Tensile benefits of nanofibers in commercial paint films

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SUPPLEMENTARY INFORMATION

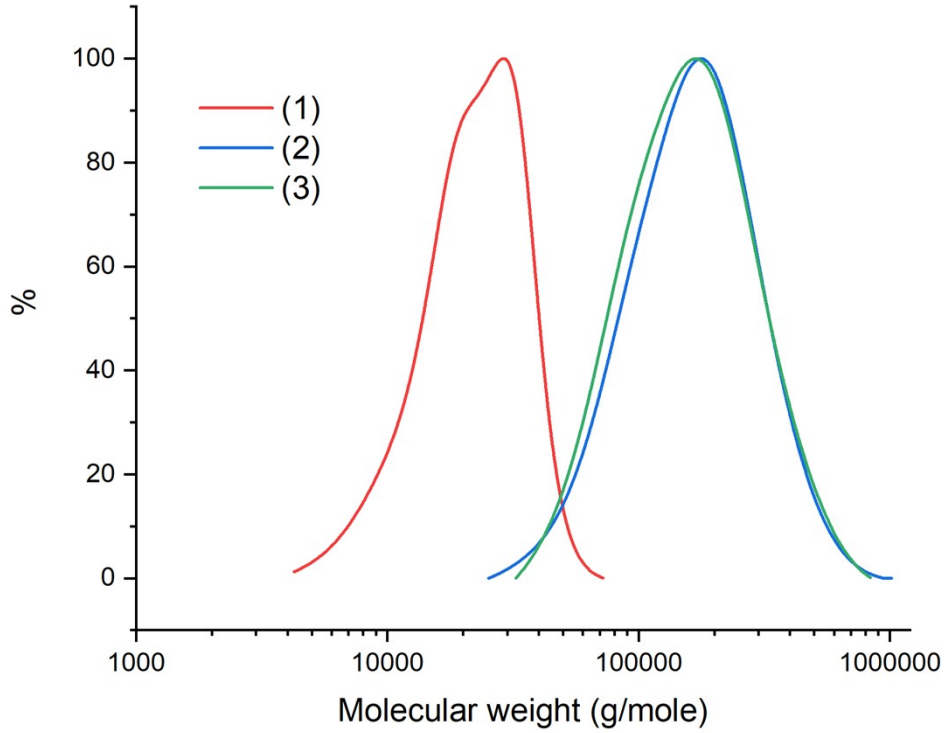

Figure S1. GPC curves characterizing molecular weight of 1) the triblock macro-RAFT copolymer; 2) PS nanofiber polymer; 3) film forming nanofiber polymer.

