Self-sorting multi-scale materials by self-assembling multi-component nanostructured gels in non-woven fabrics

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SUPPORTING INFORMATION

S1 General experimental methods
S2 Gel formation and tabletop gel studies
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S4 ^{1}H NMR Studies
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S1 General experimental methods

All chemicals and solvents were purchased from commercial suppliers (Sigma Aldrich, Alfa Aesar or VWR) and used as provided. T_{gel} measurements were obtained using a high precision thermoregulated oil bath at a heating rate of 0.5 °C min^{-1} using tube inversion to determine the T_{gel} values. Rheological measurements were obtained using a Malvern Instruments Kinexus Pro+ rheometer fitted with 20 mm parallel plate geometry using a 2.5 mm gap at 25 °C, with data being analysed using rSpace software. ^{1}H NMR spectra were recorded on a JEOL ECX400 (^{1}H 400 MHz, ^{13}C 100 MHz) spectrometer. SEM images were obtained on a FEI Sirion XL30 or a JEOL 7800F Prime after splutter coating with 6 nm of Pt/Pd at a density of 19.52 g cm^{-3}.

S2 Gel formation and tabletop gel studies

Gel formation. A known amount of gelator was accurately weighed into a 2 mL glass vial with an internal diameter of 9 mm. A Gilson pipette was used to add solvent to the vial. The sample was heated to just below the boiling point of the solvent with the cap on until the gelator dissolved and a homogeneous solution formed. The sample was then left overnight at room temperature to cool, forming a gel.

Minimum gelation concentration (MGC). Gels of decreasing concentration were formed. A sample of each concentration in a 2 mL glass vial with an internal diameter of 9 mm, was inverted to identify if the gel was self-supporting under gravity. The lowest concentration at which the gel could support its own weight when inverted was reported as the minimum gelation concentration (MGC).

T_{gel} measurements. The temperature at which the gel sample was converted to a sol (T_{gel}) was determined using the vial 'inversion' method. Gels were made in 2 mL transparent screw-capped vials with an internal diameter of 9 mm and a solvent volume of 0.5 mL. The gel was immersed and heated in a thermostated oil bath with a 0.5 °C min^{-1} ramp. At each 0.5 °C temperature increment, the gel was removed from the oil bath and inverted. The temperature at which the gel could no longer hold its own weight upon inversion of the vial was recorded as the T_{gel}.

Table S1. T_{gel} values of 0.6 wt/v% DBS with a range of loadings of BTA, indicating that the thermal properties of the DBS gel remain essentially constant in the presence of BTA.

DBS (% wt/vol)	BTA (% wt/vol)	T_{gel} (°C) 2-butanone	T_{gel} (°C) methanol
0.6	0.1	40	40
0.6	0.2	40	40
0.6	0.3	41	42
0.6	0.4	39.5	40
0.6	0.5	39.5	40
0.6	0.6	41	41
0.6	0.7	39	42.5
0.6	0.9	41.5	42.5

S3 Rheology

All gels (1 mL volume) were prepared in a transparent 5 mL vial with an internal diameter of 13 mm, then de-moulded using a spatula and carefully transferred onto the bottom plate. Oscillatory amplitude sweeps were performed from 0.05% to 50% strain at 1 Hz, to determine the linear viscoelastic region (LVR) for each sample. Oscillatory frequency sweeps were performed from 0.1 Hz to 50 Hz under a shear strain of 0.1%, which was within the linear viscoelastic region for all samples, and G’ values were extracted from the data.

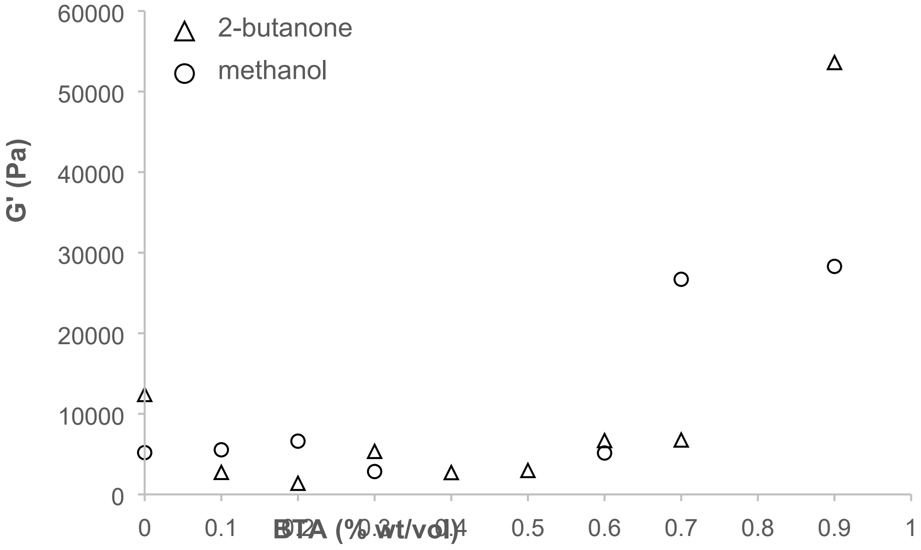

Figure S1. G’ values from frequency sweep rheological analysis of mixtures containing 0.6% wt/vol DBS and varying loadings of BTA in either methanol or 2-butanone as solvent. Data indicate that stiffness is significantly increased in the presence of higher BTA loadings.

S4 ^{1}H NMR Studies

A known amount of gelator was accurately weighed into a 2 mL glass vial. Deuterated methanol was added (1 mL) and then 2 µl of DMSO added as internal standard. Gilson pipettes were used to add solvent to the vial. The sample was heated to just below the boiling point of the solvent with the cap on until the gelator dissolved and a homogeneous solution formed. The sample was then transferred into a NMR tube and left overnight to form a gel. Where more than one gelator was present, each gelator was weighed separately then dissolved in 0.5 mL methanol spiked with 1 µl of DMSO before being mixed as two solutions in a glass vial then transferred to a NMR tube.

