Supporting Information

A Journey Along the Extruder with Polystyrene:C_{60} Nanocomposites: Effect of Feeding Formulation on Dispersion and Re-Agglomeration Phenomena

Hugo Gaspar[1], Paulo Teixeira[1], Raquel Santos[1], Liliana Fernandes[1], Loic Hilliou[1], Michael P. Weir[2], Andrew J. Parnell[2], Kerry J. Abrams[3], Christopher J. Hill[4], Wim G. Bouwman[5], Steven R. Parnell[5], Stephen M. King[6], Nigel Clarke[2], José A. Covas[1,]*, Gabriel Bernardo[1,]*

[1]Institute for Polymers and Composites/I3N, University of Minho, 4800-058 Guimarães, Portugal

[2]Department of Physics and Astronomy, The University of Sheffield, Sheffield S3 7RH, United Kingdom

[3]Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, United Kingdom

[4]Department of Biomedical Science, The University of Sheffield, Sheffield S3 7HF, United Kingdom

[5]Faculty of Applied Sciences, Delft University of Technology, Mekelweg 15, 2629 JB Delft, Netherlands

[6]ISIS Pulsed Neutron Source, STFC Rutherford Appleton Laboratory, Harwell Campus, Didcot, OX11 0QX, United Kingdom
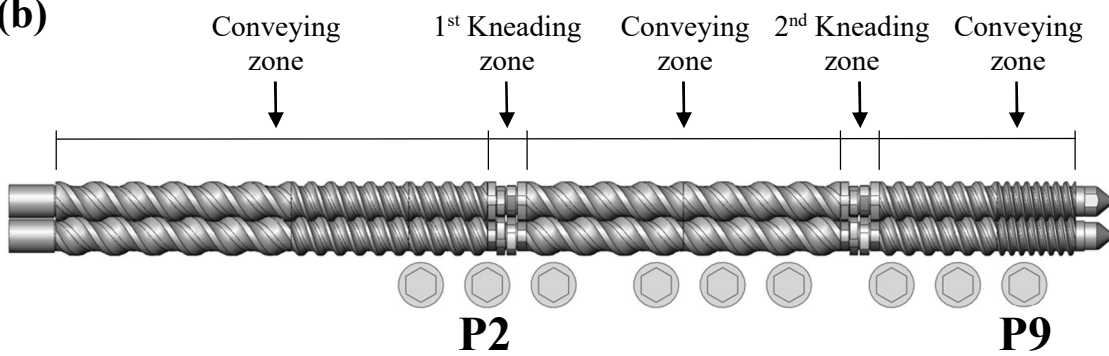
(a)
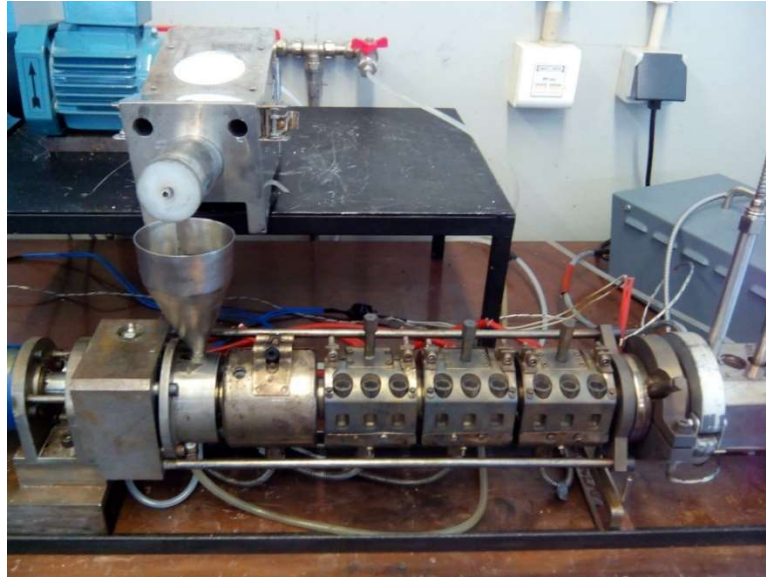
(b)

Figure S.I.1. (a) Prototype twin-screw extruder with sampling ports and volumetric feeder; (b) geometry of the screws and identification of the sampling locations P2 and P9.
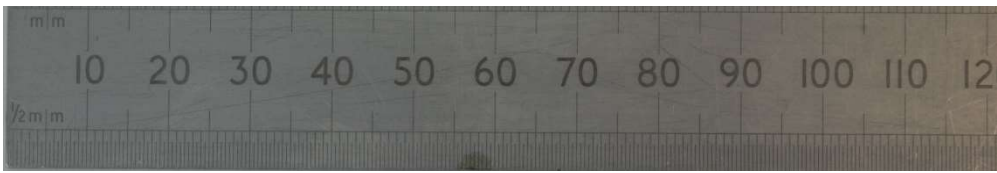
(a)	Initial	P2	P9	Ribbon
Mixed Powders				
Pre-Solvent Blended				