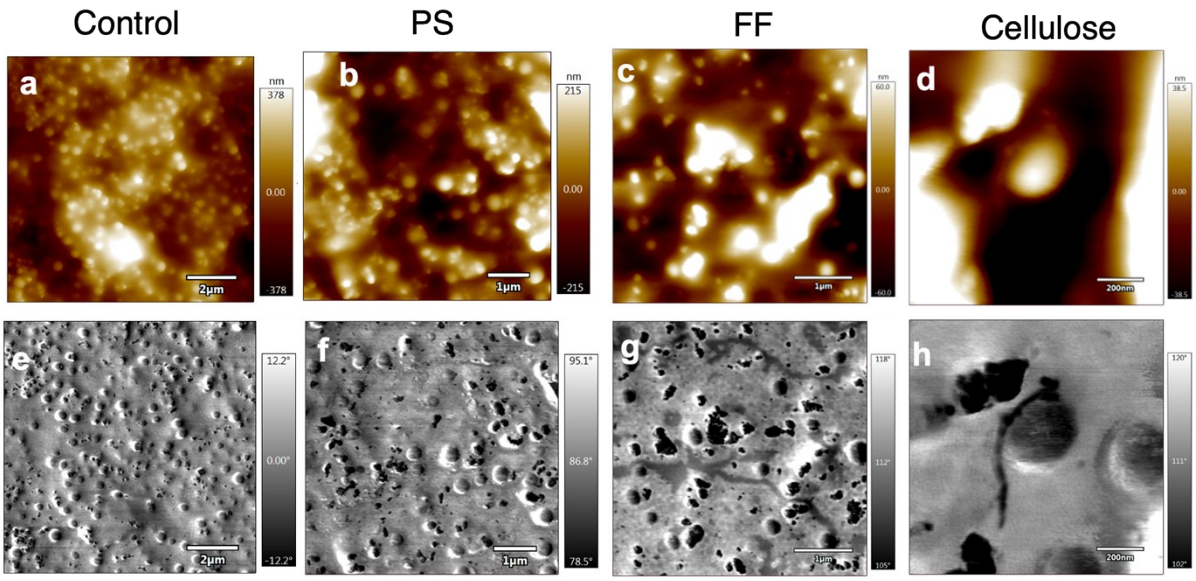

Figure S2. AFM height profiles of dried paint films containing nanofiber additives. a) Control measurement showing height profile of high Tg commercial acrylic paint. b-d) Height profiles of same commercial paint, containing 6 wt% PS fibers, 6 wt% FF fibers, and 0.75 wt% microfibrillated cellulose fibers respectively. e-h) Corresponding phase measurements of same systems included to show better resolution between latex, fiber, and pigments.

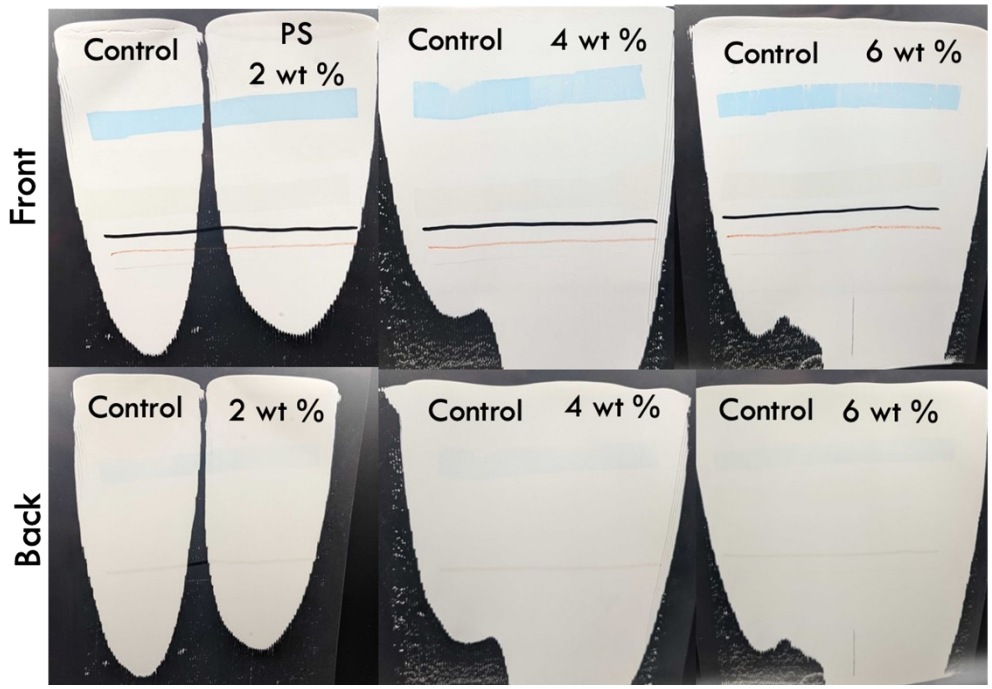

Figure S3. Stain resistance testing results comparing a high Tg commercial acrylic paint control system to the same system with increasing loadings of PS fibers. Stains tested (top-down) were blue food dye, coffee, red wine, permanent marker, crayon, grey lead pencil. Back images have been mirrored so orientation matches front for ease of interpretation.

