

Supporting Information

Toughening Cellulose: Compatibilizing Polybutadiene and Cellulose Triacetate Blends

Kyle J. Arrington^{‡,ψ}, James V. Haag IV^Φ, Eric French^{‡,ψ}, Mitsuhiro Murayama^Φ, Kevin J. Edgar^{‡,ψ}, John B. Matson^{‡,ψ}*

Department of Chemistry[‡], Department of Material Science and Engineering^Φ, Department of Sustainable Biomaterials[†], and Macromolecules Innovation Institute^ψ, Virginia Tech, Blacksburg, Virginia 24061, United States

Email: jbmatson@vt.edu

Materials and Methods

All reagents were obtained from commercial vendors and used as received unless otherwise stated. CTA had a calculated DS of 2.82 as determined by quantitative ¹³C NMR spectroscopy and a M_n of 200,000 g/mol as reported by the manufacture Acros Organics. Dry solvents were purified by passage through a solvent purification system (MBraun). NMR spectra were measured on an Agilent 400 MHz spectrometer. ¹H and ¹³C NMR chemical shifts are reported in ppm relative to internal solvent resonances. Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. THF size exclusion chromatography was carried out at 30 °C on two Agilent PLgel 10 μm MIXED-B columns connected in series with a Wyatt Dawn Helios 2 light scattering detector and a Wyatt Optilab Rex refractive index detector. No calibration standards were used, and dn/dc values were obtained by assuming 100 % mass elution from the columns. CHCl₃ size exclusion chromatography was carried out at 35 °C on two 10 μm Shodex KF-806M columns connected in series with a 2414 refractive index detector. Polystyrene standards were used to determine molar mass and dispersity. Thermogravimetric analysis was carried out with a TA-Q50 TGA under a dry nitrogen purge (40 mL/min for the balance and 60 mL/min for the sample) from room temperature to 600 °C at a heating rate of 10 °C /min. Dynamic mechanical analysis was performed on a TA Instruments Q800 DMA in oscillatory tension mode at 3 °C/min and 1 Hz with an oscillatory amplitude of 10 μm. Tensile testing was performed on an Instron 5500R in accordance with ASTM 638 at a rate of 5 mm/min or 20 mm/min. Scanning electron microscopy (SEM) was performed using a FEI Environmental SEM at 5 kV. Samples were sputtered with a 7 nm PtPd coating before imaging. Film casting of the blends was performed from a 10 wt% solution in CHCl₃. The films were casted to a desired height using a doctor blade, and the solvent was allowed to evaporate at rt in a glass enclosure for 24 h. Remaining solvent was removed by placing the resulting films under vacuum for 24 h. Differential scanning calorimetry studies (DSC) were carried out on a Q-2000 DSC in aluminum pans operated with a dry nitrogen purge from -150 °C to 200 °C with a heating and cooling rate of 10 °C /min.

Polymer Functionalization and Synthesis

Synthesis of CTA-Br. A round bottom flask was charged with a stir bar, cellulose triacetate (CTA) (20 g, DS = 2.82), and CHCl₃ (200 mL). After CTA was fully dissolved (24 h), 33 wt% HBr in acetic acid (17.5 mL) was

added. The solution was stirred at rt for 30 min. The reaction mixture was precipitated into EtOH (3 L). The resulting precipitate was isolated by filtration and washed 3x with EtOH (500 mL) to remove residual acid. The final product was dried in a vacuum oven at 50 °C for 12 h to give a white powder (12.2 g, 61% yield).

Synthesis of CTA-olefin. A round bottom flask was charged with a stir bar, undec-10-en-1-ol (4.6 mL, 24 mmol), **CTA-Br** (10 g, 0.8 mmol of Br) and CHCl₃ (50 mL). DBU (1.81 mL, 12 mmol) was then added to the solution. The reaction mixture was stirred for 4 h at rt. Afterwards, the solution was precipitated twice into EtOH (1L). The resulting precipitate was isolated by filtration and dried under vacuum for 12 h to give a white powder (9.9 g, 98% yield).