Figure S.I.2. (a) Close-up photo of the experimental samples, namely: compression moulded samples of the initial feeding formulations; extruded samples P2; extruded samples P9 and extruded ribbons. A ruler is also shown to indicate the real dimension of the samples.; (b) Close-up photo of the pre-solvent blended initial sample (compression molded at 170 ºC), lit from the back to highlight its purple colour.
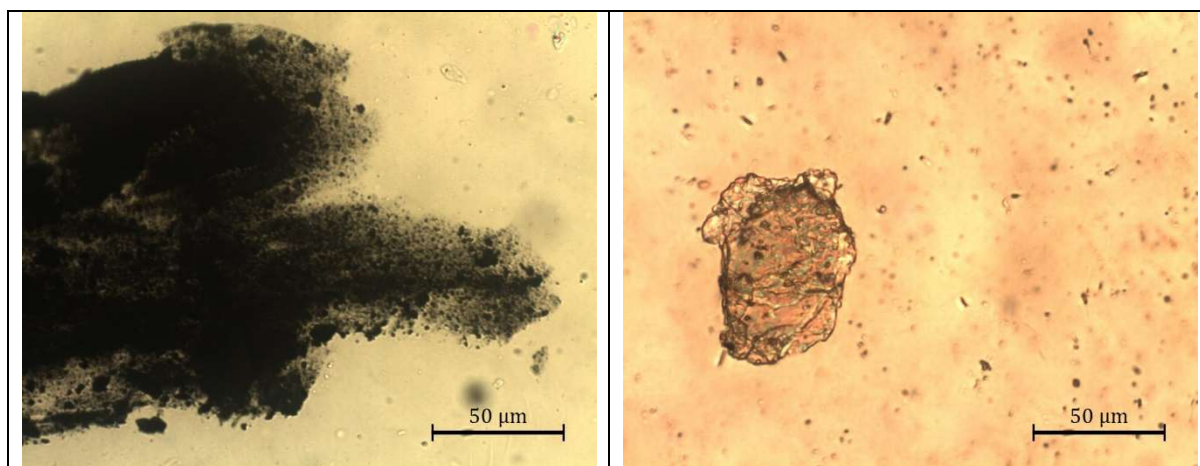
Figure S.I.3. Optical microscopy images of the initial feeding formulations: (left) mixed powders; (right) solvent blended composite. For obtaining these microscopy images, the initial feeding formulations (in powder form) were softened at 160 °C and spread onto a glass slide. The larger, approximately circular, feature with ~50 µm diameter in the image on the right corresponds to material that did not melt during the preparation of the optical microscopy sample.
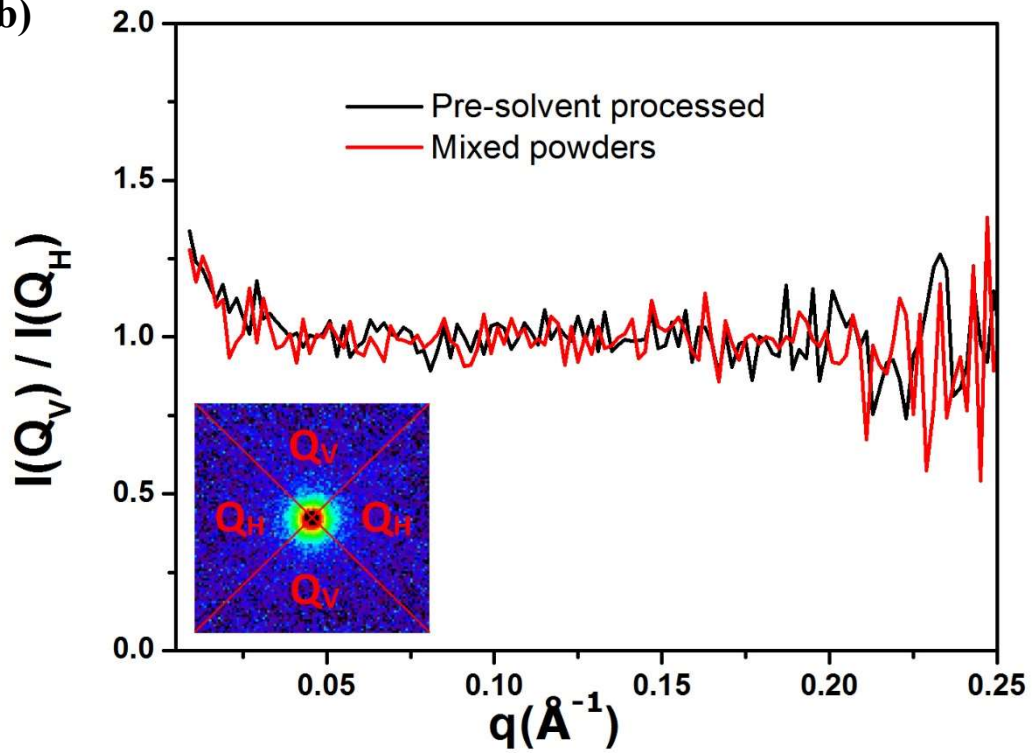
(a)
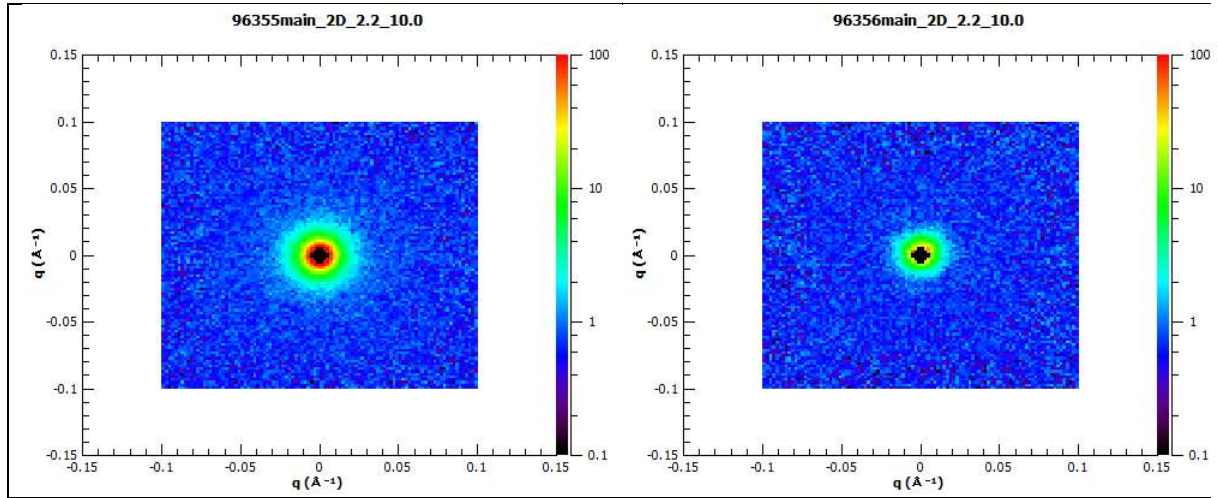
(b)

