Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Nanoplastics Prepared with Uniformly Distributed Metal-tags: A Novel Approach to Quantify Size Distribution and Particle Number Concentration of Polydisperse Nanoplastics by Single Particle ICP-MS

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Supporting Information

25 Pages, 17 Figures, 2 Tables

Additional Experimental Details:

Photodegradation: Photochemical reactions were performed in a merry go-round photochemical reactor (RPR 100, Southern New England Ultraviolet Company) equipped with 16 low pressure mercury lamps emitting 300 light in quartz glass tubes (15 mL, 1.5 cm outer diameter x 10 cm, The Southern New England Ultraviolet Co., Model RQV-5).

Zebrafish (ZF) Larvae Exposure: ZF eggs were collected 30 minutes after spawning and at 6 hours were dechorionated, allowing NP uptake to be directly determined without the confounding factor of the chorion. Using a 96-well plate each ZF egg was exposed to 10 mg NP/L (1 w/w % Ta-PMMA). After 24 hours the larvae were removed, washed with DI water, and transferred to 1 mL centrifuge tubes. Prior to spICP-MS analysis the tube was bath-sonicated for 5 minutes. The stock NP suspension and the tissue suspension of individual ZF larvae were analyzed by spICP-MS during the same analysis run. Roughly 10^4 NPs were observed per ZF larvae using spICP-MS detection of the metal (Ta) tag.

Materials Characterization:

ATR-FTIR. Attenuated total reflectance-infrared spectroscopy measurements of the metal-tagged plastic composites were obtained using a Nicolet iS5 (Thermo Fisher, Waltham, MA) spectrometer with an iD5 ATR attachment using a scan range from 3800-600 cm^{-1} with 64 scans at 0.964 cm^{-1} resolution.

Water Contact Angle. Contact angle measurements of the metal-tagged plastic composites were performed using a KSV Instruments CAM 100.

Differential Scanning Calorimetry. DSC measurements were made with a TA Instruments DSC 25, in which approximately 5 mg of sample was loaded in a aluminum crucible. PS, PMMA, and PE samples were heated to 250, 190, or 200°C, respectively, at a rate of 10°C min^{-1} under a constant and simultaneous flow of N2 (300 mL/min) and O2. Once the desired temperature was achieved, heat was maintained for 1 minute and then cooled to initial starting temperature at 10°C min^{-1}. Initial equilibration temperatures were 30°C for PMMA and 40°C for PS and PVC.

X-Ray Photoelectron Spectroscopy. XPS spectra of micro- and nanoplastics were collected using a Thermo Fisher Scientific K-Alpha X-ray Photoelectron Spectrometer with an Al Kα source (1486.6 eV). Survey scans were collected from 1350 eV to 0 eV with a pass energy of 100 eV and resolution of 1.00 eV/step. Detailed scans of the C(1s), O(1s), Sn(3d), Cl(2p), and Ta(4f) regions were acquired at a pass energy of 50 eV and a 0.20 eV/step resolution. Spectra were analyzed using CASA XPS software.

Scanning Electron Microscopy. Prior to analysis, a colloidal suspension of 1 w/w% Ta-PMMA NPs was prepared and drop-cast onto a silicon wafer. Data was collected at a 10 mm working distance and a beam energy of 5.0 kV. Irregular NP shapes measured in SEM were converted into an equivalent spherical diameter using Image J. The edge of each particle was traced to determine the cross-sectional area, which was subsequently converted into the equivalent spherical diameter.

Tables.

Table SI-1. Full summary of all composite syntheses. All sonication times are approximate.

Polymer	Organometallic Additive	Solvent	Mass Polymer (mg)	Mass Additive (mg)	Volume Solvent (mL)	Sonication Time (hrs)	Result
Polystyrene (PS) MW= 280,000	Tantalum (V) ethoxide	Benzene	2000	20	30	3	Success
		Tetrahydrofuran	2000	20	30	2.5	Success
	Dibutyltin diacetate	Tetrahydrofuran	2000	20	30	2	Success
	Zirconium (IV) ethoxide	Benzene	2000	20	30	3	Success
	Platinum 2, 4-pentanedionate	Chloroform	2000	20	30	3	Failed
		Tetrahydrofuran	2000	20	30	3	Failed
	Tantalum (V) chloride	Chloroform	2000	20	30	2	Failed
Polymethyl methacrylate (PMMA) MW= 168,000	Tantalum (V) ethoxide	Toluene	2000	20	30	3	Success
		Tetrahydrofuran	2000	20	30	2.5	Success
	Dibutyltin diacetate	Tetrahydrofuran	2000	20	30	2	Success
	Zirconium (IV) ethoxide	Toluene	2000	20	30	3	Failed
	Platinum 2, 4-pentanedionate	Toluene	2000	20	30	3	Failed
	Tantalum (V) chloride	Chloroform	2000	20	30	2.5	Failed
Polyvinylpyrrolidone (PVP) MW= 10,000	Tantalum (V) ethoxide	Methanol	2000	20	30	3	Success
Low-density Polyethylene (LDPE) MW= 4,000	Tantalum (V) ethoxide	Toluene	2000	20	45	24	Success
Polyvinyl chloride (PVC) MW= 35,000	Tantalum (V) ethoxide	Tetrahydrofuran	2000	20	30	4	Success
	Dibutyltin diacetate	Tetrahydrofuran	2000	20	30	6	Failed

Table SI-2. Summary of water contact angle measurements for composite plastics PS, PMMA, LDPE, and PVC with and without organometallic additive (tantalum (V) ethoxide).

	Additive Loading	
	0 wt. %	**1 wt. %**
PS	90 ± 1	89 ± 1
PMMA	78 ± 2	77 ± 2
LDPE	89 ± 1	88 ± 1
PVC	79 ± 2	82 ± 1

Figures.