ROMP of COD and CTA-olefin. A round bottom flask was charged with a stir bar, **CTA-olefin** (2 g, 0.16 mmol), cyclooctadiene (COD) (0.75 mL, 8 mmol), and THF (33 mL). The solution was bubbled with N₂ for 15 min to remove oxygen. Hoveyda–Grubbs second-generation catalyst (HG2) was dissolved in THF in a separate vial. An aliquot of HG2 solution (2.0 mg, 3.2 μmol in 0.2 mL of THF) was injected into the first round bottom flask. The round bottom flask was stirred for 24 h. Polymer **CTA-*b*-PB-*b*-CTA** was precipitated into EtOH (1 L), recovered by filtration, and dried overnight on a vacuum line (2.37 g, 83% yield). The polymer was then stored in the freezer to prevent possible crosslinking of the PB block.

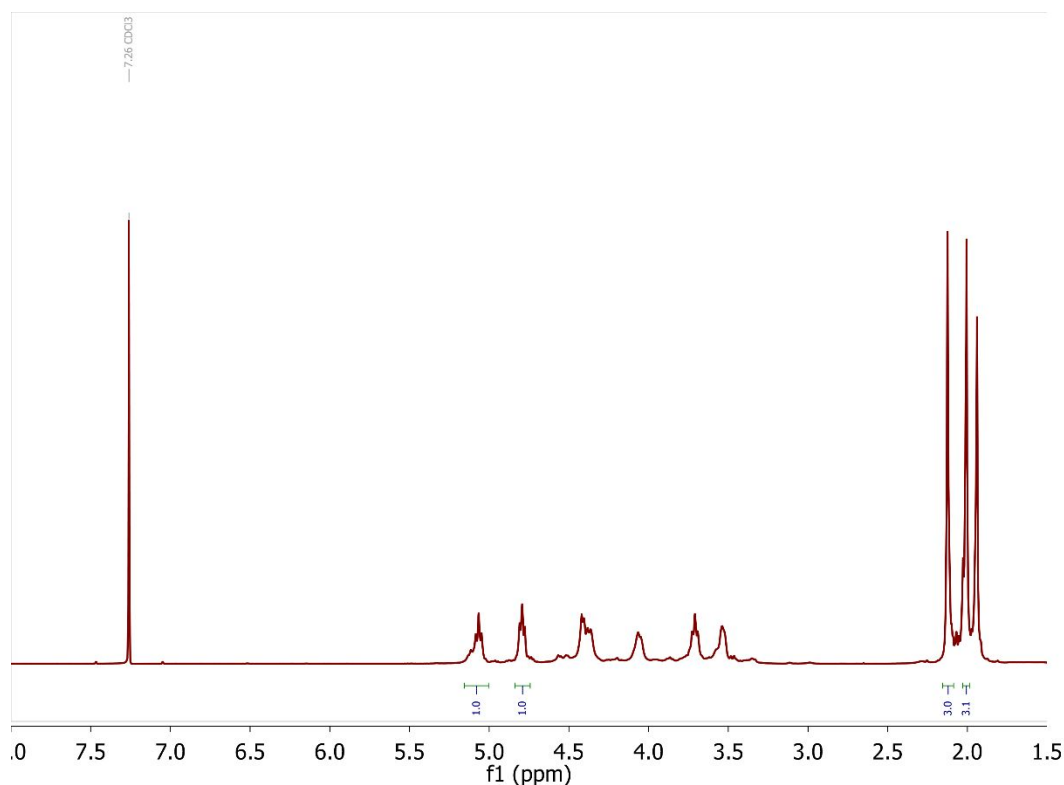


Figure S1: Full ^1H NMR spectrum of **CTA-Br** after isolation and drying. Note: A zoomed-in image of the spectrum showing the chain end signals is shown in Figure 1.

