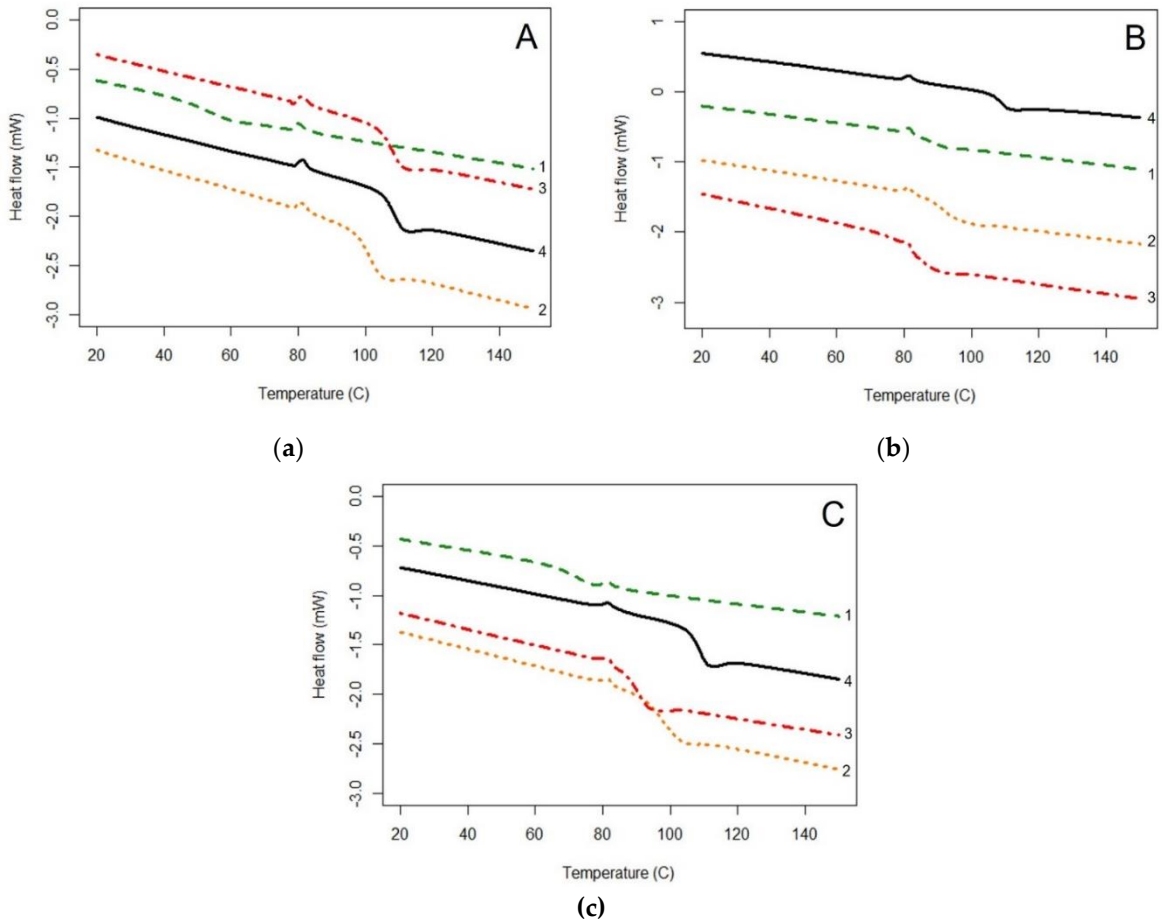


**Figure S21.** DSC thermograms of synthesized materials: A) cellobiose-m materials; B) cellotriose-m materials; C) Sigmacell-m materials. Numbers indicate: (1) linear poly(styrene) extracted from the corresponding network, (2) filler/poly(styrene) mixture, (3) not extracted semi-IPN, (4) Extracted network.