Large Format Additive Manufacturing and Machining using High Melt Temperature Polymers. Part II: Characterization of Particles and Gases

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Supporting Information

METHODS

Bubbler (Liquid Impinger) Sample Analysis for Aldehydes

For all carbonyl impinger samples, after collection, the water was decanted into 40 mL vials, then derivatized with 100 µL aqueous 250 mM O-tert-butylhydroxylamine hydrochloride (TBOX, Sigma Aldrich, St. Louis, MO) and placed in a heated water bath at 70°C for 2 hours. After removing the vial from the water bath and allowing to cool to room temperature, 0.5 mL of toluene was added to the vial. The vial was then shaken for 30 seconds and allowed to separate into a toluene layer and aqueous layer. Then 100 µL of the toluene layer was removed with a pipette and placed in a 2 mL autosampler vial with a 100 µL glass insert (Restek, Bellefonte, PA). Then 1 µL of the TBOX-derivatized extract was analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 gas chromatograph-mass spectrometer (GC-MS) system operated in the electron impact (EI) mode. Full-scan EI ionization spectra were collected from m/z 40-650. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (30 m long x 0.25 mm ID x 0.25 µm film thickness) column and the following gas chromatograph oven parameters: 40 °C for 2 min, then 5 °C/min to 200°C, then 25 °C/min to 280 °C and held for 5 min. One µL of each sample was injected in the splitless mode with the following injector temperature parameters: 130 °C for 2 min then 200 °C/min to 300 °C and held for 10 min. Samples were injected in the splitless mode and was returned to split mode 1 min after sample injection. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43).

Glass and Quartz Fiber Filter and Surface Swab Sample Analysis for BPA and BPS

All samples were sent on cold packs to the NIOSH laboratory as the original air sampling cassettes or as single swabs in 20 mL screw-capped polypropylene vials. On arrival they were refrigerated at approximately -8 °C until processing and analysis began. Samples were brought to ambient lab temperature before workup proceeded. Air samples (glass fiber or quartz fiber filters) were removed from the cassettes and transferred to 20 mL amber glass vials with Teflon-lined screw caps

(Fisher Scientific, Pittsburgh, PA, USA) using steel tweezers. Samples were fortified with 40.0 µL of 5.00 µg/mL of BPA-d_8 (MilliporeSigma, Burlington, MA, USA). 2.00 mL of Optima liquid chromatography-mass spectrometry (LC-MS) grade acetonitrile (Fisher Scientific) was added to each vial and samples were extracted on a tumbler (one turn per sec) for 2 hours. 2.00 mL of LC-MS grade water (Fisher Scientific) was added to each vial followed by brief agitation on a vortex mixer. Extracts were put through 13 mm polyvinylfluoridene 0.22 µm syringe filters (Millex, MilliporeSigma) using 5 mL disposable polypropylene syringes (Becton-Dickinson, Franklin Lakes, NJ) and collected in 8 mL amber glass vials with Teflon-lined screw caps (Fisher Scientific). Swab samples were processed in the original polypropylene vials. Workup procedure was identical except that acetonitrile and water aliquots were both increased to 5.0 mL and 100 µL of 5.0 µg/mL BPA-d_8 was added. The fortification volumes provided 50 ng/mL BPA-d_8 in the extracts for both air and wipe samples. Polypropylene pipet tips were used for all liquid transfers. Next, 990 µL of each sample extract was pipetted into glass LC-MS certified autosampler vials with PTFE/silicone slit-septa screw caps (Waters Corp., Bedford, MA, USA). 10 µL of 5.00 µg/mL $^{13}C_{12}$-BPA (Isotec/Sigma-Aldrich) was added to each vial, which was recapped and briefly vortexed, providing 50 ng/mL. The isotopically labeled standards allowed tracking of potential sample losses during workup (BPA-d_8) and of issues encountered during instrumental analysis (BPA-$^{13}C_{12}$).