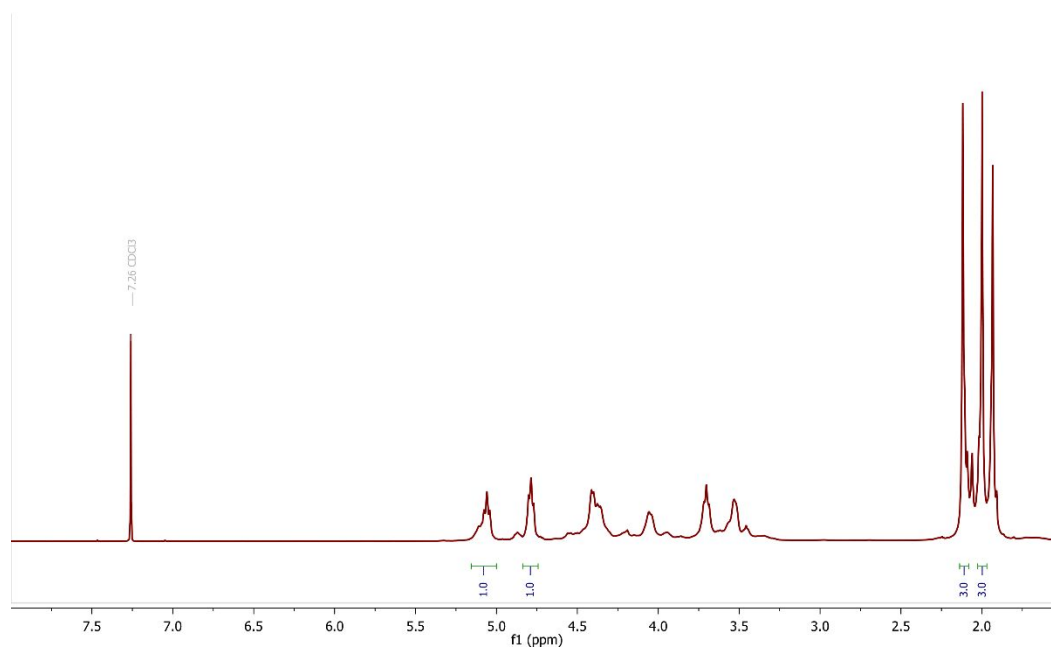


Figure S2: Full ^1H NMR spectrum of **CTA-Olefin** after isolation and drying. Note: A zoomed-in image of the spectrum showing the chain end signals is shown in Figure 1.

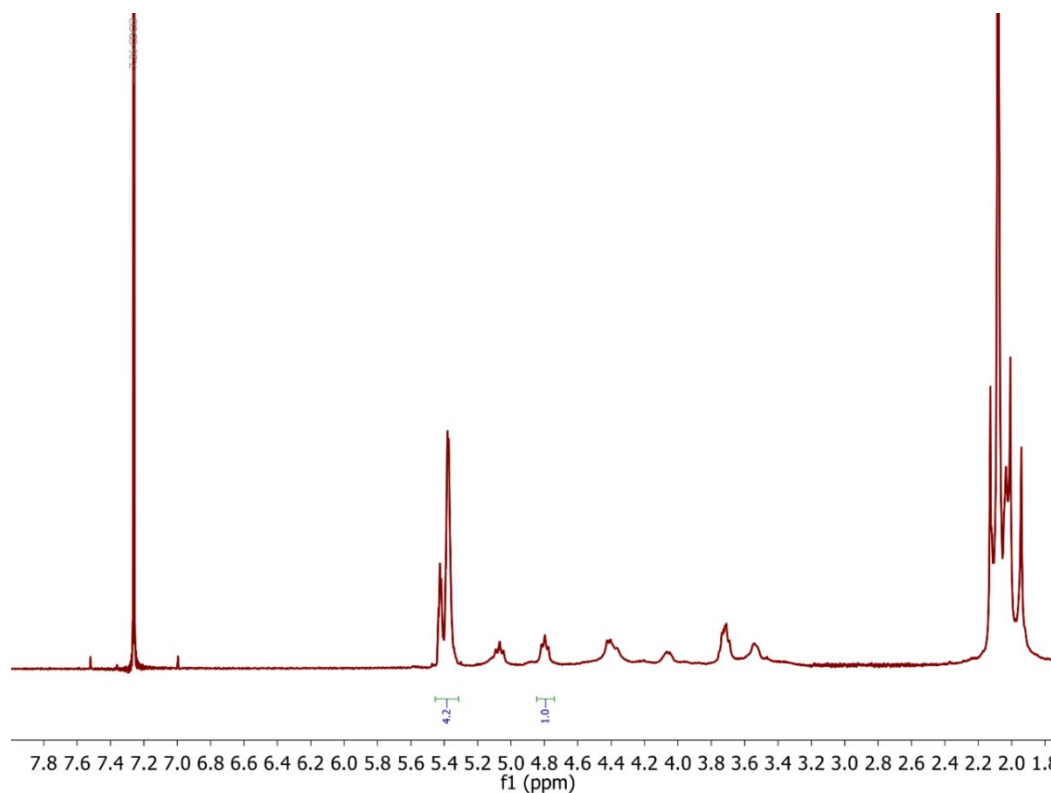


Figure S3: Full ^1H NMR spectrum of **CTA-*b*-PB-*b*-CTA** after isolation and drying.