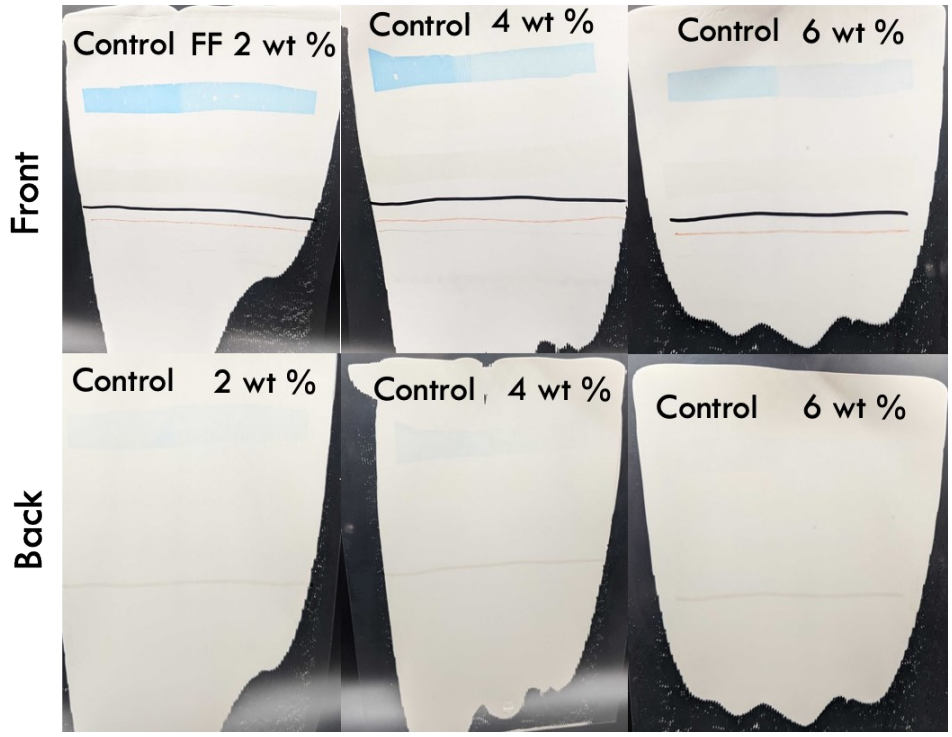

Figure S4. Stain resistance testing results comparing a high Tg commercial acrylic paint control system to the same system with increasing loadings of FF fibers. Stains tested (top-down) were blue food dye, coffee, red wine, permanent marker, crayon, grey lead pencil. Back images have been mirrored so orientation matches front for ease of interpretation.

