



<https://helda.helsinki.fi>

Helda

Constructing Spacecraft Components Using Additive Manufacturing and Atomic Layer Deposition : First Steps for Integrated Electric Circuitry

Nyman, Leo

American Society of Civil Engineers (ASCE)

2021-09-01

Nyman, L, Kestilä, A, Porri, P, Pudas, M, Salmi, M, Silander, R, Miikkulainen, V, Kaipio, M, Kallio, E & Ritala, M 2021, 'Constructing Spacecraft Components Using Additive Manufacturing and Atomic Layer Deposition : First Steps for Integrated Electric Circuitry', Journal of Aerospace Engineering, vol. 34, no. 5, 04021049.

[https://doi.org/10.1061/\(ASCE\)AS.1943-5525.0001298](https://doi.org/10.1061/(ASCE)AS.1943-5525.0001298), [https://doi.org/10.1061/\(ASCE\)AS.1943-5525.0001298](https://doi.org/10.1061/(ASCE)AS.1943-5525.0001298)

<http://hdl.handle.net/10138/334184>

10.1061/(ASCE)AS.1943-5525.0001298

acceptedVersion

Downloaded from Helda, University of Helsinki institutional repository.

This is an electronic reprint of the original article.

This reprint may differ from the original in pagination and typographic detail.

Please cite the original version.

1 **Constructing Spacecraft Components Using Additive Manufacturing and** 2 **Atomic Layer Deposition – First Steps for Integrated Electric Circuitry**

3 Leo Nyman¹, Antti Kestilä², Paavo Porri³, Marko Pudas⁴, Mika Salmi⁵, Rudolf Silander⁶, Ville
4 Miikkulainen⁷, Mikko Kaipio⁸, Esa Kallio⁹, and Mikko Ritala¹⁰

5 ¹Ph.D. Student, School of Electrical Engineering, Aalto University, P.O. Box 15500, FI-00076
6 Aalto, Finland (corresponding author). Email: leo.nyman@aalto.fi

7 ²Dr.Tech., Researcher, Finnish Meteorological Institute, Dynamicum Erik Palménin aukio 1,
8 FI-00560 Helsinki, Finland. Email: antti.kestila@fmi.fi

9 ³M.Sc., Engineer, VTT Technical Research Centre of Finland, Tietotie 4E, FI-02150 Espoo,
10 Finland. Email: paavo.porri@vtt.fi

11 ⁴Dr.Tech., IP Manager, Picosun Oy (Ltd.), Tietotie 3, FI-02150 Espoo, Finland. Email:
12 marko.pudas@picosun.com

13 ⁵D.Sc., Staff Scientist, Department of Mechanical Engineering, Aalto University, P.O. Box 14100,
14 FI-00076 Aalto, Finland. Email: mika.salmi@aalto.fi

15 ⁶M.Sc., Research Assistant, School of Electrical Engineering, Aalto University, P.O. Box 15500,
16 FI-00076 Aalto, Finland. Email: silander.r@gmail.com

17 ⁷Ph.D., University Teacher, School of Chemical Engineering, Aalto University, P.O. Box 16100,
18 FI-00076 Aalto, Finland. Email: ville.v.miikkulainen@aalto.fi

19 ⁸Ph.D. Student, Department of Chemistry, University of Helsinki, P.O. Box 55, FI-00014
20 University of Helsinki, Finland. Email: mikko.kaipio@helsinki.fi

21 ⁹Prof., School of Electrical Engineering, Aalto University, P.O. Box 15500, FI-00076 Aalto,
22 Finland. Email: esa.kallio@aalto.fi

23 ¹⁰Professor of Inorganic Materials Chemistry, Department of Chemistry, University of Helsinki,
24 P.O. Box 55, FI-00014 University of Helsinki, Finland. Email: mikko.ritala@helsinki.fi

25 **ABSTRACT**

26 Many fields including the aerospace industry have shown increased interest in the use of plastics
27 to lower the mass of systems. However, the use of plastics in space can be challenging for a number
28 of reasons. Ultraviolet radiation, atomic oxygen and other phenomena specifically associated with
29 space cause the degradation of polymers. Here we show a path towards creation of space-grade
30 components by combining additive manufacturing (AM) and atomic layer deposition (ALD). Our
31 method produced ALD Al_2O_3 coated thermoplastic parts, suitable for space applications. The
32 highlight of this work is a significant reduction in outgassing, demonstrated using residual gas
33 analyzer (RGA) sampling. Compared to uncoated parts, the ALD- Al_2O_3 coating decreased the
34 outgassing of polyether ether ketone (PEEK), acrylonitrile butadiene styrene (ABS), polycarbonate
35 (PC) and nanodiamond-doped polylactide (ND-PLA) by 46%, 49%, 58% and 65% respectively.
36 The manufacturing method used in this work enables the use of topology optimization already in
37 the early concept creation phase. The method is ideally suited for spacecraft applications, where
38 the volume and mass of parts is critical, and could also be adapted for in-space manufacturing.

39 **Keywords** Spacecraft, atomic layer deposition, additive manufacturing, material extrusion, fused
40 filament fabrication, fused deposition modeling

41 **INTRODUCTION**

42 The small-satellite market has rapidly expanded due to increasingly frequent launch opportu-
43 nities and reduced payload costs. Currently, the capabilities of small satellites, such as CubeSats,
44 are restricted in many ways, especially for active microwave instruments (Grau 2019). This is
45 because the power requirements for such instruments easily exceed the amount of electrical power
46 generated by the solar cell arrays of small satellites, even though the solar cells themselves are
47 thin enough to be packaged in large numbers into a small volume. However, this is difficult in
48 practice, since foldable structures require space and complicate the routing of electric connections.
49 Also, additional engineering is required, in order to make the structure of foldable solar cell arrays
50 able to withstand mechanical loads. One approach for overcoming these challenges is to combine

51 additive manufacturing (AM) and atomic layer deposition (ALD), to construct large foldable solar
52 cell array assemblies based on integrated electric circuitry. If these were manufactured in orbit,
53 the system mass and volume could be further reduced, since the microgravity environment would
54 be more benign to the structures. In addition, this combined AM-ALD production process would
55 allow efficient use of promising new concept creation techniques, such as topology optimization,
56 which would enable further reductions in the mass of such structures. Many fields including the
57 aerospace industry have shown increased interest in the use of plastics to lower the mass of systems
58 (Kutz 2002, p. 336). However, the use of plastics in space can be challenging. Hence overcoming
59 these challenges is of critical importance.

60 The space environment is destructive for many thermoplastics. Materials with high outgassing
61 in a vacuum are typically excluded from spacecraft designs. When moving outside of the Earth's
62 protective atmosphere and magnetosphere, many materials are degraded by high-flux ionizing
63 radiation across a wide spectrum. Ultraviolet radiation (UV) affects the top surface layers and has
64 sufficient energy to break the C-C, C-O and other polymer bonds (Grossman and Gouzman 2003).
65 Other radiation species penetrate materials to such a high degree that surface coatings alone cannot
66 provide comprehensive protection. In space, the temperature range can be extreme, depending on
67 the location of the component in a spacecraft (Gilmore 2003). This makes some materials brittle or
68 elastic, resulting in mechanical failure. Each material has a unique coefficient of thermal expansion
69 (CTE). When materials with different CTE are joined together to form a structure, thermal stresses
70 and cycles cause non-equal expansion or contraction of parts, causing failures if not taken into
71 account in the design. Apart from CTE, the concentration of atomic oxygen (AO) limits the choice
72 of materials particularly for low Earth orbit (LEO) satellites, due to its highly reactive nature
73 (Cruise et al. 2006) and relatively high concentrations, which can reach up to $9 \cdot 10^{21}$ atoms/cm²
74 in LEO (Stein 1993). Indeed, a long duration exposure facility (LDEF) experiment on an LEO
75 satellite demonstrated that no polymeric material can be completely resistant to atomic oxygen and
76 UV-inflicted erosion (Stein 1993). LDEF findings have shown that the combination of AO and UV
77 eroded uncoated graphite-epoxy surfaces on the leading edge structure (Stein 1992). Atomic layer

78 deposition (ALD) has been proposed for protecting polymers in space (Minton et al. 2010) and
79 recently the combination of AM and ALD has been studied (Kestilä et al. 2018). These studies
80 were partly driven by the capability of ALD to create conformal coatings over parts with complex
81 shapes or sharp edges. When properly designed and applied, the conformal ALD coating provides
82 an excellent gas barrier and UV shield.

83 **Coatings for Spacecraft**

84 Many metals and oxides protect against AO. However, since silver and copper can be degraded by
85 AO, these should not be implemented in the outer layer. The LDEF experiment (Stein 1993) showed
86 that cracks and holes in the coating allow AO to attack the underlying polymer. The associated
87 undercutting process erodes the polymer material under the coating near the coating defect (Stein
88 1992). Even a thin coating (e.g., 120 nm) of some inorganic material, such as aluminum, nickel
89 or silica, can provide excellent protection with good adhesion. An important property of these
90 thin-film overcoatings is their resistance to crazing (Stein 1992). A related finding from LDEF was
91 that surface micro-cracking was influenced by the thermal cycling temperature range.