<u>LC-MS Analysis of BPA and BPS</u>

Samples were analyzed on an Acquity Sample Manager/Binary Solvent Manager/Triple Quadrupole liquid chromatography-mass spectrometry unit (Waters Corp.) controlled by MassLynx 4.0 software. Loaded vials were placed into the autosampler tray which was maintained at 10 °C by a built-in chiller. Strong autosampler needle wash was 50% water/50% methanol and weak needle wash was 75% water/25% methanol, each 600 µL. The pump seal wash was 90% water/10% methanol. Sample injection volume was 10 µL using full loop option with 2X overfill. The analytical column was Waters

X-Bridge C18, 3.5 µm, 150 mm x 2.1 mm, preceded by a 10 mm x 2.1 mm guard column with identical content. Connections between autosampler and column were stainless steel and connections between column exit and MS detector were polyetheretherketone polymer using the lowest practical tubing length. Analytical and guard columns were maintained at 30 °C in the autosampler heating compartment. Mobile phases were Optima LC-MS grade water and Optima grade methanol (Fisher Scientific) with no fortification. The following gradient steps were employed using a linear ramp at a constant flow rate of 250 µl/min:

Time (min)	%Water	%Methanol
0.00	70	30
2.00	70	30
7.00	25	75
9.00	25	75
10.50	70	30
12.00	70	30

In practice, column re-equilibration was extended by about 90 seconds for the time required to load each subsequent sample for injection. Observing column backpressures demonstrated that re-equilibration was complete using this gradient. Elution of BPS and BPA under these conditions occurred at approximately 5.5 min and 7.5 min, respectively.

The detector was operated with desolvation gas flow rate of 850 L/hr nitrogen at 475 °C with cone gas at instrument setting 40, provided by a NitroFlow generation system (Parker-Balston, Gateshead, United Kingdom). Electrospray voltage was 3.50 kV in negative ion mode. Source block temperature was nominally 125 °C and collision-induced fragmentation was accomplished using ultra high purity argon at approximately 5 x 10^{-3} Torr in the collision cell. Values for other MS detector parameters are available on request. The following parent-fragment ion transitions were used to monitor the two most intense signals for both BPA and BPS and the most intense signal for each of the two isotopically labeled internal BPA standards.

BPA m/z 227 > 212 (quantification) and 133 (confirmatory)

BPS	m/z 249 > 108 (quantification) and 92 (confirmatory)
BPA-d_8	m/z 235 > 220
BPA-$^{13}C_{12}$	m/z 239 > 224

MassLynx software adjusted collision energies during each analysis to provide optimal signal intensity for each fragment ion that was monitored. The span monitored for all fragment ions was 0.1 m/z and dwell time for each ion was 0.100 sec. Exact values for parent and fragment ion signals were determined to 0.10 m/z by infusing a mixed standard of the four compounds prior to analysis of field samples; detector ion sampling hardware was thoroughly cleaned before analyses began.

Quality Control Measures

Analytes used to prepare in-house calibration standards and quality control samples were BPA > 99% and BPS analytical standard > 98.0% (both MilliporeSigma). Separate stock solutions were prepared at 100 µg/mL by weighing 10.0 mg of the analytes into dry 100 mL volumetric flasks and dissolving in 50% acetonitrile/50% water. Stocks of the isotopically labeled BPA compounds were similarly prepared at 1000 µg/mL in 10 mL flasks. Stocks were prepared fresh for each analytical session and serially diluted as needed.

For each sampling media, limits of detection and quantification were determined by NIOSH protocol by spiking four low levels of BPA and BPS onto blank media from the same lot used for field samples. Levels were chosen to be within about 10 times the estimated limits of detection (LODs) based on prior experience analyzing the compounds. Spikes were prepared in duplicate for each level and (along with two unspiked media blanks) were processed identically to field samples, including one day of refrigerated storage and fortification with internal standards. A regression curve was plotted for the responses and LOD was determined as $3Se_y$/slope where Se_y is the standard error for the y-axis intercept. The limit of quantification (LOQ) was 3.3 x LOD or $10Se_y$/slope. Due to larger extract volume, LOD/LOQ for swabs were typically higher than for air samples. LOD were determined for each analysis session, since instrument sensitivity varies somewhat depending on time elapsed since calibration, cleaning or annual maintenance.