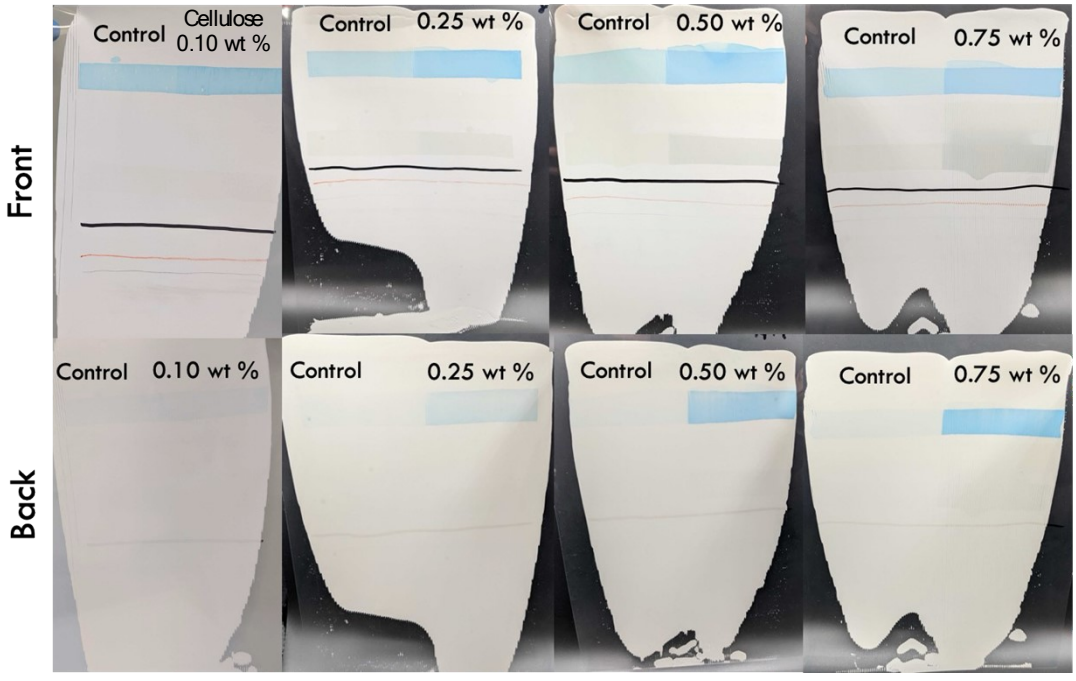

Figure S5. Stain resistance testing results comparing a high Tg commercial acrylic paint control system to the same system with increasing loadings of microfibrillated cellulose fibers. Stains tested (top-down) were blue food dye, coffee, red wine, permanent marker, crayon, grey lead pencil. Back images have been mirrored so orientation matches front for ease of interpretation.

