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Title: 3-Dimensional Printing with Nano-Enabled Filaments Releases Polymer Particles Containing Carbon Nanotubes into Air

3-Dimensional Printing with Nano-Enabled Filaments Releases Polymer Particles Containing Carbon Nanotubes into Air

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# Supplemental File

# Methods

## Chamber set-up and air monitoring

Figure S1 is a photograph of the NIST test artifact used for all 3-D printing tests.1

## Carbonyl sample analysis

All samples derivatized using O-tert-Butylhydroxylamine hydrochloride (TBOX) were analyzed using an Agilent (Santa Clara, CA) 7890B GC coupled to an Agilent 240 Internal EI/CI ion trap mass spectrometer. Samples were analyzed in both electron ionization (EI) and chemical ionization (CI) modes with liquid methanol serving as the CI reagent. Compound separation was achieved by an Agilent (Santa Clara, CA) DB-5MS (0.25 mm I.D., 30 m long, 0.25 µm film thickness) column and the following GC 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 injector temperature at 130 °C. The ion trap mass analyzer was tuned using perfluorotributylamine (FC-43). Full-scan mass spectra were collected in the m/z range 40-1000.

All samples derivatized using O-(2,3,4,5,6-Pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) were analyzed using a Varian (Palo Alto, CA) 3800/Saturn 2000 GC/MS system operated in the electron impact (EI) mode. Compound separation was achieved by an Agilent (Santa Clara, CA) HP-5MS (0.25 mm I.D., 30 m long, 0.25 µm film thickness) column and the following GC 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, and the GC injector was returned to split mode 1 min after sample injection, with the following injector temperature parameters: 130 °C for 2 min then 200 °C/min to 300 °C and held for 10 min. The Saturn 2000 ion trap mass spectrometer was tuned using perfluorotributylamine (FC-43). Full-scan EI ionization spectra were collected from m/z 40-650.

Calibration plots were made by analyzing triplicate measurements of standard solutions (glyoxal, methylglyoxal, and 4-oxopentanal) that were injected into an 80 L Teflon® chamber at 50% RH, ranging in concentration from 10 – 30 ppb (2.4 – 7.4 x 1011 molecules/cm3). Samples were obtained by pulling 60 L of air from the chamber using a pump (URG 3000-02Q, Chapel Hill, NC) into 25 mL of DI H2O in a 60 mL Teflon® impinger (Savillex, Eden Prairie, MN). After collection, samples were decanted into 40 mL vials and derivatized with 100 µL of aqueous 250 mM TBOX or 250 mM PFBHA. Vials were analyzed in the same manner as the 3-D printer samples as described above.

# Results

## Filament characterization

The mean EC content (wt%) of the sample was determined as follows:

EC (wt%) = (EC/TC)(TC fraction of base polymer) x 100,

where EC/TC is the mean (3 ≤ n ≤ 5) EC fraction of Total Carbon (TC) in the sample. The EC/TC ratio was multiplied by the mean TC mass fraction of the base polymer filament, determined through analyses of pre-weighed samples of the milled base materials. The mean (n ≥ 4) TC contents (wt%) of the ABS, PLA, and PC base polymers were 83 ± 10%, 56 ± 6%, and 75 ± 7%, respectively. To account for a potential positive bias due to carbonization of the polymer matrix, EC results for the ABS and PLA composites were corrected for residual char. Corrected EC contents were calculated by subtracting the mean ‘EC’ fraction (wt%) found for the base polymer (i.e., subtracting char) from that for the corresponding composite. The mean EC/TC fractions for the ABS and PLA base polymers were relatively low: about 0.4% and 2%, respectively. These carbon fractions correspond to mean (n = 4) residual char contents (wt%) of 0.34 ± 0.07% for ABS and 1.04 ± 0.11% for PLA.

As with the ABS and PLA materials, an OC-EC split was assigned for comparison of the base and composite filaments, but the EC fractions for both samples were identical, about 24%. Note that although the EC fractions were identical, a direct comparison may not be valid as the filaments were from different commercial sources. Therefore, an estimate of the EC content of the PC composite was based on the pyrolysis correction feature of the thermal-optical method. With a transmittance-based correction, EC contents (wt%) of about 2.2% and 3.7% were determined for the base PC (Gizmo Dorks) and PCCNT (3DX-Tech) filaments (Table S1). The (base polymer) corrected EC content of the composite was estimated at about 1.5% (wt%), though the accuracy of this result is uncertain.

Table S2 presents details of the thermogravimetric analysis results for all filaments tested.

