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Dimensional accuracy and impact resistance of 3D printed clay reinforced with scrap polymer powder

Abstract

Purpose The purpose of this paper is to give an insight into relevant aspects of 3D printing of clay paste enhanced with scrap polymer powder which have not been investigated by previous studies. Specifically, the geometrical features of the deposited lines, dimensional accuracy of benchmarks and mechanical properties of printed parts are investigated.

Design/methodology/approach

Firstly, the 3D printer is used to deposit lines of the paste under various combinations of material composition and process parameters. 3D scanning is used to measure their dimensional and geometrical errors. The results are elaborated through statistics to highlight the role of material and processing conditions. Then, four benchmark parts are printed using materials with different percentages of polymer powder. The parts are scanned after each step of the post-processing to quantify the effects of printing, drying and melting on dimensional accuracy. Finally, drop weight tests are carried out to investigate the impact resistance of specimens with different powder contents.

Findings

It is found that the quality of deposition varies with the printing speed, nozzle acceleration and material composition. Also, significant differences are observed at the ends of the lines. Materials with 10 wt% and 40 wt% of powder exhibit relevant shape variations due to the separation of phases.

Accuracy analyses show significant deformations of parts at the green state due to material weight. This effect is more pronounced for higher powder contents. On the other hand, the polymer reduces shrinkage during drying.

Further, the impact test results showed that the polymer caused a large increase in impact resistance as compared to pure clay. Nonetheless, a decrease is observed for 40 wt% due to the higher amount of porosities.

Research implications

The results of this study advance the knowledge on the 3D printing of clay paste reinforced with a scrap polymer powder. This offers a new opportunity to reuse leftover powders from powder bed fusion processes. The findings presented here are expected to foster the adoption of this technique reducing the amount of waste powder disposed of by additive manufacturing companies.

Originality/value

This study offers some important insights into the relations between process conditions and the geometry of the deposited lines. This is of practical relevance to toolpath planning.

The dimensional analyses allow for understanding the role of each post-processing step on the dimensional error. Also, the comparison with previous findings highlights the role of part dimensions.

The present research explores, for the first time, the impact resistance of parts produced by this technology. The observed enhancement of this property with respect to pure clay may open new opportunities for the application of this manufacturing process.

Keywords: Material Extrusion, Clay, Recycling, Additive Manufacturing, Polyamide

List of acronyms

3DP	Three-Dimensional Printing	3
AM	Additive Manufacturing	3
ANOVA	Analysis Of Variance	8
DOE	Design Of Experiment	7
DF	Degrees of Freedom	13
FFF	Fused Filament Fabrication	4

GLM	General Linear Model	8
HSS	High-Speed Sintering	3
KS	Kolmogorov-Smirnov	13
LPBF	Laser Powder Bed Fusion	3
mCF	milled Carbon Fibres	4
MEAM	Material Extrusion Additive Manufacturing	5
Mg	Magnesium	4
MJF	Multi Jet Fusion	3
MS	Means Square	13
PA12	Polyamide 12	4
PBF	Powder Bed Fusion	3
PE	Polyethylene	9
SIS	Selective Inhibition Sintering	3
SLS	Selective Laser Sintering	3
SS	Sum of Squares	13
SMEs	Small and Medium Enterprises	5
TPU	Thermoplastic Polyurethane	4
WC	Tungsten Carbide	4

1. Introduction

The Additive Manufacturing (AM) of polymeric powders dates back to 1980, when Carl R. Deckard patented the Laser Powder Bed Fusion (LPBF) process, originally termed Selective Laser Sintering (SLS) [1]. LPBF is still one of the most widespread Three-Dimensional Printing (3DP) technologies, with numerous applications in industry and research [2-4]. In recent years, several Powder Bed Fusion (PBF) technologies to transform polymer materials have been introduced besides LPBF [5], such as High-Speed Sintering (HSS) [6, 7], Selective Inhibition Sintering (SIS) [8, 9] and Multi Jet Fusion (MJF) [10-12]. These processes allow for a dramatic reduction of production time if compared with LPBF and foster the adoption of polymer PBF on a large scale. Accordingly, a

12 constantly increasing trend in the industrial applications of these technologies
13 has been observed in recent years [13, 14].

14 The rapid spread of AM technologies requires a critical analysis of their envi-
15 ronmental impacts [15-17]. Specifically, PBF processes suffer from an intrinsic
16 limitation related to feedstock material. In fact, in all the PBF processes men-
17 tioned above, the non-transformed powder undergoes thermal ageing [18-21].
18 Ageing determines a modification of powder properties which in turn may lead
19 to a drop in mechanical performances and to non-correct sintering of the part
20 [22, 23]. As a consequence, the non-transformed material has to be mixed with
21 virgin polymer for reusing [24, 25]. This means that a considerable amount
22 of powder must be disposed of at the end of each print. The management of
23 this waste is thus a key topic as far as the sustainability of polymer PBF is
24 concerned.

25 The primary method that has been used in literature is reusing the scrap
26 powder to produce filament for Fused Filament Fabrication (FFF). This strat-
27 egy has been first adopted by Mägi et al., who characterised the mechanical
28 properties of filament produced by leftover Polyamide 12 (PA12) from LPBF.
29 In order to tune the mechanical properties, the authors mixed the scrap powder
30 with Thermoplastic Polyurethane (TPU) pellet and aramid fibres [26]. Kumar
31 and Aleksander presented a detailed investigation into the properties of filament
32 produced by reinforcing PA12 powder with various percentages of Tungsten Car-
33 bide (WC) [27]. Similar studies were proposed by Wang et al. [28] and Uddin
34 et al. [29], who used milled Carbon Fibres (mCF) and Magnesium (Mg) par-
35 ticles, respectively, to reinforce PA12. A comparison between PA12 filament
36 obtained from the virgin pellet and scrap powder was presented by Feng et al.
37 [30], who highlighted the influence of the printing speed on mechanical proper-
38 ties. These studies demonstrated the opportunity to use FFF to recycle scrap
39 powder from PBF. Nevertheless, this method suffers from serious drawbacks
40 due to the need for producing the feedstock filament. Firstly, the powder must
41 undergo full remelting, which might modify its physical and thermal properties
42 [31, 32]. Moreover, strict control of the filament diameter is necessary since the

43 FFF process is extremely sensitive to filament diameter [33, 34]. This problem
44 is exacerbated by the limited performances of desktop filament extruders, which
45 limit the opportunities for distributed recycling [35].

46 A different method for recycling scrap PA12 powders through clay Material
47 Extrusion Additive Manufacturing (MEAM) has been recently proposed [36].
48 The AM of clay is an increasingly important area of research due to the ap-
49 pealing properties of these materials [37, 38]. Accordingly, numerous potential
50 applications of 3D-printed clay parts have been shown in the literature [39, 40].
51 MEAM is arguably the most widespread technique used for clay AM and can be
52 performed using various technological solutions [41]. Over the last few years, an
53 increasing interest in low-cost desktop MEAM machines can be observed, eas-
54 ing the adoption of these technologies by private users and Small and Medium
55 Enterprises (SMEs) [42, 43].

56 To date, the study presented in [36] has been the only application of clay
57 MEAM for the recycling of scrap polymer from PBF. That paper demonstrated
58 the feasibility of the process and the upper limit of the polymer concentration in
59 the clay paste. Also, it was shown that the addition of scrap powder mitigates
60 shrinkage in the drying phase, which is the most influential on part accuracy
61 [36]. Nevertheless, a number of questions regarding this process remain to be
62 addressed. Firstly, [36] performed test extrusions by measuring the mass of
63 paste extruded in a given time span. This method does not allow for under-
64 standing the actual dimensional stability of the deposited line. Also, the authors
65 highlighted the need for further studies on geometrical accuracy when scaling
66 up the benchmarks [36]. Finally, no information on the mechanical properties
67 of the manufactured parts was given. The latter point is especially important
68 to determine the actual fields of applicability of this technology. Specifically,
69 the impact resistance of clay-based material is often a critical aspect to be con-
70 sidered [44]. Several studies investigated the impact resistance of polymer-clay
71 nanocomposites [45, 46]. These studies showed that the addition of clay disper-
72 sions to a polymer matrix leads to little or no loss in impact toughness [47, 48].
73 Nonetheless, the final behaviour strongly depends on the specific polymer and

74 clay used in the mixture [49, 50]. To date, no study investigated the impact
75 behaviour of clay reinforced by the addition of polyamide.

76 The aim of the present study is to fill the gaps mentioned above through
77 an experimental investigation into the MEAM of clay paste enhanced by scrap
78 powder. To this end, the accuracy of the deposited lines is investigated by
79 means of 3D scanning. Then, the impact resistance of parts with different
80 powder percentages is measured through drop weight impact tests.

81 2. Materials and methods

82 2.1. Equipment

83 The printing processes were carried out using the equipment presented in
84 [36]. The frame of a Replicator 2X FFF machine was used. The original moth-
85 erboard of the printer was replaced with a RAMPS 1.4 - Arduino Mega 2560.
86 This allows for processing custom G-Code using Marlyn 1.9 firmware, which is
87 necessary to adapt the printer to clay printing [36]. Clay extrusion was carried
88 out through a two-step solution. Specifically, namely a Stoneflower ceramic 3D
89 printing kit 2.1 was used. In the first stage, a mechanic piston feeds the clay
90 paste through a hose to the second step. Here, an Archimedes' screw extrudes
91 the clay paste through the deposition nozzle [41]. The secondary extrusion
92 system was mounted on the X-carriage of the machine in place of the original
93 filament extruder. The custom 3D printed parts made available in [36] were
94 used to adapt the kit to the original printer frame. Figure 1 shows a picture of
95 the machine.