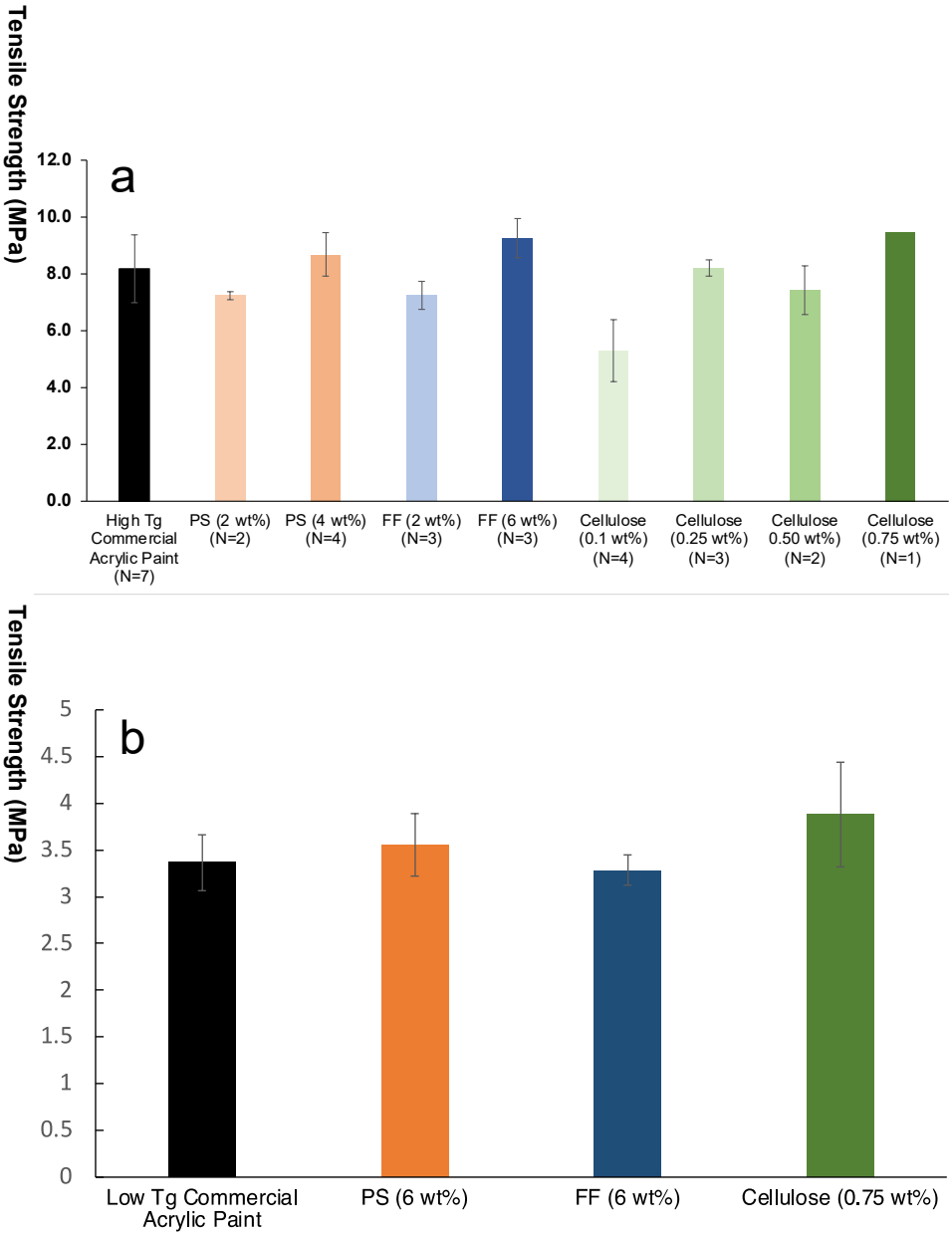

Figure S6 Impact of nanofiber additives on tensile strength of a) High Tg commercial acrylic paint and b) Low Tg commercial acrylic paint. Film forming and polystyrene fibers showed no significant ($p>0.05$) change in strength for either paint system.