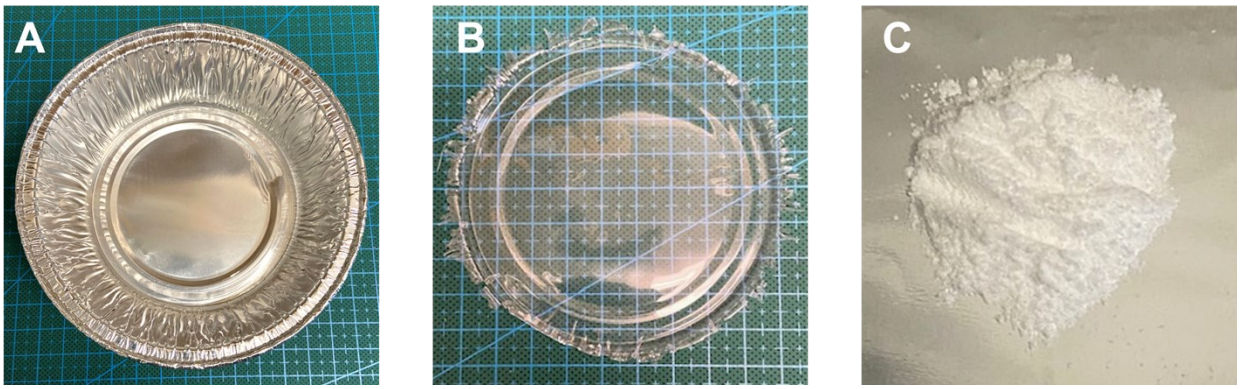

Figure SI-1: Digital images of (A) 1 w/w % Ta-PS composite in aluminum pan after solvent evaporation. (B) 1 w/w % Ta-PS composite after removal from aluminum pan. (C) 1 w/w % Ta-PS nanoplastics prepared after cryogenic milling of (B). Note: the solid grid lines in A and B represent 1 cm.

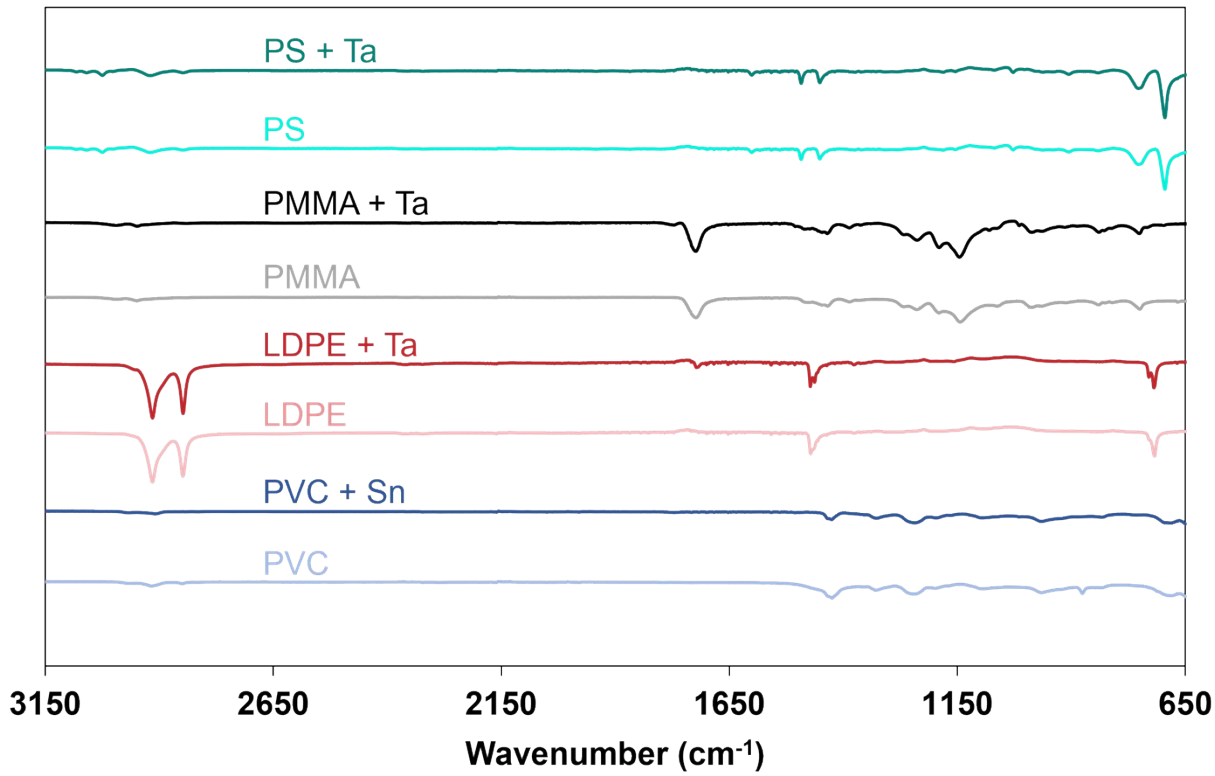

Figure SI-2: Infrared spectra of composite plastics PS (dark teal, light teal), PMMA (black, grey), and LDPE (red, pink) with and without organometallic additive (tantalum (V) ethoxide, 1 w/w % loading), and PVC (dark blue, light blue) with and without organometallic additive (dibutyltin (IV) dilaurate, 1 w/w % loading).

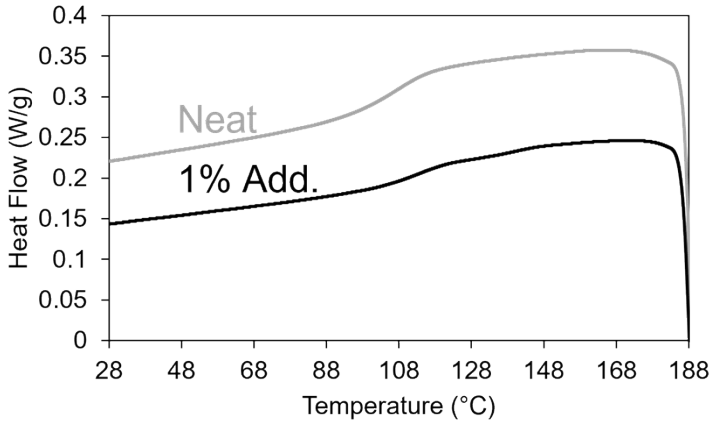

Figure SI-3: Differential scanning calorimetry results obtained for samples of PMMA NPs prepared with and without organometallic additive (tantalum (V) ethoxide, 1 w/w %). All data is mass corrected.