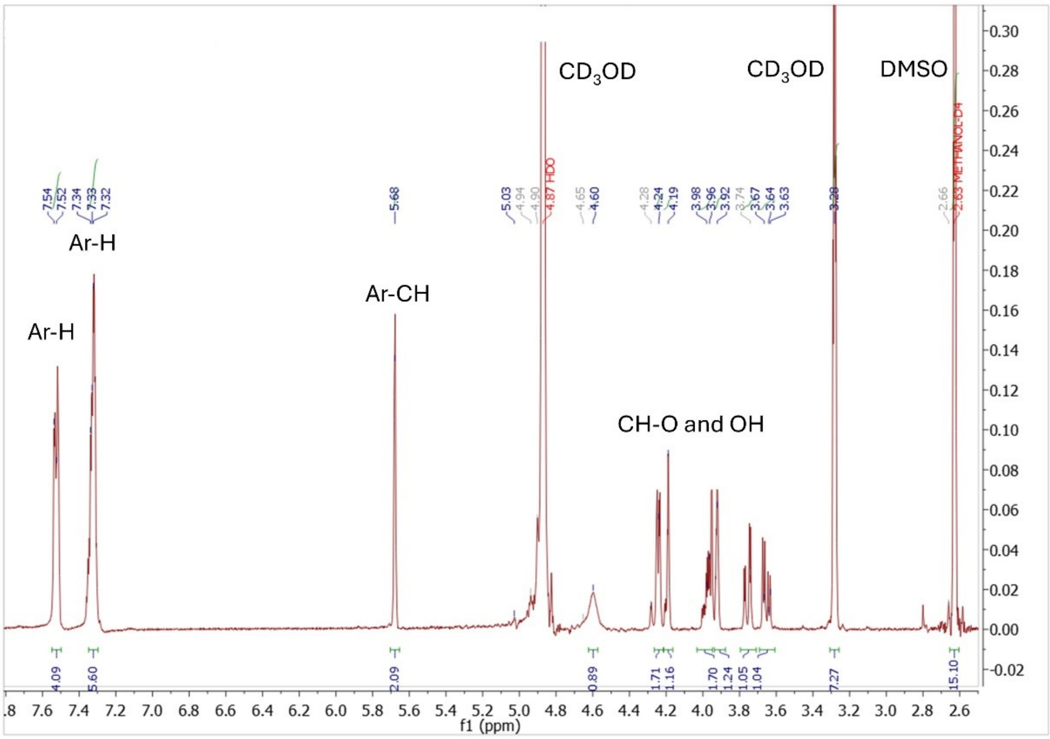

Figure S2. ^{1}H NMR spectrum of gel formed by 0.6% wt/vol DBS in deuterated methanol with DMSO present as internal standard, allowing the quantification of mobile DBS in the gel.

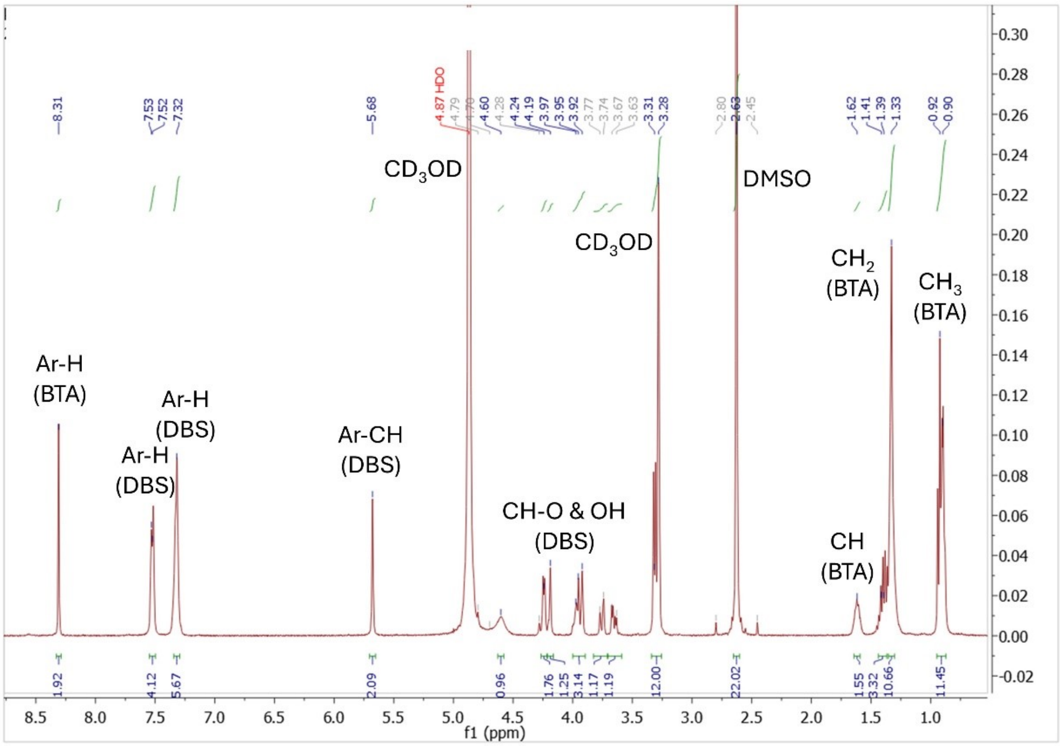

Figure S3. ^{1}H NMR spectrum of gel formed by 0.6% wt/vol DBS and 0.6%wt/vol BTA in deuterated methanol with DMSO present as internal standard, allowing the quantification of mobile DBS and BTA in the gel.

S5 SEM Imaging

SEM samples were prepared by weighing a known mass of gelator into 2 mL vials, followed by the addition of 0.5 mL of solvent. The samples were then heated until all the gelator had dissolved. A few drops of the solution were then pipetted directly onto the SEM stub and left to dry overnight at ambient conditions. Fabric samples were prepared using a dipping methodology. A known amount of gelator was weighed into a 10 mL vial, followed by addition of 2 mL of solvent. The sample was then heated to dissolve the gelator, and then the whole solution was poured into a metal weighing boat containing the pre-weighed fabric. The fabric was left to soak in the solution for 5 min, before removing and placing on an aluminium block to dry. After drying overnight, the samples were reweighed and stuck onto the SEM stubs using double-sided tape.

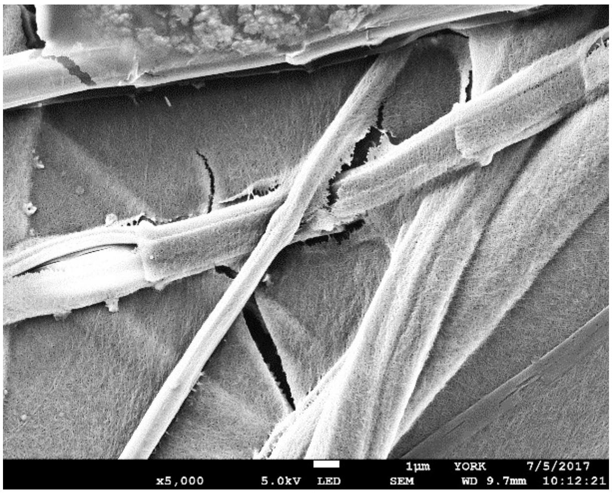

Figure S4. SEM image of DBS and BTA gel (0.6% wt/vol of each component) dried from methanol showing large rigid BTA nanofibres and smaller flexible DBS nanofibres spanning between them. Scale bar 1µm.