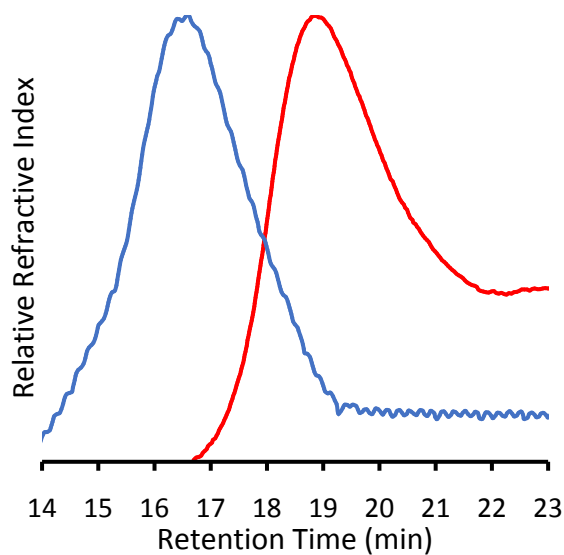


Figure S4: SEC trace of **CTA-Olefin** (red trace, $M_n = 12.5$ kg/mol, $\bar{D} = 2.3$) and **CTA-*b*-PB-*b*-CTA** (blue trace, $M_n = 32.4$ kg/mol, $\bar{D} = 2.3$) in CHCl_3 relative to polystyrene standards. Note: The red trace does not return to baseline because the solvent peak elutes at 22 min and due to the low refractive index of CTA in chloroform.

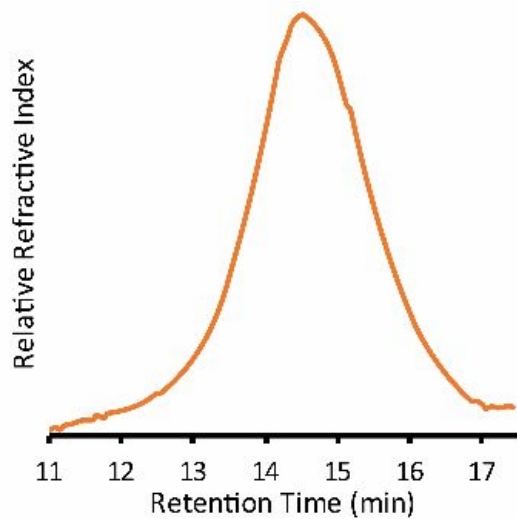


Figure S5: SEC trace of **CTA-*b*-PB-*b*-CTA** in THF ($M_n = 34.3$ kg/mol, $\bar{D} = 2.1$). M_n and \bar{D} values were measured by SEC in THF at 30 °C using refractive index and light scattering detectors.

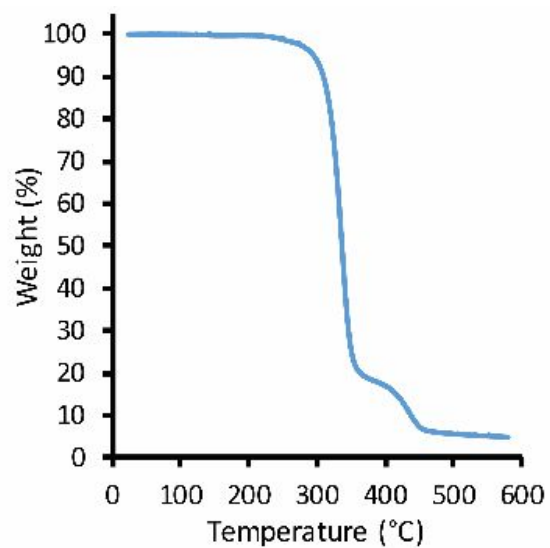


Figure S6: TGA trace of **CTA-*b*-PB-*b*-CTA** from RT to 600 °C with a heating rate of 10 °C/min run under N₂. The onset of degradation (5% weight loss) occurred at 294 °C.