92 When the International Space Station (ISS) was designed, the LDEF results were useful in the
93 design work. The Kapton solar array blankets manufactured for the ISS were coated on both sides
94 with 130 nm of SiO₂ for protection against AO. Recently, ALD coatings have been used to protect
95 polymers for usage in spacecraft (Minton et al. 2010). This study used Al₂O₃ to provide protection
96 against AO, and another layer of TiO₂ to block damaging UV radiation. Another good UV-shield
97 material is ZnO. A coating thickness of approximately 35 nm of Al₂O₃ provided protection against
98 AO. However, some substrate materials, such as FEP (fluorinated ethylene propylene or Teflon®),
99 required a thicker coating for efficient protection, most likely caused by the different film-forming
100 mechanisms of ALD Al₂O₃ on various substrate materials (Tynell and Karppinen 2014; Cooper
101 et al. 2008).

102 Spacecraft components may be exposed to large temperature ranges. It is commonly known
103 that coatings are susceptible to cracking, if the CTE values differ greatly between the coating
104 material and underlying substrate. Therefore, materials with similar CTE values are preferred.

105 Coating thickness also plays a role. The negative effects of cracking will depend on the application.
106 For example, when an Al₂O₃ ALD film is used as a gas diffusion barrier, cracks will degrade its
107 efficiency (Jen et al. 2011). Several studies have shown that for hard coatings, thinner films are less
108 susceptible to cracking (McGuigan et al. 2003).

109 **Atomic Layer Deposition**

110 ALD is a type of chemical vapour deposition (CVD) technique. This paper focuses on an
111 Al₂O₃ coating, a well-known ALD process. Other relevant materials are briefly discussed when
112 appropriate. Al₂O₃ is well suited for coating of polymers, partly because it can be deposited over
113 a wide process temperature range. In earlier studies, Al₂O₃ has been deposited at temperatures
114 ranging from 500 °C to as low as 33 °C (Groner et al. 2004). Due to their low glass transition
115 temperatures (T_g), many polymers require relatively low process temperatures. On the other hand,
116 the CTE of Al₂O₃ is very low compared to most polymers. This must be taken into account, since
117 large difference in CTE between the substrate and the coating will induce cracking during thermal
118 cycling.

119 As-deposited ALD Al₂O₃ is known to be amorphous and easily dissolvable into water. This
120 type of amorphous coating structure has been shown to possess excellent gas barrier properties
121 (Heidary and Randall 2015). However, the coating shall be protected from water and high levels
122 of humidity. Degradation of ALD Al₂O₃ has been reported after exposure to liquid water or high-
123 temperature and high-humidity environment (124 °C, 95 % rH) (Abdulagatov et al. 2011; Ruckerl
124 et al. 2017). In general, non-corrosive environment is provided for spacecraft components before
125 and during launch. Broas (2018) reports, that an ALD deposited Al₂O₃ coating may be subjected
126 to tensile stresses. This is at least partly caused by the CTE difference of the substrate and the
127 coating. Tensile stress can lead to cracking and delamination of the coating.

128 The outcome of the film deposition is subject to many quality factors. Properties such as amount
129 and type of impurities, film phase (crystallinity), stoichiometry, stress state, film uniformity, thick-
130 ness, interface structure and conformity are more or less important, depending on the application
131 (Broas 2018). Regarding distinct polymer layers (structural or functional, e.g. electrically conduct-

132 ing), interfacial adhesion between layers must be ensured (Varadan et al. 2001, p. 16). Naturally,
133 this adhesion requirement also applies for ALD layers.

134 For spacecraft, the evaporation of any condensable volatiles may adversely contaminate optical
135 sensors (Fortescue et al. 2011, p. 40). One benefit of using ALD in the encapsulation of polymers
136 is that prior to the coating process the substrates are evacuated and heated to the deposition
137 temperature. This *stabilization time* effects a degassing of the part. Further, the ALD coating is
138 then deposited while the substrates are hot, dry and in a vacuum, as they are in space. As a result,
139 the ALD coating reduces outgassing of the polymer part in space. The ALD barrier coating can
140 also prevent gas absorption from ambient atmosphere, before the satellite is delivered to orbit where
141 it will operate.

142 Another possible use case for ALD is the inhibition of tin whiskers. This is a known phe-
143 nomenon, causing complications in the design and manufacturing of space-grade electronics. Until
144 now, the solution has been the use of lead-tin alloys for soldering, where Pb provides mitigation
145 against the growth of tin whiskers. However in the European Union, legislation to ban lead-tin alloys
146 is moving ahead. Therefore the use of Al₂O₃ ALD coating is one promising lead-free alternative
147 to inhibit tin whisker growth in space-grade electronics (Kutilainen et al. 2019).

148 **METHODOLOGY**

149 This section explains how the test articles were made and the test setup used. All results and
150 conclusions are shown in later sections.

151 For the experiments, thin-film coated thermoplastic parts were manufactured using AM, epoxy
152 impregnation and ALD. The fabricated parts were tested to determine outgassing properties. For
153 AM, material extrusion (MEX) was used.

154 The first phase of the research focused on finding suitable thermoplastics, taking into account
155 the space environment and potential use cases. Based on our tests and a literature review, a list of
156 promising material candidates for space applications was created. The list included polyether ether
157 ketone (PEEK), polycarbonate (PC), nanodiamond doped polylactide (ND-PLA) and polyimide
158 (PI, Kapton®). As the melting of polyimide is highly problematic, it was not considered for this

159 study as it was not possible to use it with our AM process. Instead acrylonitrile butadienestyrene
160 (ABS) was included in our list of potentially viable test materials. Finally, the following four
161 thermoplastics were selected as substrate materials for this study.

162 **ABS** was used in the ISS *Made in Space* experiment (Prater et al. 2019). It is a widely used
163 material with many good properties (Kutz 2002, p. 339). ABS has good mechanical properties,
164 but the usable temperature range is low. At low temperatures ABS may become brittle, however it
165 does possess a good radiation tolerance (Shulman and Ginell 1970).

166 **PC** is used in many industries, including aerospace. The following has been reported (Mark
167 2009, p. 480): "*The polymer has an excellent balance of high heat resistance, stiffness, strength,*
168 *dimensional stability, low creep, ignition resistance, and exceptional impact strength*". The radiation
169 tolerance and outgassing properties of PC are sufficient for space applications. PC has been
170 widely used in space suit helmet visors. It has also been used in space-based science instruments
171 (Kirn 2013).

172 **PEEK** is an aerospace-grade high-strength material. It has good mechanical properties over a
173 wide temperature range. PEEK has a good tolerance to radiation and it is suitable for relatively high
174 temperature environments, compared to other plastics. It also has good (low) outgassing properties
175 for space applications and water absorption is low (Murari et al. 2002). PEEK has been used in
176 the main structure of the ISS remote manipulator arm, as a matrix for the carbon fibre composite
177 (Lanouette et al. 2015). It has also been proposed as a candidate material for the manufacturing of
178 spare parts and other items in orbit, using AM (Zanjanijam et al. 2020). Initially, these items will
179 mostly be used inside pressurised habitats. Due to the excellent mechanical properties of PEEK, it
180 can also find good use cases outside habitats. If this will be the case, robust protective coatings will
181 be beneficial in protecting such exposed parts from the degrading effects of the space environment.

182 **ND-PLA** Carbodeon uDiamond PLA® is a special nanodiamond doped polylactide filament
183 for material extrusion. In particular, the addition of nanodiamonds can improve the mechanical
184 properties of PLA filaments used in *3D printing*. It also results in improved thermal conductance
185 of the plastic material (VTT 2018). Plain PLA has a fair level of radiation tolerance (Krzysztof
186 et al. 2011). In 2019, Tethers Unlimited and NASA installed the *Refabricator* device on ISS. This
187 device is capable of recycling PLA waste material and 3D printing new parts from it (Prater et al.
188 2019). PLA can be readily utilised for printing generic items used inside space habitats. At this
189 moment, it is difficult to predict how extensively PLA parts will be used in the vacuum of space. A
190 robust protective coating will be a key enabler for such use cases. In light of recent studies, the use
191 of printed PLA parts in vacuum looks promising (Johnson et al. 2020; Nogales et al.2018).



Figure 1. CAD model for the test articles. The outer dimensions of this part were $46 \times 23 \times 2.6$ mm. The coordinate axes shown were used in the material extrusion machines.

192 **Step 1 – Design and Additive Manufacturing of Test Articles**

193 The geometry of the test articles was designed with Autodesk Fusion 360 CAD software and
194 exported as an *.stl* file (Fig. 1). This was further refined (sliced) into G-code files using Intamsys
195 IntamSuite 3.2.0 and Ultimaker Cura 3.5.0 software. The outer dimensions of this part were $46 \times$
196 23×2.6 mm. The part geometry and features were designed in a way to mimic a typical small
197 circuit board, having a placeholder for a microcontroller (Texas Instruments® MSP430) and areas
198 for electrically conductive tracks in three dimensions (3D). The 3D features included holes and

199 small tunnels. One end of the part was designed as a custom 5-pin connector, enabling a quick
200 connect and disconnect to external electric circuits. The part design was created for the purpose of
201 testing 3D electric circuit manufacturing using AM and ALD. It was envisioned that a follow-up
202 research would add area-selective ALD-copper layers to create the conductive tracks.

203 The ABS and PEEK parts were printed with an Intamsys Funmat HT, while PC and ND-PLA
204 parts were printed with an Ultimaker 3 (Fig. 2). For the ABS, PC and ND-PLA parts, a *Dimafix*®
205 glue pen was applied on the build platform to improve adhesion. The much higher bed temperature
206 of the PEEK printing, however, required a different adhesive. After trials, a *Tresemme*® hairspray
207 was used to improve the build-plate adhesion. Table 1 and Table 2 contain a summary of the print
208 parameters used. The parts were printed flat on the build platform, so that the top surface normal
209 was pointing along the printer Z-axis. No raft or brim was used, except for the PEEK parts, which
210 had a 14 mm wide brim. The brim was removed by cutting, after the part had been removed from
211 the printer.