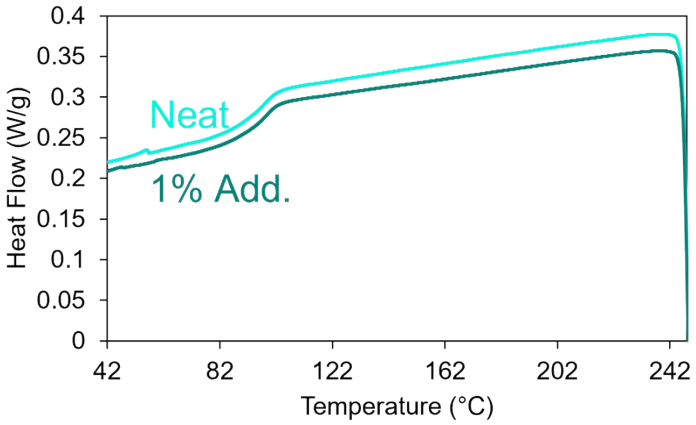

Figure SI-4: Differential scanning calorimetry results obtained for samples of PS NPs prepared with and without organometallic additive (tantalum (V) ethoxide, 1 w/w %). All data is mass corrected.

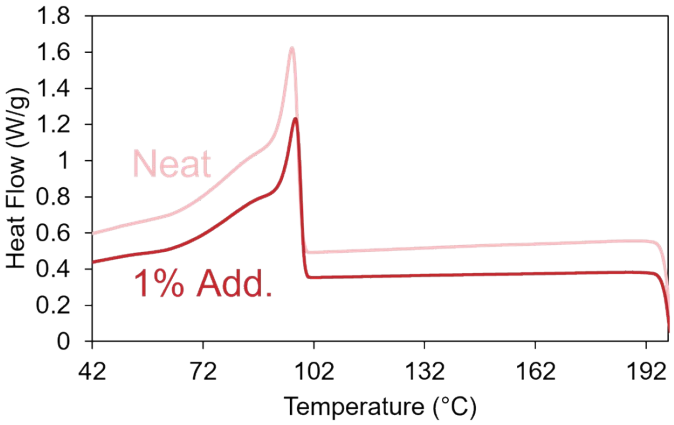

Figure SI-5: Differential scanning calorimetry results obtained for samples of PE NPs prepared with and without organometallic additive (tantalum (V) ethoxide, 1 w/w %). All data is mass corrected.

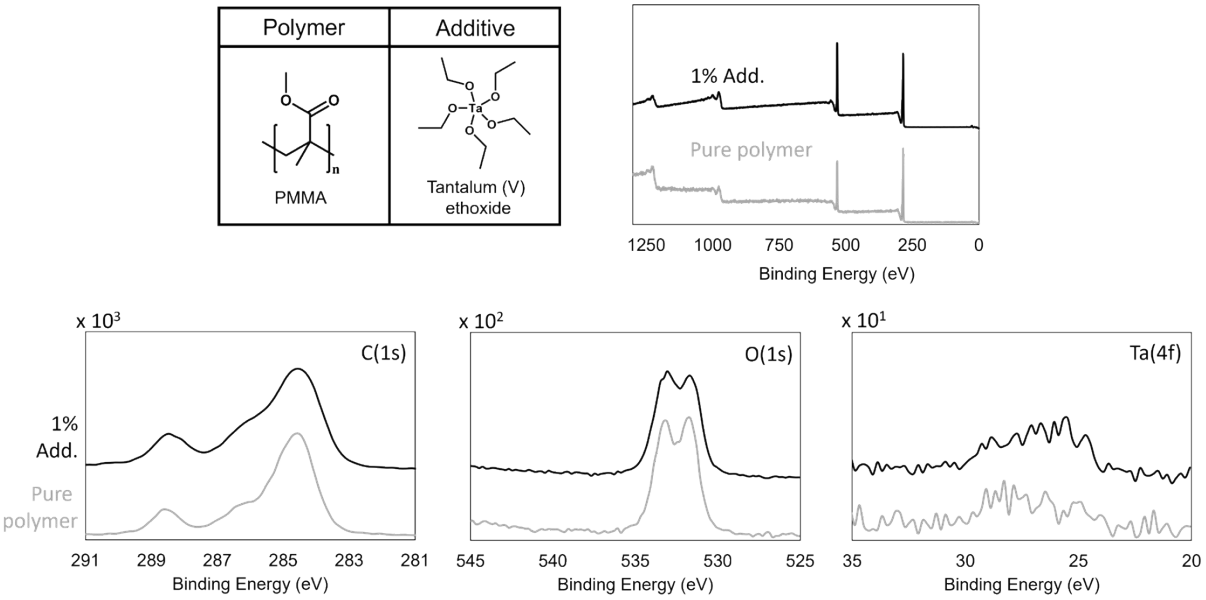

Figure SI-6. X-ray photoelectron spectra of 1% Ta-PMMA composite (black) and neat PMMA control composite (light grey). a) Full survey scan. b) C(1s) region. c) O(1s) region. d) Ta(4f) region.