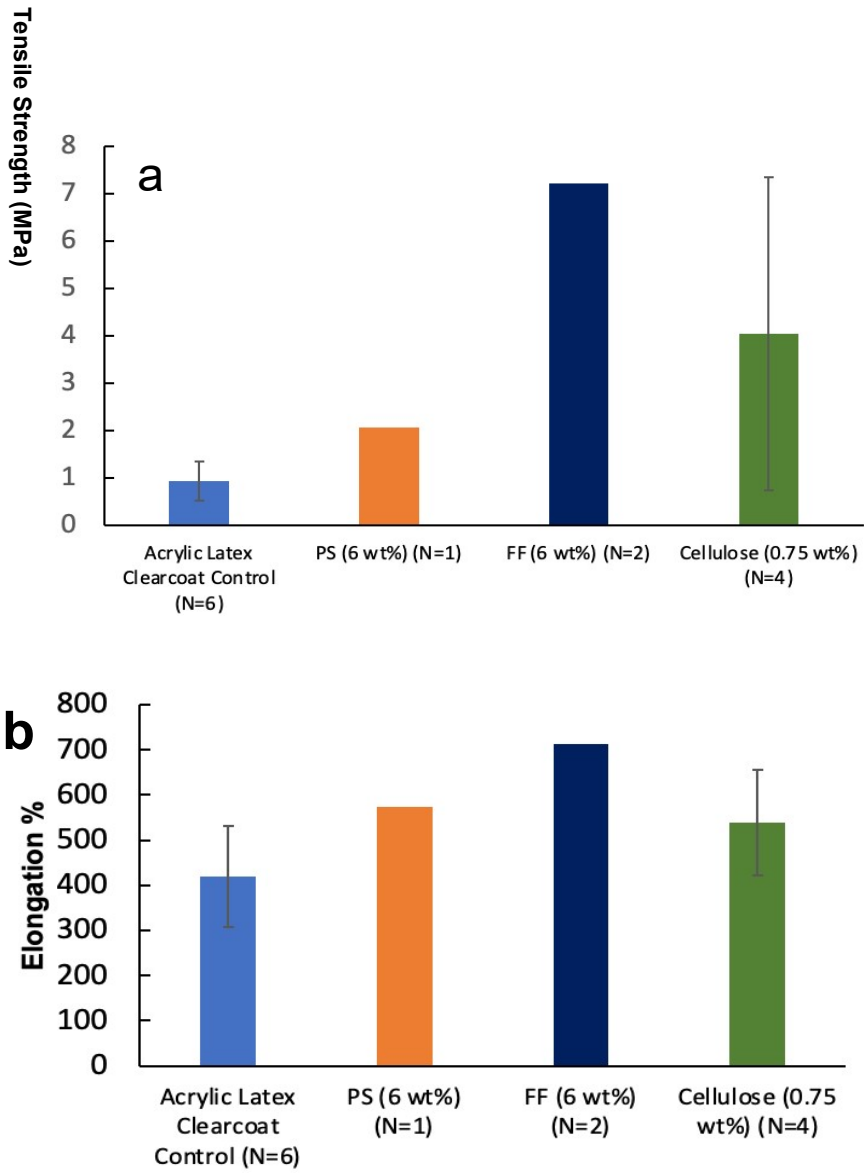

Figure S7. Impact of high loadings of nanofibers on a) tensile strength and b) tensile elongation in pigment-free clearcoat films. Note: FF films did not break, and so maximal strength and elongation values are reported rather than values-at-break.

Clear coat films were problematic because 60% of the samples were too sticky or fragile to handle, and therefore the measurements were hard to reproduce. These experiments are to be taken as a provisional indication of behaviour rather than statistically rigorous measurements. Figure S6(b) shows that high loadings of FF fibers increased extensibility, but high loadings of PS fibers or microfibrillated cellulose did not decrease extensibility as observed in both paint systems.

Scale-up of macro-RAFT Triblock D synthesis

The synthesis of Macro-RAFT Triblock D was successfully scaled to double that which was reported in the main paper as follows: RAFT DBTC (1.24 g, 4.2 mmol), AIBN (0.20 g, 1.2 mmol), AA (18.4 g, 255 mmol), BA (65.24 g, 509 mmol) and dioxane (80 g) were thoroughly mixed in a 500 mL round bottom flask. This was stirred magnetically and purged with nitrogen for 10 minutes. The flask was then heated at 70 ℃ for 2.5 hours under constant stirring. After heating, the clear polymer had a solids content of 51 wt% (98% conversion). At the end of the heating, Sty (35.4 g, 340 mmol) and AIBN (0.2 g, 1.2 mmol) were added to the polymer solution. The flask was sealed, deoxygenated with nitrogen for 10 minutes and then heated at 70 ℃ for another 12 hours under constant stirring. The final copolymer solution had 53.8% solids.

Scale-up of PS nanofiber synthesis

The synthesis of Polystyrene (PS) nanofibers was successfully scaled to a kilogram-scale reaction as follows: A solution of St (315 g), AIBN (2.52 g) and macro-RAFT Triblock D solution (105 g) was prepared. To this solution, 126 mL of 1.07 M NaOH solution was added dropwise while the solution was stirred at 1500 rpm using an overhead mixer (Labortechnik, IKA) to produce a viscous white mixture. A further 280 g of water was slowly added as stirring continued to produce a white emulsion. A final 392 g of water was further added to the emulsion under stirring for another 5 minutes. The container was sealed, sparged with nitrogen for 10 min then heated at 80℃ for 1.5 hours in an oil bath while being magnetically stirred at 150 rpm. The final ~1.2 kg product contained 33.3 wt% solids, with about 42% of those exhibiting fiber morphology as assessed via TEM (Figure S8).