96 2.2. Material

97 The extruded paste was prepared by mixing clay with scrap PA12 powder.
98 The latter was collected from the leftover powder of an HP MJF 4200 machine
99 operating in *balanced* mode [51]. As discussed in [36], using the equipment
100 detailed above, the mass percentage of PA12 cannot exceed 40% to prevent
101 clogging of the extruder. Accordingly, tests with 10%, 20%, 30% and 40% of
102 PA12 were carried out. 30% of water was included in all the mixtures.

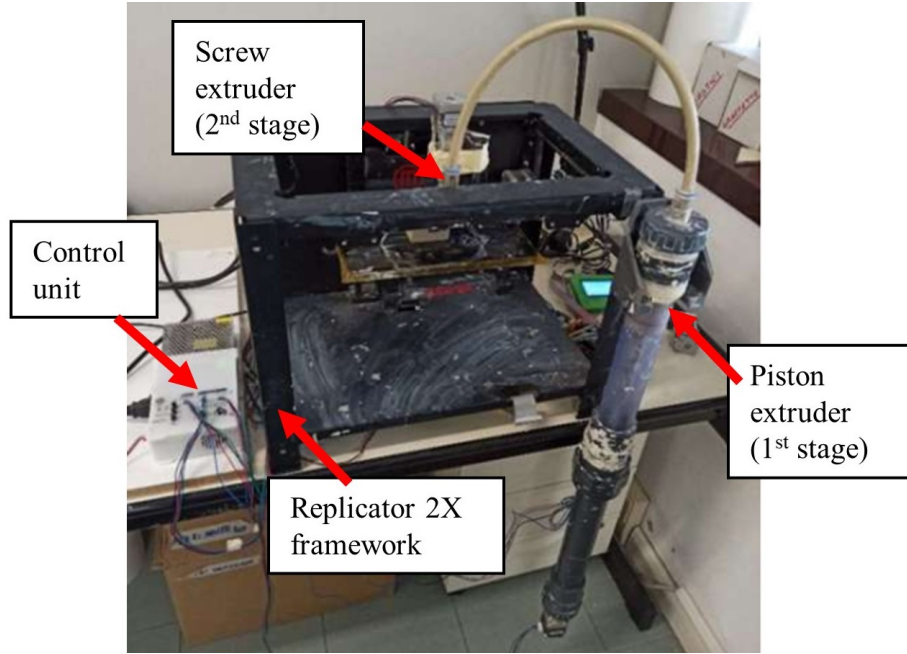


Figure 1: Equipment used for clay paste extrusion. Figure by authors.

2.3. Deposition tests

To investigate the quality of the deposition process, single lines of the clay paste were extruded using different parameters and then digitalised through a 3D scanner. Lines measured 180 mm and were oriented along the X-axis of the machine. A nozzle of 1 mm in diameter was used for the deposition. The experiment was designed by varying the nozzle acceleration (a_n), deposition speed (v_n) and PA12 mass percentage according to the values reported in Table 1. The deposition parameters that were not varied in the experiment are summarised in Table 2. A full-factorial Design Of Experiment (DOE) was used [52]. Three lines distanced by 13 mm were printed for each testing condition. Two repetitions of the experiment were carried out, resulting in 144 measured lines.

Lines were printed on a glass plate. After printing, the plate with the deposited lines was scanned by means of a Faro CAM2 Edge ScanArm HD [36, 53].

Table 1: Parameters varied in the experiment. Table by authors.

Parameter	Levels	Values	Unit of measurement
Nozzle acceleration (a_n)	2	(150, 800)	$\frac{mm}{s^2}$
Nozzle speed (v_n)	3	(30,60,90)	$\frac{mm}{s}$
PA12 percentage	4	(10,20,30,40)	wt%

Table 2: Deposition parameters of single lines. Table by authors.

Parameter	Value	Unit of measurement
Layer Height	0.6	mm
Extrusion Width	1.2	mm
Extrusion Multiplier	0.56	-
Retraction	0.01	mm
Extra Restart Distance	0.1	mm
Vertical Lift	1	mm
Retraction Speed	50	mm/s
Coasting Distance	0.2	mm
Wipe Distance	1	mm

117 The scanner was controlled through the software Geomagic Studio by 3D Sys-
 118 tem. The acquired point cloud was cleaned to isolate the deposited lines. The
 119 *wrap* function of Geomagic was then used to create a polygonal mesh from the
 120 point cloud. To quantify the accuracy of the extrusion, the scan of each line
 121 was divided into 5 segments with a length of 36 mm. Each segment was fitted
 122 to a cylinder through the *best-fit* function of Geomagic, as shown in Figure **2**.
 123 This function returns the average diameter and the standard deviation of points.
 124 These values were then used for statistical analyses. The influence of the pro-
 125 cess parameters was investigated by means of Analysis Of Variance (**ANOVA**).
 126 Specifically, the General Linear Model (**GLM**) approach was applied using the
 127 statistical software Minitab **52**, **54**.

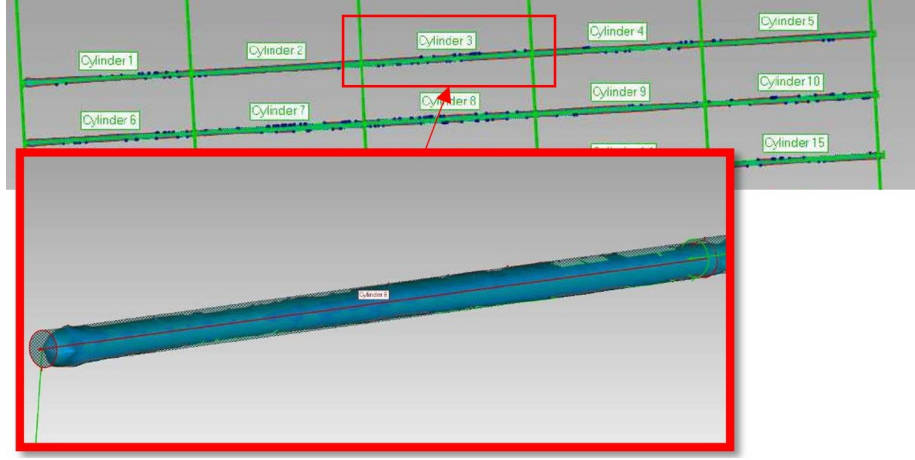


Figure 2: Fitting of cylinders to segments of the scanned lines. Figure by authors.

2.4. Accuracy tests

The accuracy tests were performed on the same geometries proposed by [36], namely a cube, a cylinder and a hollow cylinder. The parts have been scaled up to investigate the accuracy of larger dimensions. Also, a hollow cube was added to the experiment to observe the behaviour of planar thin walls. The specimens are shown in Figure 3, which highlights the nomenclature of dimensions along the X, Y and Z direction. The numerical values of these dimensions are made explicit in the figure caption.

The parts were printed using four mixtures with, respectively, 10%, 20%, 30% and 40% of PA12 powder. Three replicas of each specimen were printed for each material composition, resulting in 48 total specimens. The parameters used for printing are summarised in Table 3.

The build platform was covered with a Polyethylene (PE) film to ease the removal at the end of the printing process. Immediately after printing, the specimens were scanned by means of the FARO CAM2 Edge ScanArm HD 3D scanner mentioned in section 2.3.

After this acquisition, the parts were dried according to the method described by [36]. This method consisted of two phases, namely the conditioning

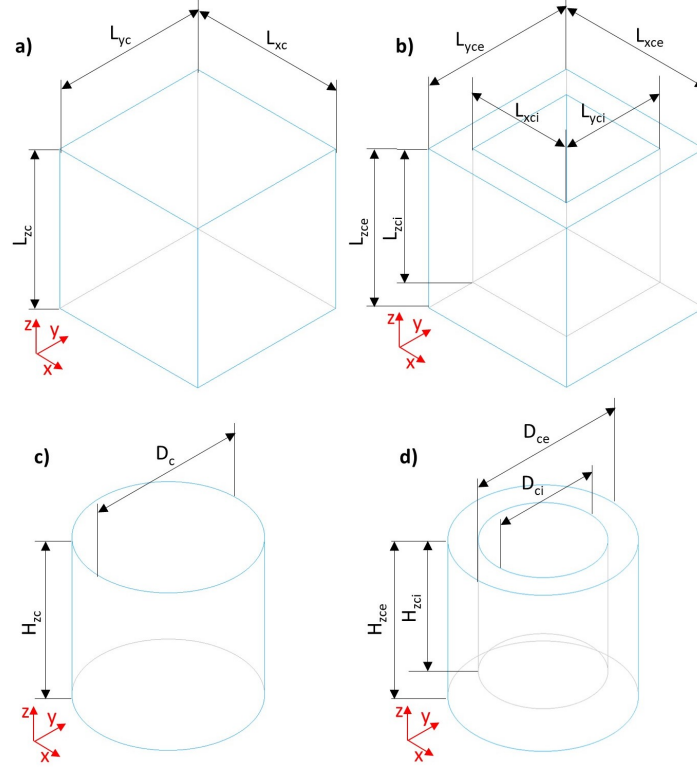


Figure 3: Specimens used for accuracy tests: a) Full cube ($L_{xc} = L_{ye} = L_{zc} = 50\text{ mm}$), b) hollow cube ($L_{xce} = L_{yce} = L_{zce} = 50\text{ mm}$, $L_{xci} = L_{yzi} = 34\text{ mm}$, $L_{zci} = 42\text{ mm}$), c) full cylinder ($D_c = H_{zc} = 50\text{ mm}$), d) hollow cylinder ($D_{ce} = H_{zce} = 50\text{ mm}$, $D_{ci} = 34\text{ mm}$, $H_{zci} = 42\text{ mm}$). Figure by authors.

and the drying phases. In the first phase, the part is maintained in an environment with humidity between 85% and 98%. During this phase, microwaves are used to warm the internal part of the component between 27°C and 35°C so as to promote the migration of water towards external surfaces. In the second phase, the temperature of the chamber is raised to 70°C for 120 minutes while maintaining a high humidity of the chamber. Finally, additional 60 minutes at 85°C are used to complete drying [36]. After drying, a second scanning of the parts was performed.