For each sample media, a set of laboratory quality controls (LQC) were prepared using blank media from the same lot used for field samples. These were spiked at four different target levels of BPA and BPS (two replicates per level) covering the range of the calibration standards and prepared identically to field samples. LQC were interspersed with samples during analysis, and average recoveries relative to nominal target levels were determined for each analyte and used as correction factors for field sample quantification results. Particular attention was paid to whether significantly different recoveries were observed for different target levels.

Several field samples of each media type and (when time permitted) LQC samples were rerun during each session and the results were compared to first-run values.

Data Assessment

Chromatographic elution peaks for each ion were smoothed and integrated using MassLynx software. Area for the most intense (quantification) ion for each analyte was divided by area for the BPA-$^{13}C_{12}$ ion and this ratio was used for calibration plot generation and subsequent sample quantification. Peak areas for both isotopically labeled BPA standards were tracked to monitor sample workup or instrumental issues. The ratio of quantification and confirmatory ions was calculated for both analytes during the initial run of each calibration standard, and the average ratio for all the standards was noted for each compound. The same ion ratio was calculated for field samples and quality controls. The latter are prepared from analyte standards so the ion ratio should match well with the expected average. If the ion ratio for a field sample deviated significantly from the expected average, it may indicate inflated positive analyte signal (via interferent overlap) or other problems in peak integration or analysis.

If a result exceeded the calibration plot range, the original sample extract was diluted with 50% acetonitrile/50% water, 990 µl of the diluent was fortified with 10 µL of 5.0 µg/mL $^{13}C_{12}$-BPA, and reanalyzed to ensure that analyte signal now fell within range. This procedure reduced BPA-d_8 signal according to extent of dilution, but $^{13}C_{12}$-BPA signal was unaffected relative to undiluted samples or calibration standards since it was added afterwards. Dilution factors were incorporated into calculation of sample analyte content. Required dilutions were occasionally fairly extensive (e.g., >100 fold).

Number and Type of Time-integrated Samples by Polymer and Print Job

The number and type of time-integrated samples collected for each polymer and print job are summarized in the tables below. This summary does not include background samples that were collected prior to each print job. If a cell in a table indicates n = 2, it means that one sample was collected inside the LFAM enclosure (at the front of the machine) and one sample was collected at the operator's location for that polymer/print job combination. If a cell indicates n = 4, it means that pairs of samples were collected inside and outside of the LFAM enclosure at the front and side of the machine. If a cell indicates n = 6, it means that pairs of samples were collected inside and outside of the LFAM enclosure at the front, side, and rear of the machine. For Ultem® only, one impinger sample was collected for each print job at the operator's platform. Additionally, only three MCE filter and three canister samples were collected for print job 2 (operator's platform, side, and rear of LFAM); all were positioned outside of the enclosure. Sampling times in minutes are included in [brackets].

Acrylonitrile butadiene styrene (ABS)											
Job	MCE	Canister	GFF	QFF	Impinger	DNPH	OVS-7	Charcoal	XAD-7	CEF	ST/GFF
1	2	2			2		2				
	[264]	[264]			[264]		[264]				
2	4	4					2				
	[578]	[540]					[578]				
3	6	6				6	6				
	[852]	[548]				[852]	[852]				
4 + 5		6									
		[360]									
6		6				2					
		[575]				[864]					
7	2	2				2	2				
	[311]	[311]				[311]	[311]				
Total	14	26			2	10	12				

					*Polycarbonate (PC)**						
Job	MCE	Canister	GFF	QFF	Impinger	DNPH	OVS-7	Charcoal	XAD-7	CEF	ST/GFF
1	6	6									
	[196]	[196]									
2	6	6	6								
	[184]	[184]	[184]								
3	6	6	6								
	[125]	[123]	[125]								
4	2	2					2				
	[363]	[363]									
Total	20	20	12				2				

					Ultem®						
Job	MCE	Canister	GFF	QFF	Impinger	DNPH	OVS-7	Charcoal	XAD-7	CEF	ST/GFF
1	2	2			1						
	[70]	[60]			[64]						
2	3	3			1						

	[210]	[205]			[205]						
Total	5	5			2						

Polyphenylene sulfide (PPS)											
Job	MCE	Canister	GFF	QFF	Impinger	DNPH	OVS-7	Charcoal	XAD-7	CEF	ST/GFF
1 – 3	6	6									2
	[389]	[389]									[389]
Total	6	6									2