## Particle emission rates

Figure S2 illustrates that particle number concentration values measured by the FMPS for sizes from 5.6 to 19.8 nm were orders of magnitude higher than for the P-Trak instrument (range: 20 nm to 1 µm). This observation indicates that particles with size below 20 nm dominated emissions but could not be measured using the P-Trak. As shown in the main text, yield and ER values are, in turn, higher when calculated from FMPS data compared to the P-Trak data. Figure S3 is an example number concentration distribution measured using the APS for sizes from 0.5 to 20 µm. The tabulated Npeak, ER, and yield values for each tested filament type are presented in Tables S3 – S5 for particle number (P-Trak, 20 nm to 1 µm), Tables S6 – S8 for submicrometer number (FMPS, 5.6 to 560 nm), and Tables S9 – S11 for micron-scale number (APS, 0.5 to 20 µm) measurements. The tabulated geometric mean (GM) particle diameters and corresponding geometric standard deviation (GSD) values for each tested filament type are presented in Table S12 for FMPS data and Table S13 for APS data.

**Table S1**. Elemental carbon characterization of thermoplastic filaments (all values are arithmetic mean ± standard deviation)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
|  |  |  |  |  | EC wt% |
| Typea | Filler | Manufacturer | Product | EC/TCb | Uncorrectedc | Correctedd |
| ABS | MWCNT | 3DXTech | 3DXStat | 0.056 ± 0.003 | 4.66 ± 0.60 | 4.32 ± 0.67 |
| ABS | N/A | 3DXTech | ABS  | 0.004 ± 0.001 | 0.34 ± 0.07 | N/A |
| PLA | MWCNT | Functionalize F-Electric | Highly conductive | 0.112 ± 0.005 | 6.25 ± 0.72 | 5.20 ± 0.83 |
| PLA | N/A | 3DXTech | PLA | 0.0186 ± 0.0001 | 1.04 ± 0.11 | N/A |
| PC | CNT | 3DXTech | 3DXStat | 0.03 ± 0.05 | 3.68 ± 6.10 | N/A |
| PC | N/A | Gizmo Dorks | PC | 0.05 ± 0.06 | 2.23 ± 4.89 | 1.5e |

a ABS = acrylonitrile butadiene styrene; PLA = poly lactic acid; PC = polycarbonate

b Mean (n ≥ 3) elemental to total carbon ratio (EC/TC)

c Mean EC content of filament. Estimates for ABS and PLA materials are based on mean (n ≥ 3) EC/TC and TC/base polymer mass fractions. Estimates for PC based on pyrolysis correction. See main text for details.

d Composite results corrected for char residue from respective polymer matrix

e Estimate based on pyrolysis correction. See supporting text for details.

N/A = Not applicable

**Table S2**. Oxidation temperatures and residual ash results for thermoplastic filaments, determined by thermogravimetric analysis.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Typea | Filler | Manufacturer | Product | Oxidation onsetb, °C | RPD | Sample weight, mg | Residual ash, mg | Residual ash, % |
| ABS | MWCNT | 3DXTech | 3DXStat | 329 | 0.04 | 9.044 | 0.078 | 0.86 |
| ABS | N/A | 3DX Tech  | ABS | 333 | 0.79 | 8.588 | 0.018 | 0.21 |
| PLA | MWCNT | Functionalize F-Electric  | Highly conductive | 314 | 1.41 | 9.871 | 0.105 | 1.07 |
| PLA | N/A | 3DX Tech  | PLA | 314 | 1.54 | 15.041 | 0.048 | 0.32 |
| PC | CNT | 3DX Tech  | 3DXStat | 474 | 0.74 | 20.945 | 0.061 | 0.29 |
| PC | N/A | Gizmo Dorks  | PC | 434 | 0.46 | 5.138 | 0.003 | 0.06 |

a ABS = acrylonitrile butadiene styrene; PLA = poly lactic acid; PC = polycarbonate

b Average of duplicate analyses.