Finally, the parts were put in an oven at 200°C to melt the polymer powder [36]. The third scan of parts was taken at the end of this treatment.

Table 3: Deposition parameters of impact specimens. Table by authors.

Parameter	Value	Unit of measurement
Layer Height	0.6	<i>mm</i>
Extrusion Width	2	<i>mm</i>
Deposition Speed	45	$\frac{mm}{s}$
Extrusion Multiplier	0.57	-
Infill density	100	%
Infill angle	± 45	$^{\circ}$
Infill/contour overlap	35	%

The scans were analysed by using the software Geomagic Studio by 3D System to inspect the geometrical accuracy. Specifically, the dimensions shown in Figure 3 were measured at each stage of the post-processing cycle. The measurements were used to calculate the percentage deviation of each dimension with respect to the previous stage ($E_r\%$) and to the nominal value ($E_a\%$) [36].

2.5. Impact tests

Drop weight impact tests were performed according to the ASTM D7136 [55]. The specimen used for testing is a parallelepiped measuring $110\text{ mm} \times 160\text{ mm} \times 11\text{ mm}$. These dimensions are higher than those prescribed in the standard in order to account for dimensional shrinkage occurring during drying and heat treatment [36]. A nozzle of 2 mm in diameter was used for printing specimens. The hatching was performed through parallel lines oriented at $\pm 45^{\circ}$. The infill parameters used for printing are reported in Table 4. Other process parameters are as in Table 2.

Specimens with 0 wt%, 10 wt%, 20 wt%, 30 wt% and 40 wt% of scrap PA12 powder were tested. For each composition, 5 replications of the test were carried out.

After printing, specimens were dried and heat treated as described in Section 2.3 and 3.6.

Table 4: Deposition parameters of impact specimens. Table by authors.

Parameter	Value	Unit of measurement
Layer Height	1.2	<i>mm</i>
Extrusion Width	2	<i>mm</i>
Deposition Speed	30	$\frac{mm}{s}$
Extrusion Multiplier	0.57	-
Infill density	100	%
Infill/contour overlap	35	%

Figure 4 shows the equipment used for drop weight impact tests. The machine is equipped with a laser cell (shown in Figure 4b) to measure the velocity of the impactor before and after the impact. The signal was acquired at 100 kHz. Figure 4c) shows the impactor used for testing, which was a semi-sphere with a diameter of 1 inch (i.e. 25.4 mm). The impactor was made of stainless steel with a hardness of 61 HRC. The mass of the impactor and sledge was equal to 1.530 kg. A piezoelectric load cell PCB 208C05 was mounted on the impactor to measure the force during the impact. NI-DAQmx by National Instruments® and Data Acquisition Toolbox™ Support Package by MATLAB® were used for acquiring the signal. The acquisition frequency was equal to 100 kHz.

After preliminary tests, the drop height of the impactor was set to 750 mm to ensure the breaking of all the specimens. Impact force and adsorbed energy were calculated according to [55].

3. Results and discussion

3.1. Deposition tests

As mentioned in section 2.3, the average value and standard deviation of the best-fit cylinder of each extrusion segment were used for analyses. The average value of the cylinder diameter provides information about the amount of deposited clay paste, while the standard deviation values quantify the geometrical consistency of the extruded tracks.

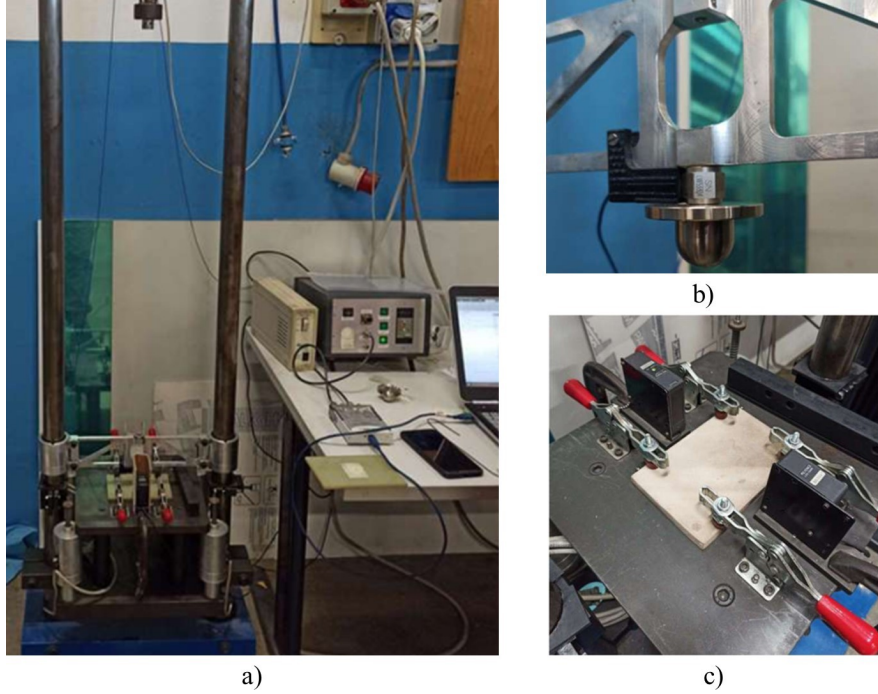


Figure 4: a) Equipment used for drop weight impact tests, b) detail view of the impactor, c) detail view of the specimen clamping and optical cells. Figure by authors.

3.1.1. Average diameter

Table 5 reports the Degrees of Freedom (DF), adjusted Sum of Squares (SS), adjusted Means Square (MS), F-value and p-value of each parameter obtained by means of ANOVA.

The adjusted R^2 of the GLM was equal to 73.02%. Figure 5 shows the normal probability plot for standardised residuals. A Kolmogorov-Smirnov (KS) test for normality was performed on the standardised residuals [56, 57]. The KS test returned a p-value equal to 0.071 and a KS coefficient equal to 0.045. This allows rejecting the hypothesis of non-normal distribution, thus validating the results of ANOVA [52].

The results in Table 5 show that the p-value of v_n is higher than 0.05, i.e. the deposition speed has no effect on the average diameter of the deposited line. This result confirms that the extrusion process is stable in the investigated

Table 5: ANOVA on the average diameter of the best-fitting cylinder

Parameter	DF	Adj SS	Adj. MS	F-value	P-value
v_n	2	2.37×10^{-2}	1.18×10^{-2}	6.10×10^{-1}	5.46×10^{-1}
wt% PA12	3	1.35×10	4.51	2.31×10^2	0.00
Position	4	2.93×10^{-1}	7.32×10^{-2}	3.74×10	5.00×10^{-3}
a_n	1	5.35	5.35×10	2.74×10^2	0.00

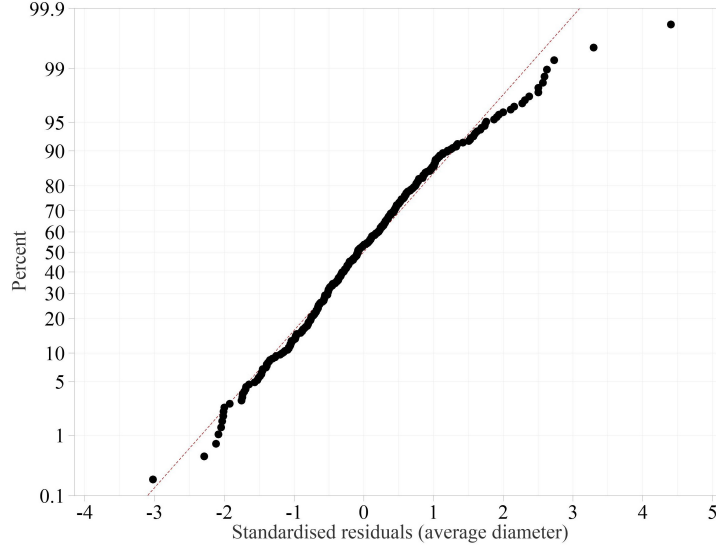


Figure 5: Normal probability plot for standardised residuals of ANOVA on the average diameter. Figure by authors.

range of velocity due to good coordination between the stepper motors of the two extrusion phases. On the other hand, the process is highly sensitive to the weight percentage of PA12, whose F-value is equal to 231. Particularly, the main effects plot in Figure 6 shows that the average diameter in the case of 10 wt% paste is significantly higher than the one observed in all the other cases.