212 **Step 2 – Epoxy Impregnation**

213 Epoxy impregnation was used to reduce the inherent porosity of the AM parts. Panacol®
214 Vitralit 2008 and Vitralit 2009F epoxies were selected for this purpose. Both are ultraviolet(UV)
215 and thermally curable compounds. For simplicity, an impregnation without a vacuum chamber
216 was chosen. At first, the test articles were cleaned using isopropanol wipes. The impregnation
217 was performed by first pouring Vitralit 2008 and Vitralit 2009F into separate Petri dishes. The test
218 articles were then placed and submerged into the selected epoxy, as per Table 3. This table also
219 shows those test articles for which the epoxy impregnation was omitted. During impregnation,
220 the epoxies, dishes and test articles were at room temperature inside a ventilated lab cabinet.
221 Mechanical vibration was applied to the dishes, in order to enhance the removal of air bubbles. The
222 parts were then lifted and excess uncured epoxy was allowed to drip off. Pressurised air was used to
223 remove uncured epoxy from small holes and cavities. The parts were then cured using an Osram®
224 Ultra-Vitalux 300 W UV lamp, which provides approximately 13.6 W of power in the wavelength
225 range between 315 nm and 400 nm. The distance to the lamp was approximately 20 cm and each
226 surface was illuminated for two hours. The second curing step was performed in an oven, where

the parts were heated at 105 °C for 30 minutes. The oven was not fitted with a UV light source.

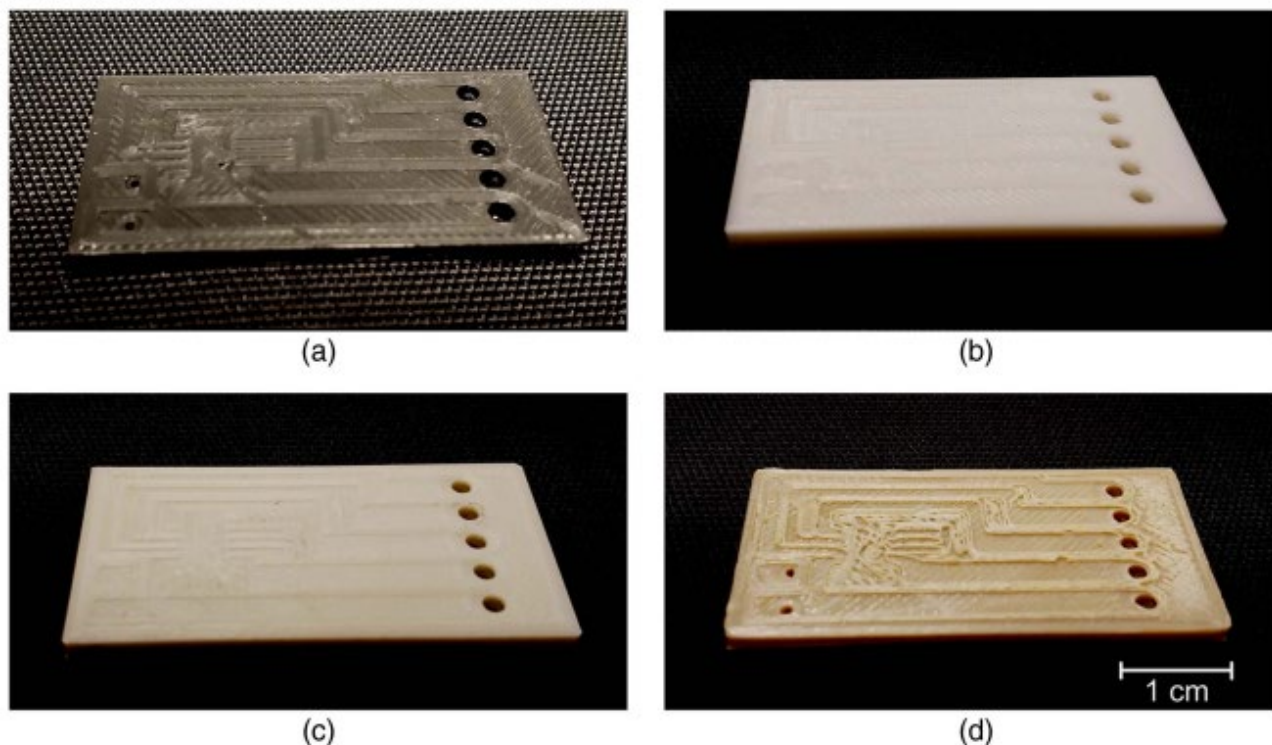


Figure 2. Test articles manufactured with material extrusion printers: (a) ABS part; (b) PC part; (c) ND-PLA; and (d) PEEK. According to visual inspection, the ABS and ND-PLA printing gave the best results in terms of fine details (actual print resolution). The noticeable warping of the part and somewhat crude details.

Table 1. Temperatures, print speed, and bed glue used in the MEX process

Device	Material	T_{BED} (°C)	T_{CHAMBER}	T_{NOZZLE} (°C)	Print speed (mm/s)	Bed glue	Part dimensions (mm)
Funmat HT	ABS	95	90°C	240	50	Dimafix	45.95 × 23.20 × 2.50
Funmat HT	PEEK	160	90°C	400	6	Tresemme	46.10 × 23.15 × 2.55
Ultimaker 3	PC	100	unheated	270	50	Dimafix	45.85 × 23.15 × 2.65
Ultimaker 3	ND-PLA	60	unheated	230	50	Dimafix	46.20 × 23.60 × 2.55

Note: T_{BED} = temperature of the build plate; T_{CHAMBER} = temperature of the print chamber of the printer used; and T_{NOZZLE} = temperature of the printer's extrusion nozzle. A much slower print speed was used for the PEEK parts. The last column shows actual part dimensions, as measured using a vernier caliper.

Table 2. Diameters and other settings for material extrusion

Device	Material	D_{NOZZLE} (mm)	Gap (bed-nozzle)	RAFT/BRIM	Material flow (%)	Print fan
Funmat HT	ABS	0.4	Leveling card	None	100	On
Funmat HT	PEEK	0.4	0.35 mm	Brim, 14 mm wide	105 for initial layers, then 100	Off
Ultimaker 3	PC	0.4	Leveling card	None	100	Off
Ultimaker 3	ND-PLA	0.4	Leveling card	None	100	Off

Step 3 – ALD Al₂O₃ Coating

Selected test articles (Table 3) were coated with ALD-alumina as follows. The parts were

cleaned with isopropanol alcohol wipes and dried with clean compressed air, then placed inside a

R150 ALD reactor (Picosun Oy, Finland) for the first coating layer. The coating process started with an initial phase of 24 hours of thermo–vacuum baking at 90 °C, to remove moisture and other volatiles as much as practically possible. The same chamber temperature was maintained for the subsequent ALD coating process, with a vacuum of approximately 0.3 mbar. Because the test articles were thermoplastic parts, the ALD process temperature had to be limited, in order to avoid damaging the parts. Based on an earlier study (Groner et al. 2004), 90 °C was chosen as this gives near the maximum growth rate and is not too hot to severely damage the test articles.

A targeted thickness of 95 nm was selected for the ALD-alumina layer. In lack of better information of the thickness needed, thickness significantly exceeding the minimum used for barrier applications (Jen et al. 2011) was selected, but below the level which was known by experience to cause delamination issues due stress from CTE mismatch. To achieve this target thickness, the ALD cycle count was set to 1000.

Table 3. Substrate material, type of epoxy used for impregnation, estimated thickness of the ALD coating, and outgassing results for test articles

Test article label	Substrate material	Epoxy impregnation	ALD Al ₂ O ₃ thickness (nm)	Outgassing results
A1	PEEK	Vitralit 2008	95	Not tested
A2	PC	Vitralit 2009F	95	Not tested
A3	ABS	Vitralit 2008	95	Not tested
A4	PEEK	Vitralit 2009F	95	Not tested
A5	ND-PLA	Vitralit 2008	95	Not tested
A6	ND-PLA	Vitralit 2009F	95	Not tested
A7	PC	None	95	Not tested
A8	PC	Vitralit 2008	95	Not tested
A9	PC	None	95	Not tested
A10	ABS	Vitralit 2009F	95	Not tested
A11	PC	None	95	Tested
A12	PEEK	None	None	Tested
A13	ND-PLA	None	None	Tested
A14	PC	None	None	Tested
A15	ABS	None	None	Tested
B1	ABS	Vitralit 2008/2009F	95	Not tested
B2	ND-PLA	Vitralit 2008/2009F	95	Tested
B3	ABS	Vitralit 2008/2009F	95	Tested
B4	ABS	Vitralit 2008/2009F	95	Not tested
B5	PC	Vitralit 2008/2009F	95	Not tested
B6	PEEK	Vitralit 2008/2009F	95	Tested

Note: The selection of epoxy was not recorded for Test articles B1–B6. These parts received either Vitralit 2008 or 2009F.

The ALD Al₂O₃ deposition was carried out using trimethylaluminium (TMA) and deionized water. The precursor dose times were 0.3 s for TMA and 0.2 s for water. Purge time was 60 s for both dose types to ensure egress of the reactants from the reaction chamber between pulses. This chemistry was selected, because it is known to produce films of high quality and good adhesion. Water is a common reactant for ALD-grown metal oxides, as it is gentle to the substrate surface (Johnson et al. 2014). Using this setup, a layer of ALD Al₂O₃ was then deposited on the epoxy

249 impregnated thermoplastic substrate or non-impregnated thermoplastic substrate as per Table 3.