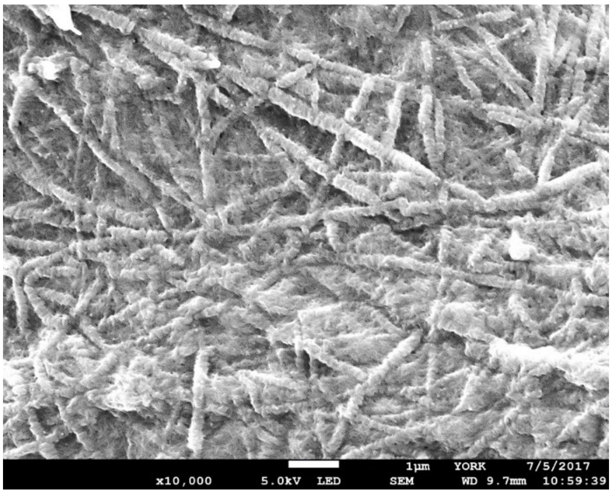

Figure S5. SEM image of DBS and BTA gel (0.6% wt/vol of each component) dried from 2-butanone showing smaller more flexible BTA fibres than in the case of methanol and very small DBS nanofibres forming a network between them. Scale bar 1 µm.

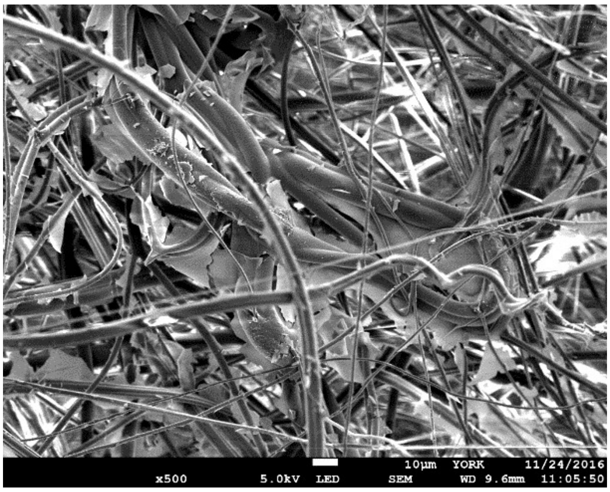

Figure S6. SEM image of DBS (0.4% wt/vol) dried from 2-butanone onto non-woven fabric showing some sheet like aggregates of small nanofibres spanning between fabric fibres. Scale bar 10 μm.

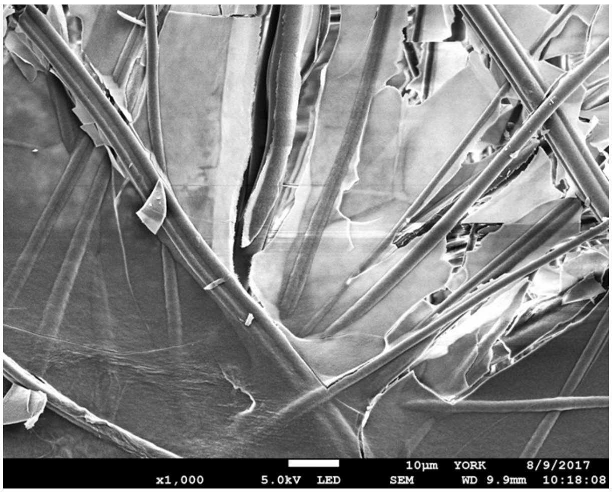

Figure S7. SEM image of DBS (0.6% wt/vol) dried from 2-butanone onto non-woven fabric showing sheet like aggregates of small nanofibres spanning across the whole sample between larger fabric fibres. Scale bar 10 μm.

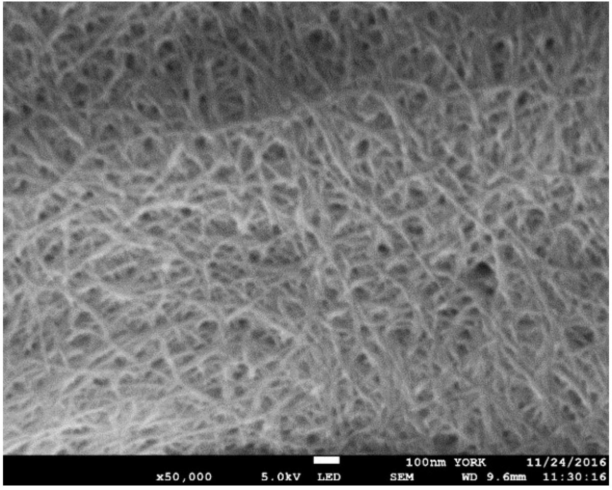

Figure S8. SEM image of DBS (0.6% wt/vol) dried from 2-butanone onto non-woven fabric zoomed in onto the sheet-like DBS aggregates, showing the small nanofibres that comprise these objects that span across the whole sample. Scale bar 100 nm.

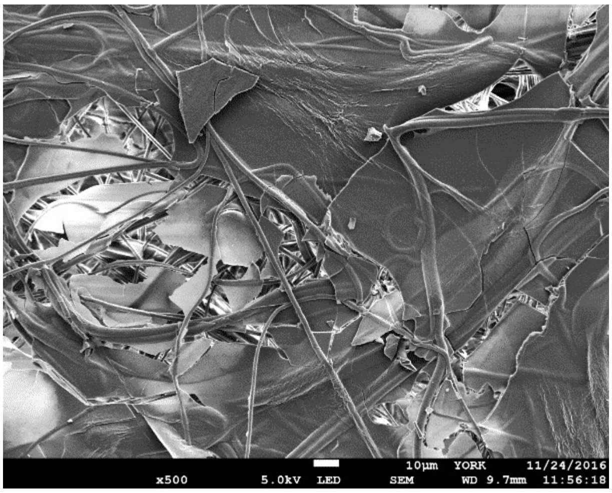

Figure S9. SEM image of DBS (1.0% wt/vol) dried from 2-butanone onto non-woven fabric showing sheet like aggregates of small nanofibres between larger fabric fibres. Scale bar 10 μm.

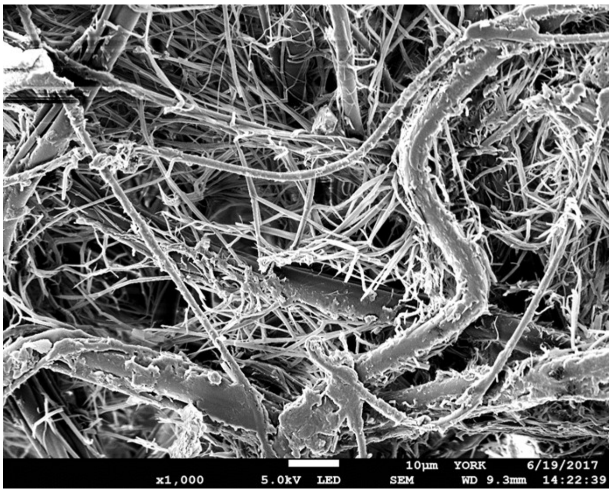

Figure S10. SEM image of BTA (0.6% wt/vol) dried from 2-butanone onto non-woven fabric showing larger fabric fibres and smaller BTA nanofibres. Scale bar 10 μm.