Figure S.I.4. (a) Neutron scattering 2D patterns of extruded ribbons processed from a pre-solvent blend (left) and from mixed powders (right); (b) Intensity ratio $I(Q_V)/I(Q_H)$ as a function of q, for the vertical and horizontal quadrants of the 2D scattering patterns (see inset). The average ratio is ~1 which means that the samples are completely isotropic.
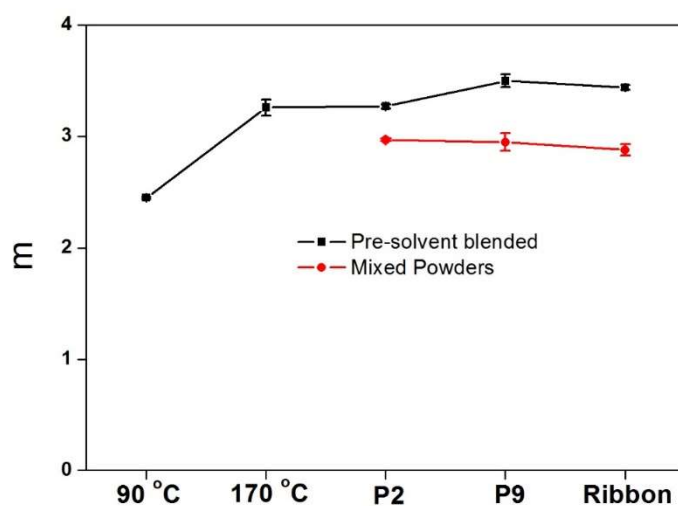
Figure S.I.5. Variation of the slope of the SAXS curves with processing. For ease of comparison the scale used is identical to the scale in Figure 5.
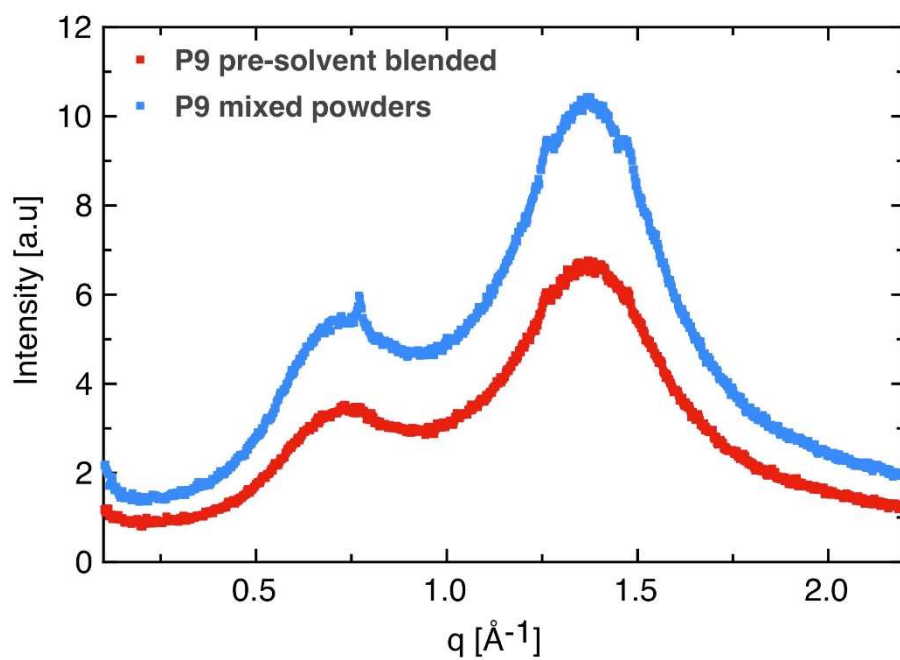

Figure S.I.6. 1D WAXS patterns of samples collected from sampling port #9. The data has been translated vertically for clarity.

Experimental Procedure for the TEM characterization

Samples were snap frozen in Liquid Nitrogen and placed in the FC6 cryo-chamber to equilibrate for approximately 30 minutes. Ultrathin sections, approximately 90-100nm thick, were cut using a Leica UC 6 ultra-microtome and FC6 cryobox attachment onto uncoated 200 mesh copper grids at temperatures of between -60 to -100 degrees C.

Sections were examined using a FEI Tecnai Transmission Electron Microscope at an accelerating voltage of 80 kV. Electron micrographs were recorded using a Gatan Orius 1000 digital camera and Gatan digital micrograph software.