250 Following the ALD coating, the parts were examined with an Olympus® BH-2 optical stere-
251 omicroscope. Images were captured using an Olympus® SC30 camera module attached to the
252 microscope.

253 **Step 4 – Thermal-Vacuum Outgassing Test**

254 For the thermal–vacuum outgassing test, the ALD-coated parts A11, B2, B3 and B6 were
255 selected. It should be noted that A11 was not epoxy impregnated, whereas the other three parts
256 were epoxy impregnated (Table 3). This was so, because an associated coating test (not reported in
257 this paper) consumed all the epoxy impregnated PC parts. Although not planned, this did provide
258 an opportunity to see on a coarse level how a missing impregnation could affect the outgassing.
259 The A11 part had only ALD Al₂O₃ coating on top of the polymer substrate.

260 Reference parts (A12, A13, A14 and A15) were selected and these were not epoxy impregnated
261 nor ALD coated. These uncoated parts were manufactured using AM in the same way as for the
262 coated parts and using the same G-code file.

263 All in all, eight test articles were tested for outgassing: four with an ALD coating and four
264 reference parts with no ALD coating. The other parts listed in Table 3 were not included in
265 the outgassing test. They were retained in the table, as they were relevant for other observations
266 included in this paper, including the AM, ALD and impregnation.

267 Next, an outgassing test using an MKS Vision 2000-C quadrupole residual gas analyzer (RGA)
268 and a thermal–vacuum chamber was conducted. For each of the four plastics (PEEK, ND-PLA,
269 PC and ABS), the outgassing was measured for the uncoated part and coated part using the same
270 setup.

271 The tests were conducted with a custom-made setup. The vacuum chamber was constructed
272 from a KF-40 type T-shaped steel tubing component (Fig. 3). One open end of this T-tube was
273 connected to the RGA. The second open end was fitted with an extension tube, which incorporated
274 connections to a secondary vacuum pump, a manometer (MKS 722B Baratron), and a positive
275 pressure dry nitrogen purge line. The third open end, of this T-shaped chamber, was fitted with a
276 KF-40 stainless steel end cap with a clamp.

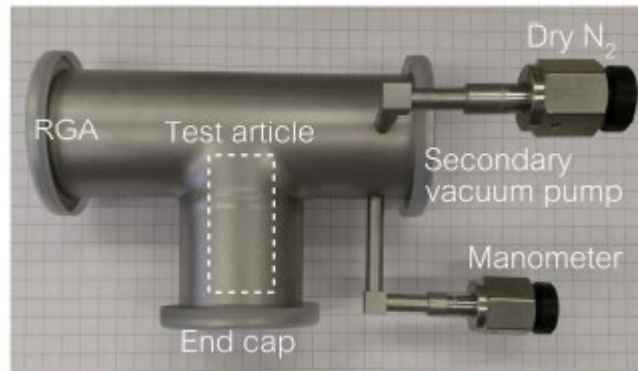


Figure 3. KF-40 steel thermal-vacuum chamber used in the outgassing tests. The secondary vacuum connection and nitrogen line were closed during the RGA measurements. The end cap opening was fitted with an Aldrich two-hand AtmosBag and a steel cap with a clamp. The test articles were first placed inside the nitrogen filled AtmosBag, and then placed from there inside the vacuum chamber via the end cap. The openable end cap also resided inside the AtmosBag. Using this setup, the test articles could be moved inside the vacuum chamber after base-line measurements, without contaminating the chamber with ambient air. The vacuum chamber tube diameter was 39.5 mm and flange outer dimension was 55.0 mm.

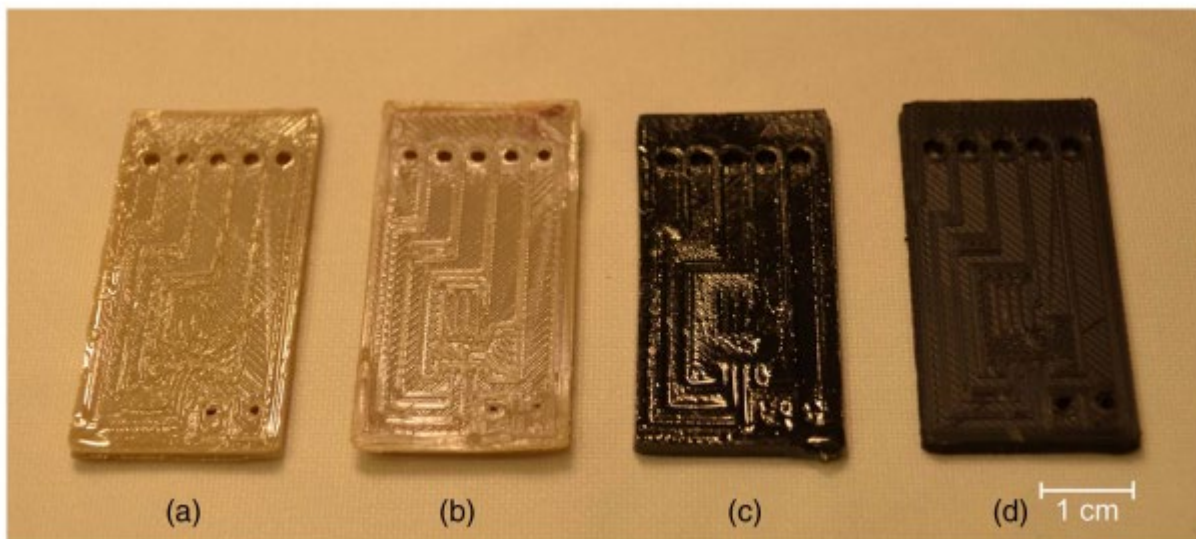


Figure 4. PEEK and ABS parts used in the outgassing test taken after the test runs: (a) coated PEEK; (b) uncoated PEEK; (c) coated ABS; and (d) uncoated ABS. The coating system comprised of epoxy impregnation (thickness $> 1 \mu\text{m}$), followed by ALD Al_2O_3 overcoat (thickness approximately 95 nm). The PC and ND-PLA parts were similar.

The vacuum chamber was then externally wrapped with

277 a heating wire element and a temperature sensor, both of which were connected to a digital heater
 278 controller (Horst HT MC1). The outside of this assembly was wrapped using silicone insulating
 279 mats and aluminum foil, in order to isolate the hot vacuum chamber from its surroundings as much
 280 as possible. The role of the secondary vacuum pump was to provide a vacuum for purging, and
 281 to get the chamber pressure below the threshold of the RGA's turbomolecular pump. During RGA
 282 measurements, the secondary vacuum pump vent and nitrogen line vent were closed. This way, all

283 outgassing particles were routed via the RGA and into an external trap, forced by the turbomolecular
284 pump of the MKS Vision 2000. During RGA measurements, the vacuum level was in the range of
285 0.02..0.89 mbar, depending on the amount of outgassing from the test article. The test flow was as
286 follows:

- 287 1. The steel vacuum chamber was heated to 55 °C.
- 288 2. A baseline measurement was conducted with the chamber being empty.
- 289 3. The empty vacuum chamber was purged with dry nitrogen gas threetimes.
- 290 4. A coated test article was placed into the chamber (see Fig. 3 and Fig. 4), via an N₂ filled
291 glove bag.
- 292 5. The vacuum chamber was purged with dry nitrogen gas three times, with the test article
293 residing in the chamber.
- 294 6. A *coarse* resolution measurement was conducted using the RGA. This was labelled as TVC
295 Test 1. The duration of this step was approximately 15 minutes. Only the recorded RGA
296 data from the first 12 minutes and 55 seconds was used for the actual analysis. Using this
297 cropping of data, exactly the same number of measurement cycles was analyzed for all the
298 test articles.
- 299 7. Following the previous step, with the test setup running continuously, a *fine* resolution
300 measurement was conducted using the RGA. This was labelled as TVC Test 2. The duration
301 of this step was approximately 50 minutes, while the recorded RGA data from the first 45
302 minutes and 44 seconds, counted from the moment when RGA switched to fine resolution,
303 was cropped for the actual analysis.
- 304 8. The test article was removed from the chamber.
- 305 9. An uncoated reference test article, made from the same thermoplastic as the coated test
306 article in step 4, was placed in the chamber.
- 307 10. The vacuum chamber was purged with dry nitrogen gas three times, with the reference test
308 article residing in the chamber.
- 309 11. RGA measurements were made in the same way as in steps 6 and 7.
- 310 12. The test article was removed from the chamber. End of the test. The steel vacuum chamber

311 was kept at 55 °C during all the steps shown above.

312 An identical test flow (as explained above) was used for each of the thermoplastics tested. The
313 only exception was for the testing of the two ABS parts, where the uncoated part was moved into
314 the chamber in step 4 and the coated part in step 9. This was done in order to evaluate whether the
315 small deviation in the vacuum chamber temperature towards the end of a test run could affect the
316 outgassing rate.

317 The collected RGA data was then analyzed as follows. The flux measurements of detected
318 ion species were organized into a table, with scans (temporal range) representing Y-axis rows
319 and particle mass range (1–300) forming X-axis columns. The average flux of each column was
320 calculated. Static noise in the measurement data was detected by observing very small negative
321 flux values. Based on this observation, a threshold value was set and columns having an average
322 value below it were discarded as noise. These filtered average fluxes were then used to produce
323 bar graphs and logarithmic mass spectrum plots as follows: For the bar graphs (Fig. 6 and 7), the
324 constituents of N, N₂, H₂O, OH and O₂ were removed from the RGA data before analysis, as these
325 were most likely traces of trapped ambient air and residuals of nitrogen gas used during chamber
326 purging. For spacecraft design purposes, it is important to narrow down the data to the outgassing
327 of condensable contaminants, in relation to the space environment. After this filtering, the average
328 fluxes of the remaining columns were integrated and this value was used as the outgassing of the
329 corresponding test article. For the logarithmic mass spectrum plots (Fig. 8), the same filtered data
330 set was used. However, the constituents of N, N₂, H₂O, OH and O₂ were retained in this case, so
331 that these peaks are visible in the mass spectrum plots. The logarithmic plots were only used for
332 an RGA peak detection (qualitative analysis).