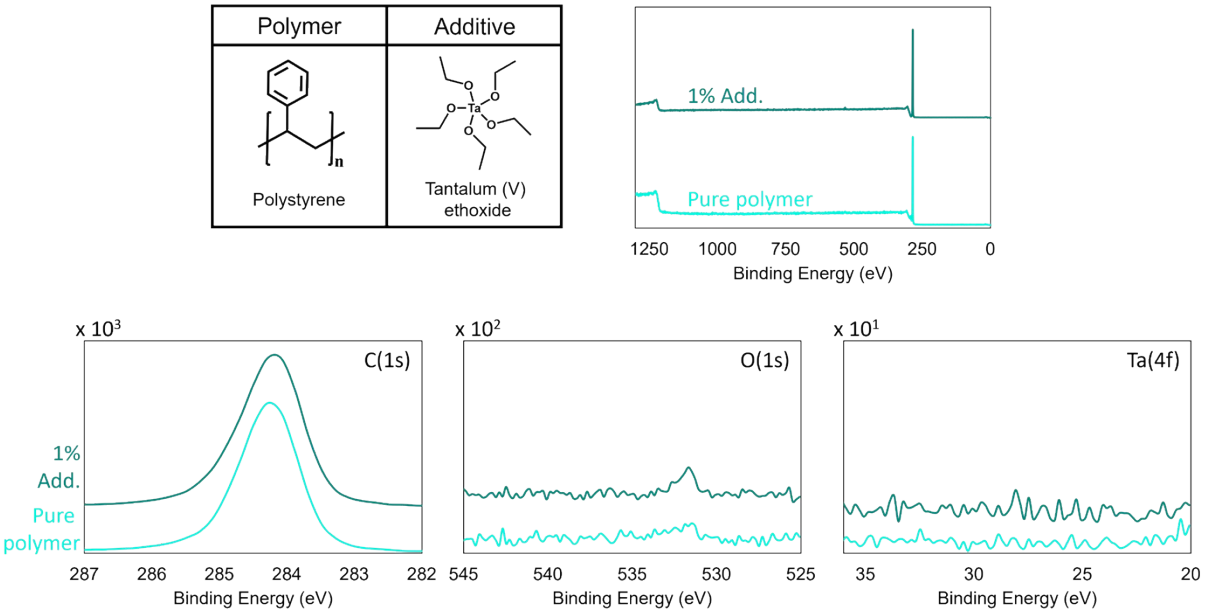

Figure SI-7. X-ray photoelectron spectra of 1% Ta-PS composite (dark teal) and neat PS control composite (light teal). a) Full survey scan. b) C(1s) region. c) O(1s) region. d) Ta(4f) region.

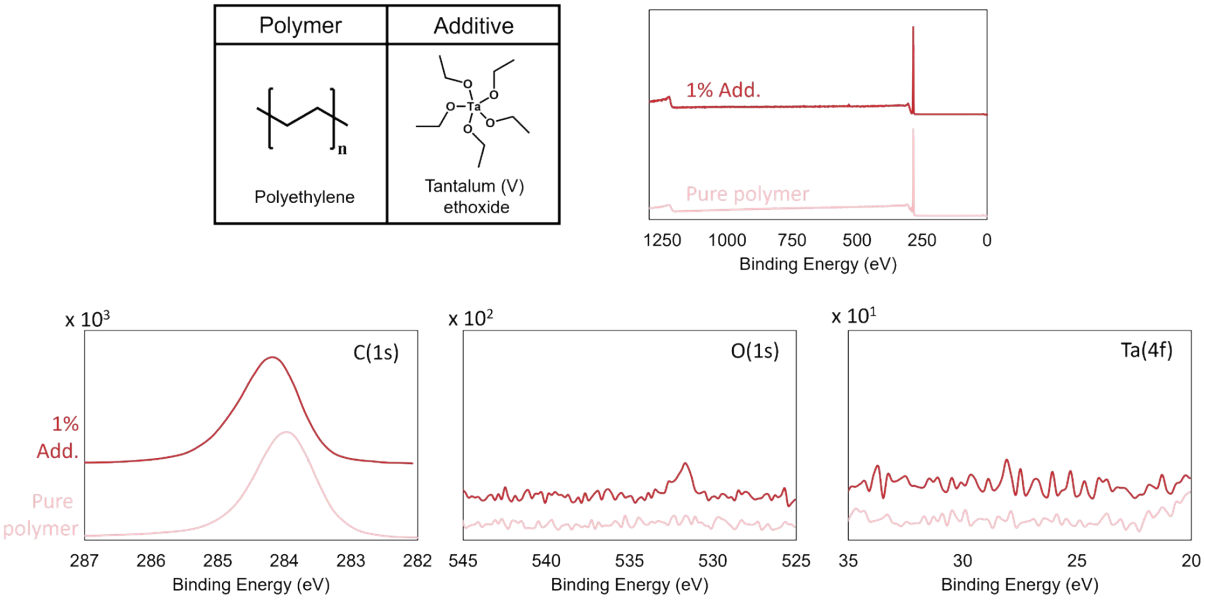

Figure SI-8. X-ray photoelectron spectra of 1% Ta-LDPE composite (red) and neat LDPE control composite (pink). a) Full survey scan. b) C(1s) region. c) O(1s) region. d) Ta(4f) region.

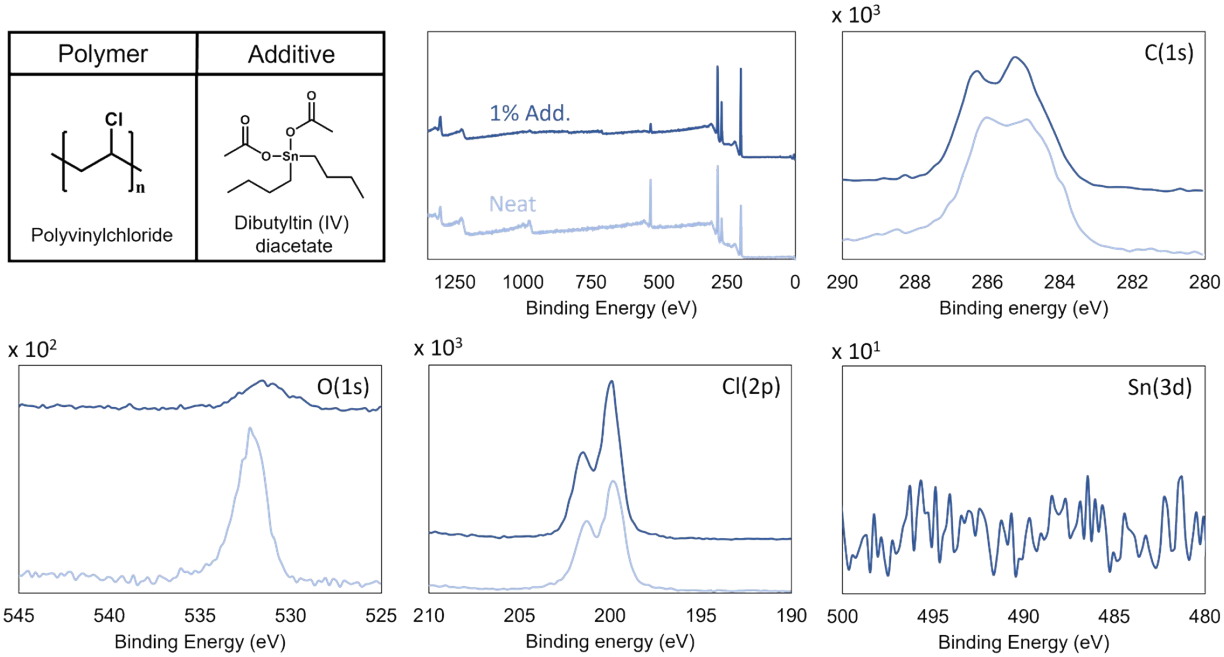

Figure SI-9. X-ray photoelectron spectra of 1% Sn-PVC composite (dark blue) and neat PVC control composite (light blue). a) Full survey scan. b) C(1s) region. c) Cl(2p) region. d) O(1s) region. e) Sn(3d) region.