Experimental Procedure for the STEM characterization

Sections on TEM grids were examined in FEI Helios UC SEM in Transmission Mode utilizing the STEM3++ detector with an accelerating voltage of 29 kV and a working distance of 5 mm. Images were processed in ImageJ 1.51j.
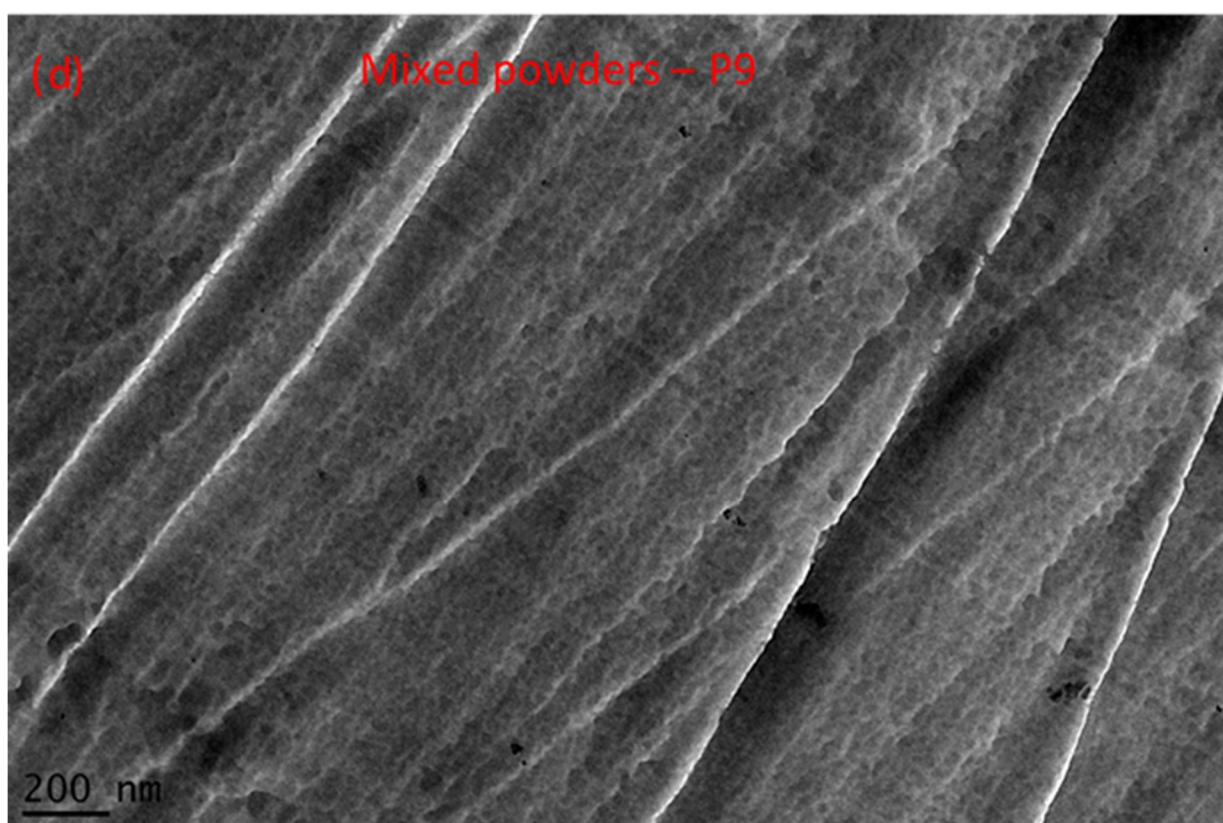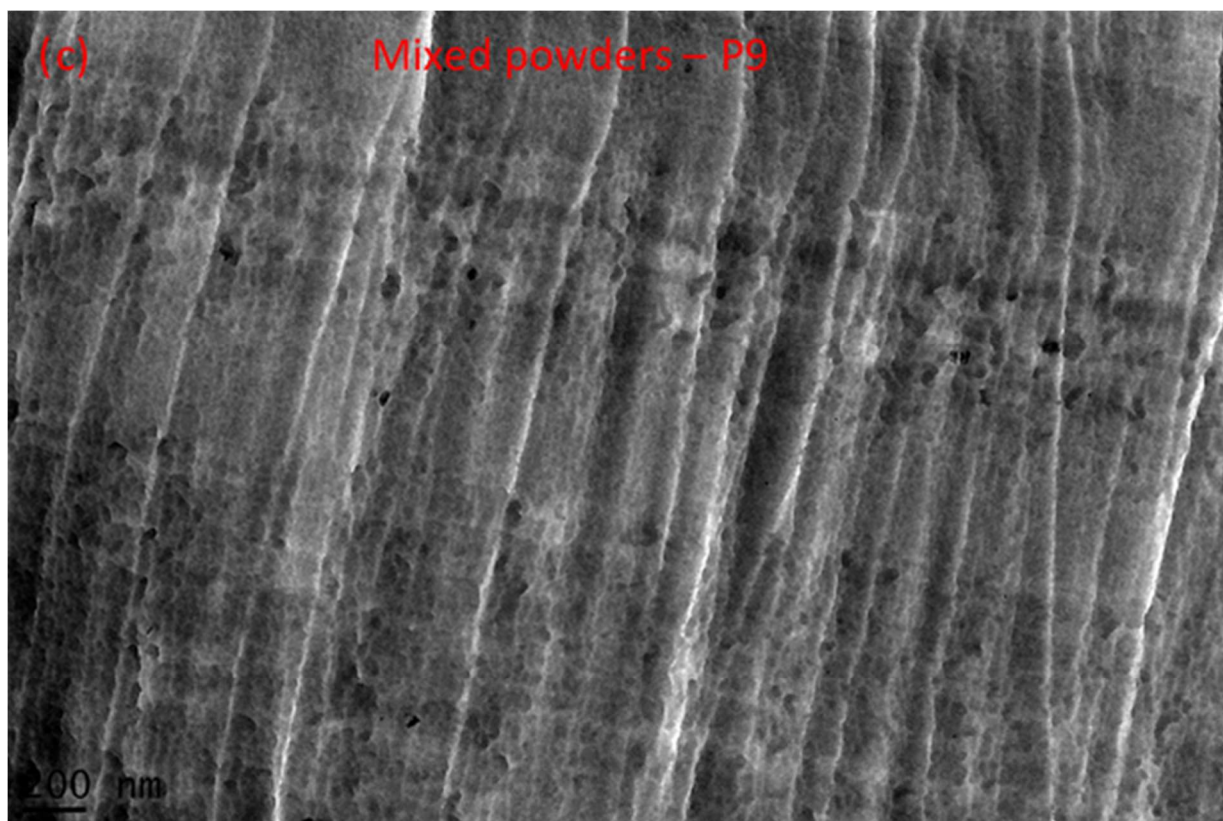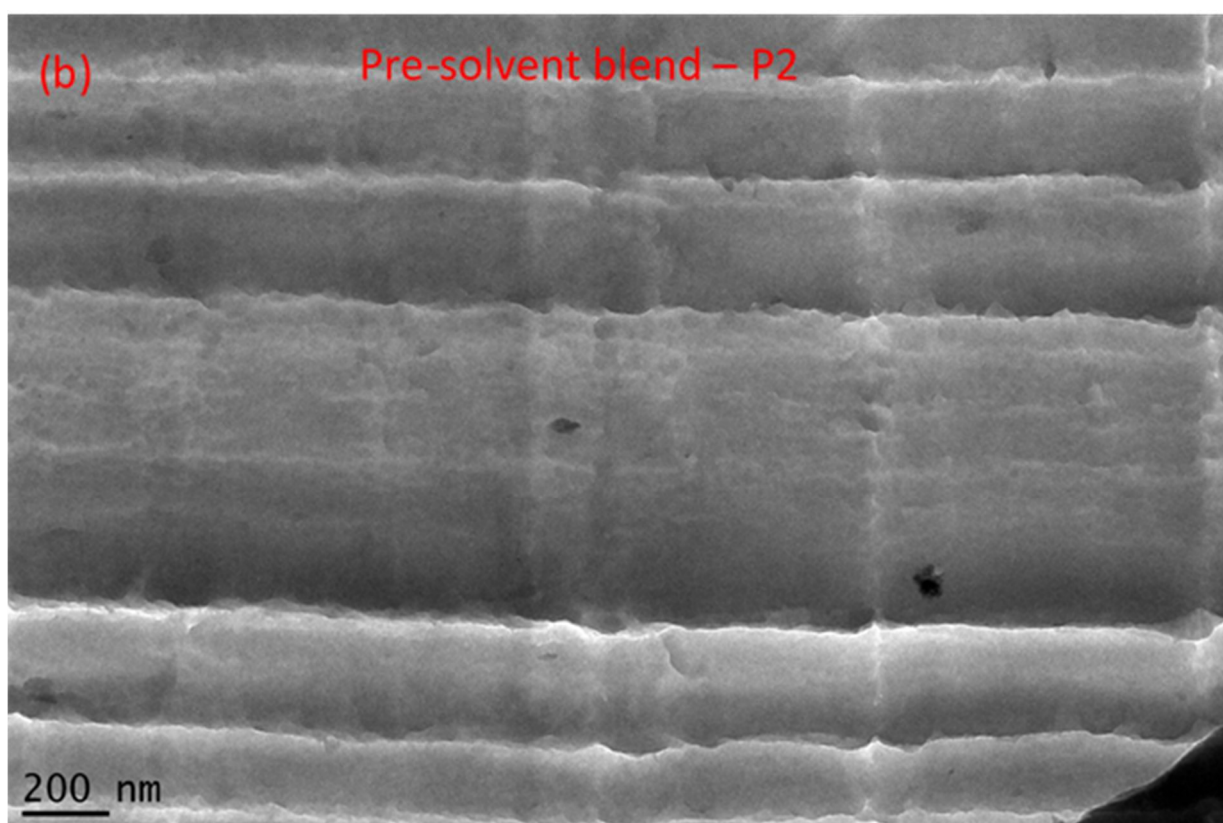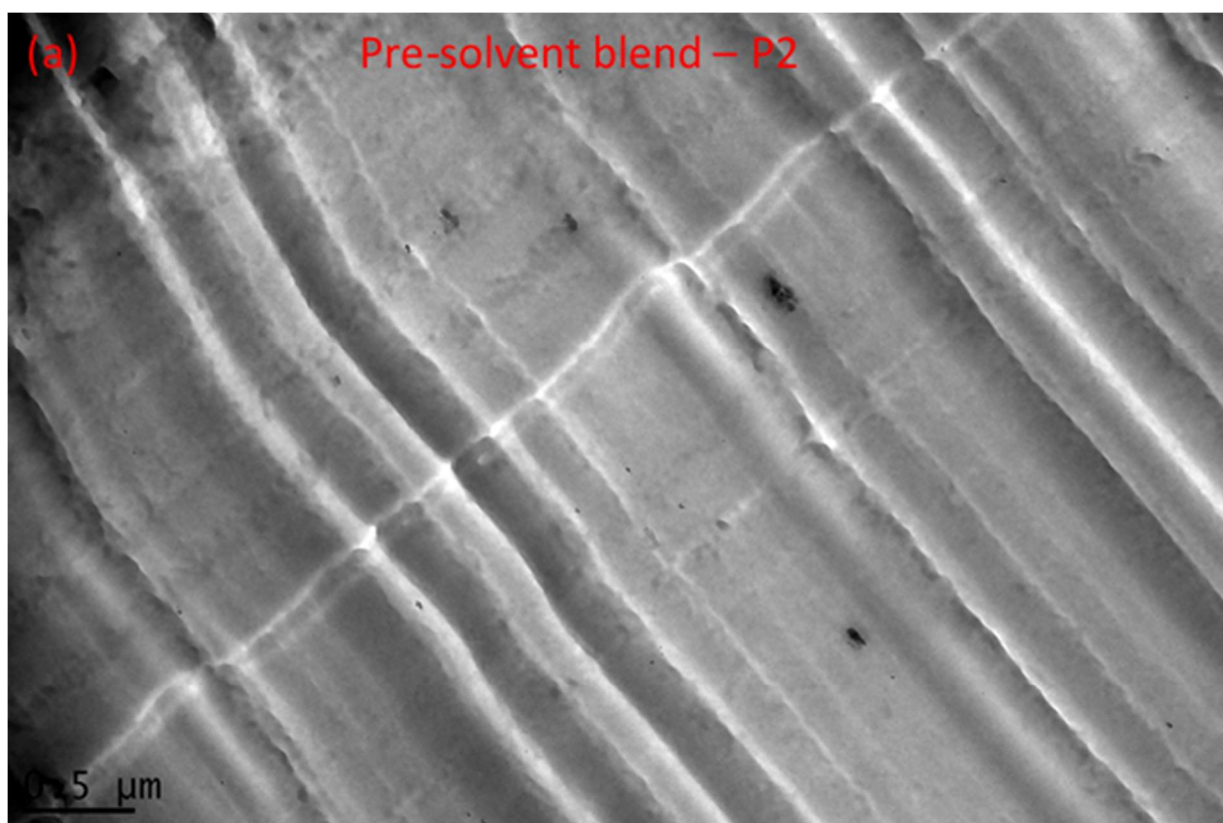
(a) Mixed powders – P2