333 The *MKS Process Eye Professional* software outputs the data as *pressure in millibars*. However,
334 a careful calibration process is needed if accurate values for partial pressures of ion species need
335 to be obtained. Therefore, we report our measurements using an arbitrary unit (arb. unit). The
336 reported values are not factored. We have simply replaced "millibar" with "arb. unit" in this paper.

337 **RESULTS AND DISCUSSION**

338 Here we report the results of the tests in the same order as they were introduced in the previous

339 section.

340 **Results of Step 1 – Additive Manufacturing**

341 In order to achieve proper adhesion between the printed part and the heated build platform, it is
342 important to apply glue or another suitable compound on the platform before printing. Commercial
343 3D-printing build-surface sheets are also available. Kapton and other tapes are also used for this
344 purpose. As the build plate temperature is increased, the choice of options gets narrower. These
345 additives aim to ensure sufficient adhesion, ensuring a successful print. Also, they make the part
346 removal easier after the print. This could otherwise be a challenge, especially for PC.

347 The manufacturing time of the ABS, PC and ND-PLA test articles was about 1 hour per part,
348 regardless of the device used. The PEEK articles took about 2 hours to print. The pre-heating phase
349 is longer and the print speed lower when using PEEK. Bed leveling and calibration is important, in
350 order to ensure good quality and adhesion for the initial printed layers. We noticed that when using
351 the Funmat HT with PEEK, the printer bed, chamber and nozzle must be pre-heated to operating
352 temperatures before the bed leveling and calibration. Otherwise, the gap between the nozzle and
353 the bed will not be correctly adjusted.

354 The measured dimensions of the AM parts, as they were removed from the printer and cleaned,
355 are included in Table 1.

356 *Additive Manufacturing with PEEK*

357 PEEK was the most difficult of these materials to print successfully using material extrusion.
358 The parts were initially always warping and detaching from the bed during printing. This was
359 caused by thermal expansion and subsequent contraction. Different settings for the bed and nozzle
360 temperatures were tried, without noticeable improvement. Dimafix®, UHU® polyvinylpyrrolidone
361 (PVP) and Dremel® glue gun adhesives were trialled without success. Finally, a *Tresemme®*
362 hairspray combined with a brim provided sufficient adhesion for the print. The hairspray was able
363 to provide adhesion only for approximately 10 minutes, while the brim was printing. After this, the
364 hairspray dried and no longer provided sufficient adhesion. Based on our trials, a better solution
365 for bed adhesion in high temperature polymer printing is needed.

366 Other relevant parameters are listed in Tables 1 and 2. This setup produced partially successful

367 prints. Finished parts were still slightly warped, and the quality of fine details was inferior to the
368 ABS prints, in particular. We expect that higher bed and chamber temperatures could reduce the
369 warping of the PEEK prints. This was, however, not tested because the Intamsys Funmat HT was
370 already operating with its highest bed and chamber temperature settings.

371 **Results of Step 2 – Epoxy Impregnation**

372 In several industrial processes, the porosity of manufactured parts is removed or reduced with
373 the use of impregnation compounds. Earlier studies by our consortium had found issues with the
374 porosity of AM prints, resulting in ALD layers depositing inside the porous cavities of test articles.
375 This phenomenon is unwanted in many cases. For example, when creating electrically conductive
376 surface paths with ALD Cu, any conductive material deposited in the porous cavities inside the
377 part are an issue. To avoid this, an epoxy impregnation step was added between the AM and ALD
378 processes. The assumption was that epoxy-impregnated AM prints would not exhibit the porosity
379 issue in the ALD coating step.

380 The actual impregnation step revealed that the viscosity of the two epoxies used was too high,
381 for the intended purpose. The viscosity controls, to a great degree, the impregnation capability and
382 the thickness and uniformity of the epoxy coating. Our method of using pressurised air to remove
383 any excess Vitralit compound before curing is an option, but it did not result in a uniform coating
384 thickness. Other mechanical methods may also be used to enforce a thin and uniform epoxy film
385 before the curing step. At the end of the research, a simple self-made *centrifuge* was tested. When
386 an uncured epoxy coated AM print was attached to the centrifuge and rotated at 1500 rpm, excess
387 epoxy was effectively removed and a smooth epoxy layer remained, ready for UV curing.

388 In general, the UV curing of the parts was easy. However, if a UV lamp generates heat
389 significantly, it needs to be placed at a safe distance away, so that the polymer parts are not
390 overheated and deformed. This increases the UV curing time. The use of cooling fans may
391 possibly be able to mitigate this issue. When the parts were removed from the oven following the
392 second curing step, we noticed that the ABS parts were slightly warped. This is not surprising,
393 since the oven temperature exceeded the continuous use temperature of ABS, which is 80 °C.
394 Overall, the impregnation was successful. We were able to successfully eliminate the porosity of

395 the AM prints, at least near the surface of the parts. This was evident based on visual inspection of
396 the parts after impregnation (continuous layer of epoxy on the surface). Also, an inspection with
397 an optical microscope after the ALD coating showed a bulk epoxy layer under the transparent ALD
398 layer.

399 The viscosity of the liquid compound used in impregnation must be controlled precisely. If
400 the viscosity is too high, it becomes necessary to use high pressure gradients to overcome the
401 hydraulic resistance. This will complicate the manufacturing process. Vacuum impregnation is a
402 well-known industrial process, and would probably be needed to ensure that no air bubbles remain
403 in the AM prints. The use of high temperatures, to lower the viscosity, is problematic in many
404 cases (Buevich and Kalinnikov 1979). Ideally, the properties of the liquid and the AM print would
405 allow impregnation by capillary action.

406 Epoxy impregnation might bring additional benefits. For example, it is possible that elimination
407 of the porosity with epoxy impregnation could improve the mechanical properties of an AMprint,
408 effectively creating a part made of *composite material*.

409 **Results of Step 3 – ALD Al₂O₃ Coating**

410 The applied top-coat layer was ALD Al₂O₃. There were no problems encountered during this
411 coating process. The resulting Al₂O₃ layer was estimated to be approximately 95 nm thick, based on
412 the actual ALD process parameters. After the coating, numerous surface microcracks were found
413 when the test articles were examined with an optical microscope (Fig. 5). This was the case for
414 the PC, PEEK and ND-PLA parts. The ABS parts appeared to have much less cracks, but because
415 these parts were black, we suspect that the colour of the parts affected the visual inspection. These
416 cracks in the ALD coating were evident in both the epoxy impregnated and non-impregnated parts.

417 As the main plastic material was fully covered under the epoxy film, it was the cured epoxy
418 compound that controlled the ALD-related chemical reactions for the initial ALD layers, except for
419 the three non-impregnated PC parts. Since the aim was to find an efficient manufacturing process,
420 as few processing steps as possible were planned. For this reason, no surface pretreatment of the
421 test articles was conducted before ALD. Depending on the material and the surface characteristics,
422 a surface pretreatment may improve the quality of an ALD coating.