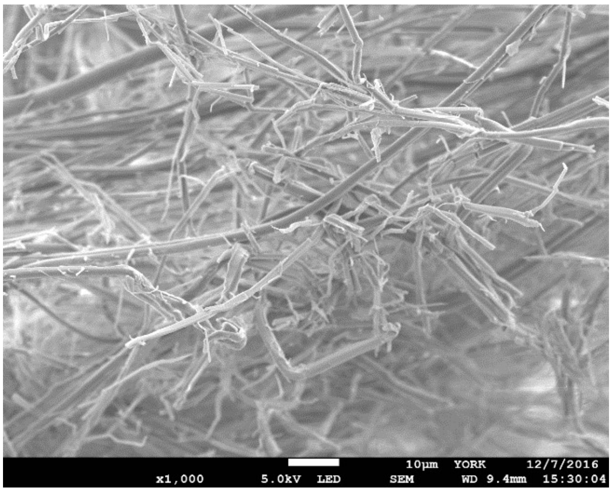

Figure S11. SEM image of BTA (0.6% wt/vol) dried from methanol onto non-woven fabric showing larger fabric fibres and smaller BTA nanofibres. Scale bar 10 μm.

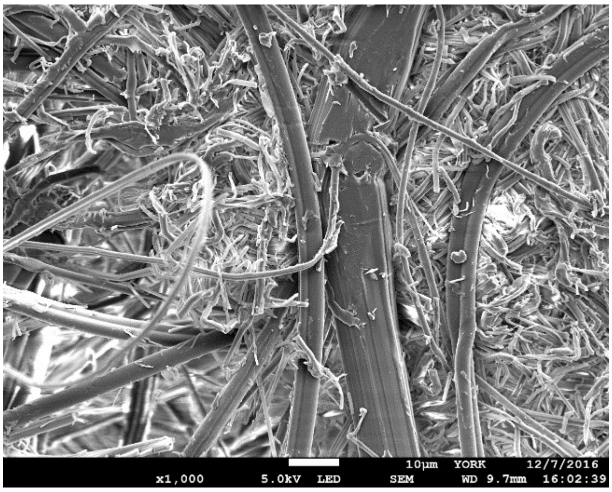

Figure S12. SEM image of BTA (1.0% wt/vol) dried from methanol onto non-woven fabric showing larger fabric fibres and smaller BTA nanofibres present at higher loading than when using a 0.6% wt/vol sample. Scale bar 10 μm.

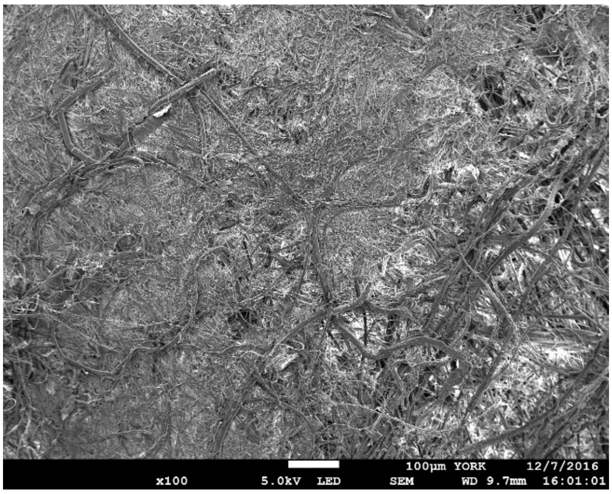

Figure S13. SEM image of BTA (1.0% wt/vol) dried from methanol onto non-woven fabric – zoomed out view showing sample-spanning nature of larger fabric fibres and smaller BTA nanofibres present at higher loading than when using a 0.6% wt/vol sample. Scale bar 100 μm.

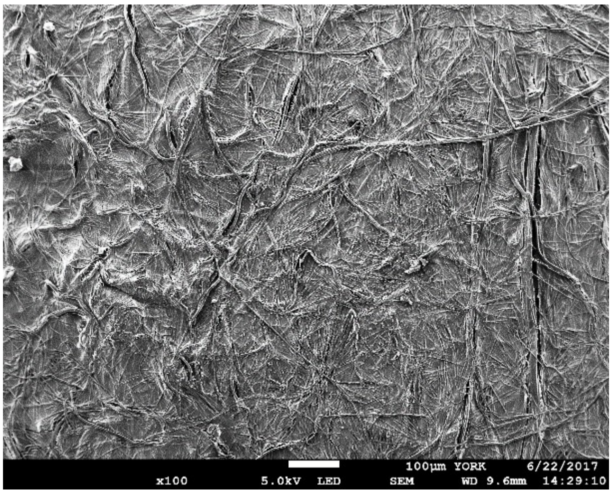

Figure S14. SEM image of DBS and BTA (each 0.6% wt/vol) dried from methanol onto non-woven fabric zoomed out to show sample spanning three-fibre self-sorted system. Scale bar 100 μm.

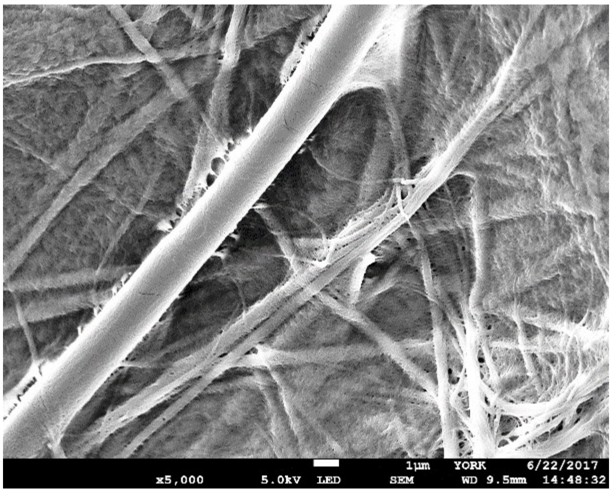

Figure S15. SEM image of DBS and BTA (each 0.6% wt/vol) dried from 2-butanone onto non-woven fabric showing the three-fibre self-sorted system in one of the homogeneous regions. Scale bar 1 μm.

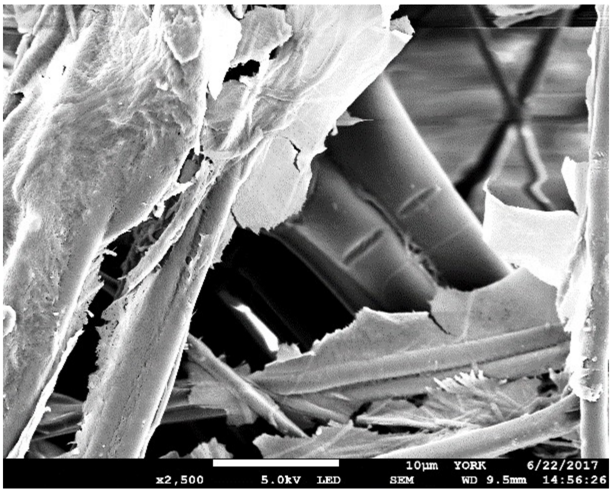

Figure S16. SEM image of DBS and BTA (each 0.6% wt/vol) dried from 2-butanone onto non-woven fabric showing the three-fibre self-sorted system in one of the regions where aggregation has led to porosity. Scale bar 1 μm.