1 μm

(b) Mixed powders – P2

200 nm
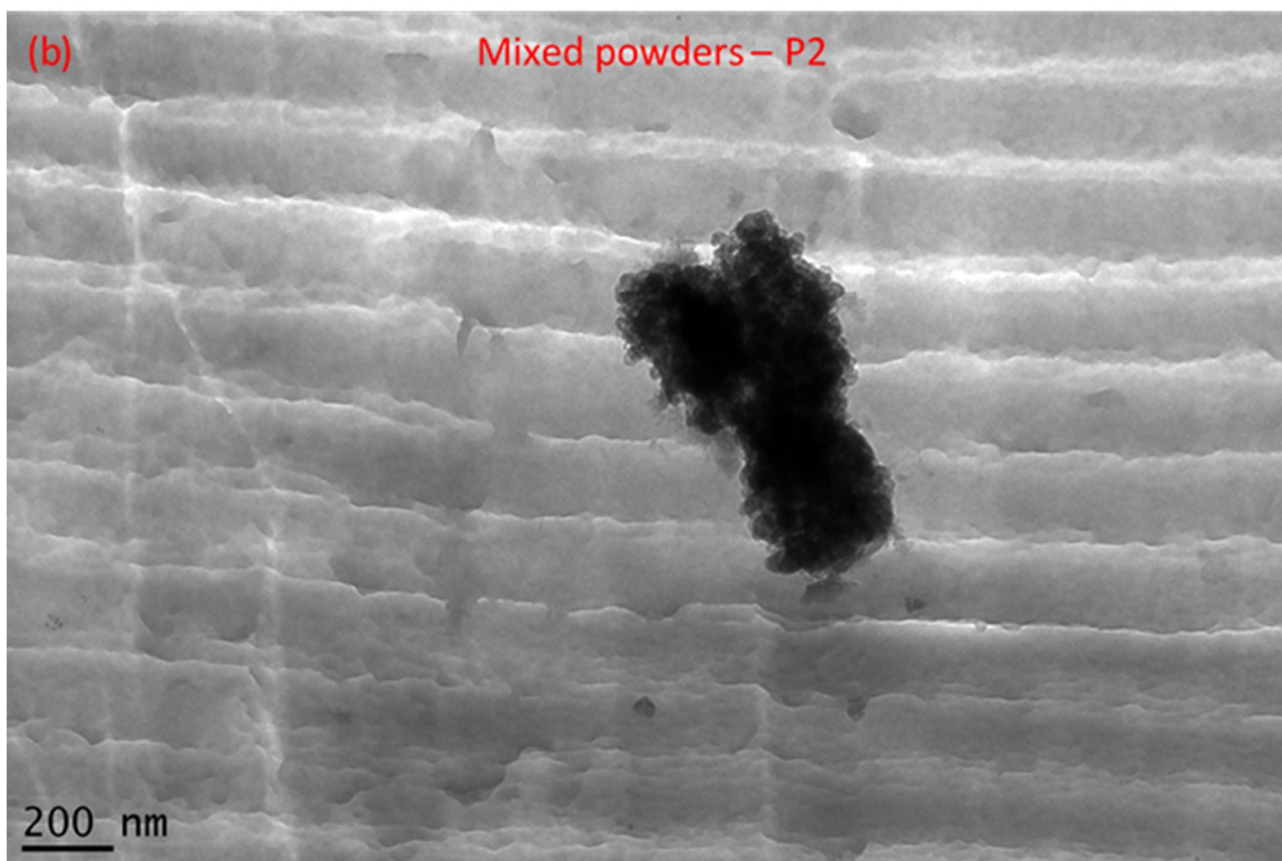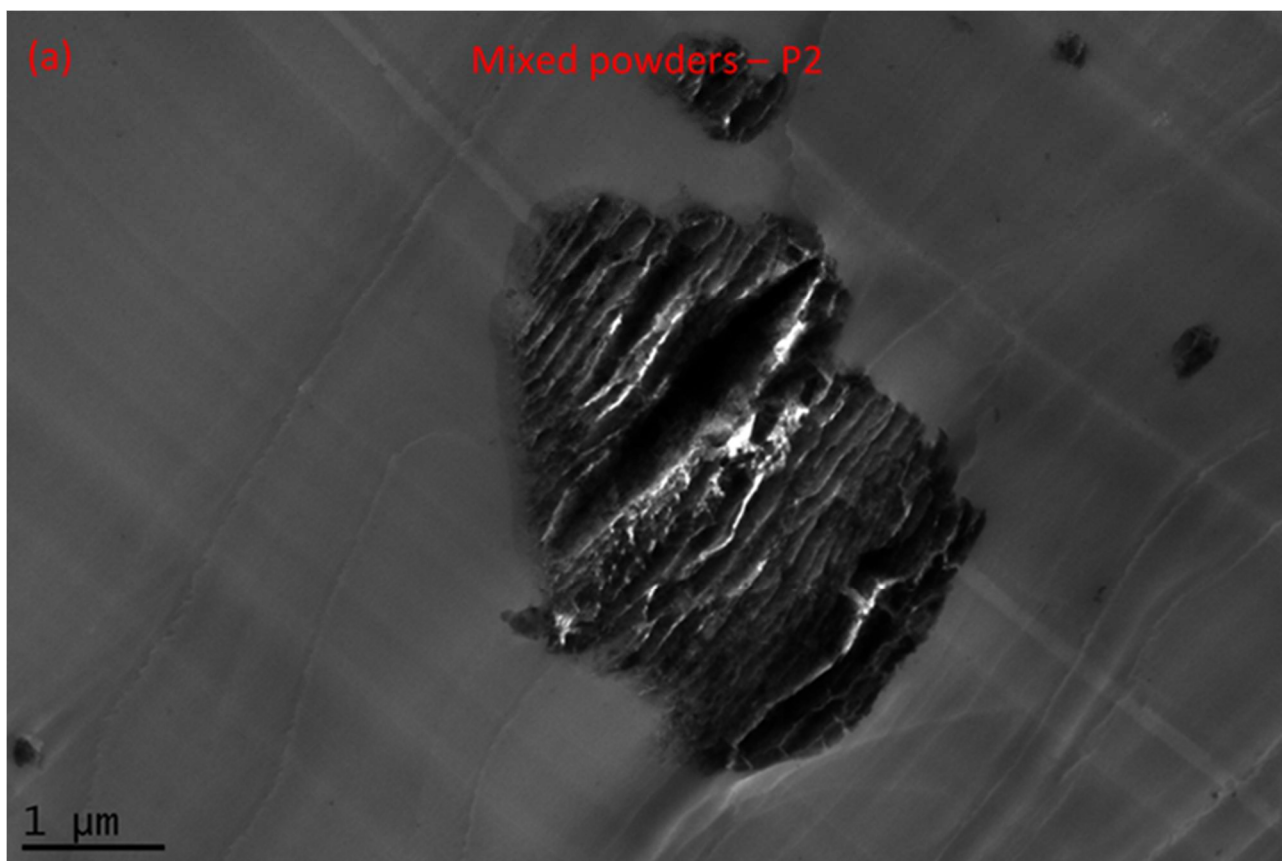
Figure S.I.7. TEM of composites processed from mixed powders: (a) and (b): P2; (c) and (d) P9