Polysulfone (PSU)											
Job	MCE	Canister	GFF	QFF	Impinger	DNPH	OVS-7	Charcoal	XAD-7	CEF	ST/GFF
1	2	2									
	[166]	[155]									
2	6	6								6	
	[741]	[486]								[741]	
Total	8	8								6	

Polyether sulfone (PESU)[†]											
Job	MCE	Canister	GFF	QFF	Impinger	DNPH	OVS-7	Charcoal	XAD-7	CEF	ST/GFF
1	2	2		2				2	2	2	
	[680]	[600]		[680]				[680]	[681]	[680]	
2	2	2		2				2	2	2	
	[761]	[596]		[761]				[761]	[761]	[761]	
Total	4	4		4				4	4	4	

[*] 11 surface wipe samples collected for BPA and BPS
[†] 24 surface wipe samples collected for BPA and BPS
MCE = mixed cellulose ester filter for elements (NMAM 7303)
Canister = evacuated canister sampler for individual volatile organic compounds (NMAM 3900)
GFF = glass fiber filter for BPA using liquid chromatography-mass spectrometry (LC-MS)
QFF = quartz fiber filter for BPA and BPS using LC-MS
Impinger = liquid impinger sampler for select carbonyls using GC-MS
DNPH = silica gel coated with 2,4-dinitrophenylhydrazine for formaldehyde (NMAM 2016)
OVS-7 = OSHA versatile sampler tube – glass fiber filter and two sections of XAD-7 adsorbent for caprolactam (OSHA Method PV2012)
Charcoal = coconut shell charcoal tubes for chlorobenzene (NMAM 1003)
XAD-7 = XAD-7 tube samplers for phenol (NMAM 2546)
CEF = 0.8-µm cellulose ester filter followed by a Na_2CO_3-treated cellulose ester filter for particulate sulfate (SO_4) and sulfur dioxide (SO_2), respectively (NMAM 6004)
ST/GFF = sorbent tube that contained silica gel coated with silver nitrate and a glass fiber filter treated with sodium carbonate/glycerol silver nitrate for hydrogen sulfide (H_2S) gas (OSHA Method 1008)

RESULTS

Nanoscale cluster particles that, from EDX analysis, consisted of carbon and oxygen (Figure S1), were ubiquitous in filter samples collected during extrusion of all polymers.