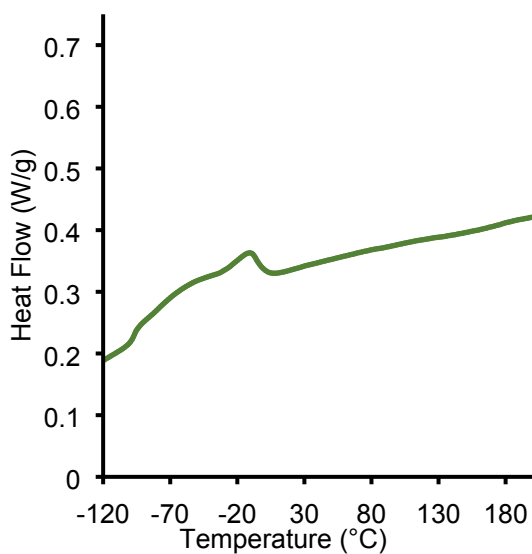


Figure S7: Second heat DSC trace of **CTA-*b*-PB-*b*-CTA**, 10 °C/min, exo down. Glass transitions are observed at -110 °C (PB component) and 187 °C (CTA component); the endotherm observed at -18 °C is attributed to melting of the nonamethylene linkers between the polymer blocks.

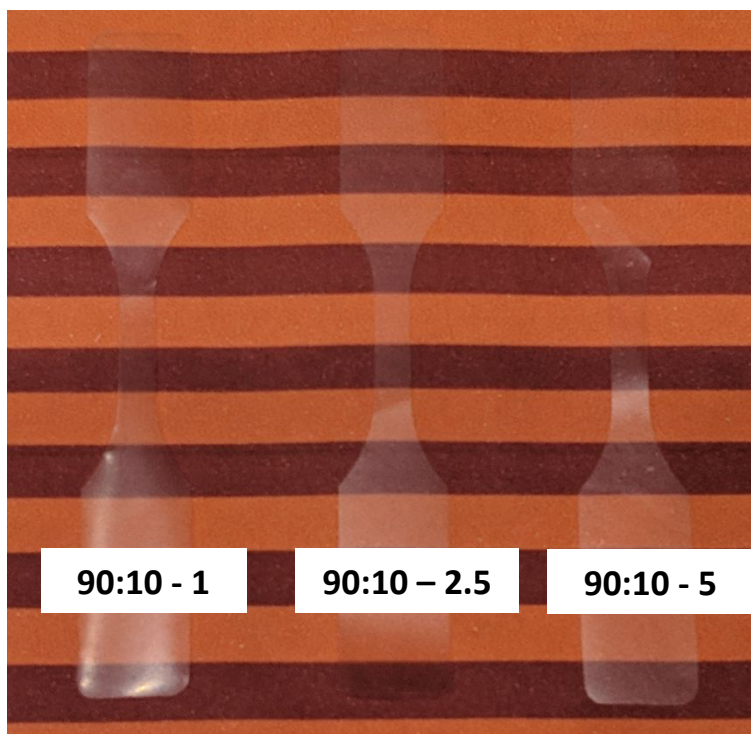


Figure S8: Images of the 90:10 Hi-C series.