**Table S3**. Peak number concentrations, emission rates, and emission yields for acrylonitrile butadiene styrene (ABS) polymer filaments with and without carbon nanotube additives (P-Trak data)

|  |  |  |
| --- | --- | --- |
| ABSCNT |  | ABS |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 6.0 x 104 | 8.0 x 108 | 3.5 x 109 |  | 1.3 x 105 |  1.4 x 1010 |  5.6 x 1010 |
| 5.3 x 103 | 4.8 x 108 | 2.1 x 109 |  | 4.4 x 104 | 6.4 x 109 | 2.6 x 1010 |
| 1.1 x 104 | 4.2 x 108 | 1.8 x 109 |  | 6.3 x 104 | 6.6 x 109 | 2.7 x 1010 |
| 9.1 x 104 | 2.5 x 109 |  1.1 x 1010 |  | 5.5 x 104 | 7.0 x 109 | 2.9 x 1010 |
| 4.1 x 103 | 2.8 x 108 | 1.2 x 109 |  | 3.7 x 104 | 6.6 x 109 | 2.7 x 1010 |

**Table S4**. Peak number concentrations, emission rates, and emission yields for poly lactic acid (PLA) polymer filaments with and without carbon nanotube additives (P-Trak data)

|  |  |  |
| --- | --- | --- |
| PLACNT |  | PLA |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 9.3 x 103 | 8.4 x 107 | 3.7 x 108 |  | 2.4 x 103 | 1.6 x 106 | 7.9 x 106 |
| 3.2 x 103 | 3.0 x 108 | 1.4 x 109 |  | 3.8 x 103 | 6.4 x 108 | 3.0 x 109 |
| 1.1 x 104 | 2.4 x 108 | 1.0 x 109 |  | 1.9 x 103 | 1.3 x 108 | 5.7 x 108 |
| 5.9 x 103 | 8.3 x 108 | 3.5 x 109 |  | 3.1 x 103 | 1.1 x 108 | 4.8 x 108 |
| --a | -- | -- |  | 1.3 x 103 | 4.9 x 107 | 2.2 x 108 |

a Only four replicates (filament broke during repeated attempts to obtain fifth replicate)

**Table S5**. Peak number concentrations, emission rates, and emission yields for polycarbonate (PC) polymer filaments with and without carbon nanotube additives (P-Trak data)

|  |  |  |
| --- | --- | --- |
| PCCNT |  | PC |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 3.8 x 104 | 3.2 x 109 | 1.0 x 1010 |  | 4.2 x 104 | 2.6 x 109 | 8.5 x 109 |
| 2.7 x 104 | 9.8 x 108 | 3.1 x 109 |  | 3.6 x 104 | 1.8 x 109 | 5.9 x 109 |
| 5.2 x 104 | 3.4 x 109 | 1.1 x 1010 |  | 2.3 x 104 | 1.5 x 109 |  9.5 x 1010 |
| 3.1 x 103 | 1.4 x 107 | 4.6 x 107 |  | 2.2 x 104 | 1.4 x 109 | 4.5 x 109 |
| 3.7 x 104 | 3.9 x 109 | 1.2 x 1010 |  | 5.6 x 104 | 6.6 x 109 |  2.1 x 1010 |

**Table S6**. Peak number concentrations, emission rates, and emission yields for acrylonitrile butadiene styrene (ABS) polymer filaments with and without carbon nanotube additives (FMPS data)

|  |  |  |
| --- | --- | --- |
| ABSCNT |  | ABS |
| Npeak (#/cm3) | Rate (#/min)  | Yield (#/g printed)  |  | Npeak (#/cm3) | Rate (#/min)  | Yield (#/g printed)  |
| 3.2 x 107 | 5.0 x 1010 | 2.2 x 1011 |  | 2.4 x 107 | 1.5 x 1012 | 6.2 x 1012 |
| 2.1 x 105 | 4.4 x 1010 | 1.9 x 1011 |  | 5.9 x 106 | 4.9 x 1011 | 2.0 x 1012 |
| 3.0 x 105 | 1.6 x 1010 | 6.7 x 1010 |  | 7.0 x 106 | 6.2 x 1011 | 2.5 x 1012 |
| 5.6 x 106 | 6.0 x 1010 | 2.7 x 1011 |  | 1.4 x 107 | 5.7 x 1011 | 2.3 x 1012 |
| 2.5 x 105 | 1.3 x 1010 | 5.7 x 1010 |  | 1.2 x 107 | 6.2 x 1011 | 2.6 x 1012 |

**Table S7**. Peak number concentrations, emission rates, and emission yields for poly lactic acid (PLA) polymer filaments with and without carbon nanotube additives (FMPS data)

|  |  |  |
| --- | --- | --- |
| PLACNT |  | PLA |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 3.7 x 107 |  4.4 x 109 | 2.0 x 1010 |  | 1.4 x 105 | 9.4 x 108 | 4.6 x 109 |
| 1.2 x 106 |  4.4 x 109 | 2.0 x 1010 |  | 9.6 x 104 | 2.2 x 109 | 8.2 x 109 |
| 6.5 x 105 | 1.0 x 1010 | 4.5 x 1010 |  | 5.5 x 104 |  1.1 x 1010 | 4.9 x 1010 |
| 1.9 x 106 | 7.9 x 108 | 3.4 x 109 |  | 8.5 x 104 | 9.2 x 109 | 4.1 x 1010 |
| --a | -- | -- |  | 6.6 x 104 | 1.7 x 1010 | 7.9 x 1010 |

a Only four replicates (filament broke during repeated attempts to obtain fifth replicate)