Scale-up of FF nanofiber synthesis

The synthesis of Film Forming (FF) nanofibers was successfully scaled to 45 g of monomers as follows: A solution of tert-butyl acrylate (t-BA) (22.5 g), AIBN (0.18 g) and macro-RAFT Triblock D solution (8.5g)was prepared in a 500 mL glass container. To this solution, 9 mL of 1.19 M NaOH solution was added in drop wise while the solution was stirred at 1500 rpm using an overhead mixer (Labortechnik, IKA) to produce a viscous white mixture. A further 20 g of water was slowly added into the beaker while the stirring was maintained to produce a white emulsion before a final 28 g of water was further added to the emulsion under stirring for another 5 minutes. The container was sealed, sparged with nitrogen for 10 min, then heated at 80℃ for 2 hours in an oil bath while being magnetically stirred at 150 rpm. The final product contained 30.6 wt% solids, with morphology assessed via SEM (Figure S9).

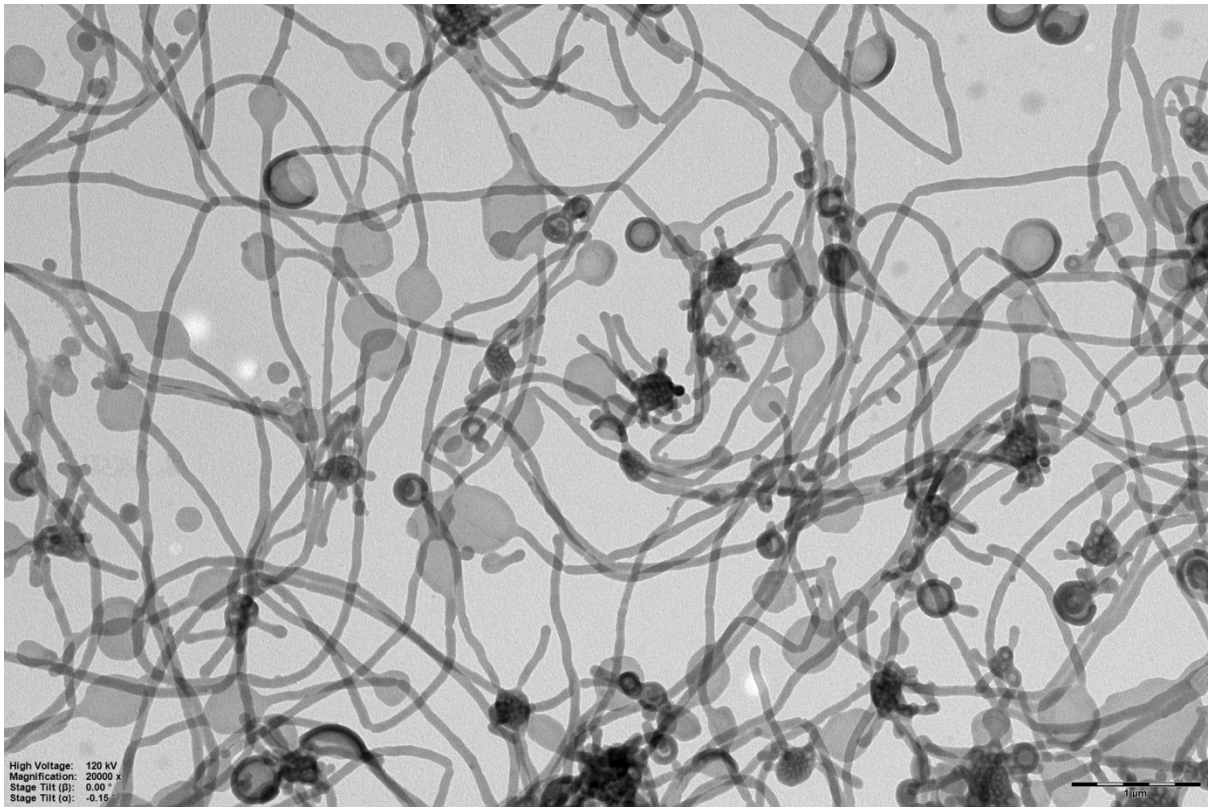

Figure S8. TEM micrograph depicting scaled-up PS nanofibers.