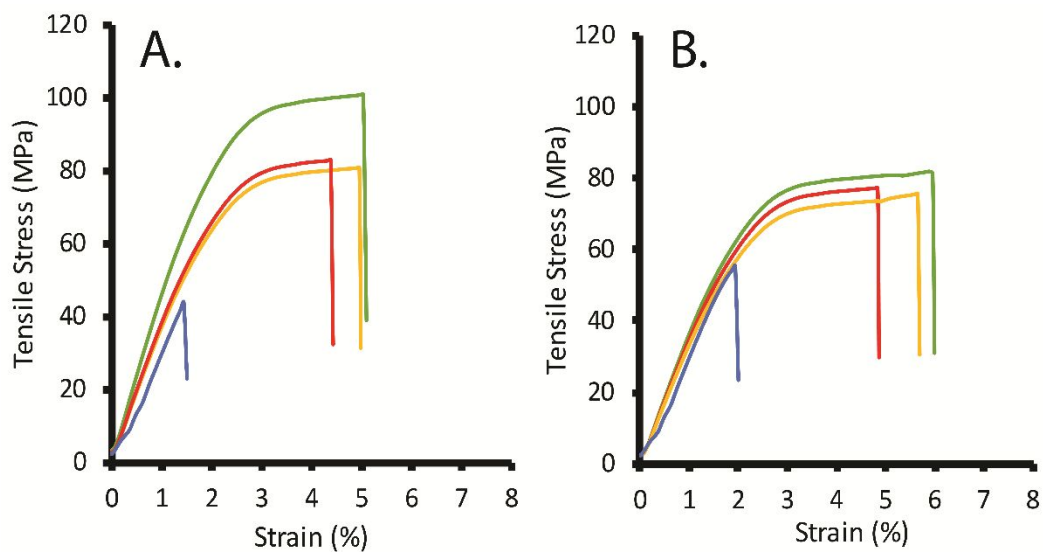


Figure S9: Tensile tests (strain vs. stress) for Hi-C films with variable wt% of compatibilizer. Tensile testing was performed on dog bones in accordance with ASTM D638 at a rate of 20 mm/min. A) 90:10 Hi-C series. **90:10 - 0** (blue trace); **90:10 - 1** (red trace); **90:10 - 2.5** (yellow trace); **90:10 - 5** (green trace). B) 80:20 Hi-C series. **80:20 - 0** (blue trace); **80:20 - 1** (red trace); **80:20 - 2.5** (yellow trace); **80:20 - 5** (green trace).

Table S1: Domain sizes (diameter) of droplets for blends. Domains were sized by ImageJ, sampling 30 spots per sample.

Material	Droplet diameter (μm)
80:20 – 0	6 ± 3
80:20 – 1	4 ± 2
80:20 – 2.5	3 ± 1
80:20 – 5	2 ± 1
90:10 – 0	5 ± 2
90:10 – 1	3 ± 1
90:10 – 2.5	2.0 ± 0.9
90:10 – 5	1.6 ± 0.6

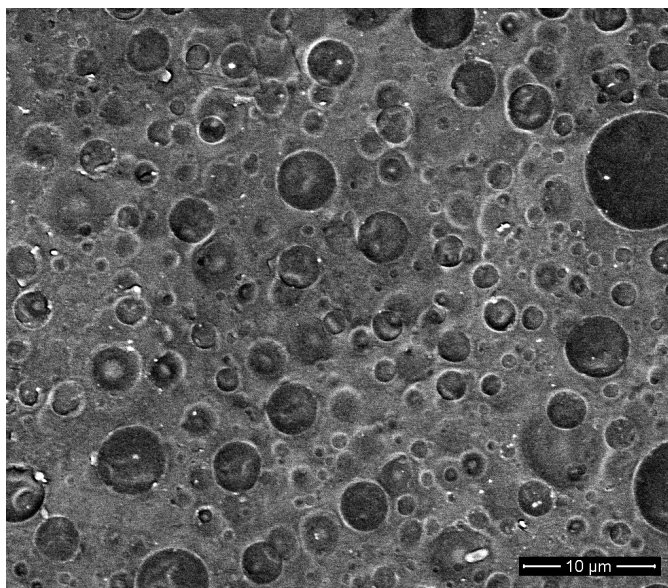


Figure S10: SEM image at 5000x magnification of **80:20 – 0**. Dark circles are PB in a matrix of light colored CTA.

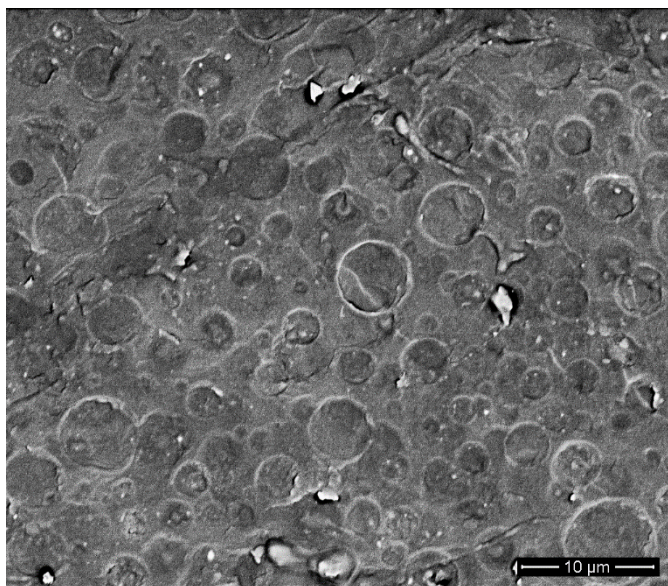


Figure S11: SEM image at 5000x magnification of **80:20 – 1**. Dark circles are PB in a matrix of light colored CTA.