**Table S8**. Peak number concentrations, emission rates, and emission yields for polycarbonate (PC) polymer filaments with and without carbon nanotube additives (FMPS data)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | PCCNT |  |  |  | PC |  |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 1.2 x 107 | 4.1 x 1011 | 1.3 x 1012 |  | 6.6 x 104 | 4.8 x 108 | 1.5 x 109 |
| 3.5 x 106 | 2.0 x 1011 | 6.4 x 1011 |  | 1.4 x 107 | 1.5 x 1011 | 4.8 x 1011 |
| 3.1 x 107 | 4.0 x 1011 | 1.3 x 1012 |  | 4.4 x 106 | 1.8 x 1011 | 5.8 x 1011 |
| 2.8 x 106 | 1.9 x 1011 | 6.3 x 1011 |  | 1.7 x 107 | 2.1 x 1011 | 6.8 x 1011 |
| 3.3 x 107 | 4.3 x 1011 | 1.4 x 1012 |  | 1.1 x 107 | 9.4 x 1011 | 3.1 x 1012 |

**Table S9**. Peak number concentrations, emission rates, and emission yields for acrylonitrile butadiene styrene (ABS) polymer filaments with and without carbon nanotube additives (APS data)

|  |  |  |
| --- | --- | --- |
| ABSCNT |  | ABS |
| Npeak (#/cm3) | Rate (#/min)  | Yield (#/g printed)  |  | Npeak (#/cm3) | Rate (#/min)  | Yield (#/g printed)  |
| 1.8 x 102 | 1.0 x 107 | 4.5 x 107 |  | 4.6 x 103 | 1.4 x 108 | 5.7 x 108 |
| 3.5 x 103 | 7.8 x 107 | 3.4 x 108 |  | 3.6 x 103 | 1.2 x 108 | 4.7 x 108 |
| 5.2 x 102 | 1.6 x 107 | 6.6 x 107 |  | 2.7 x 103 | 1.9 x 108 | 7.7 x 108 |
| 8.8 x 102 | 6.8 x 107 | 3.0 x 108 |  | 5.3 x 102 | 9.3 x 106 | 3.8 x 107 |
| 2.2 x 103 | 9.7 x 107 | 4.2 x 108 |  | 8.1 x 102 | 7.7 x 106 | 3.2 x 107 |

**Table S10**. Peak number concentrations, emission rates, and emission yields for poly lactic acid (PLA) polymer filaments with and without carbon nanotube additives (APS data)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | PLACNT |  |  |  | PLA |  |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 1.4 x 103 | 3.5 x 107 | 1.6 x 108 |  | 1.2 x 103 | 7.2 x 107 | 3.5 x 108 |
| 6.7 x 102 | 1.9 x 107 | 8.7 x 107 |  | 3.6 x 103 | 1.0 x 108 | 5.0 x 108 |
| 4.3 x 102 | 1.4 x 107 | 5.9 x 107 |  | 4.7 x 103 | 1.1 x 108 | 5.0 x 108 |
| 1.2 x 103 | 3.9 x 107 | 1.7 x 108 |  | 4.6 x 103 | 9.1 x 107 | 4.1 x 108 |
| --a | -- | -- |  | 7.3 x 102 | 1.3 x 108 | 5.8 x 108 |

a Only four replicates (filament broke during repeated attempts to obtain fifth replicate)

**Table S11**. Peak number concentrations, emission rates, and emission yields for polycarbonate (PC) polymer filaments with and without carbon nanotube additives (APS data)

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
|  | PCCNT |  |  |  | PC |  |
| Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |  | Npeak (#/cm3) | Rate (#/min) | Yield (#/g printed) |
| 2.0 x 103 | 5.8 x 106 | 1.8 x 107 |  | 1.1 x 104 | 1.7 x 108 | 5.5 x 108 |
| 4.5 x 103 | 9.0 x 106 | 2.9 x 107 |  | 2.9 x 103 | 2.7 x 107 | 8.7 x 107 |
| 5.5 x 103 | 1.4 x 108 | 4.3 x 108 |  | 8.4 x 102 | 2.3 x 107 | 7.4 x 107 |
| 2.5 x 103 | 2.2 x 108 | 7.0 x 108 |  | 2.1 x 103 | 9.0 x 107 | 3.0 x 108 |
| 1.0 x 103 | 7.2 x 107 | 2.3 x 108 |  | 1.7 x 103 | 7.0 x 107 | 2.3 x 108 |