This result is partially explained by the findings of [36], who showed that the mass flow decreases when the PA12 percentage increases. Nevertheless, other factors need to be considered to justify the observed difference. A possible explanation is that the higher percentage of clay intensifies the swelling phenomenon

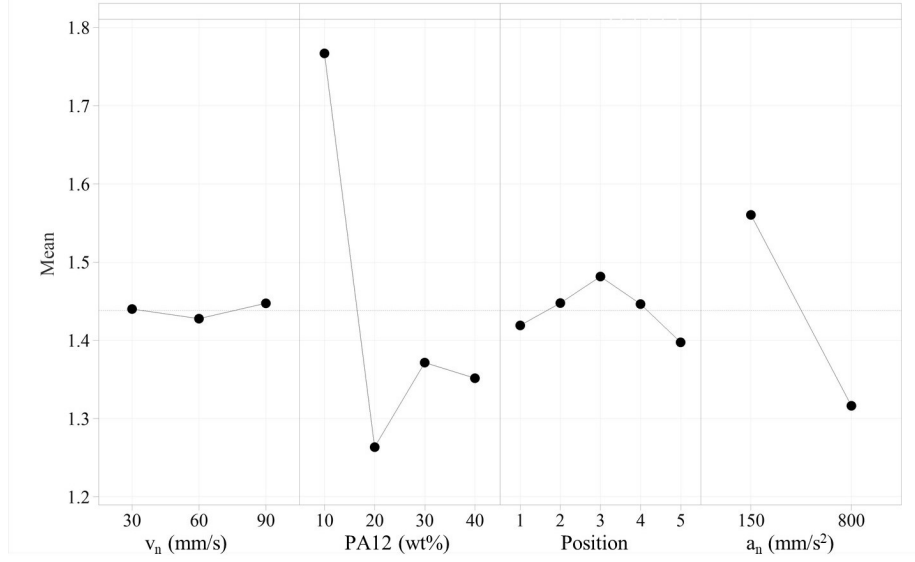


Figure 6: Main effects plot for average diameter. Figure by authors.

217 due to water absorption [58, 59]. Also, the PA12 increases the viscosity of the
 218 paste. Therefore, the 10 wt% material is more prone to collapse under the effect
 219 of its own weight.

220 Results in Table 5 also show a significant role of a_n on the results. In partic-
 221 ular, the measured diameter decreases while increasing the nozzle acceleration.
 222 Finally, the diameter depends on the position within the extruded line. Specifi-
 223 cally, the diameter is maximum in the central region and minimum at the ends
 224 of the deposited lines.

225 3.1.2. Standard deviation

226 The results of the ANOVA performed on the standard deviation values are
 227 reported in Table 6. The adjusted R^2 of the GLM was equal to 66.93%. The
 228 normal probability plot for standardised residuals is shown in Figure 7. The
 229 p-value and KS coefficient calculated by means of the KS normality test were
 230 equal to 0.087 and 0.044, respectively. It is thus possible to validate also in this
 231 case the hypothesis of normally distributed residuals.

Table 6: ANOVA on the standard deviation of points. Table by authors.

Parameter	DF	Adj SS	Adj. MS	F-value	P-value
v_n	2	1.28×10^{-3}	6.40×10^{-4}	9.20	0.00
wt% PA12	3	1.34×10^{-2}	4.47×10^{-3}	6.42×10	0.00
Position	4.00	3.65×10^{-2}	9.12×10^{-3}	1.31×10^2	0.00
a_n	1	8.70×10^{-5}	8.70×10^{-5}	1.25	2.64×10^{-1}

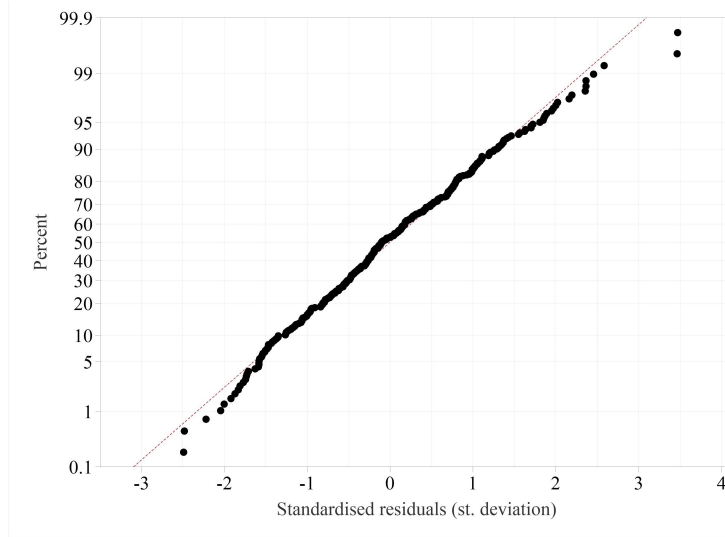


Figure 7: Normal probability plot for standardised residuals of ANOVA on standard deviations. Figure by authors.

232 The results in Table 6 show that the standard deviation, and thus the geo-
233 metrical accuracy, is mainly affected by the PA12 wt% and the position within
234 the deposited line. The influence of these parameters can be seen in Figure 8,
235 which shows the plot of the main effects on standard deviation.

236 By observing Figure 8 it can be noticed that the compositions with 10 wt%
237 and 40 wt% of PA12 exhibit the maximum standard deviation. This effect is
238 arguably attributable to the unstable behaviour of these compositions during
239 extrusion. Specifically, the high water content in the 10 wt% material (already
240 discussed in section 3.1.1) may determine the separation of phases. In the case of

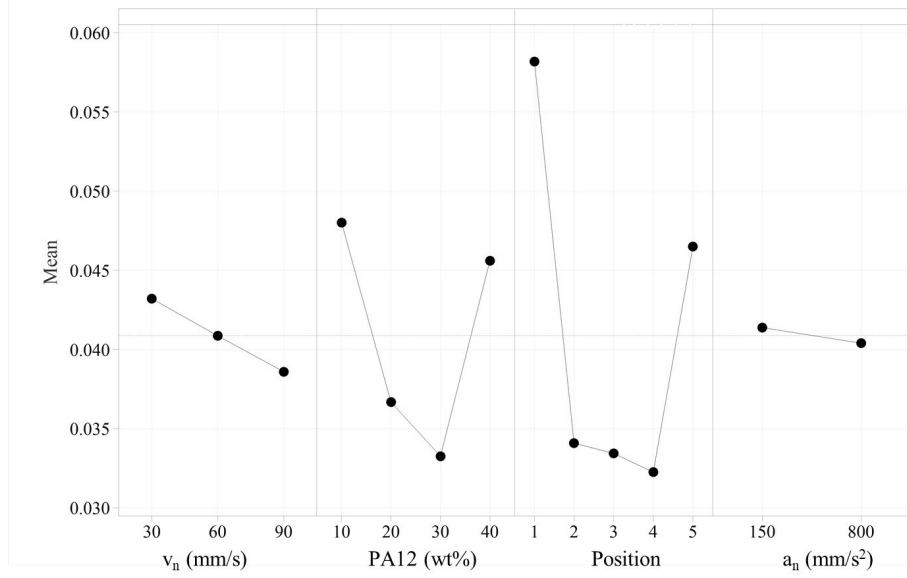


Figure 8: Main effects plot for standard deviation. Figure by authors.

the 40 wt% mixture, the variation is arguably attributable to the high content of the polymer, which might determine a non-homogeneous blend between powder and clay paste.

The shape error is maximum at the ends of the deposited lines, namely positions 1 and 5. This can be explained if considering the material accumulation within the second extruder and the changes in velocity occurring at the ends of the path.

3.2. Dimensional accuracy

The measurements of dimensional accuracy are reported in supplementary Tables 1-4. As shown in Figure 3, the bounding box of each specimen in the cartesian coordinate system is equal to $50mm \times 50mm \times 50mm$. Also, the internal dimensions L_{xci} and L_{yci} of the hollow cube are both equal to $34mm$. Since the dimensional accuracy of 3D printed parts may significantly depend on the direction, a preliminary analysis of measurements has been performed to understand which dimensions can be considered together and which must be

256 analysed independently. Specifically, two-sample t-tests [52] have been carried
 257 out to compare the dimensions of each specimen having the same nominal value.
 258 The results of these analyses are summarised in Table 7

Table 7: Results of T-tests on measured values of nominally equal dimensions. Table by authors.