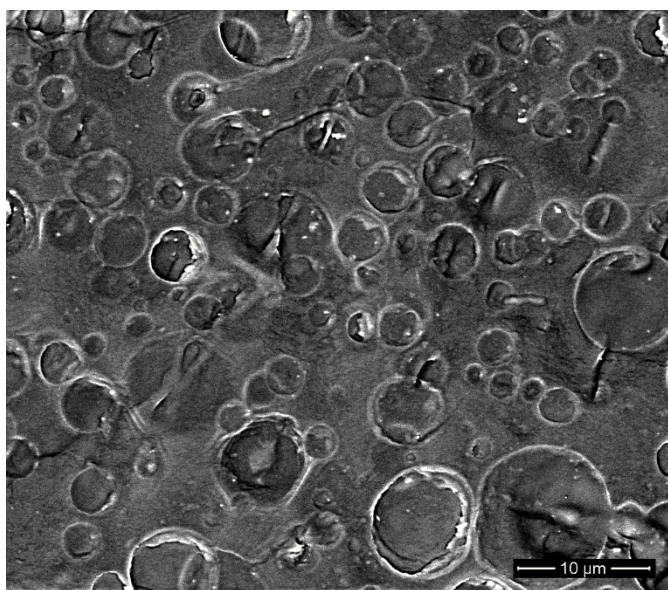


Figure S12: SEM image at 5000x magnification of **80:20 – 2.5**. Dark circles are PB in a matrix of light colored CTA.

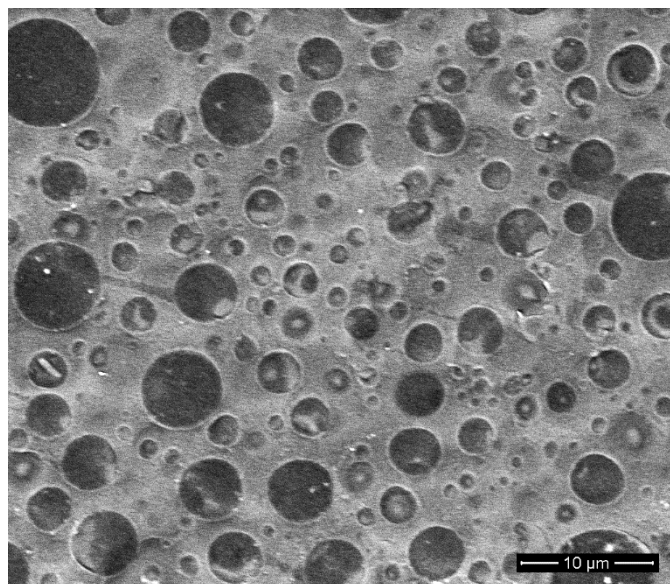


Figure S13: SEM image at 5000x magnification of **80:20 – 5**. Dark circles are PB in a matrix of light colored CTA.

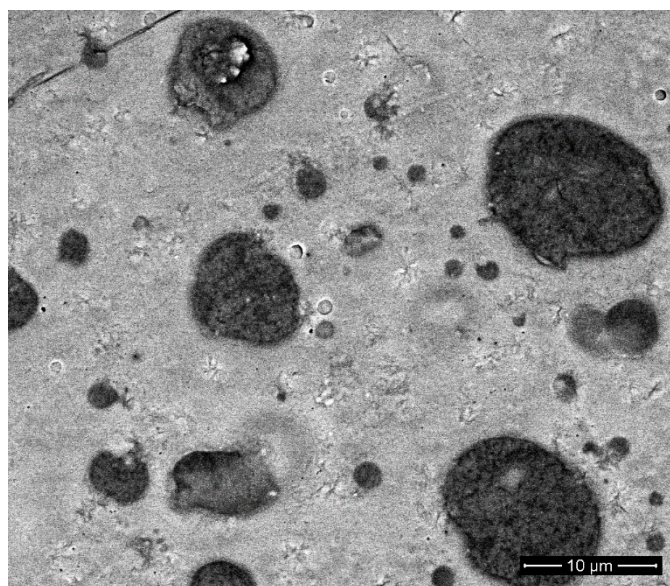


Figure S14: SEM image at 5000x magnification of **90:10 – 0**. Dark circles are PB in a matrix of light colored CTA.