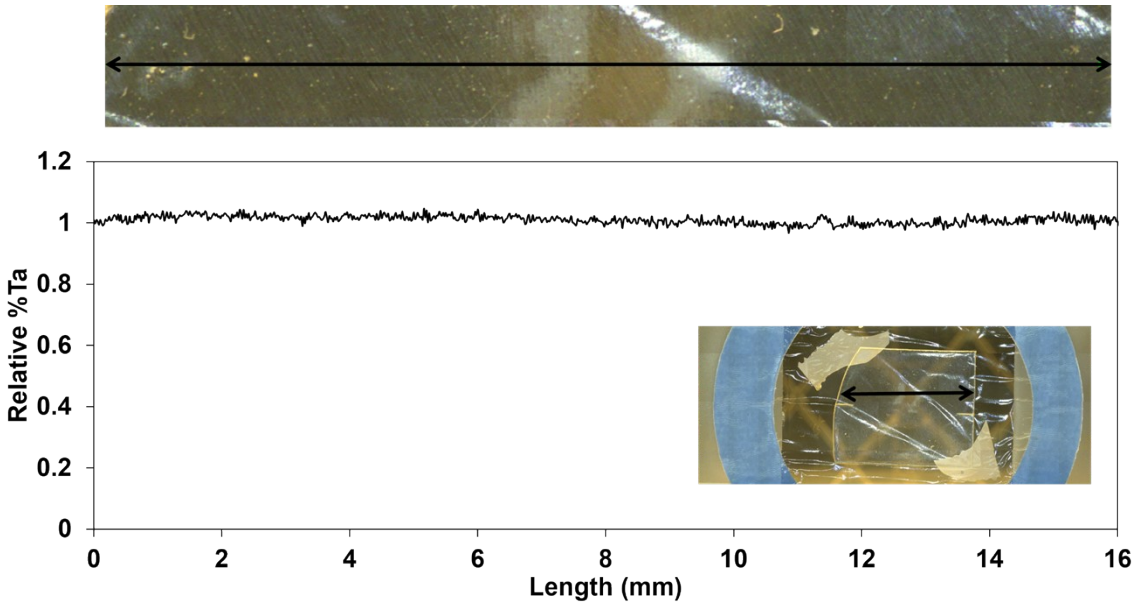

Figure SI-10: uXRF of a 1 w/w % Ta-PMMA composite. Shown is the relative % Ta detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 20 µm spot size over a sample distance of 16 mm.

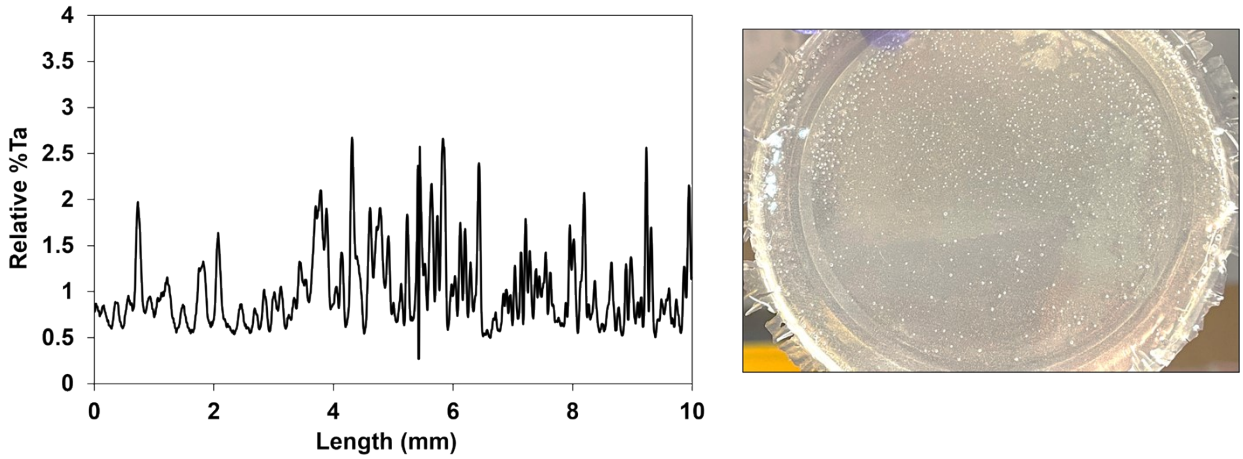

Figure SI-11: uXRF of a 1 w/w % Ta-PS composite prepared with tantalum (V) chloride. Shown is the relative %Ta detected as a function of composite length with data collected at a 20 μm spot size over a sample distance of 10 mm. Inset image depicts additive aggregation within composite.