(a) Pre-solvent blend – P2

0.25 μm
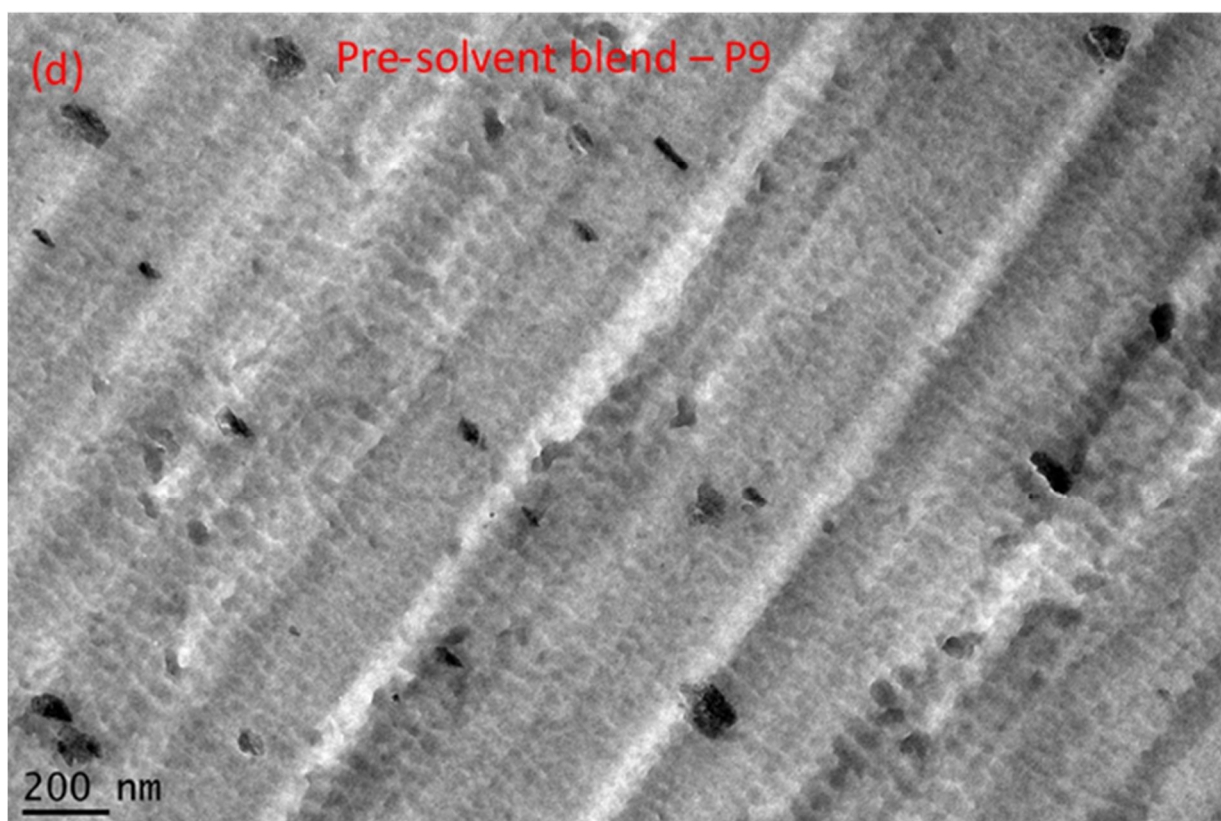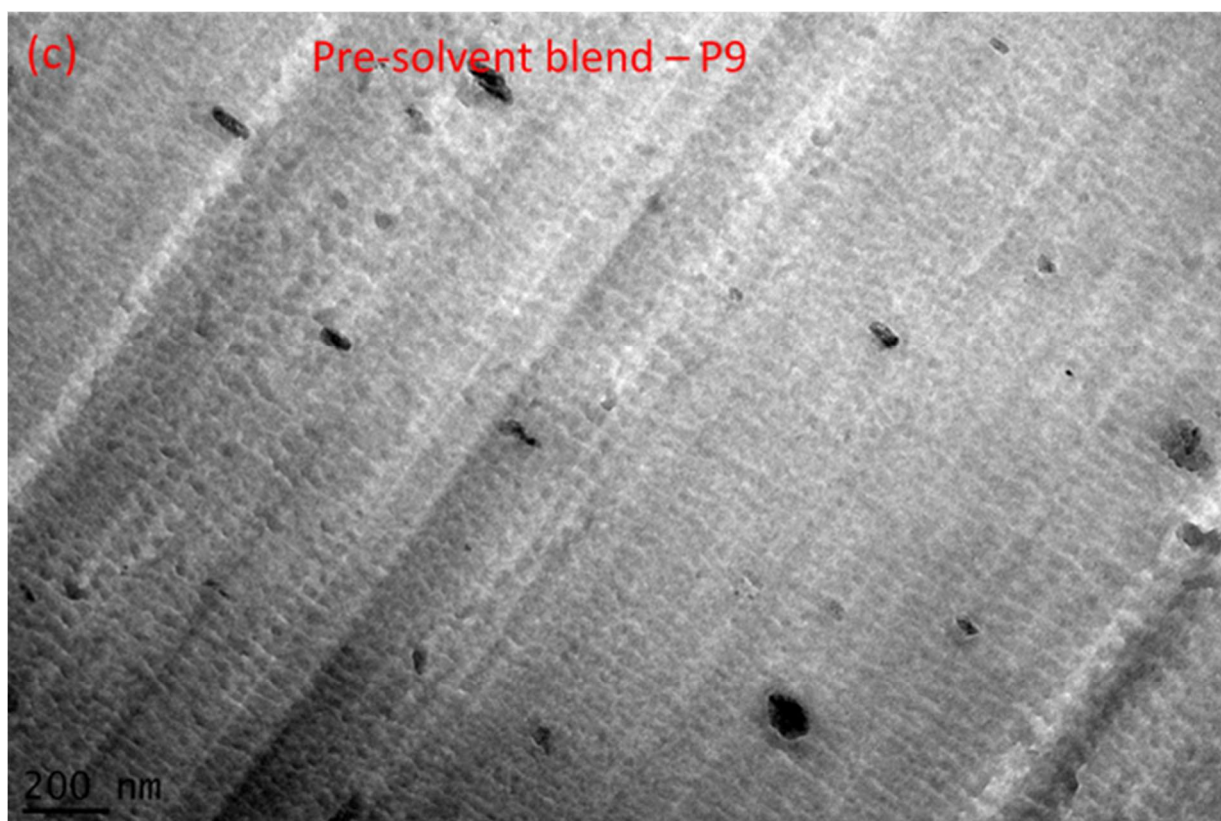