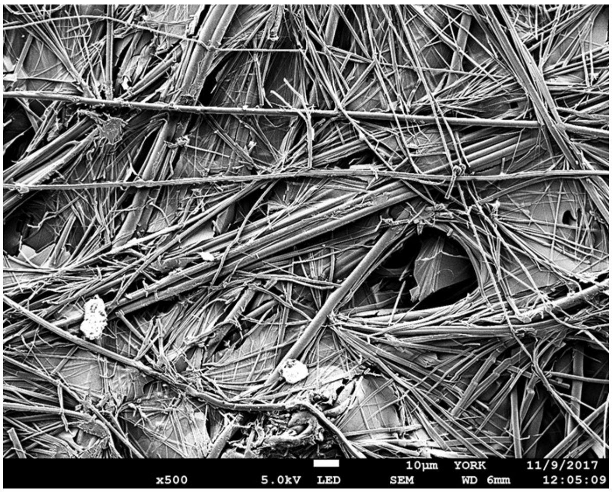

Figure S17. SEM image of DBS and BTA (each 0.3% wt/vol) dried from methanol onto non-woven fabric showing sample spanning nature of the three-fibre self-sorted system. Scale bar 10 μm.

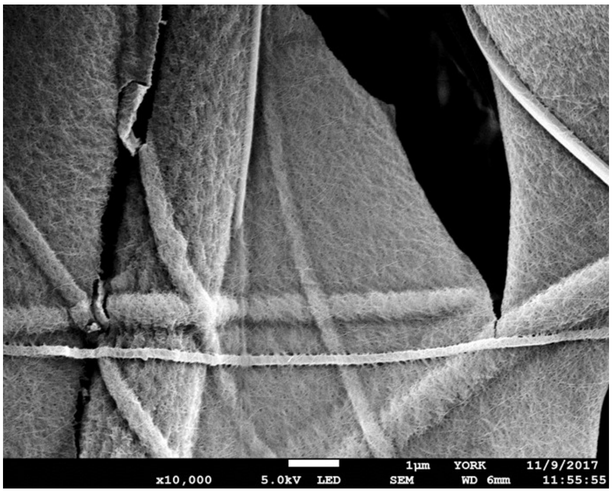

Figure S18. SEM image of DBS and BTA (each 0.3% wt/vol) dried from methanol onto non-woven fabric zoomed in to clearly show the three different types of self-sorted fibres. Scale bar 1 μm.

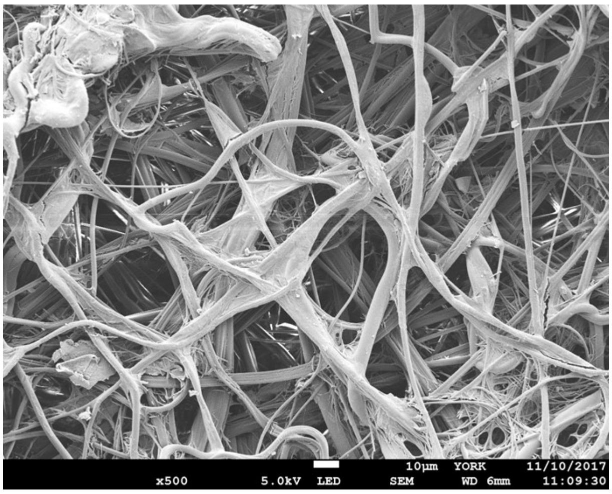

Figure S19. SEM image of DBS and BTA (each 0.3% wt/vol) dried from 2-butanone onto non-woven fabric. Scale bar 10 μm.

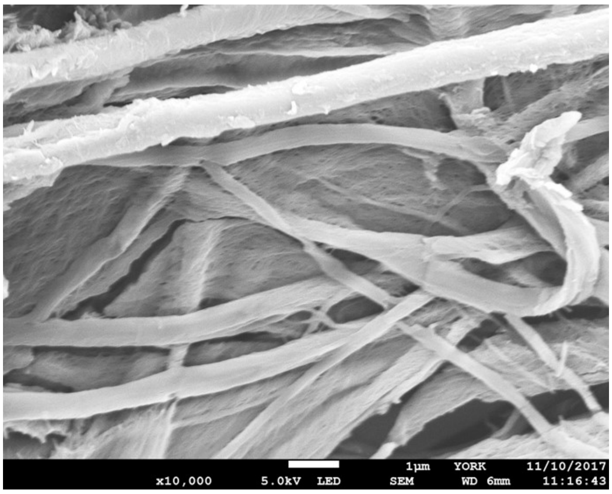

Figure S20. SEM image of DBS and BTA (each 0.3% wt/vol) dried from 2-butanone onto non-woven fabric zoomed in to clearly show the three different types of self-sorted fibres. Scale bar 1 μm.

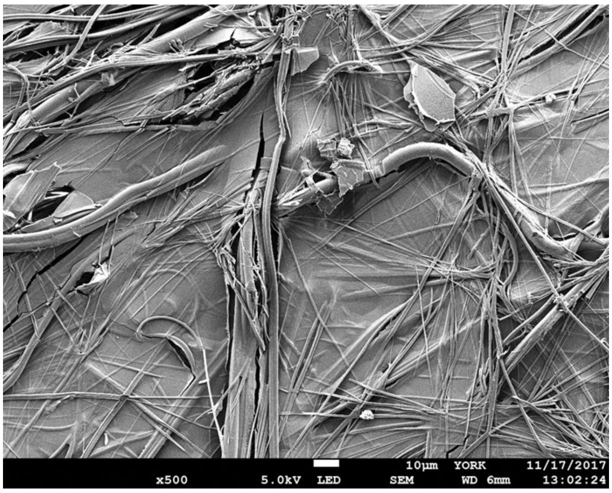

Figure S21. SEM image of DBS (0.4% wt/vol) and BTA (0.2% wt/vol) dried from methanol onto non-woven fabric showing sample spanning nature of the three-fibre self-sorted system with a lower loading of BTA nanofibres. Scale bar 10 μm.

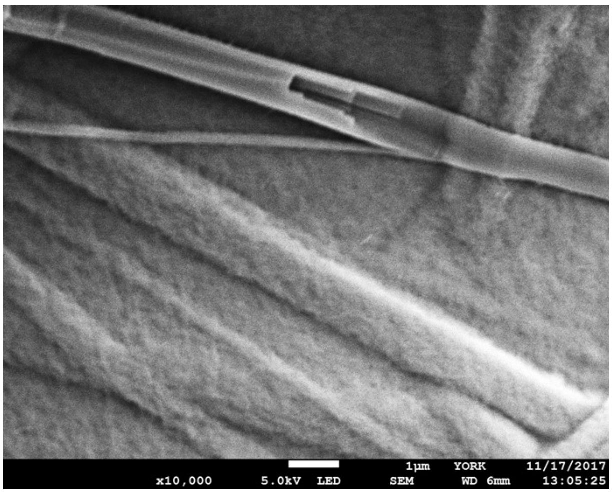

Figure S22. SEM image of DBS (0.4% wt/vol) and BTA (0.2% wt/vol) dried from methanol onto non-woven fabric zoomed in to show the three different nanofibres in the self-sorted system. Scale bar 1 μm.