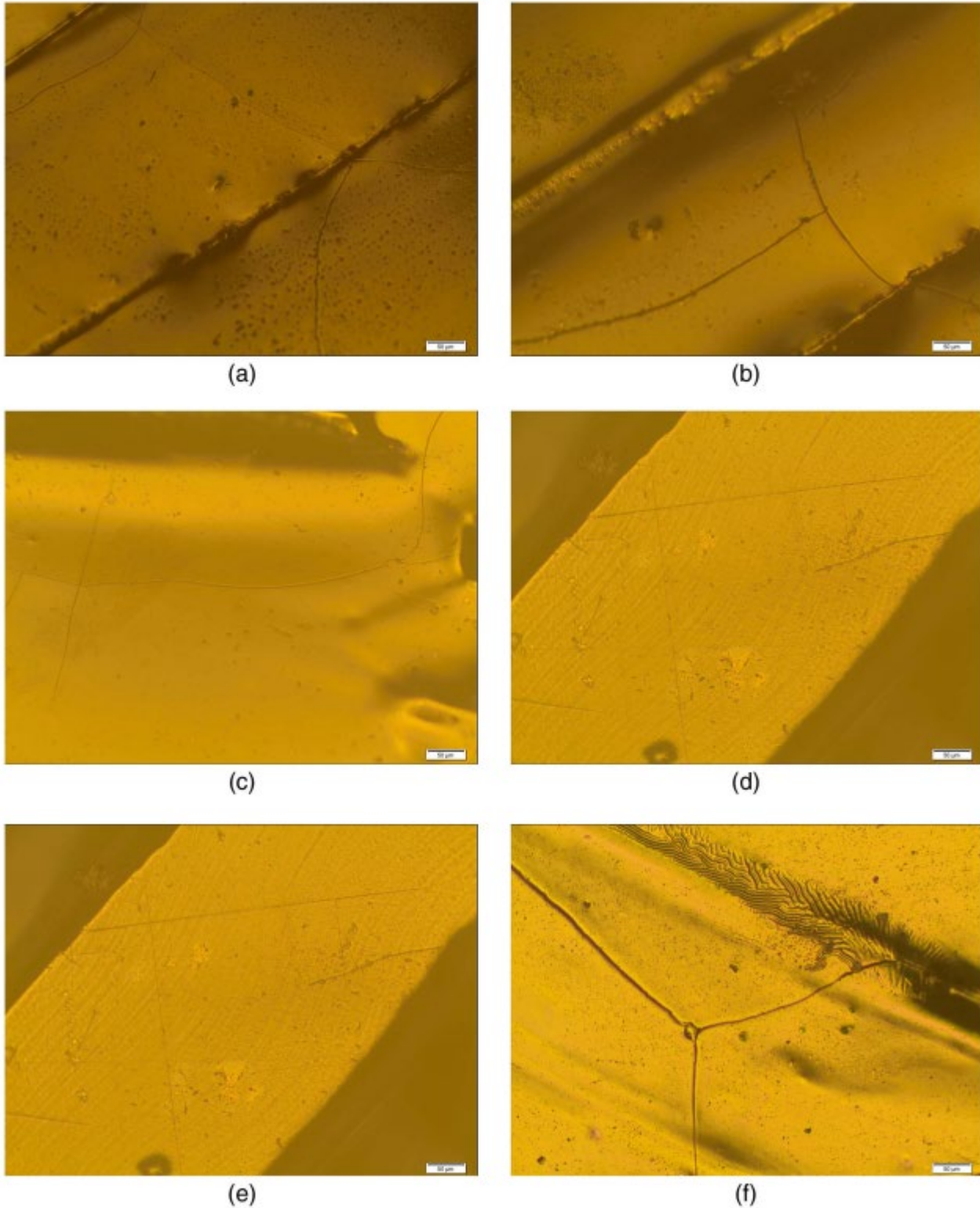


Figure 5. Images from visual inspection of the ALD coating with an optical microscope: (a) Test article A4 (PEEK); (b) A4 (PEEK); (c) A2 (PC) with epoxy impregnation; (d) A11 (PC) without impregnation (ALD coating on polymer substrate); (e) A6 (ND-PLA); and (f) B5 (ABS). Large scale tracks (approximately 400 μm) are features from material extrusion process. Thin lines (estimated 1–3 μm from the images) are cracks in the ALD Al_2O_3 thin-film coating, found in all coated test articles.

424 a sufficient layer thickness. The selection of a proper coating thickness for the ALD layers is
425 important. With ALD Al₂O₃, a coating thickness of 100 nm is common. At least one study (Jen
426 et al. 2011) has shown a smaller cracking tendency for thinner Al₂O₃ coatings.

427 The adhesion between the ALD coatings and substrates was not measured in this study. However,
428 this type of adhesion has been previously evaluated for thermoplastics and epoxies (Chen et al.
429 2019). In order to test coating adhesion, a similar scratch test as explained by Bull could be used
430 (Bull 1997).

431 **Results of Step 4 – Thermal-Vacuum Outgassing Test**

432 The results of our thermal–vacuum tests show a significant reduction in the outgassing of the
433 ALD coated test articles. Compared to the uncoated parts, the ALD Al₂O₃ coating decreased the
434 outgassing of PEEK by 46%; ABS, by 49%; PC, by 58%; and ND-PLA, by 65%.

435 As the PC part (A11) was lacking epoxy impregnation, the comparison of this substrate and the
436 other three substrates is somewhat complicated (Table 3). The outgassing results of the impregnated
437 PEEK, ABS and ND-PLA parts can be directly compared against each other, as they all had the
438 epoxy impregnation and ALD coating. On the other hand, the outgassing results of the non-
439 impregnated PC part (A11) clearly show that the presence of the ALD coating was the main reason
440 for the reduced outgassing. Regarding the reference parts, all four were non-impregnated and
441 without any ALD coating, printed from PEEK, ABS, PC and ND-PLA using the same AM process
442 as used for the coated parts.

443 It is well known that all polymeric substances exhibit some level of outgassing, as absorbed
444 gases, moisture and extraneous solvents egress. However, it is more important to detect and study
445 the evaporation of substances related to the basic polymer structure itself (Muraca and Whittick
446 1967). For this reason, we chose to measure the outgassing using RGA. Fig. 6 and 7 report the
447 measured outgassing of the TVC Test 1 and 2, respectively.

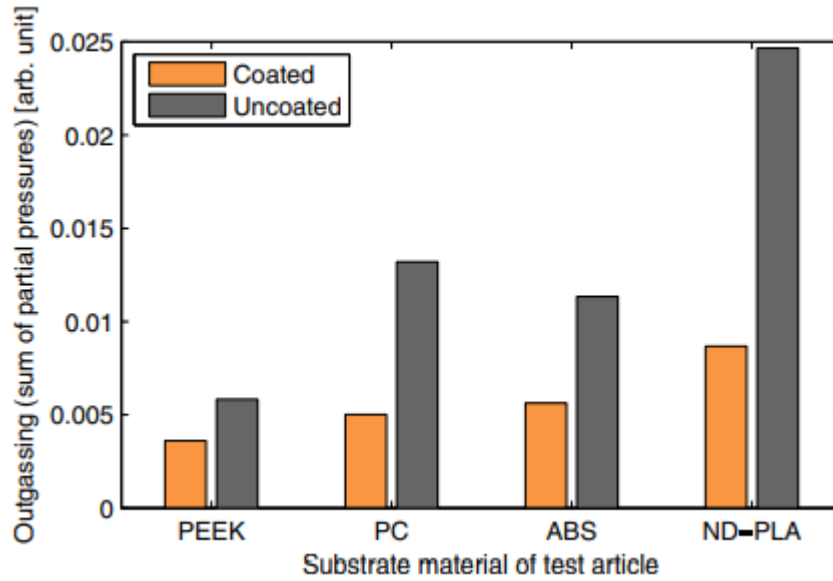


Figure 6. Outgassing of the test articles, measured by using the *coarse* resolution mode of the RGA during initial exposure to a vacuum (thermal-vacuum chamber Test 1). The constituents of N, N₂, H₂O, OH, and O₂ were removed from the RGA data before analysis, because these are most likely traces of trapped ambient air and residuals of nitrogen gas used during chamber purging.

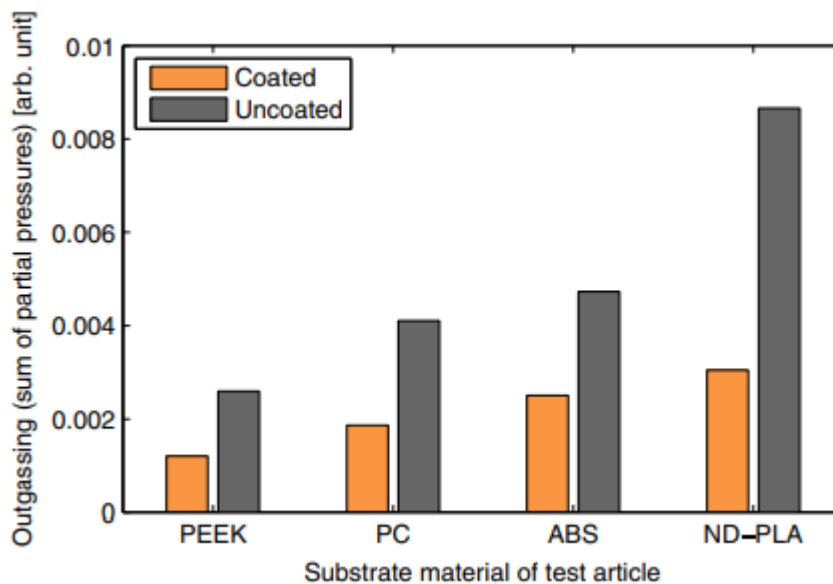


Figure 7. Outgassing of the test articles, measured by using the *fine* resolution mode of the RGA. The figure shows the results for the thermal-vacuum chamber Test 2. The constituents of N, N₂, H₂O, OH, and O₂ were removed from the RGA data before analysis, because these are most likely traces of trapped ambient air and residuals of nitrogen gas used during chamber purging.

448 Qualitative analysis of the obtained RGA spectras should include: 1) fragmentation patterns;
 449 2) multiply charged ions, and; 3) isotope ratios. For the uncoated ABS test article, the measured
 450 RGA spectra (Fig. 8) shows a distinct peak for ions with an atomic mass unit (AMU) of 40. This
 451 peak could be associated with 1,3-butadiene which is one constituent of ABS. However, this peak is

452 more likely associated with argon gas, especially when taking into account the lower peak at AMU
453 20 and the fact that the peak is also visible in the spectras of PEEK, PC and ND-PLA parts. No
454 other peaks clearly associated with a polymer structure were detected. It is likely that the parts must
455 be heated to higher temperatures before the outgassing of these polymer structures produce distinct
456 peak patterns. Although our results clearly indicate a reduced outgassing rate for each of the coated
457 test articles, a more comprehensive test campaign would be required to analyse the composition of
458 the outgassed particles. This campaign would necessarily include elevated temperatures, at least
459 125 °C and possibly up to 250 °C for PEEK, in order to gain better knowledge of the behaviour of
460 this type of components in various locations in a spacecraft. In this study and in future studies, the
461 logarithmic RGA spectra (Fig. 8) is useful for the peak detection.

462 ALD coatings thicker than 10 nm can be used as a gas diffusion barrier (Jen et al. 2011). The
463 type of ALD Al₂O₃ coating used in this study has been shown to be amorphous and having excellent
464 gas barrier properties (Heidary and Randall 2015). This can effectively reduce the outgassing of
465 many polymers in space. The coating will also protect the polymer from highly reactive atomic
466 oxygen particles. Our findings support this.