(b) Pre-solvent blend – P2

200 nm

Figure S.I.8. TEM of composites processed from solvent-blend: (a) and (b): P2; (c) and (d) P9
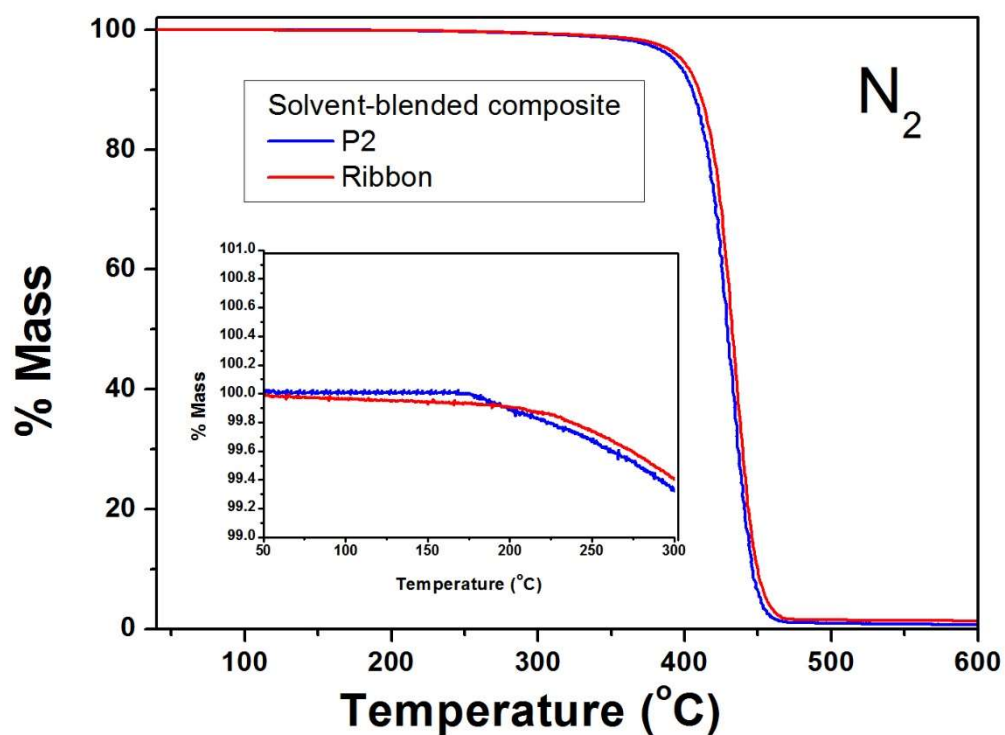
Figure S.I.9. Thermogravimetry measurements of pre-solvent-blended composites collected from P2 and ribbon.
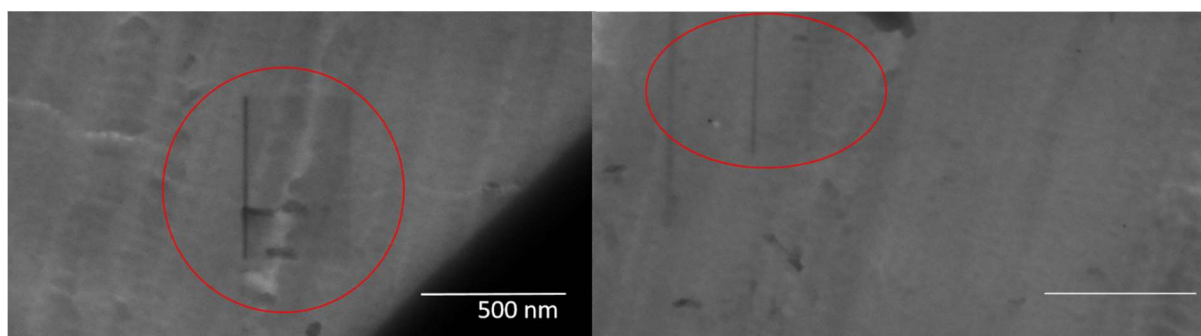