Specimen	Null hypothesis	t-Student	p-value
Full cube	$L_{xc} = L_{yc}$	0.6703	0.5049
Full cube	$L_{xc} = L_{zc}$	9.5521	< 0.0001
Full cube	$L_{yc} = L_{zc}$	8.7769	< 0.0001
Hollow cube	$L_{xce} = L_{yce}$	0.5468	0.5862
Hollow cube	$L_{xc} = L_{zc}$	5.3497	< 0.0001
Hollow cube	$L_{yc} = L_{zc}$	4.648	< 0.0001
Hollow cube	$L_{xci} = L_{yci}$	1.4482	0.152
Hollow cube	$L_{xci} = L_{zci}$	110.1464	< 0.0001
Hollow cube	$L_{yci} = L_{zci}$	108.5768	< 0.0001
Full cylinder	$D_c = H_{zc}$	8.5995	< 0.0001
Hollow cylinder	$D_{ce} = H_{zce}$	6.1364	< 0.0001
Hollow cylinder	$D_{ci} = H_{zci}$	104.4002	0.5862

259 As can be seen in Table 7, the tests between dimensions along the Z direction
 260 and those along the X and Y directions return p-values less than 0.0001. This
 261 allows for rejecting the null hypothesis, i.e. the vertical dimensions (i.e. those
 262 along the Z-axis) are statistically different from others. The accuracy results in
 263 this direction are discussed in Section 3.2.1

264 On the other hand, p-values higher than 0.05 are found when comparing dimen-
 265 sions along the X and Y directions. This finding suggests that the dimensional
 266 accuracy does not depend on the orientation in the XY plane. For this reason,
 267 the dimensions along the X and Y directions will be analysed together in Section
 268 3.2.2

3.2.1. Accuracy along the Z-axis

By looking at the parts after the printing process (Figure 9), a severe slumping can be clearly observed on those with higher PA12 content. This result is consistent with findings by [36] and supports the idea that most of the dimensional error occurring during printing is due to the collapse of the part under its own weight [60]. This is more evident when increasing the percentage of PA12 since, being the water content constant, the amount of solid clay decreases. It is worth mentioning that this phenomenon is more evident in this study than it was in [36] due to the larger dimensions of the investigated parts. The slumping at the green state for high PA12 wt% was observed in all the investigated geometries, as can be seen in Figure 10, which shows the measured height of each specimen. This height corresponds to the dimensions L_{zc} , L_{zce} , H_{zc} and H_{zce} for the full cube, the hollow cube, the full cylinder and the hollow cylinder, respectively (see also Figure 3).

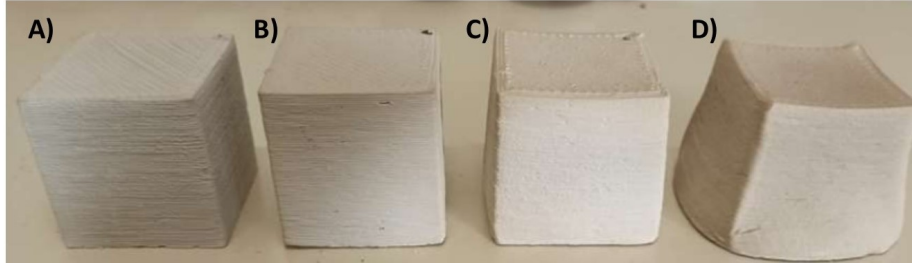


Figure 9: Picture of the specimens after printing. A) 10 wt% PA12, B) 20 wt% PA12, C) 30 wt% PA12, D) 40 wt% PA12. Figure by authors.

3.2.2. Accuracy in the XY plane

In order to quantify the distortion induced by each step of the post-processing cycle, the relative error with the previous operation is calculated as in Equation 1 [36]:

$$E_{r,\%} = \frac{L_{i-1} - L_i}{L_{i-1}} \times 100 \quad (1)$$

where L_i is the value of dimension L at the generic i -th step.

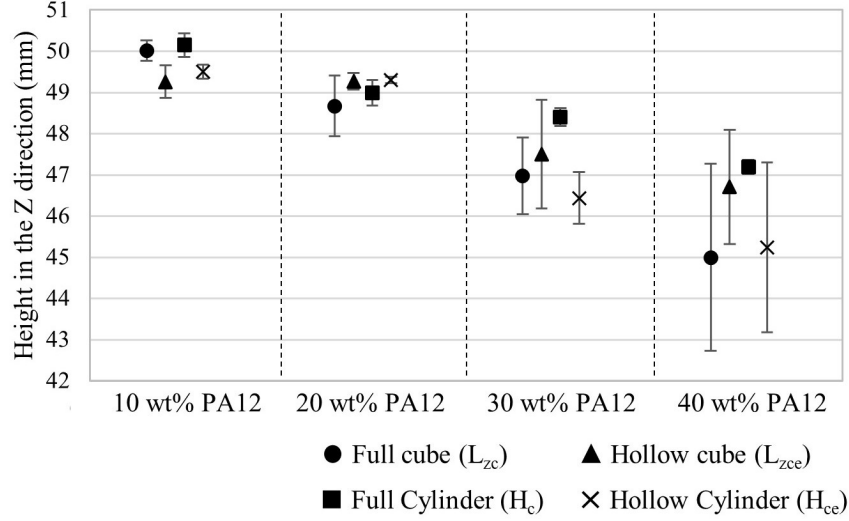


Figure 10: Height of the different specimens according to the content of **PA12**. Figure by authors.

Figure 11 shows the relative errors for dimensions in the XY plane. These dimensions are L_{xc} and L_{yc} for the full cube, L_{xce} and L_{yce} for the full cube, D_c for the full cylinder and D_{ce} for the hollow cylinder.

As can be observed in Figure 11, the dimensional error after deposition (wet) is higher for mixtures with high percentages of powder. This is coherent with the results found for Z dimensions. The collapse due to the lower self-supporting capability of the material is thus responsible also for a loss of accuracy in the XY plane.

An opposite trend is observed after the drying phase. Specifically, the specimens with more **PA12** content show less shrinkage in this phase. This is likely attributable to the lower water absorption of the polymer if compared to clay. The results also show that the effect of melting on dimensional error is marginal if compared to those of previous phases.

These findings are consistent with those of [36]. Nevertheless, a far more clear relation between the **PA12** content and the dimensional error is observed in this study. This is arguably due to the larger dimension of specimens, which

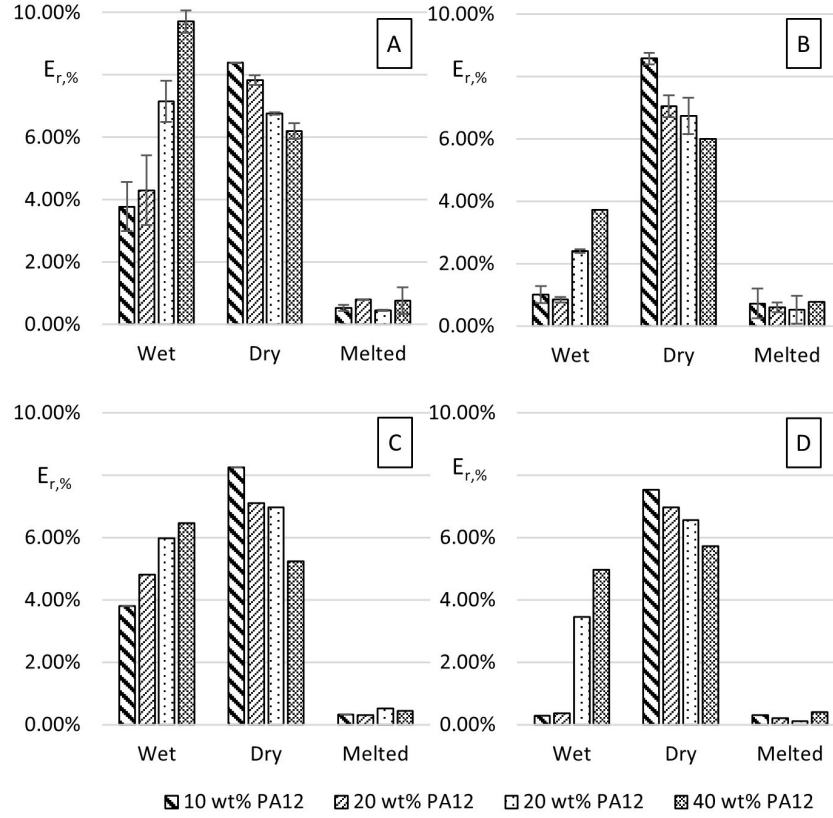


Figure 11: Relative error $E_{r,\%}$ observed in the XY plane for the four geometries: A) full cube (L_{xc} , L_{yc}), B) hollow cube (L_{xce} , L_{yce}), C) full cylinder (D_c), D) hollow cylinder (D_{ce}). Figure by authors.

allows for a better observation of the effects on dimensional accuracy.

One significant difference with previous findings is that the dimensional error observed at the green state is highly more relevant in the present study. This suggests that the dimensional error after printing is mainly attributable to the collapse of geometries under the effects of material weight. On the other hand, the per cent error occurring during drying is related to the material composition and does not show significant differences varying the dimensions of parts. This idea is also supported by the fact that the highest errors are observed in the case of full geometries, namely A and C, in which more weight acts on the parts.

3.3. Impact resistance

Table 8 summarises the actual weight and dimensions of the specimens used for impact tests.

Table 8: Actual weight and dimensions of the manufactured specimens. Table by authors.