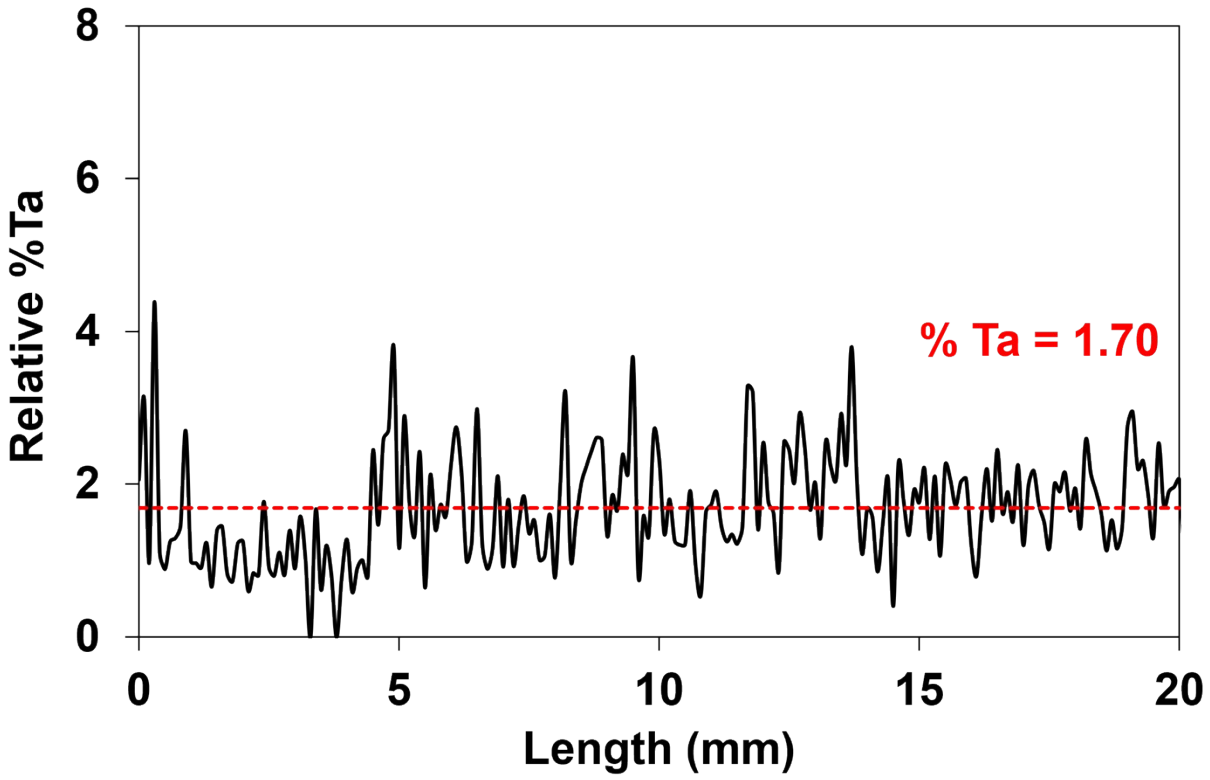

Figure SI-12: *uXRF of a 1 w/w % Ta-PS composite prepared with tantalum (V) ethoxide. Shown is the relative % Ta detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 100 µm spot size over a sample distance of 20 mm.*

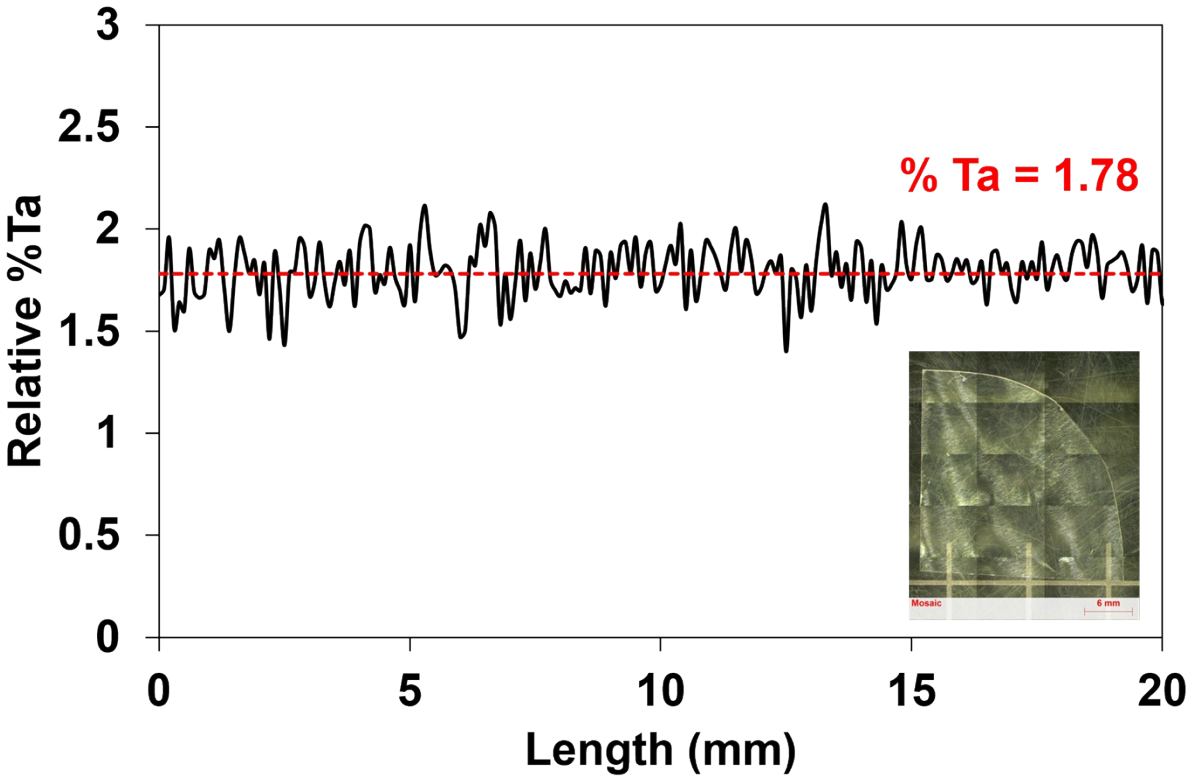

Figure SI-13: *uXRF of a 1 w/w % Ta-PVC composite prepared with tantalum (V) ethoxide. Shown is the relative % Ta detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 100 µm spot size over a sample distance of 20 mm.*