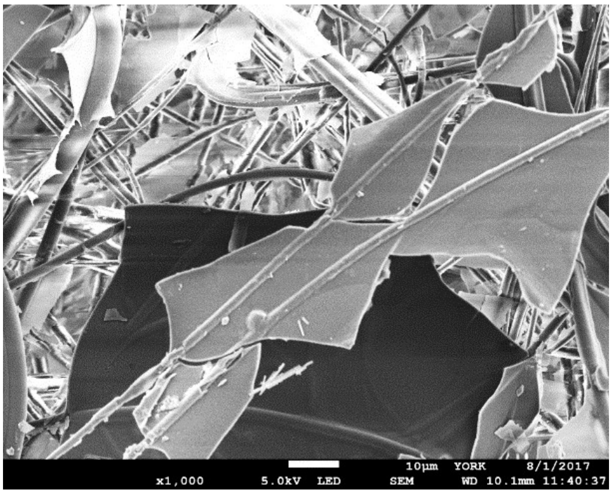

Figure S23. SEM image of DBS (0.4% wt/vol) dried from methanol onto non-woven fabric showing regions of sheet-like aggregates of DBS. Scale bar 10 μm.

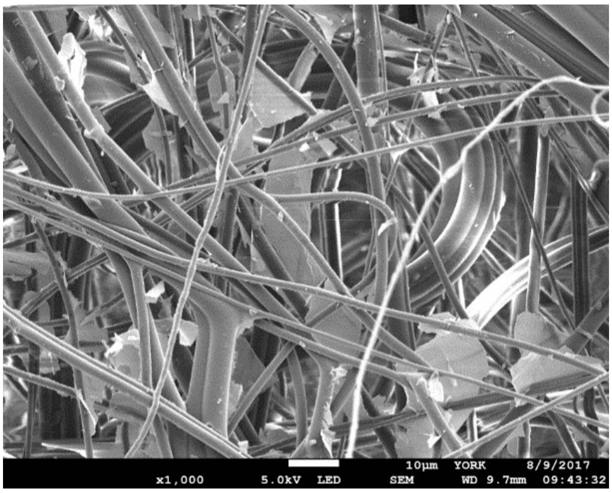

Figure S24. SEM image of DBS (0.4% wt/vol) dried from 2-butanone onto non-woven fabric showing regions of sheet-like aggregates of DBS. Scale bar 10 μm.

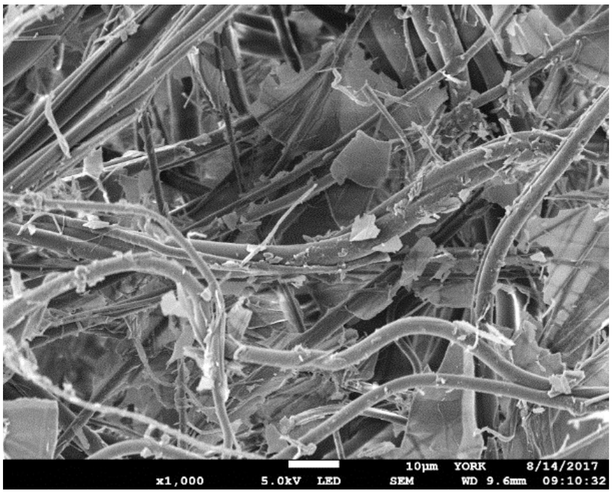

Figure S25. SEM image of DBS (0.3% wt/vol) and BTA (0.1%) dried from methanol onto non-woven fabric showing regions of sheet-like aggregates of DBS and a small number of BTA nanofibres. Scale bar 10 μm.

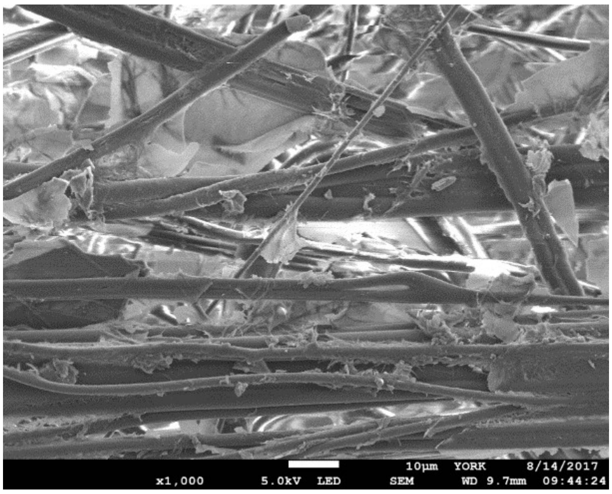

Figure S26. SEM image of DBS (0.3% wt/vol) and BTA (0.1%) dried from 2-butanone onto non-woven fabric showing regions of sheet-like aggregates of DBS and a small number of BTA nanofibres. Scale bar 10 μm.

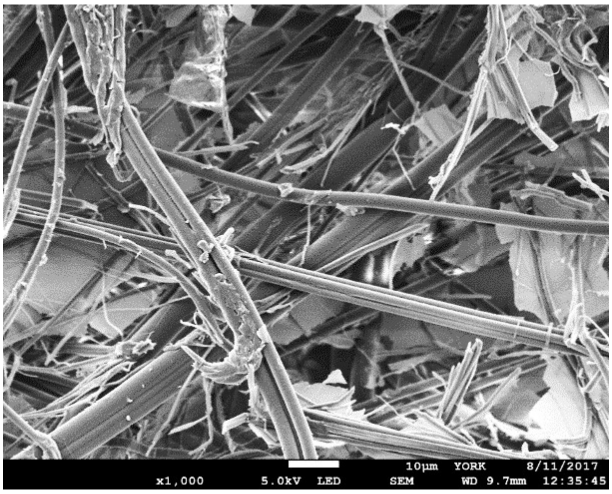

Figure S27. SEM image of DBS (0.2% wt/vol) and BTA (0.2%) dried from methanol onto non-woven fabric showing regions of sheet-like aggregates of DBS and some BTA nanofibres. Scale bar 10 μm.

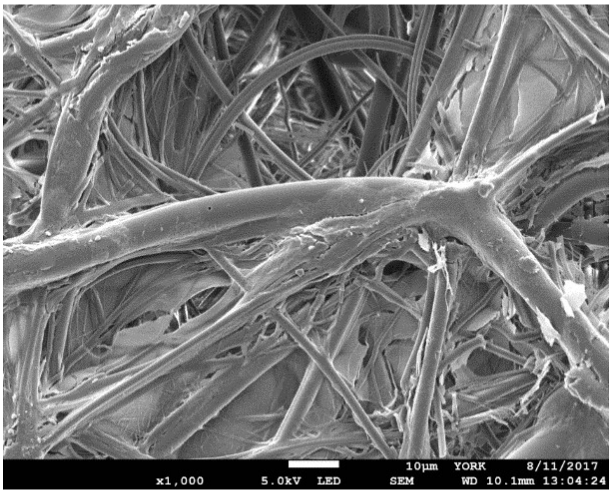

Figure S28. SEM image of DBS (0.2% wt/vol) and BTA (0.2%) dried from 2-butanone onto non-woven fabric showing regions of sheet-like aggregates of DBS and some BTA nanofibres. Scale bar 10 μm.