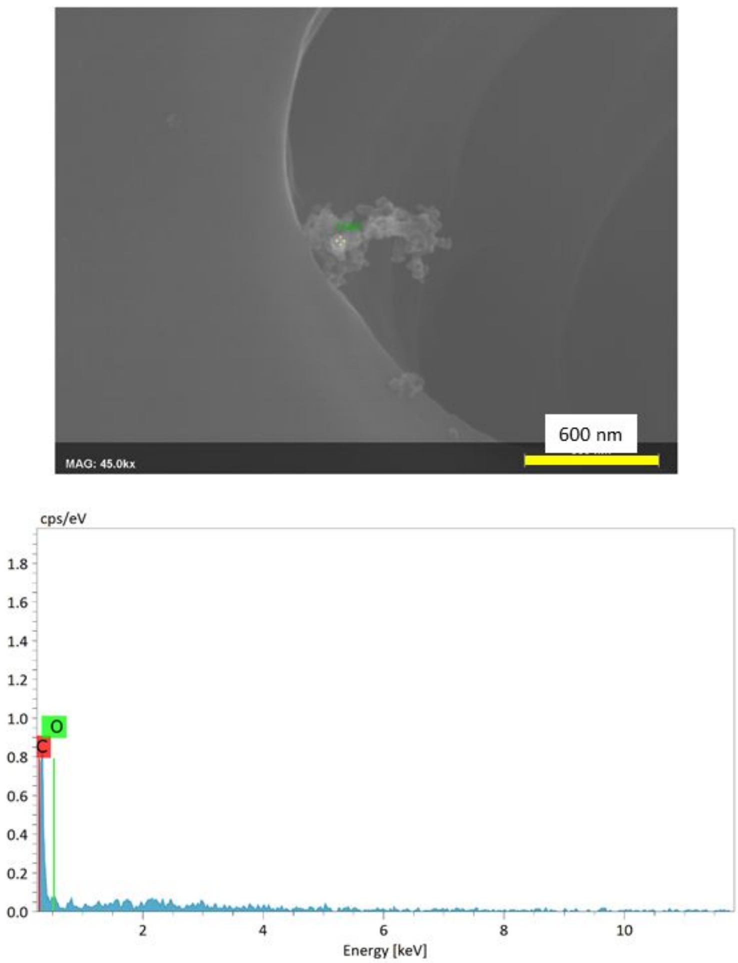

Figure S1. Morphology and elemental composition of representative nanoscale cluster particle composed of carbon and oxygen released during extrusion of all polymers.

Table S1. Average ± StDev (range) concentrations of elements and gases by print job during extrusion of ABS polymer.* Single value indicates that substance was detected on only one sample. All values in μg/m³.

	Job 1		Job 2		Job 3		Jobs 4 + 5		Job 6		Job 7	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
MCE												
Aluminum	0.1±0.1 (0.05-0.2)	--			0.1	1.8±0.7 (1.3- 2.3)	--	--	--	--	0.3	0.4
Arsenic		--				0.2±0.04 (0.2-0.3)	--	--	--	--		
Barium	0.01	--			0.01±0.01 (0.01-0.02)	0.02±0.01 (0.01-0.02)	--	--	--	--		
Chromium		--				0.2±0.05 (0.2-0.2)	--	--	--	--	0.4	0.4
Iron	558	--			24		--	--	--	--		
Manganese	1.0±1.4 (0.05-2.0)	--			0.09±0.03 (0.06-0.1)	0.02	--	--	--	--		
Tin		--			0.04	0.4±0.4 (0.1-0.7)	--	--	--	--		0.2
Titanium	5.9	--			0.01	0.05±0.02	--	--	--	--		

	Job 1		Job 2		Job 3		Jobs 4 + 5		Job 6		Job 7	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
						(0.03-0.06)						
Zinc	3.0	--		0.1±0.1 (0.04-0.2)	0.07±0.01 (0.06-0.07)	0.3±0.01 (0.3-0.3)	--	--	--	--		0.3
Canister												
Acetaldehyde	26.0±12.2 (17.4-34.6)	--		26.4±4.9 (22.9-29.9)		22.6±5.9 (18.4-26.7)				13.9±7.8 (7.0-22.3)		
Acetone	248.7±21.1 (233.7 – 263.6)	--	25.8±6.9 (20.9-30.7)		10.6±12.9 (2.2-25.4)	3.7±1.1 (2.9-4.5)	178.7±2.7 (176.8-180.6)	150.8±43.6 (100.7-179.7)	6.7	8.6	10.5	13.4
α-Pinene		--						5.1				
Benzene	11.6	--						25.9±34.9 (1.2-50.6)	40.1	3.9	2.8	
d-Limonene	36.1	--	10.6±2.4 (8.9-12.3)	11.0	25.1	19.3±5.7 (15.2-23.3)	19.3±5.0 (16.0-25.0)	27.2±5.8 (23.1-31.3)			21.0	

	Job 1		Job 2		Job 3		Jobs 4 + 5		Job 6		Job 7	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
MM	43.2	--	12.3±1.8 (11.0-13.5)	5.7±1.6 (4.6-6.9)	1.1±1.1 (0.3-1.9)	5.0±4.2 (2.5-9.8)		7.8±1.3 (6.9-8.7)			10.6	13.5
m,p-Xylene	43.9	--					6.3±0.1 (6.2-6.3)	5.4±3.2 (1.7-7.3)				
o-Xylene	36.8	--										
Styrene	103.2±95.7 (35.5-170.9)	--	13.3±1.4 (12.3-14.3)	81.0±81.3 (23.5-138.5)	18.1	50.7±2.4 (49.0-52.4)	12.2±0.5 (11.8-12.5)	35.9±25.7 (8.5-59.5)	11.6	73.3±40.5 (45.0-102.3)		
Toluene	23.8±16.3 (12.2-35.3)	--	6.3±1.5 (5.2-7.3)	18.2±14.9 (7.6-28.7)	3.9±2.2 (2.3-5.4)		27.1±5.8 (20.4-30.6)	186.1±21.5 (170.9-201.3)		74.3		9.1
Impinger												
Acetone	5.2±0.1 (5.1-5.2)	--	--	--	--	--	--	--	--	--	--	--
Benzaldehyde	0.8±0.0 (0.8-0.8)	--	--	--	--	--	--	--	--	--	--	--
Formaldehyde	12.8±0.0	--	--	--	--	--	--	--	--	--	--	--