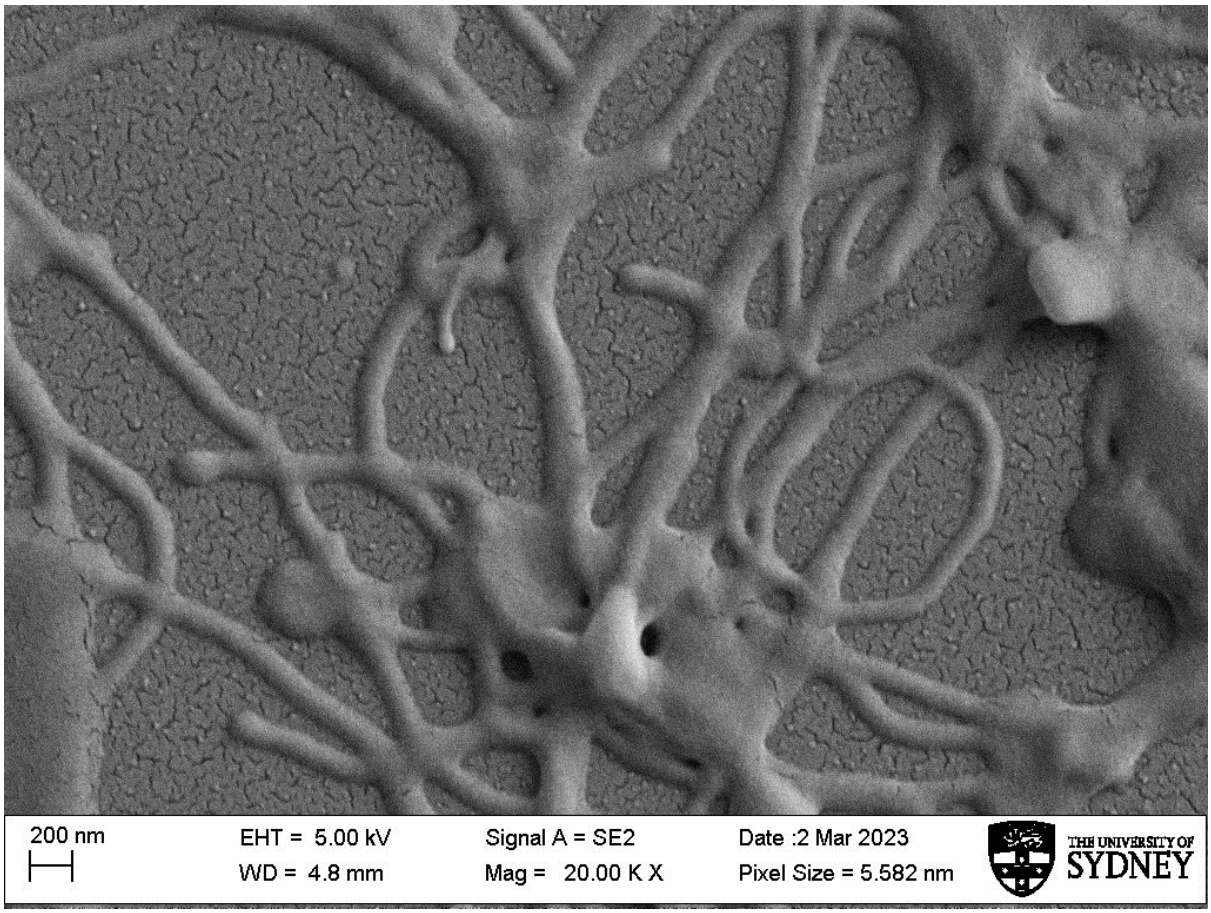

Figure S9. SEM micrograph depicting scaled-up FF nanofibers.