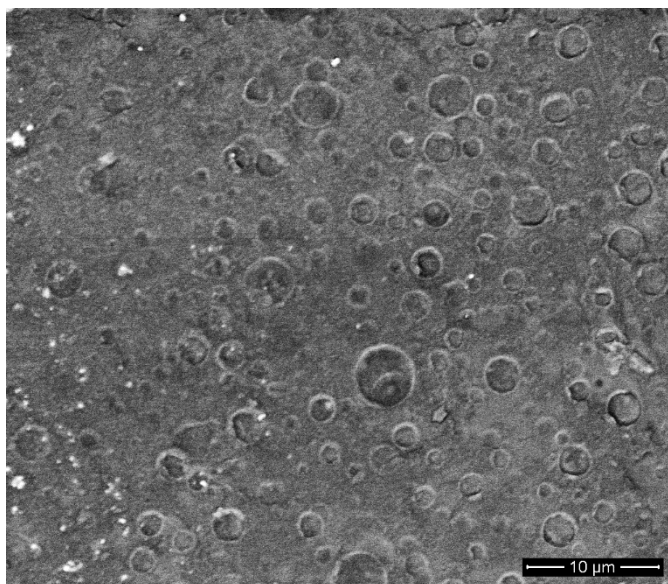


Figure S15: SEM image at 5000x magnification of **90:10 – 1**. Dark circles are PB in a matrix of light colored CTA.

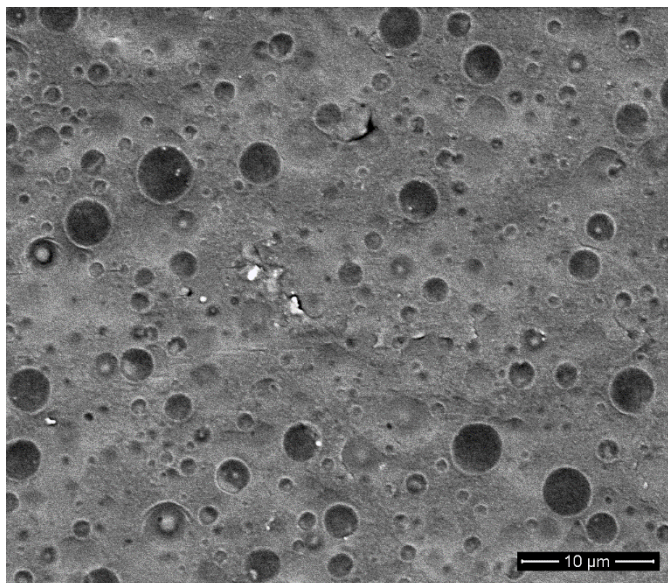


Figure S16: SEM image at 5000x magnification of **90:10 – 2.5**. Dark circles are PB in a matrix of light colored CTA.

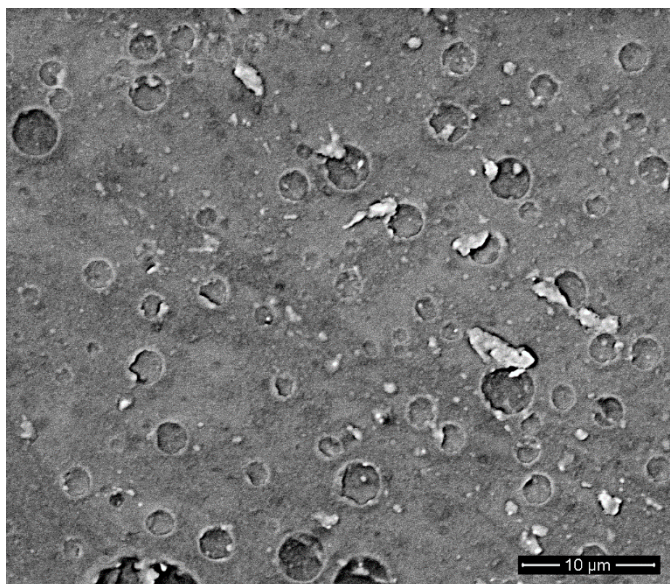


Figure S17: SEM image at 5000x magnification of **90:10 – 5**. Dark circles and craters are PB in a matrix of light colored CTA.