**Table S12**. Geometric mean (GM) in nanometers and geometric standard deviation (GSD) mobility particle diameters for polymer filaments with and without carbon nanotube additives (FMPS data)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ABSCNT | ABS | PLACNT | PLA | PCCNT | PC |
| GM  | GSD | GM  | GSD | GM  | GSD | GM  | GSD | GM  | GSD | GM  | GSD |
| 29.3 | 1.3 | 24.0 | 1.3 | 20.1 | 1.3 | 18.7 | 1.3 | 23.2 | 1.3 | 58.0 | 1.3 |
| 35.0 | 1.4 | 23.3 | 1.3 | 21.9 | 1.4 | 28.6 | 1.4 | 27.5 | 1.3 | 47.8 | 1.3 |
| 32.1 | 1.3 | 22.3 | 1.3 | 18.5 | 1.2 | 21.7 | 1.5 | 24.7 | 1.3 | 44.5 | 1.3 |
| 32.5 | 1.2 | 22.4 | 1.3 | 26.4 | 1.3 | 20.6 | 1.5 | 27.8 | 1.3 | 45.7 | 1.3 |
| 34.9 | 1.4 | 21.6 | 1.3 | --a | -- | 18.4 | 1.3 | 22.8 | 1.3 | 41.4 | 1.2 |
| 32.8b | 1.3c | 22.7 | 1.3 | 21.7 | 1.3 | 21.6 | 1.4 | 25.2 | 1.3 | 47.5 | 1.3 |

ABS = acrylonitrile butadiene styrene, PLA = poly lactic acid, PC = polycarbonate

a Only four replicates (filament broke during repeated attempts to obtain fifth replicate)

b Mean GM (nm)

c Mean GSD

**Table S13**. Geometric mean (GM) in nanometers and geometric standard deviation (GSD) aerodynamic particle diameters for polymer filaments with and without carbon nanotube additives (APS data)

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| ABSCNT | ABS | PLACNT | PLA | PCCNT | PC |
| GM  | GSD | GM  | GSD | GM  | GSD | GM  | GSD | GM  | GSD | GM  | GSD |
| 651 | 1.2 | 649 | 1.2 | 674 | 1.2 | 670 | 1.2 | 661 | 1.2 | 683 | 1.2 |
| 652 | 1.2 | 643 | 1.2 | 663 | 1.2 | 659 | 1.2 | 659 | 1.2 | 667 | 1.2 |
| 702 | 1.3 | 668 | 1.2 | 689 | 1.2 | 654 | 1.2 | 641 | 1.2 | 658 | 1.2 |
| 666 | 1.2 | 678 | 1.2 | 670 | 1.2 | 673 | 1.2 | 652 | 1.2 | 645 | 1.2 |
| 661 | 1.2 | 668 | 1.2 | --a | -- | 687 | 1.2 | 654 | 1.2 | 724 | 1.3 |
| 666b | 1.2c | 661 | 1.2 | 680 | 1.2 | 669 | 1.2 | 653 | 1.2 | 675 | 1.2 |

ABS = acrylonitrile butadiene styrene, PLA = poly lactic acid, PC = polycarbonate

a Only four replicates (filament broke during repeated attempts to obtain fifth replicate)

b Mean GM (nm)

c Mean GSD



Figure S1. Photograph of NIST artifact used for 3-D printing tasks

Figure S2. Example fast mobility particle sizer (FMPS) and P-Trak (range: 20 nm – 1 µm) concentration measurements (#/cm3). Top panel: FMPS data for all size channels and P-Trak concentration measurements. Bottom panel: FMPS data for size channels <20 nm and the same P-Trak concentration measurements illustrating that particles below 20 nm dominated number-based emissions. FMPS data on left axis, P-Trak data on right axis. Data are from emissions test with ABSCNT filament.

Figure S3. Example aerodynamic particle sizer (APS) instrument concentration measurements for particles sizes from 0.5 – 20 µm. Data are from emissions test with ABS filament.

# References

1. Moylan S, Slotwinski J, Cooke A, Jurrens K, Donmez MA. An additive manufacturing test artifact. *Journal of Research of the National Institute of Standards and Technology* 2014, **119:** 429-459.