PA12 content	Weight (g)	Length (mm)	Height (mm)	Depth (mm)
0%	272.6 ± 4.1	147.1 ± 0.7	99.5 ± 0.7	10.1 ± 0.2
10%	235.8 ± 9.4	148.9 ± 0.7	100.3 ± 0.4	10.0 ± 0.2
20%	209.8 ± 5.8	149.7 ± 0.4	100.2 ± 0.3	10.3 ± 0.1
30%	184.8 ± 9.5	150.1 ± 0.4	100.1 ± 0.2	10.3 ± 0.2
40%	155 ± 14.0	149.0 ± 0.8	100.3 ± 0.9	10.3 ± 0.2

Figure 12 shows the force (F) versus displacement (z) diagrams obtained for each material composition. The highest point of these graphs represents the maximum force, while the area under each line is equal to the absorbed energy. These values are also reported in Table 9.

Table 9: Maximum force and absorbed energy of specimens according to the PA12 content. Table by authors.

wt% PA12	Maximum force (kN)	Absorbed energy (J)
0%	0.344 ± 0.049	0.758 ± 0.131
10%	1.379 ± 0.147	2.896 ± 0.441
20%	1.953 ± 0.28	4.458 ± 0.286
30%	1.981 ± 0.204	4.746 ± 0.252
40%	1.558 ± 0.282	4.553 ± 0.992

By observing the results in Figure 12 and Table 9 it is possible to notice that the specimens made of pure clay show the lowest impact resistance. Specifically, the maximum force and the absorbed energy increase with the content of PA12 until the 30 wt% is reached. This finding can be explained by considering the higher elasticity of polyamide infiltrating between the clay grains. The resilience of these specimens determines also a more pronounced deformation

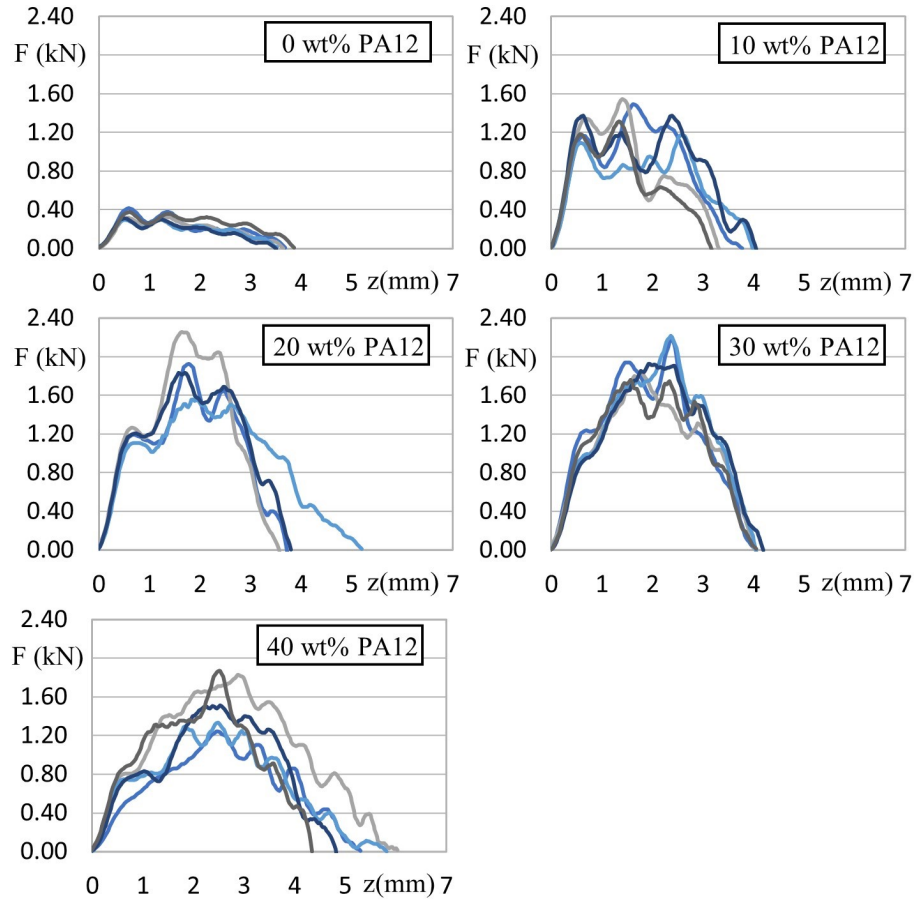


Figure 12: Variation of force in time during drop weight tests for various percentages of **PA12**.
Figure by authors.

326 before breaking, as demonstrated by the higher deformation before breaking
 327 shown in Figure **12**. Accordingly, a sharp difference can be observed in the
 328 fracture mode of the specimens, as shown by the picture in Figure **13**. Looking
 329 at Figure **13** a), it is possible to notice that the impactor passed through the
 330 specimens. On the other hand, the specimen in Figure **13** b) shows a brittle
 331 fracture with cracks connecting the impact region with the four clamps.

332 Interestingly, the maximum force and absorbed energy are observed to de-
 333 crease in the 40 wt% **PA12** paste. This may be explained by the different

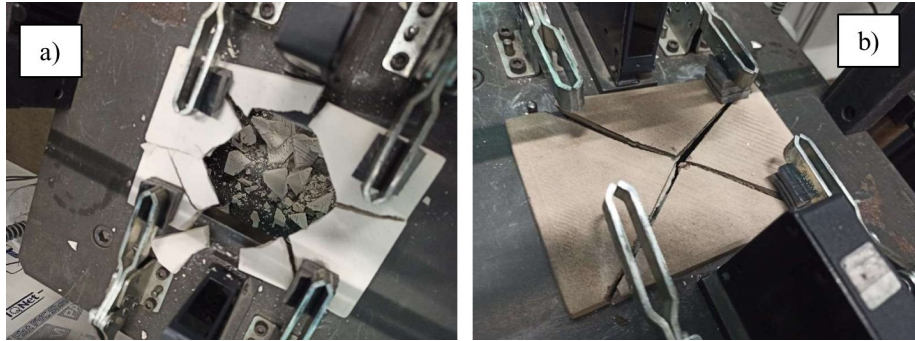


Figure 13: Picture of fractured specimens after the drop weight test. a) 0 wt% PA12 and b) 30 wt% PA12

densities of specimens at the end of the post-processing. In fact, [36] showed that the melting of the polymeric phase is responsible for porosities within the final parts. Arguably, when the powder content is too high, the detrimental effect of these voids surpasses the benefits provided by the PA12

Another possible explanation for the decrease in resistance is that the excessive amount of polymer determines a non-homogenous blend with the clay. This hypothesis is consistent with the results of deposition tests presented in section 3.1. As a consequence, the part may contain randomly distributed regions with lower impact resistance due to a higher content of clay. This idea is supported by the standard deviation of absorbed energy observed in Table 9 for the 40 wt% mixture, which is significantly higher than all the other compositions.

Most likely, a combination of these two effects contributes to the reduction of impact resistance. Future work is planned to study these phenomena more in-depth. The most important aspect of these findings is that an optimal composition maximising impact resistance exists for a PA12 content between 20 wt% and 40 wt%.

4. Conclusions

The research presented in this paper contributed to providing a more in-depth insight into the 3D printing of clay paste enhanced by PA12 powder.

353 Firstly, the factors influential to deposition have been investigated. Then, the
354 results of previous studies concerning part accuracy have been extended to larger
355 dimensions. Finally, for the first time, the mechanical properties of these mate-
356 rials have been observed by impact tests. The main findings can be summarised
357 as follows:

- 358 • The PA12 content, deposition speed and acceleration contribute to de-
359 termining the width and regularity of the deposited lines. These outputs
360 change significantly at the beginning and end of the deposition,
- 361 • Material with 10 wt% PA12 shows larger lines since it is more prone to
362 collapse under its own weight. Lines deposited with 10 wt% and 40 wt%
363 PA12 mixtures exhibit irregular shapes due to the separation of phase,
- 364 • For high dimensions, the effect of material weight at the green state sig-
365 nificantly affects the dimensional accuracy both along the Z-axis and in
366 the XY plane,
- 367 • The effect of weight on dimensional accuracy is more pronounced for spec-
368 imens with higher content of PA12,
- 369 • PA12 positively affects dimensional accuracy during post-processing since
370 it reduces the shrinkage provoked by drying,
- 371 • PA12 determines a tremendous increase in the impact resistance of man-
372 ufactured parts if compared to pure clay,
- 373 • A decrease in the maximum force and absorbed energy can be observed
374 on benchmarks with 40 wt% PA12

375 Overall, the results suggest that a percentage of PA12 around 20-30% should
376 be preferred for the 3D printing process. In fact, these percentages showed
377 the highest repeatability of deposited lines. As far as dimensional accuracy
378 is concerned, these compositions exhibited a good compromise between loss
379 of resistance at the green state and shrinkage reduction during drying. Finally,

the 30% mixture exhibited the maximum resistance to impacts. Future research should be carried out around these compositions investigating the physical and mechanical properties of the printed material. Also, further studies are needed to compare the environmental and economic impacts of this novel technique to those of current practices used to dispose of scrap powder.