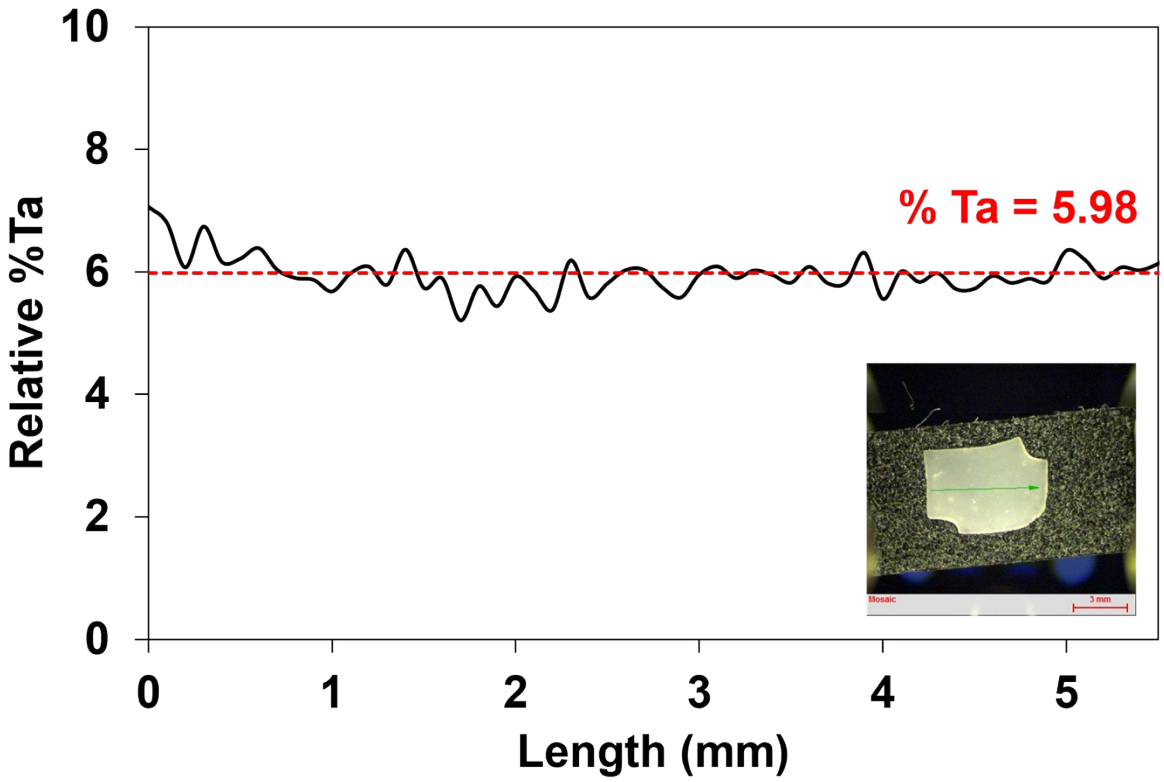

Figure SI-14: *uXRF of a 1 w/w % Ta-PE composite. Shown is the relative % Ta detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 100 µm spot size over a sample distance of 5.5 mm.*

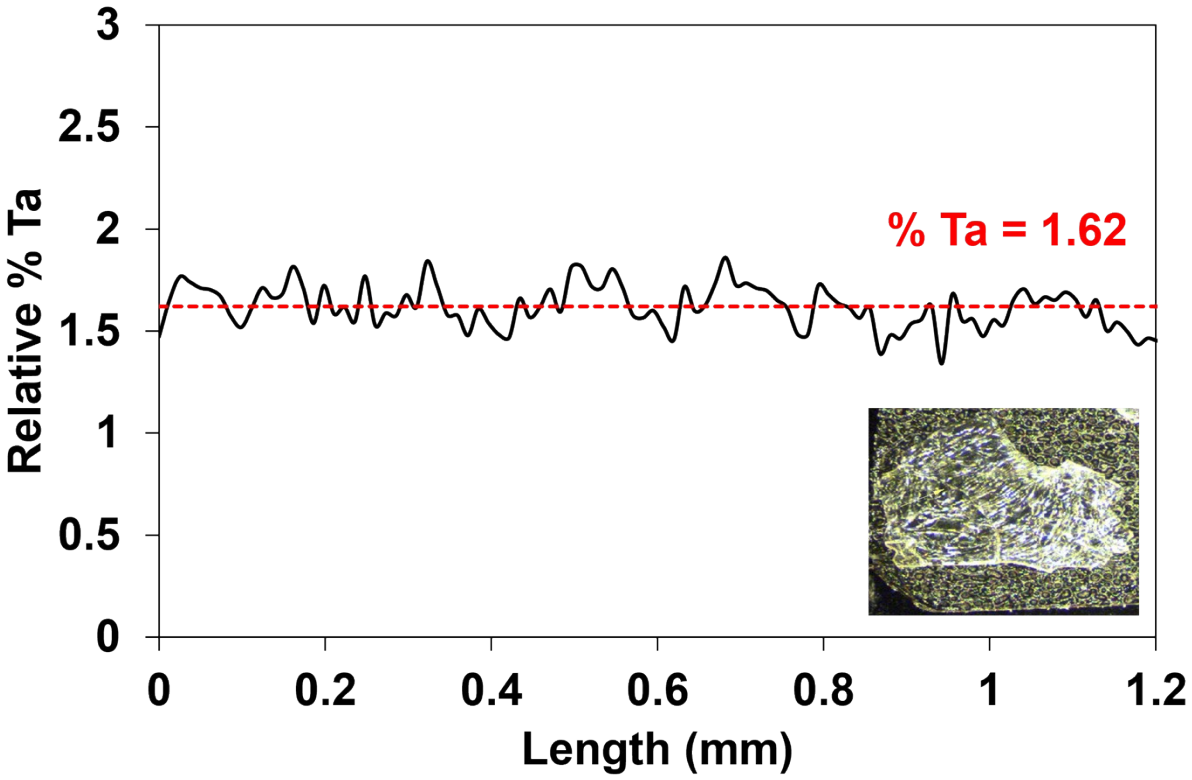

Figure SI-15: *uXRF of a 1 w/w % Ta-PVP composite. Shown is the relative % Ta detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 12 µm spot size over a sample distance of 1.2 mm.*