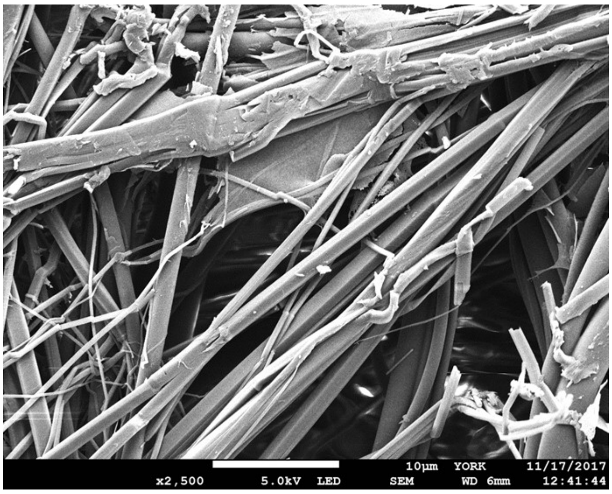

Figure S29. SEM image of DBS (0.1% wt/vol) and BTA (0.3%) dried from methanol onto non-woven fabric showing a small number of regions of sheet-like aggregates of DBS and BTA nanofibres. Scale bar 10 μm.

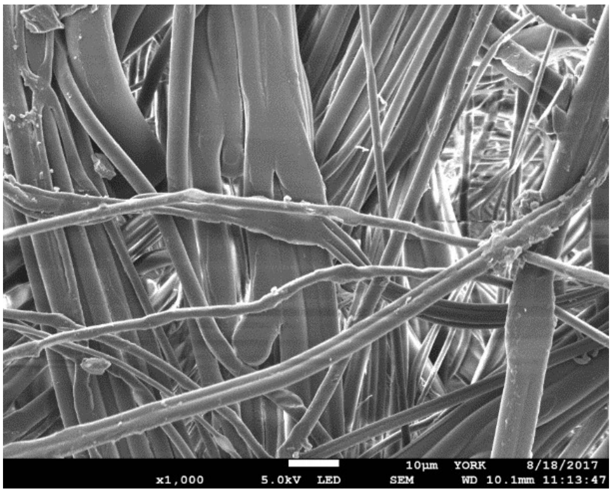

Figure S30. SEM image of DBS (0.1% wt/vol) and BTA (0.3%) dried from methanol onto non-woven fabric showing a small number of regions of sheet-like aggregates of DBS and BTA nanofibres. Scale bar 10 μm.

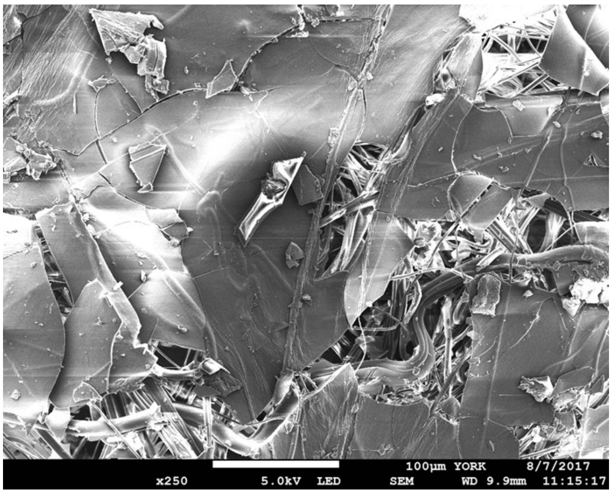

Figure S31. SEM image of DBS (1.0% wt/vol) dried from methanol onto non-woven fabric showing extensive sheet-like aggregates of DBS. Scale bar 100 μm.

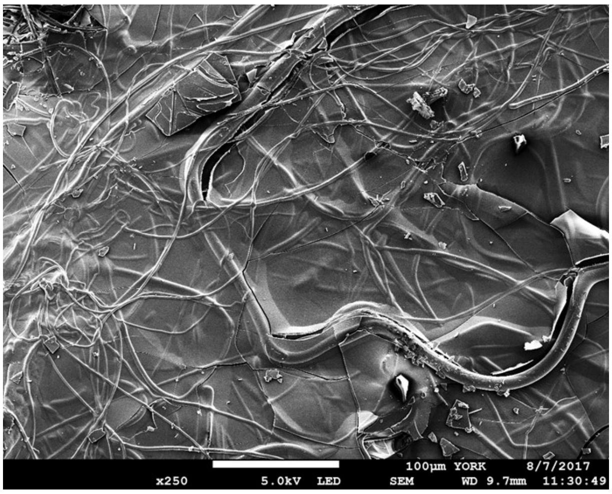

Figure S32. SEM image of DBS (1.0% wt/vol) dried from methanol onto non-woven fabric after air permeability testing showing undamaged sheet like aggregates of DBS. Scale bar 100 μm.

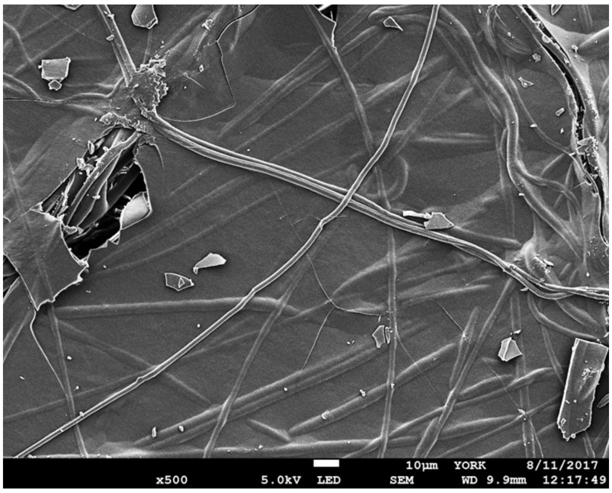

Figure S33. SEM image of DBS (1.0% wt/vol) dried from 2-butanone onto non-woven fabric after air permeability testing showing undamaged sheet like aggregates of DBS. Scale bar 100 µm.

S6 Air permeability testing

Testing was completed to British Standard EN ISO 9073-15:2008 on a TexTest instrument, FX 3300 Lab Air. This specifies a method of measuring the velocity of an air flow passing perpendicularly through a given area of test specimen fabric under a prescribed air pressure differential over a given time period. Each test sample of at least 100 mm by 100 mm was clamped on the head of the test instrument and sealed. The suction was started and the air flow regulated until the desired pressure drop was attained. The air permeability was reported in units of cm^3/cm^2/s. Each fabric sample was tested at least 5 times over a test area of 5 cm^3 at a test pressure of 100 Pa as per the British Standard.