Figure S.I.10. STEM images showing contamination on surface of solvent processed samples caused by the electron beam highlighted by the red circles. The scale bars are both 500 nm.
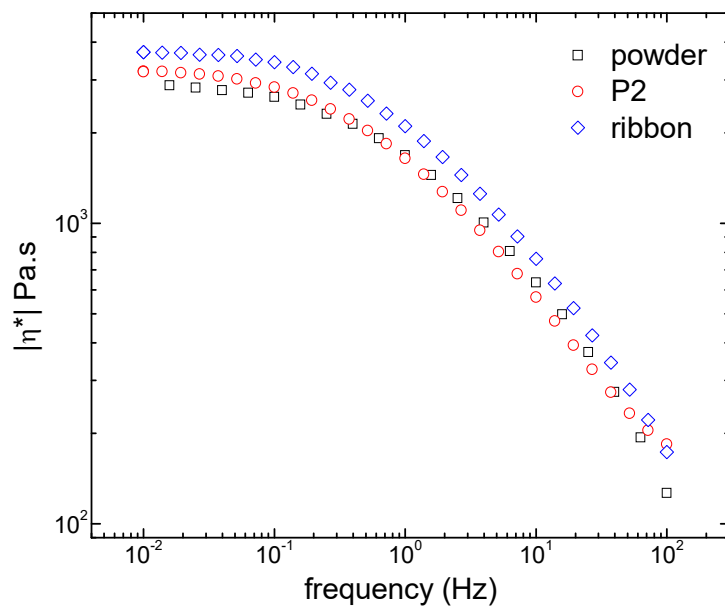
Figure S.I.11. Mechanical spectra measured at 200 °C of PS sample fed into the extrusion line (powder, squares), of PS sample collected at P2 along the extruder (P2, circles) and PS ribbon (ribbon, diamond).
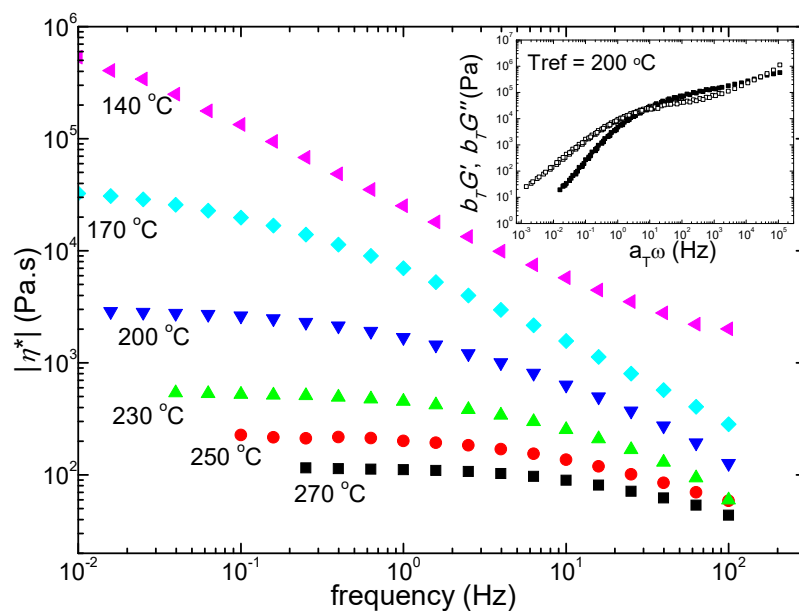

Figure S.I.12. Construction of the master curve of the PS matrix. Mechanical spectra measured at different temperatures indicated in the Figure are overlayed by shifting horizontally the curves with a factor a_T and vertically with a factor b_T to build the master curve plotted in the inset.
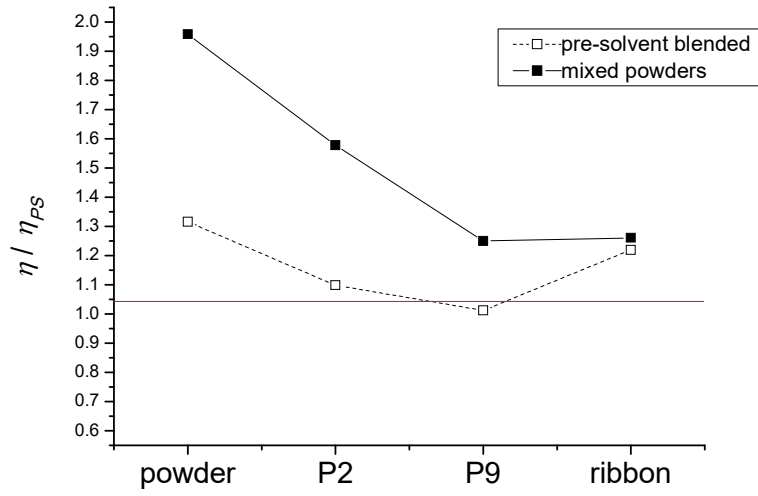
Figure S.I.13. Evolution along the extruder of the ratio between the zero shear viscosity of the composite η and the zero shear viscosity of the PS matrix η_{PS} for the two feeding formulations. The red line indicates the viscosity ratio predicted by the Einstein equation for a suspension of hard spheres in a Newtonian matrix.
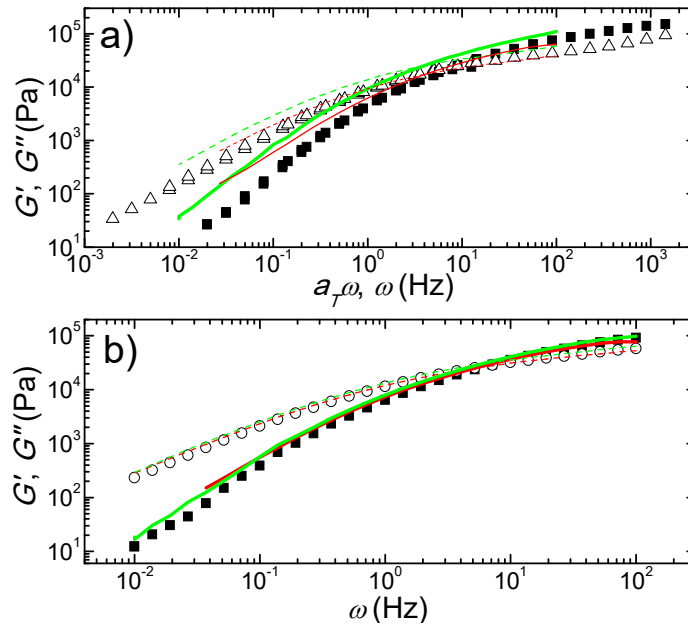

Figure S.I.14. Mechanical spectra of feeding powders (a) and of the corresponding extruded ribbons (b). Filled and empty symbols correspond to G' and G'' of the PS matrix respectively, whereas full lines and dashed lines correspond to G' and G'' respectively of the mixed powder samples (green) and the pre-solvent blended samples (red).