467 In order to qualify this type of parts for the NASA or European Space Agency (ESA) missions,
468 further outgassing testing is required. In the United States, the ASTM test methods E595 and E1559
469 are used to qualify materials for use in spacecraft, when it comes to outgassing (ASTM 2020). In
470 Europe, the ECSS-Q-ST-70C standard lays out the criteria for space-grade materials, mechanical
471 parts and processes. Related to outgassing, this document states that the ECSS-Q-ST-70-02C and
472 ECSS-Q-TM-70-52A standards are relevant (ECSS 2020).

473 **CONCLUSIONS**

474 Research has shown many benefits of using AM for space applications. Recently, Rui Hu et
475 al. studied an AM-enabled concept for the design of a space telescope primary mirror (Hu et al.
476 2016). In light of the topics covered above, we evaluated the manufacturing of thermoplastic parts
477 for spacecraft, using a combined AM-ALD technique.

478 Most importantly, we showed a path towards creation of space-grade components using a

479 combination of AM and ALD. This type of manufacturing method enables the use of *topology*
480 *optimization* already in the early concept creation phase. It is ideally suited for spacecraft appli-
481 cations, where the volume and mass of parts is often critical. In-space manufacturing using these
482 methods could be applied to various use cases. Parts printed from PEEK, PC or ABS could be
483 used for structural applications. Food packaging and general purpose items could be made from
484 PLA, which is biocompatible and environmentally friendly.

485 In this study, we used two low viscosity epoxies for the impregnation of AM parts. Surface
486 porosity was effectively removed. Interestingly, elimination of the porosity with epoxy impregnation
487 could improve the mechanical properties of an AM print. This was not verified in our tests, but
488 could be studied in future.

489 Although our results clearly demonstrate a reduction in outgassing, further testing is necessary
490 to separate the effect of the impregnation and the effect of the ALD coating.

491 The main results of the presented analysis can be summarized as follows: 1) Significant
492 reduction in outgassing was demonstrated. Low outgassing is one important criteria for the
493 selection of spacecraft materials, and; 2) The inherent porosity of AM-MEX printed thermoplastic
494 parts was effectively removed, at least near the surface, using epoxy impregnation.

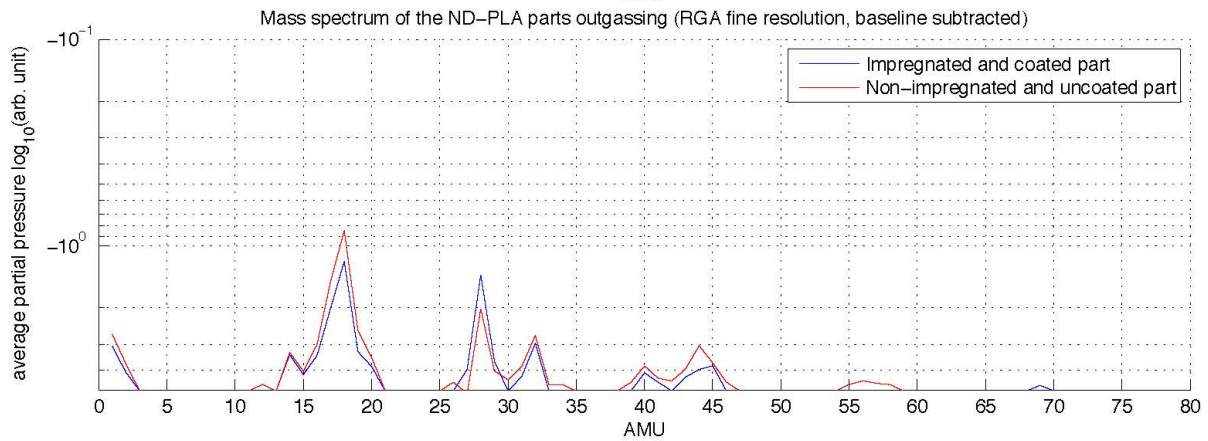
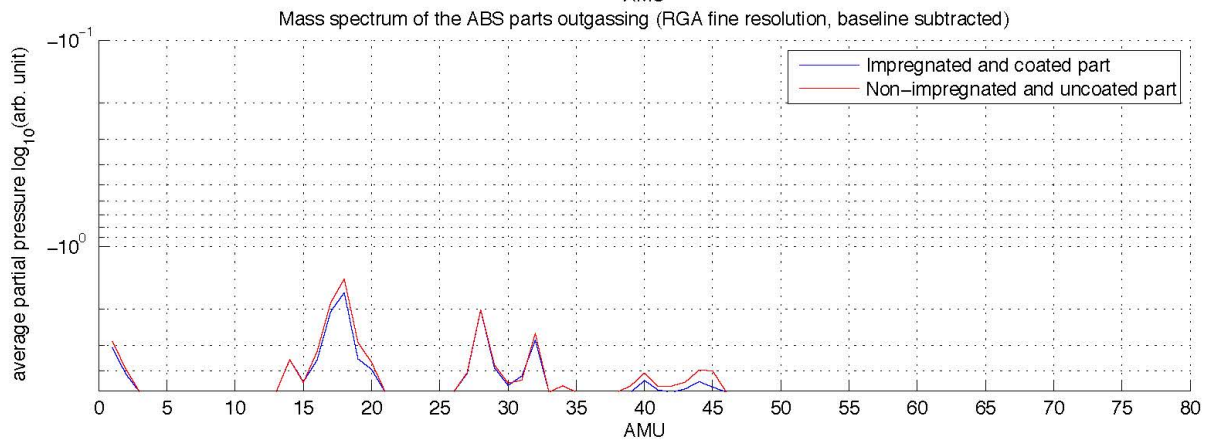
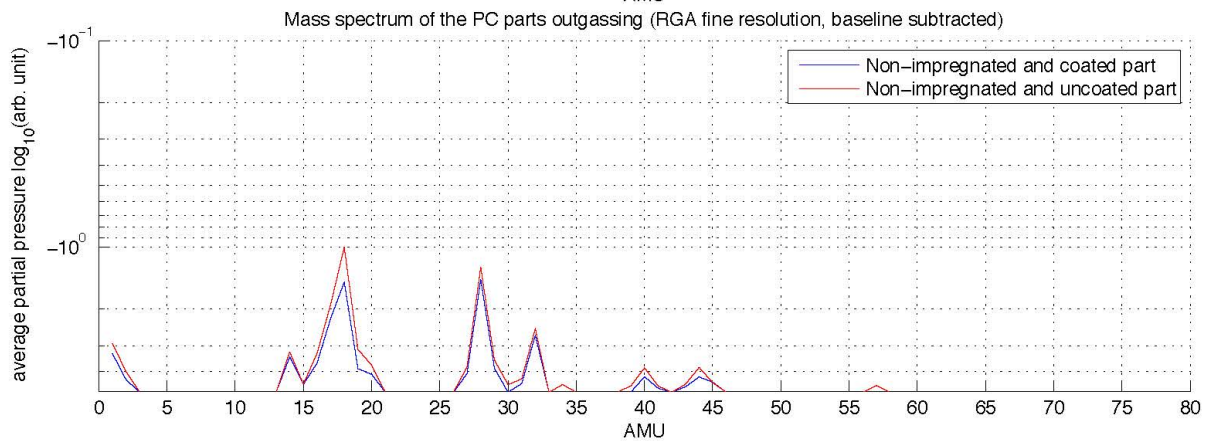
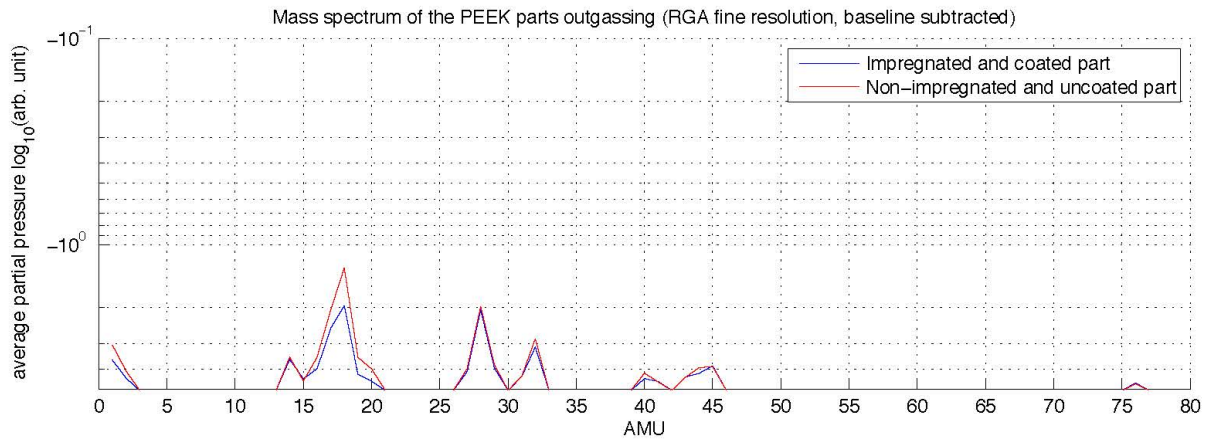


Figure 8. Mass spectrum plots of the RGA data up to AMU 80. Higher masses did not produce noticeable peaks. Chamber baseline measurement has been subtracted in these plots, to show the outgassing of the test articles solely.

495 DATA AVAILABILITY STATEMENT

496 Some or all data, models, or code generated or used during the study are available from
497 the corresponding author upon request. This includes RGA measurements, laboratory notes and
498 pictures.