	Job 1		Job 2		Job 3		Jobs 4 + 5		Job 6		Job 7	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
	(12.8-12.8)											
Glyoxal	0.3±0.3	--	--	--	--	--	--	--	--	--	--	--
	(0.1-0.5)											
Methylglyoxal	0.3±0.0	--	--	--	--	--	--	--	--	--	--	--
	(0.3-0.3)											
4-oxopentanal	0.8±0.0	--	--	--	--	--	--	--	--	--	--	--
	(0.8-0.8)											
DNPH												
Formaldehyde	--	--	--	--	0.8±0.5	3.4±3.7	--	--			0.6	0.5
					(0.4-1.1)	(0.8-6.0)						
OVS-7												
Caprolactam		--		22.0			--	--	--	--		

* Outside = outside enclosure at operator's station, side, and back; Inside = inside enclosure at front, side, and back
Empty cell = below limit of detection (see Table S7) or background
-- = No sample collected
MM = methyl methacrylate

Table S2. Average ± StDev (range) concentrations of elements, bisphenols, and gases by print job during extrusion of PC polymer.* Single value indicates that substance was detected on only one sample. All values in μg/m³.

	Job 1		Job 2		Job 3		Job 4	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
MCE								
Aluminum	0.1±0.02 (0.1-0.13)			0.7				
Antimony								0.3
Barium	0.1±0.01 (0.1-0.1)	0.1		0.05				0.02
Copper	0.3		0.04	0.03	0.01	0.04±0.03 (0.02-0.06)		0.04
Iron				0.7				
Manganese	0.6	0.1			0.05		0.02	
Nickel			0.1	0.1	0.1			
Tin	0.5	0.7±0.2 (0.5-0.8)	0.1		0.2	0.05		
Titanium			0.02	0.01±0.01 (0.01-0.02)	0.03	0.02		
Zinc		0.7±0.1		0.1				0.7

	Job 1		Job 2		Job 3		Job 4	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
		(0.6-0.8)						
GFF								
BPA	--	--	0.36±0.11	4.79±4.02	1.27±0.19	21.3±5.3	--	--
			(0.23-0.42)	(0.15-7.14)	(1.13-1.40)	(17.5-25.0)		
BPS	--	--					--	--
Canister								
Acetaldehyde							5.0	10.3
Acetone	27.9±5.8	31.0±13.6	44.7±19.0	41.8		29.3±8.6	14.3	27.9
	(22.2-33.7)	(23.1-46.7)	(26.3-64.2)			(23.2-35.3)		
Benzene	17.0±1.3	12.6±6.3						
	(16.2-18.5)	(5.4-16.5)						
d-Limonene	62.7±32.7	52.5						
	(39.5-85.8)							
Ethylbenzene	27.9±10.5	21.9±12.1						
	(15.8-34.1)	(10.1-34.3)						
MM	36.4±18.2	15.5						
	(23.5-49.2)							
m,p-Xylene	27.3±12.1	19.5±11.1						

	Job 1		Job 2		Job 3		Job 4	
	Outside	Inside	Outside	Inside	Outside	Inside	Outside	Inside
	(13.8-37.0)	(9.5-31.5)						
Styrene	38.1±17.3	30.9±16.4						
	(18.2-49.2)	(15.6-48.2)						
Toluene	32.1±11.5	33.3±2.2	26.3±9.0	202.0±157.0		104.0	81.3	
	(18.9-39.9)	(30.5-34.7)	(16.9-34.8)	(20.8-98.6)				
OVS-7								
Caprolactam	--	--	--	--	--	--		

* Outside = outside enclosure at operator's station, side, and back; Inside = inside enclosure at front, side, and back
Empty cell = below limit of detection (see Table S7) or background
-- = No sample collected
MM = methyl methacrylate

Table S3. Average ± StDev (range) concentrations of elements and gases by print job during extrusion of Ultem® polymer.* Single value indicates that substance was detected on only one sample. All values in μg/m³.