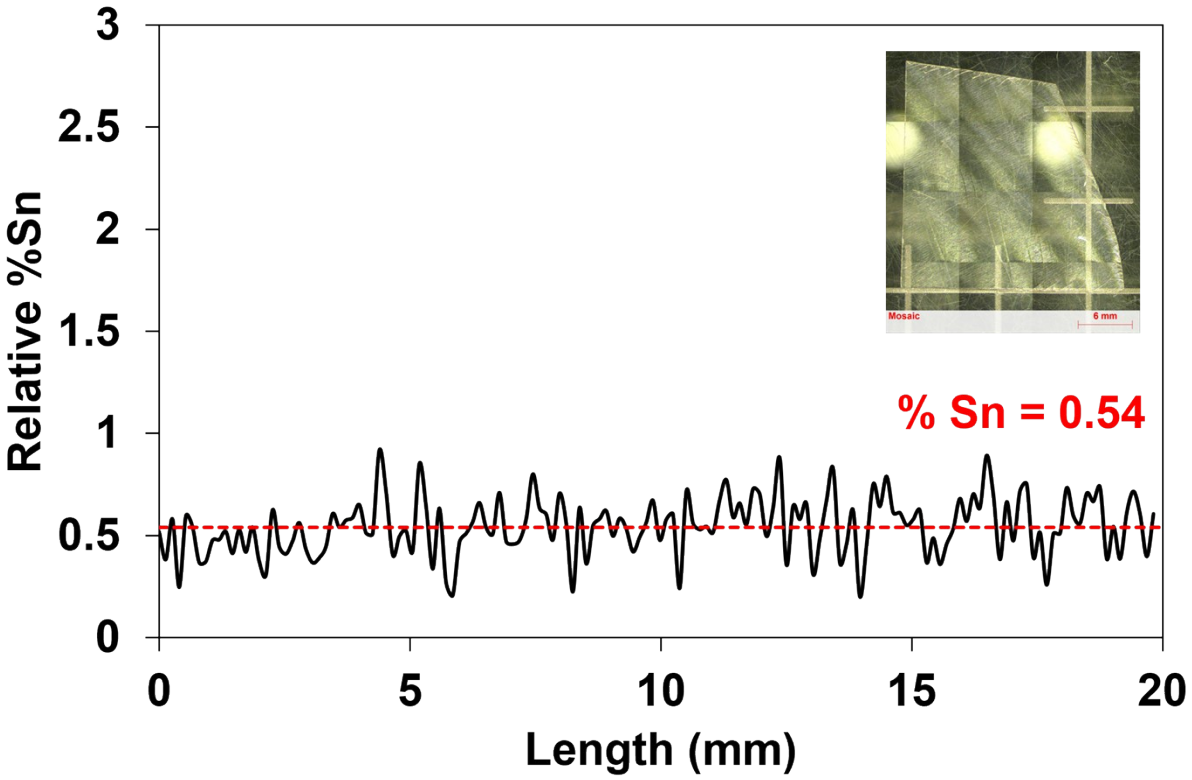

Figure SI-16: *uXRF of a 0.5 w/w % Sn-PMMA composite. Shown is the relative % Sn detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 100 µm spot size over a sample distance of 20 mm.*

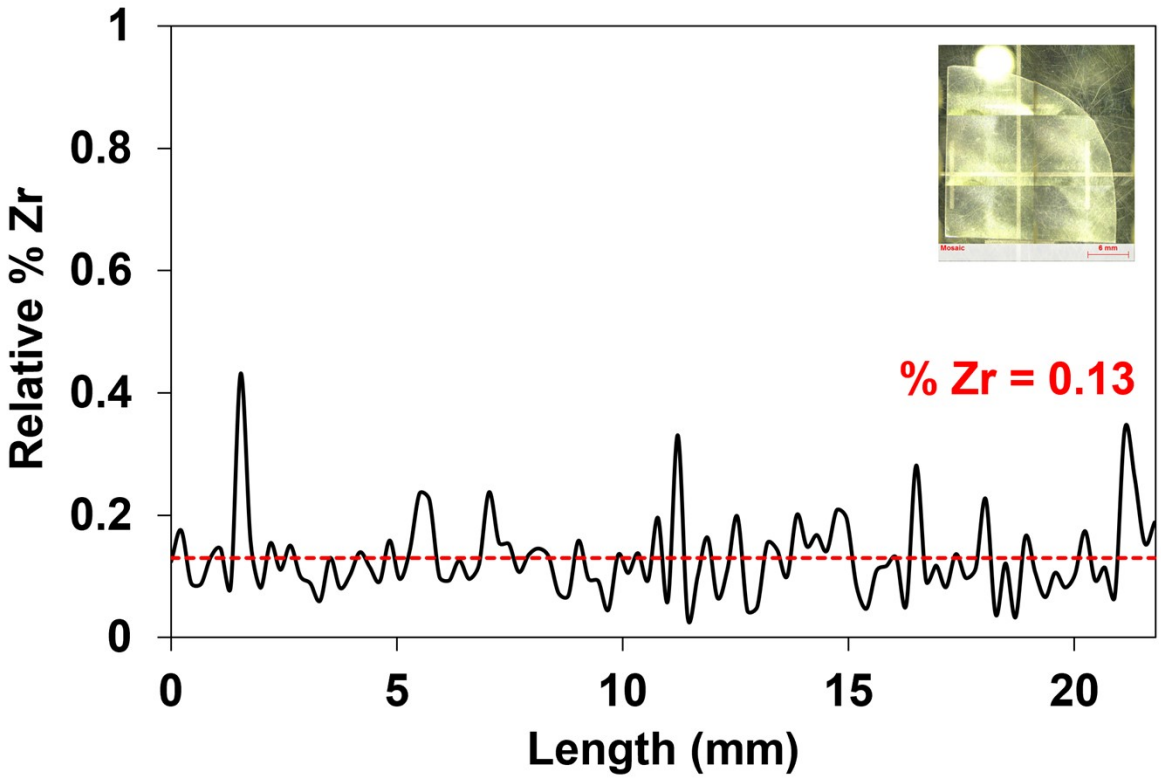

Figure SI-17: *uXRF of a 0.5 w/w % Zr-PS composite. Shown is the relative % Zr detected as a function of composite length to demonstrate the uniformity of metal loading within the plastic. Data collected at a 220 µm spot size over a sample distance of 22 mm.*