499 ACKNOWLEDGEMENTS

500 We thank the European Space Agency (ESA) who has supported parts of this research as part
501 of the HighPEEK project (ESA Contract N° 4000127834/19/UK/AB). In particular, Ugo Lafont
502 and Paul Greenway (ESA) have our gratitude. We also deeply appreciate the help given by Daniel
503 Leese (exchange student at Aalto University), Kirsi Kukko, Ashish Mohite and Olli Knuuttila
504 (Aalto University), Lorenz Schmuckli and Pekka Rummukainen (Aalto University, retired) and
505 Katja Väyrynen and Marko Vehkamäki (University of Helsinki).

506 REFERENCES

- 507 Abdulagatov, A., Yan, Y., Cooper, J., Zhang, Y., Gibbs, Z., Cavanagh, A., Yang, R., Lee, Y., and
508 George, S. (2011). “Al₂O₃ and TiO₂ atomic layer deposition on copper for water corrosion
509 resistance..” *ACS applied materials & interfaces*, 3(12), 4593–4601.
- 510 ASTM (2020). “American Society for Testing and Materials., <<https://www.astm.org>>.
- 511 Broas, M. (2018). “Quality, microstructural refinement and stability of atomic-layer-deposited
512 aluminum nitride and aluminum oxide films.” Ph.D. thesis, Aalto University, Finland.
- 513 Buevich, Y. and Kalinnikov, V. (1979). “Impregnation of a heated filler with a viscous liquid.”
514 *Journal of Engineering Physics and Thermophysics*, 36(6).
- 515 Bull, S. (1997). “Failure mode maps in the thin film scratch adhesion test.” *Tribology international*,
516 30(7), 491–498.
- 517 Chen, Y., Ginga, N., LePage, W., Kazyak, E., Gayle, A., Wang, J., Rodríguez, R., Thouless, M., and
518 Dasgupta, N. (2019). “Enhanced interfacial toughness of thermoplastic–epoxy interfaces using
519 ALD surface treatments..” *ACS Applied Materials & Interfaces*, 11(46), 43573–43580.

520 Cooper, R., Upadhyaya, H., Minton, T., Berman, M., Du, X., and George, S. (2008). “Protection of
521 polymer from atomic-oxygen erosion using Al₂O₃ atomic layer deposition coatings.” *Thin Solid*
522 *Films*, 516(12), 4036–4039.

523 Cruise, A., Bowles, J., Patrick, T., and Goodall, C. (2006). *Principles of space instrument design*.
524 Cambridge University Press.

525 ECSS (2020). “European Coordination for Space Standardization., <<https://www.ecss.nl>>.

526 Fortescue, J., Swinerd, G., and Stark, J. (2011). *Spacecraft systems engineering*. John Wiley &
527 Sons, West Sussex.

528 Gilmore, D. (2003). *Spacecraft thermal control handbook*. Aerospace Press.

529 Grau, S. (2019). *Contributions to the Advance of the Integration Density of CubeSats*, Vol. 3.
530 Universitätsverlag der TU Berlin.

531 Groner, M., Fabreguette, F., Elam, J., and George, S. (2004). “Low-temperature Al₂O₃ atomic
532 layer deposition.” *Chemistry of Materials*, 16(4), 639–645.

533 Grossman, E. and Gouzman, I. (2003). “Space environment effects on polymers in low earth
534 orbit.” *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with*
535 *Materials and Atoms*, 208, 48–57.

536 Heidary, D. and Randall, C. (2015). “Evaluating the merit of ALD coating as a barrier against
537 hydrogen degradation in capacitor components..” *RSC Advances*, 5(63), 50869–50877.

538 Hu, R., Chen, W., Li, Q., Liu, S., Zhou, P., Dong, Z., and Kang, R. (2016). “Design optimization
539 method for additive manufacturing of the primary mirror of a large-aperture space telescope.”
540 *Journal of Aerospace Engineering*, 30(3).

541 Jen, S., Bertrand, J., and George, S. (2011). “Critical tensile and compressive strains for cracking
542 of Al₂O₃ films grown by atomic layer deposition.” *Journal of Applied Physics*, 109(8).

543 Johnson, P., Copeland, P., Ayodele, A., Tarekegn, E., Bromley, S., Harrell, W., Sosolik, C., and
544 Marler, J. (2020). “In-vacuum performance of a 3D-printed ion deflector.” *Vacuum*, 172, 109061.

545 Johnson, R., Hultqvist, A., and Bent, S. (2014). “A brief review of atomic layer deposition: from
546 fundamentals to applications..” *Materials today*, 17(5), 236–246.

547 Kestilä, A., Nordling, K., Miikkulainen, V., Kaipio, M., Tikka, T., Salmi, M., Auer, A., Leskelä, M.,

548 and Ritala, M. (2018). “Towards space-grade 3D-printed, ALD-coated small satellite propulsion
549 components for fluidics.” *Additive Manufacturing*, 22, 31–37.

550 Kirn, T. (2013). “The AMS-02 TRD on the international space station..” *Nuclear Instruments and
551 Methods in Physics Research Section A: Accelerators, Spectrometers, Detectors and Associated
552 Equipment*, 706, 43–47.

553 Krzysztof, M., Kubera, H., Głuszewski, W., and Zimek, Z. (2011). “Effect of ionizing radiation on
554 the properties of PLA packaging materials.” *Nukleonika*, 56, 65–69.

555 Kutilainen, T., Pudas, M., Ashworth, M., Lehto, T., Wu, L., Wilcox, G., Wang, J., Collander, P., and
556 Hokka, J. (2019). “Atomic layer deposition (ALD) to mitigate tin whisker growth and corrosion
557 issues on printed circuit board assemblies.” *Journal of Electronic Materials*, 48(11), 7573–7584.

558 Kutz, M. (2002). *Handbook of materials selection*. John Wiley & Sons.

559 Lanouette, A., Potvin, M., Martin, F., Houle, D., and Therriault, D. (2015). “Residual mechanical
560 properties of a carbon fibers/PEEK space robotic arm after simulated orbital debris impact.”
561 *International Journal of Impact Engineering*, 84, 78–87.

562 Mark, J. (2009). *Polymer data handbook*. Oxford University Press.

563 McGuigan, A., Briggs, G., Burlakov, V., Yanaka, M., and Tsukahara, Y. (2003). “An elastic-plastic
564 shear lag model for fracture of layered coatings.” *Thin Solid Films*, 424(2), 219–223.

565 Minton, T., Wu, B., Zhang, J., Lindholm, N., Abdulagatov, A., O’Patchen, J., George, S., and
566 Groner, M. (2010). “Protecting polymers in space with atomic layer deposition coatings.” *ACS
567 applied materials & interfaces*, 2(9), 2515–2020.

568 Muraca, R. and Whittick, J. (1967). “Polymers for spacecraft applications..” *Report No. N67-40270*,
569 Stanford Research Institute.

570 Murari, A., Vinante, C., and Monari, M. (2002). “Comparison of PEEK and VESPEL SP1 charac-
571 teristics as vacuum seals for fusion applications..” *Vacuum*, 65(2), 137–145.

572 Nogales, C., Grim, B., Kamstra, M., Campbell, B., Ewing, A., Hance, R., Griffin, J., and Parke,
573 S. (2018). “MakerSat-0: 3D-printed polymer degradation first data from orbit.” *32th Annual
574 AIAA/USU Conference on Small Satellites*.

575 Prater, T., Edmunson, J., Ledbetter, F., Fiske, M., Hill, C., Meyyappan, M., Roberts, C., Huebner,

576 L., Hall, P., and Werkheiser, N. (2019). "NASA's in-space manufacturing project: Update on
577 manufacturing technologies and materials to enable more sustainable and safer exploration."
578 *70th International Astronautical Congress (IAC), Washington, D.C., 21-25 October 2019.*

579 Ruckerl, A., Zeisel, R., Mandl, M., Costina, I., Schroeder, T., and Zoellner, M. (2017). "Char-
580 acterization and prevention of humidity related degradation of atomic layer deposited Al₂O₃."
581 *Journal of Applied Physics*, 121(2).

582 Shulman, H. and Ginell, W. (1970). "Nuclear and space radiation effects on materials." *Report No.*
583 *SP-8053*, NASA.

584 Stein, B. (1992). "An interim overview of LDEF materials findings." *Report No. 107664*, NASA.

585 Stein, B. (1993). "LDEF materials overview." *Report No. 93-28255*, NASA.

586 Tynell, T. and Karppinen, M. (2014). "Atomic layer deposition of ZnO: a review." *Semiconductor*
587 *Science and Technology*, 29(4), 043001.

588 Varadan, V., Xiaoning, J., and Varadan., V. (2001). *Microstereolithography and other fabrication*
589 *techniques for 3D MEMS*. John Wiley and Sons, New Jersey.

590 VTT (2018). "VTT and Carbodeon speed up 3D printing with nanodiamonds (ac-
591 cessed: 12.07.2020), <[https://www.vttresearch.com/en/news-and-ideas/vtt-and-carbodeon-](https://www.vttresearch.com/en/news-and-ideas/vtt-and-carbodeon-speed-3d-printing-nanodiamonds)
592 [speed-3d-printing-nanodiamonds](https://www.vttresearch.com/en/news-and-ideas/vtt-and-carbodeon-speed-3d-printing-nanodiamonds)>.

593 Zanjanijam, A., Major, I., Lyons, J., Lafont, U., and Devine, D. (2020). "Fused filament fabrication
594 of PEEK: A review of process-structure-property relationships." *Polymers*, 12(8), 1665.