	Job 1		Job 2	
	Outside	Inside	Outside	Inside
MCE				
Aluminum		--	1.6±1.2 (0.8-3.0)	--
Arsenic	2.3	--		--
Cadmium	0.2	--		--
Chromium	0.8	--	0.3±0.1 (0.1-0.4)	--
Copper	3.6±4.3 (0.5-6.6)	--	0.1±0.04 (0.1-0.2)	--
Iron	975±870 (360-1590)	--	251±151 (144-358)	--
Manganese	9.5±5.1 (5.9-13.1)	--	0.6±0.6 (0.1-1.2)	--
Nickel		--	0.2	--
Zinc	1.2	--	35.3±57.4 (0.2-101.5)	--
Canister				
Acetaldehyde	32.6	--	21.2±4.0 (18.7-25.8)	--
Acetone	80.2±7.8 (74.7-85.7)	--	342.7±59.1 (289.9-406.5)	--

	Job 1		Job 2	
	Outside	Inside	Outside	Inside
d-Limonene	264.6	--		--
m,p-Xylene		--	10.6	--
Styrene	35.2	--	20.4±0.3 (20.1-20.7)	--
Toluene	13.9	--	22.3±3.4 (19.2-26.0)	--
Impinger				
Acetone	9.8±0.1 (9.7-9.8)	--	4.3±0.5 (3.9-4.6)	--
Benzaldehyde	2.9	--	0.7	--
Formaldehyde	8.1	--	18.8	--
Glyoxal	0.2	--	0.1	--
Methylglyoxal	0.3±0.1 (0.2-0.3)	--	0.7±0.3 (0.5-0.9)	--
4-oxopentanal	0.8	--	1.3±0.3 (1.0-1.6)	--

* Outside = outside enclosure at operator's station, side, and back; Inside = inside enclosure at front, side, and back
Empty cell = below limit of detection (see Table S7) or background
-- = No sample collected

Table S4. Average ± StDev (range) concentrations of elements and gases by print job during extrusion of PPS polymer.* Single value indicates that substance was detected on only one sample. All values in μg/m^3 unless otherwise noted.

	Jobs 1 – 3	
	Outside	Inside
MCE		
Aluminum	42.9	
Canisters		
Acetone	379.3±19.0	340.7±31.1
	(359.6-397.4)	(308.2-370.2)
Benzene	10.9±10.8	11.2±13.1
	(3.2-18.5)	(3.5-26.3)
Ethylbenzene	6.1±0.1	7.9±1.4
	(6.0-6.1)	(6.9-8.9)
d-Limonene		48.2
Methyl methacrylate	8.9	
m,p-Xylene	5.7	7.5±0.8
		(6.9-8.0)
Styrene	8.7±0.3	11.3±1.6
	(8.5-8.9)	(10.2-12.4)
Toluene	10.1±2.4	88.2±58.5
	(8.4-11.8)	(21.3-129.9)
ST/GFF		
H_2S		

* Outside = outside enclosure at operator's station, side, and back; Inside = inside enclosure at front, side, and back
Empty cell = below limit of detection or background

Table S5. Average ± StDev (range) concentrations of elements and gases by print job during extrusion of PSU polymer.* Single value indicates that substance was detected on only one sample. All values in µg/m^3.