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References

- [1] C. R. Deckard, Method and apparatus for producing parts by selective sintering (1989).
- [2] A. Awad, F. Fina, A. Goyanes, S. Gaisford, A. W. Basit, 3D printing: Principles and pharmaceutical applications of selective laser sintering, International Journal of Pharmaceutics 586 (July) (2020) 119594. doi:10.1016/j.ijpharm.2020.119594. URL <https://doi.org/10.1016/j.ijpharm.2020.119594>
- [3] N. A. Charoo, S. F. Barakh Ali, E. M. Mohamed, M. A. Kuttolamadam, T. Ozkan, M. A. Khan, Z. Rahman, Selective laser sintering 3D printing—an overview of the technology and pharmaceutical applications, Drug Development and Industrial Pharmacy 46 (6) (2020) 869–877. doi:10.1080/03639045.2020.1764027. URL <https://doi.org/10.1080/03639045.2020.1764027>

- [4] F. Lupone, E. Padovano, F. Casamento, C. Badini, Process phenomena and material properties in selective laser sintering of polymers: A review, *Materials* 15 (1) (2022). [doi:10.3390/ma15010183](https://doi.org/10.3390/ma15010183).
- [5] Y. Wang, Z. Xu, D. Wu, J. Bai, Current status and prospects of polymer powder 3D printing technologies, *Materials* 13 (10) (2020). [doi:10.3390/ma13102406](https://doi.org/10.3390/ma13102406).
- [6] N. Hopkinson, P. Erasenthiran, High speed sintering-early research into a new rapid manufacturing process, in: *Solid Freeform Fabrication Symposium, 2004*, pp. 312–320.
- [7] A. Ellis, *High Speed Sintering : The Next Generation of Manufacturing, Nanomaterials for 2D and 3D Printing* (2017) 107–118.
- [8] B. Asiabanpour, B. Khoshnevis, K. Palmer, Advancements in the selective inhibition sintering process development, *Virtual and Physical Prototyping* 1 (1) (2006) 43–52. [doi:10.1080/17452750500289910](https://doi.org/10.1080/17452750500289910).
- [9] P. Arunkumar, E. Balasubramanian, U. Chandrasekhar, Thermo Mechanical Modeling of Selective Inhibition Sintered Thermoplastic Parts, *Applied Mechanics and Materials* 813-814 (2015) 791–795. [doi:10.4028/www.scientific.net/amm.813-814.791](https://doi.org/10.4028/www.scientific.net/amm.813-814.791).
- [10] H. J. O'Connor, A. N. Dickson, D. P. Dowling, Evaluation of the mechanical performance of polymer parts fabricated using a production scale multi jet fusion printing process, *Additive Manufacturing* 22 (May) (2018) 381–387. [doi:10.1016/j.addma.2018.05.035](https://doi.org/10.1016/j.addma.2018.05.035).
- [11] Z. Xu, Y. Wang, D. Wu, K. P. Ananth, J. Bai, [The process and performance comparison of polyamide 12 manufactured by multi jet fusion and selective laser sintering](https://doi.org/10.1016/j.jmapro.2019.07.014), *Journal of Manufacturing Processes* 47 (October 2018) (2019) 419–426. [doi:10.1016/j.jmapro.2019.07.014](https://doi.org/10.1016/j.jmapro.2019.07.014).
URL <https://doi.org/10.1016/j.jmapro.2019.07.014>

- [12] S. Rosso, R. Meneghello, L. Biasetto, L. Grigolato, G. Concheri, G. Savio, In-depth comparison of polyamide 12 parts manufactured by Multi Jet Fusion and Selective Laser Sintering, Additive Manufacturing 36 (2020) 101713. doi:10.1016/j.addma.2020.101713. URL <https://doi.org/10.1016/j.addma.2020.101713>
- [13] Sculpteo, the State Printing of 3D, Tech. rep. (2021).
- [14] Grand View Research, 3D Printing Market Size, Share & Trends Analysis Report By Component, By Printer Type (Desktop, Industrial), By Technology, By Software, By Application, By Vertical, By Material, By Region, And Segment Forecasts, 2021 - 2028, Tech. rep. (2021). URL <https://www.grandviewresearch.com/industry-analysis/3d-printing-industry-analysis/methodology>
- [15] Z. Liu, Q. Jiang, F. Ning, H. Kim, W. Cong, C. Xu, H. C. Zhang, Investigation of energy requirements and environmental performance for additive manufacturing processes, Sustainability (Switzerland) 10 (10) (2018). doi:10.3390/su10103606.
- [16] F. L. Garcia, V. A. d. S. Moris, A. O. Nunes, D. A. L. Silva, Environmental performance of additive manufacturing process – an overview, Rapid Prototyping Journal 24 (7) (2018) 1166–1177. doi:10.1108/RPJ-05-2017-0108.
- [17] F. Fruggiero, A. Lambiase, R. Bonito, M. Fera, The load of sustainability for Additive Manufacturing processes, Procedia Manufacturing 41 (2019) 375–382. doi:10.1016/j.promfg.2019.09.022. URL <https://doi.org/10.1016/j.promfg.2019.09.022>
- [18] A. Martínez, A. Ibáñez, A. Sánchez, M. A. León, Comparison of aged polyamide powders for selective laser sintering, AIP Conference Proceedings 1431 (1) (2012) 5–13. doi:10.1063/1.4707544.
- [19] F. Sillani, R. G. Kleijnen, M. Vetterli, M. Schmid, K. Wegener, Selective laser sintering and multi jet fusion: Process-induced modification of the

-
- raw materials and analyses of parts performance, Additive Manufacturing 27 (November 2018) (2019) 32–41. doi:10.1016/j.addma.2019.02.004. URL <https://doi.org/10.1016/j.addma.2019.02.004>
- [20] K. Wudy, D. Drummer, Aging effects of polyamide 12 in selective laser sintering: Molecular weight distribution and thermal properties, Additive Manufacturing 25 (November 2018) (2019) 1–9. doi:10.1016/j.addma.2018.11.007. URL <https://doi.org/10.1016/j.addma.2018.11.007>
- [21] P. Chen, J. Su, H. Wang, L. Yang, M. Li, Z. Li, J. Liu, S. Wen, Y. Zhou, C. Yan, Y. Shi, Aging mechanism of polyetheretherketone powder during layer-wise infrared radiation of high-temperature laser powder bed fusion, Materials and Design 213 (2022) 110348. doi:10.1016/j.matdes.2021.110348. URL <https://doi.org/10.1016/j.matdes.2021.110348>
- [22] K. Dotchev, W. Yusoff, Recycling of polyamide 12 based powders in the laser sintering process, Rapid Prototyping Journal 15 (3) (2009) 192–203. doi:10.1108/13552540910960299.
- [23] J. Riedelbauch, D. Rietzel, G. Witt, Analysis of material aging and the influence on the mechanical properties of polyamide 12 in the Multi Jet Fusion process, Additive Manufacturing 27 (October 2018) (2019) 259–266. doi:10.1016/j.addma.2019.03.002. URL <https://doi.org/10.1016/j.addma.2019.03.002>
- [24] D. T. Pham, K. D. Dotchev, W. A. Y. Yusoff, Deterioration of polyamide powder properties in the laser sintering process, Proceedings of the Institution of Mechanical Engineers, Part C: Journal of Mechanical Engineering Science 222 (11) (2008) 2163–2176. doi:10.1243/09544062JMES839.
- [25] S. Josupeit, J. Lohn, E. Hermann, M. Gessler, S. Tenbrink, H. J. Schmid, Material properties of laser sintered polyamide 12 as function of build cycles using low refresh rates, Proceedings - 26th Annual International Solid

- 491 Freeform Fabrication Symposium - An Additive Manufacturing Conference,
492 SFF 2015 (2020) 540–548.
- 493 [26] P. Mägi, A. Krumme, M. Pohlak, Material recycling and improvement is-
494 sues in additive manufacturing, Proceedings of the International Conference
495 of DAAAM Baltic 2015-Janua (May) (2015) 63–68.
- 496 [27] S. Kumar, A. Czekanski, Development of filaments using selective laser
497 sintering waste powder, Journal of Cleaner Production 165 (2017) 1188–
498 1196. doi:10.1016/j.jclepro.2017.07.202.
499 URL <http://dx.doi.org/10.1016/j.jclepro.2017.07.202>
- 500 [28] L. Wang, A. Kiziltas, D. F. Mielewski, E. C. Lee, D. J. Gardner, Closed-
501 loop recycling of polyamide12 powder from selective laser sintering into
502 sustainable composites, Journal of Cleaner Production 195 (2018) 765–772.
503 doi:10.1016/j.jclepro.2018.05.235.
504 URL <https://doi.org/10.1016/j.jclepro.2018.05.235>
- 505 [29] M. Uddin, D. Williams, A. Blencowe, Recycling of selective laser sintering
506 waste Nylon powders into fused filament fabrication parts reinforced with
507 Mg particles, Polymers 13 (13) (2021). doi:10.3390/polym13132046.
- 508 [30] L. Feng, Y. Wang, Q. Wei, PA12 powder recycled from SLS for FDM,
509 Polymers 11 (4) (2019). doi:10.3390/polym11040727.
- 510 [31] J. Kawabata, G. Matsuba, K. Nishida, R. Inoue, T. Kanaya, Melt memory
511 effects on recrystallization of polyamide 6 revealed by depolarized light
512 scattering and small-angle X-ray scattering, Journal of Applied Polymer
513 Science 122 (3) (2011) 1913–1920.
- 514 [32] N. Vidakis, M. Petousis, L. Tzounis, A. Maniadi, E. Velidakis, N. Moun-
515 takis, J. D. Kechagias, Sustainable additive manufacturing: Mechanical re-
516 sponse of polyamide 12 over multiple recycling processes, Materials 14 (2)
517 (2021) 1–15. doi:10.3390/ma14020466.