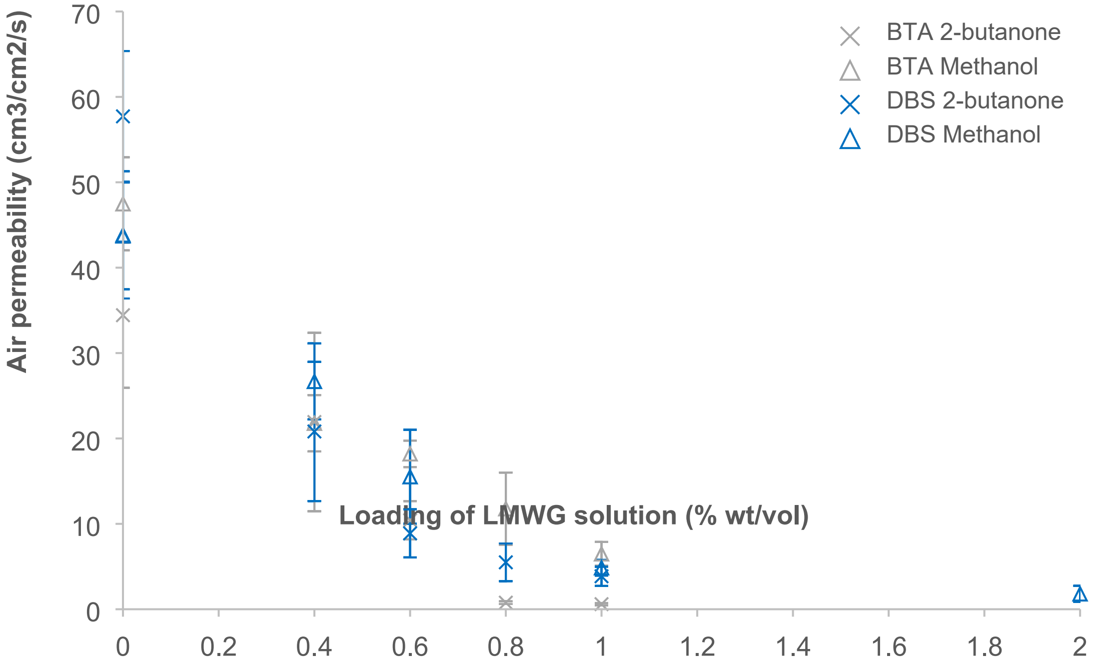

Figure S34. Graph of air permeability against concentration of gelator for methanol and 2-butanone

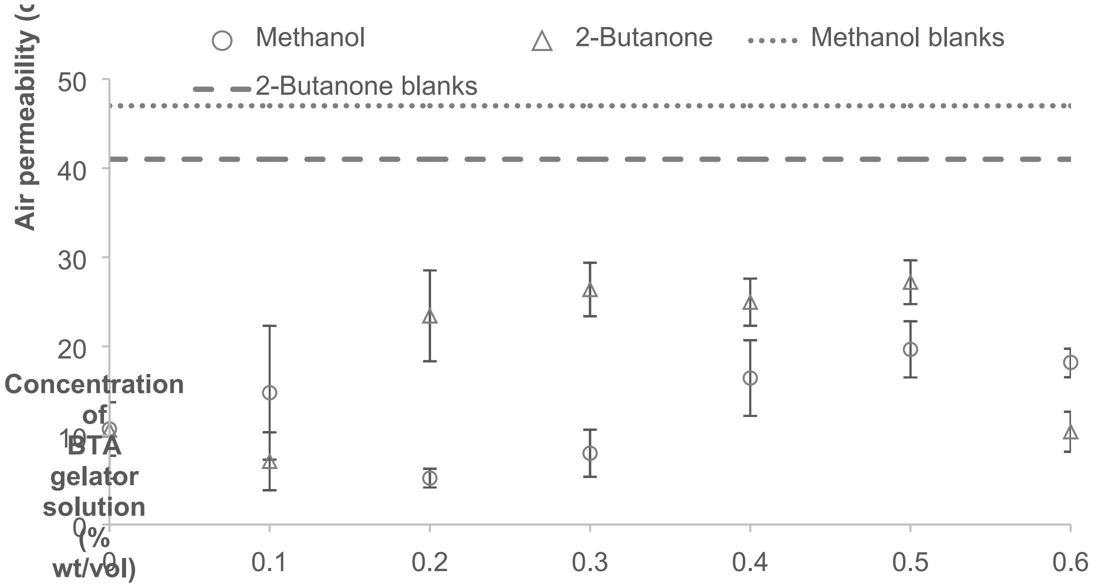

Figure S35. Air permeability of samples prepared with 0.6% wt/vol total concentration of DBS and BTA plotted against the loading of BTA in the system.

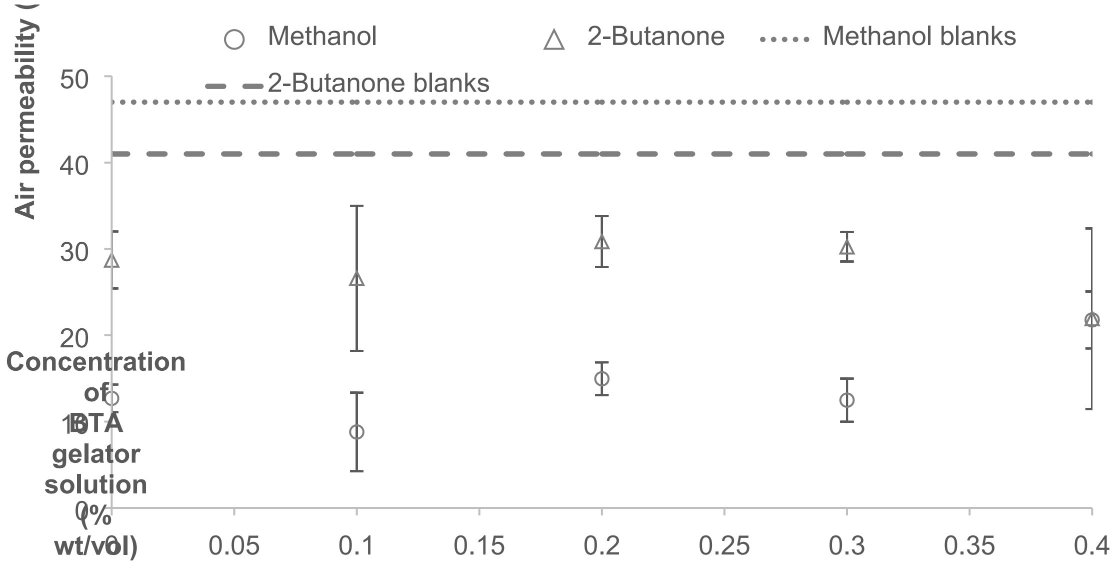

Figure S36. Air permeability of samples prepared with 0.4% wt/vol total concentration of DBS and BTA plotted against the loading of BTA in the system.