	Job 1		Print 2	
	Outside	Inside	Outside	Inside
MCE				
Aluminum			0.7±0.5	17.0±7.1
			(0.4-1.0)	(11.9-22.0)
Barium			0.01	0.2±0.1
				(0.1-0.3)
Iron			0.5±0.1	25.0
			(0.5-0.6)	
Titanium		0.01	0.1	0.06±0.01
				(0.05-0.06)
Vanadium			0.1	1.6
Zinc		0.2	0.1±0.1	1.0±1.0
			(0.1-0.2)	(0.05-1.9)
Canisters				
Acetone				34.4
Benzene			4.1	51.7±41.6
				(4.0-80.7)
d-Limonene			9.2±3.2	8.4±4.6
			(6.9-11.4)	(5.1-11.6)
Methyl methacrylate			3.6	12.3±0.4
				(12.0-12.5)
m,p-Xylene	1.0	0.1		
Styrene	14.7	5.7		

	Job 1		Print 2	
	Outside	Inside	Outside	Inside
Toluene	3.7	3.7		
CEF				
Sulfate			1.5±0.9	1.5±0.15
			(0.7-2.4)	(1.3-1.6)
Sulfur dioxide				20.1±3.2
				(17.8-22.3)

* Outside = outside enclosure at operator's station, side, and back; Inside = inside enclosure at front, side, and back
Empty cell = below limit of detection (see Table S7) or background

Table S6. Average ± StDev (range) concentrations of elements, bisphenols, and gases by print job during extrusion of PESU polymer.* Single value indicates that substance was detected on only one sample. All values in $\mu g/m^3$.

	Job 1		Job 2	
	Outside	Inside	Outside	Inside
MCE				
Aluminum			4.5	3.4
Barium	0.02		0.03	0.02
Cadmium	0.06	0.01		
Copper		0.04	0.04	0.1
Iron				1.0
Titanium				0.2
Zinc			0.3	0.3
QFF				
BPA	8.7	5.7	2.0	1.7
BPS	0.07	0.06	0.04	0.03
Canister				
Acetaldehyde	8.2	8.5	17.1	3.8
Acetone				18.2
α-Pinene	10.9	10.7		
Benzene	1.5	1.6	0.6	0.3
Ethylbenzene	0.1	0.2		
MM	0.1	0.3		
m,p-Xylene	1.8	1.9		
o-Xylene	0.4	0.4		
Styrene	0.1	0.6		
Toluene			3.2	2.9
Charcoal				

	Job 1		Job 2	
	Outside	Inside	Outside	Inside
Chlorobenzene				
XAD-7				
Phenol	25.6	20.7	14.4	15.5
CEF				
Sulfate		4.7	2.1	
Sulfur dioxide	39.7		25.0	30.9

* Outside = outside enclosure at operator's station, side, and back; Inside = inside enclosure at front, side, and back

Empty cell = below limit of detection (see Table S7) or background

Table S7. Analytical limits of detection (LOD) by sample type and analyte*

Sample/analyte	LOD (µg/m^3)
MCE	
Aluminum	0.08 – 2.00
Antimony	0.20 – 0.70
Arsenic	0.20 – 3.33
Barium	0.01 – 0.07
Cadmium	0.01 – 0.03
Chromium	0.02 – 0.47
Copper	0.02 – 0.06
Iron	0.58 – 20.0
Manganese	0.01 – 0.07
Nickel	0.04 – 0.06
Tin	0.004 – 2.00
Titanium	0.01 – 0.05
Vanadium	0.08 – 0.35
Zinc	0.02 – 0.53
Canister	
Acetaldehyde	0.51 – 1.10
Acetone	0.34 – 0.36
α-Pinene	0.50 – 0.52
Benzene	0.18 – 0.19
Ethylbenzene	0.32 – 0.32
d-Limonene	0.65 – 0.84
Methyl methacrylate	0.39 – 0.48
m,p-Xylene	0.35 – 0.46
o-Xylene	0.28 – 0.31

Styrene	0.51 – 0.70
Toluene	0.32 – 0.34
Glass fiber filter	
BPS	0.004 – 0.007
DNPH	
Formaldehyde	0.29 – 0.38
OVS-7	
Caprolactam	1.20 – 6.70
Charcoal tube	
Chlorobenzene	0.011 – 0.014
CEF	
Sulfur dioxide	0.001 – 0.01
Sulfate	0.001
ST/GFF	
Hydrogen disulfide	0.87

* Samples collected from April 2018 to November 2019 and, except for hydrogen disulfide, were analyzed in separate batches. For samples analyzed in multiple batches, values of LOD varied over time and are given as the minimum and maximum of all batches.