- [33] C. Cardona, A. H. Curdes, A. J. Isaacs, Effects of Filament Diameter Tolerances in Fused Filament Fabrication, *IU Journal of Undergraduate Research* 2 (1) (2016) 44–47. [doi:10.14434/iujur.v2i1.20917](https://doi.org/10.14434/iujur.v2i1.20917).
- [34] E. Gkartzou, E. P. Koumoulos, C. A. Charitidis, Production and 3D printing processing of bio-based thermoplastic filament, *Manufacturing Review* 4 (2017). [doi:10.1051/mfreview/2016020](https://doi.org/10.1051/mfreview/2016020).
- [35] B. Peeters, N. Kiratli, J. Semeijn, A barrier analysis for distributed recycling of 3D printing waste: Taking the maker movement perspective, *Journal of Cleaner Production* 241 (2019) 118313. [doi:10.1016/j.jclepro.2019.118313](https://doi.org/10.1016/j.jclepro.2019.118313).
URL <https://doi.org/10.1016/j.jclepro.2019.118313>
- [36] M. Mele, M. Ricciarelli, G. Campana, 3D printing of clay paste enhanced by scrap polymer from powder bed processes, *Rapid Prototyping Journal* (2021).
- [37] Y. Xing, Y. Zhou, X. Yan, H. Zhao, W. Liu, J. Jiang, L. Lu, Shell thickening for extrusion-based ceramics printing, *Computers and Graphics (Pergamon)* 97 (2021) 160–169. [doi:10.1016/j.cag.2021.04.031](https://doi.org/10.1016/j.cag.2021.04.031).
URL <https://doi.org/10.1016/j.cag.2021.04.031>
- [38] A. Wolf, P. L. Rosendahl, U. Knaack, Additive manufacturing of clay and ceramic building components, *Automation in Construction* 133 (September 2021) (2022) 103956. [doi:10.1016/j.autcon.2021.103956](https://doi.org/10.1016/j.autcon.2021.103956).
URL <https://doi.org/10.1016/j.autcon.2021.103956>
- [39] P. Biswas, S. Mamatha, K. Varghese, R. Johnson, R. Vijay, R. Kumar, 3D printing of high surface area ceramic honeycombs substrates and comparative evaluation for treatment of sewage in Phytoid application, *Journal of Water Process Engineering* 37 (June) (2020) 101503. [doi:10.1016/j.jwpe.2020.101503](https://doi.org/10.1016/j.jwpe.2020.101503).
URL <https://doi.org/10.1016/j.jwpe.2020.101503>

- [40] V. Sangiorgio, F. Parisi, F. Fieni, N. Parisi, The New Boundaries of 3D-Printed Clay Bricks Design: Printability of Complex Internal Geometries, Sustainability (Switzerland) 14 (2) (2022). [doi:10.3390/su14020598](https://doi.org/10.3390/su14020598).
- [41] A. Ruscitti, C. Tapia, N. M. Rendtorff, A review on additive manufacturing of ceramic materials based on extrusion processes of clay pastes, Ceramica 66 (380) (2020) 354–366. [doi:10.1590/0366-69132020663802918](https://doi.org/10.1590/0366-69132020663802918).
- [42] F. Zhong, W. Liu, Y. Zhou, X. Yan, Y. Wan, L. Lu, Ceramic 3D printed sweeping surfaces, Computers and Graphics (Pergamon) 90 (2020) 108–115. [doi:10.1016/j.cag.2020.05.007](https://doi.org/10.1016/j.cag.2020.05.007).
URL <https://doi.org/10.1016/j.cag.2020.05.007>
- [43] E. R. Ramírez, S. A. H. Moreno, E. T. Díaz, N. P. Burgos, G. G. Moreno-Contreras, Design of a Clay Extrusion System for Low Cost 3D Printing, ARPN Journal of Engineering and Applied Sciences 16 (12) (2021) 1235–1239.
- [44] M. Jemberu, F. Shemsu, M. Gopal, Investigation of different clay compositions and additives for energy- efficient and impact-resistant Injera baking pan, Materials Today: Proceedings (xxxx) (2023). [doi:10.1016/j.matpr.2023.02.035](https://doi.org/10.1016/j.matpr.2023.02.035).
URL <https://doi.org/10.1016/j.matpr.2023.02.035>
- [45] S. S. Ray, Recent trends and future outlooks in the field of clay-containing polymer nanocomposites, Macromolecular Chemistry and Physics 215 (12) (2014) 1162–1179. [doi:10.1002/macp.201400069](https://doi.org/10.1002/macp.201400069).
- [46] F. Ali, H. Ullah, Z. Ali, F. Rahim, F. Khan, Z. Ur Rehman, Polymer-clay Nanocomposites, Preparations and Current Applications: A Review, Current Nanomaterials 1 (2) (2016) 83–95. [doi:10.2174/2405461501666160625080118](https://doi.org/10.2174/2405461501666160625080118).
- [47] M. Tanniru, Q. Yuan, R. D. Misra, On significant retention of impact strength in clay-reinforced high-density polyethylene (HDPE) nanocom-

- posites, *Polymer* 47 (6) (2006) 2133–2146. [doi:10.1016/j.polymer.2006.01.063](https://doi.org/10.1016/j.polymer.2006.01.063).
- [48] K. Zdiri, A. Elamri, M. Hamdaoui, *Advances in Thermal and Mechanical Behaviors of PP/Clay Nanocomposites*, *Polymer - Plastics Technology and Engineering* 56 (8) (2017) 824–840. [doi:10.1080/03602559.2016.1233282](https://doi.org/10.1080/03602559.2016.1233282).
URL <http://dx.doi.org/10.1080/03602559.2016.1233282>
- [49] C. Deshmane, Q. Yuan, R. S. Perkins, R. D. Misra, On striking variation in impact toughness of polyethylene-clay and polypropylene-clay nanocomposite systems: The effect of clay-polymer interaction, *Materials Science and Engineering A* 458 (1-2) (2007) 150–157. [doi:10.1016/j.msea.2006.12.069](https://doi.org/10.1016/j.msea.2006.12.069).
- [50] B. Chen, Polymer-clay nanocomposites: An overview with emphasis on interaction mechanisms, *British Ceramic Transactions* 103 (6) (2004) 241–249. [doi:10.1179/096797804X4592](https://doi.org/10.1179/096797804X4592).
- [51] HP Development Company L.P., HP Multi Jet Fusion Handbook, Tech. rep. (2019).
- [52] D. C. Montgomery, *Design and Analysis of Experiments* Eighth Edition, 2013. [doi:10.1198/tech.2006.s372](https://doi.org/10.1198/tech.2006.s372).
- [53] M. T. Lozano, F. B. Haro, A. Ruggiero, J. A. Mendez, Systems of digitalization and processing of anatomical pieces for their three-dimensional reconstruction, *ACM International Conference Proceeding Series Part F1322* (2017) 1–5. [doi:10.1145/3144826.3145402](https://doi.org/10.1145/3144826.3145402).
- [54] A. Alin, Minitab, *Wiley Interdisciplinary Reviews: Computational Statistics* 2 (6) (2010) 723–727.
- [55] ASTM, Standard Test Method for Measuring the Damage Resistance of a Fiber-reinforced Polymer Matrix Composite to a Drop-weight Impact Event: D7136/D7136M-15, ASTM International, 2015.

- [56] H. W. Lilliefors, On the Kolmogorov-Smirnov Test for Normality with Mean and Variance Unknown Author (s): Hubert W . Lilliefors Source : Journal of the American Statistical Association , Vol . 62 , No . 318 (Jun . , 1967), pp . 399- ON THE KOLMOGOROV-SMIRNOV TEST FOR NO, journal of American Statistics 62 (318) (1967) 399–402.
- [57] B. Yazici, S. Yolacan, A comparison of various tests of normality, Journal of Statistical Computation and Simulation 77 (2) (2007) 175–183. doi:10.1080/10629360600678310.
- [58] C. L. Amorim, R. T. Lopes, R. C. Barroso, J. C. Queiroz, D. B. Alves, C. A. Perez, H. R. Schelin, Effect of clay-water interactions on clay swelling by X-ray diffraction, Nuclear Instruments and Methods in Physics Research, Section A: Accelerators, Spectrometers, Detectors and Associated Equipment 580 (1 SPEC. ISS.) (2007) 768–770. doi:10.1016/j.nima.2007.05.103.
- [59] R. L. Anderson, I. Ratcliffe, H. C. Greenwell, P. A. Williams, S. Cliffe, P. V. Coveney, Clay swelling - A challenge in the oilfield, Earth-Science Reviews 98 (3-4) (2010) 201–216. doi:10.1016/j.earscirev.2009.11.003.
- [60] S. S. Chan, R. M. Pennings, L. Edwards, G. V. Franks, 3D printing of clay for decorative architectural applications: Effect of solids volume fraction on rheology and printability, Additive Manufacturing 35 (December 2019) (2020) 101335. doi:10.1016/j.addma.2020.101335.
URL <https://doi.org/10.1016/j.addma.2020.101335>