Physical properties of wood-based materials for liquid deposition modeling

Rosenthal, Michael; Rüggeberg, Markus; Gerber, Christian; Beyrich, Lukas; Faludi, Jeremy

DOI
10.1108/RPJ-09-2022-0322

Publication date
2022

Document Version
Final published version

Published in
Rapid Prototyping Journal

Physical properties of wood-based materials for liquid deposition modeling

Michael Rosenthal, Markus Rüggeberg, Christian Gerber and Lukas Beyrich
Chair of Forest Utilization, Technische Universität Dresden, Dresden, Germany, and
Jeremy Faludi
Faculty of Industrial Design Engineering, Technische Universiteit Delft, Delft, The Netherlands

Abstract

Purpose – The purpose of this study is to quantify the vertical shrinkage rates and the mechanical strength of three-dimensional (3D) printed parts for a variety of wood-based materials for liquid deposition modeling.

Design/methodology/approach – The overall hypothesis was that a well-chosen combination of binders, fibers and fillers could reduce shrinkage in the Z dimension and increase compressive and flexural strength (DIN 52185, 52186). To test this assumption, eight sub-hypotheses were formulated. Mixtures of the ingredients were chosen in different ratios to measure the performance of prints. For time efficiency, an iterative heuristic approach was used – not testing all variations of all variables in even increments, but cutting off lines of testing when mixtures were clearly performing poorly.

Findings – The results showed that some mixtures had high dimensional accuracy and strength, while others had neither, and others had one but not the other. Shrinkage of 3D printed objects was mainly caused by water release during drying. An increase of the wood as well as the cement, sand, salt and gypsum content led to reduced vertical shrinkage, which varied between 0 and 23%. Compressive and flexural strength showed mixed trends. An increase in wood and salt content worsened both strength properties. The addition of fibers improved flexural, and the addition of cement improved compression strength. The highest strength values of 14 MPa for compressive and 8 MPa for flexural strength were obtained in the test series with gypsum.

Originality/value – This paper is an important milestone in the development of environmentally friendly materials for additive manufacturing. The potential of many ingredients to improve physical properties could be demonstrated.

Keywords Sustainability, Shrinkage, Mechanical properties, Wood

Paper type Research paper

1. Introduction

Additive manufacturing (AM) has greatly increased in importance in recent decades. The vast majority of three-dimensional (3D) prints has been based on plastic or metal, whereas wood or other cellulosic materials have been used in a few cases only (Krapež Tomec and Kariž, 2022; Wohlers and Campbell, 2017). This is of great concern because of the increasing problem of plastic waste worldwide (European Commission, 2018) and the energy-intensiveness of 3D printing plastic or metal (Faludi *et al.*, 2017). 3D printing with cellulosic materials could be far more sustainable by reducing print energy and the embodied impact of the material (Faludi *et al.*, 2018), and enabling a circular economy by upcycling waste cellulosic material from the lumber industry or agriculture (Gardan *et al.*, 2016; Gardan and Roucoules, 2014; Rael and San Fratello, 2018). However, a number of properties, such as the mechanical strength and dimensional stability, have not been adequately studied. The few existing studies have shown poor mechanical performance compared to that of AM plastics (Faludi *et al.*, 2018; Rosenthal *et al.*, 2018). The aim of this study is to quantify the mechanical strength and vertical shrinkage rates of a wide variety of cellulosic materials, and to identify factors, which could lead to improved performance (less shrinkage, higher strength), such as binding agents, reinforcing fibers or fillers.

A large number of AM processes are available, e.g. fused deposition modeling (FDM), binder jetting, selective laser sintering and stereolithography (Gibson *et al.*, 2015). The main differences between these processes lie in the way how layers are deposited to create parts and what materials are used. Liquid deposition modeling (LDM), sometimes also called paste deposition modeling (Schunemann and Silve, 2013) or dough deposition modeling (Gardan *et al.*, 2016), is an AM process originally developed to print viscous materials such as clay. Yet, it is also a promising approach for 3D printing with wood, because both materials share the physics of liquids that

The current issue and full text archive of this journal is available on Emerald Insight at: **https://www.emerald.com/insight/1355-2546.htm**

Rapid Prototyping Journal

[DOI 10.1108/RPJ-09-2022-0322]

The research projects, on which this publication is based, were funded by the German Federal Ministry of Food and Agriculture (2220HV034A) and the German Federal Ministry of Education and Research (01DH20019). Holzmühle Westerkamp GmbH (Visbek, Germany) kindly provided the softwood flour.

Received 22 September 2022
Revised 8 November 2022
Accepted 11 November 2022

must extrude easily but quickly solidify all at room temperature, unlike melting plastic.

The first descriptions of printing with wood composites by means of LDM have been made by Gardan and colleagues (Gardan *et al.*, 2016; Gardan and Roucoules, 2014). Their printing material was based on beech flour and starch. Other researchers have used either beech sawdust, polyvinyl acetate (PVAc) and urea-formaldehyde (UF) adhesives as binders (Kariz *et al.*, 2016), UF resin, spruce sawdust and glass fibers for reinforcement (Pitt *et al.*, 2017), sawdust from beech and methylcellulose as binding agent (Rosenthal *et al.*, 2018), wood flour and chitosan (Dritsas *et al.*, 2018; Ng *et al.*, 2021; Sanandiya *et al.*, 2018, 2020), spruce wood flour and starch (Kaufhold *et al.*, 2019) or wood flour microparticles dispersed in a matrix of cellulose nanocrystals and xyloglucan (Kam *et al.*, 2019).

Composites with a wood content higher than 50% (Kam *et al.*, 2019; Kaufhold *et al.*, 2019; Rosenthal *et al.*, 2018; Sanandiya *et al.*, 2018) show two problems:

1 the shrinkage of the paste during drying and curing of the manufactured objects (shrinkage in the vertical direction is usually the largest); and
2 its relatively low strength compared to FDM printed ABS. Specifically, these studies found the following values:
   - compressive strength max 2.3 MPa (Kaufhold *et al.*, 2019);
   - tensile strength 11.3 MPa, compressive strength 15.3 MPa, flexural strength 15 MPa, shrinking ca. 15% (Sanandiya *et al.*, 2018);
   - maximum compressive strength 4.3 MPa (Kam *et al.*, 2019); and
   - maximum flexural strength 7.4 MPa, vertical shrinking 17%–20% (Rosenthal *et al.*, 2018).

Cellulosic materials do not necessarily need similar material properties, e.g. mechanical strength, as traditional AM materials like ABS plastic, as AM materials are used in a range of different applications with their specific demands. However, the properties of printed ABS plastic can still be useful as a benchmark for feasible applications when developing a new material. Most studies report the compressive strength of 3D printed ABS in the range of 20–28 MPa and flexural strength in the range of 47–49 MPa (Shabana *et al.*, 2019; Wu *et al.*, 2015). Clever choice of printing orientation, raster orientation and avoidance of air gaps lead to strengths as high as 59 MPa in compression and 122 MPa for flexural loading (Hernandez *et al.*, 2016). These values are an order of magnitude higher than those recorded for wood paste prints thus far. Furthermore, the printed ABS show negligible shrinkage.

Cellulosic materials may also be combined with minerals to improve strength, reduce shrinkage or provide other performance attributes. One study showed that LDM of mineral pastes such as gypsum can have compressive strength of 5.8 MPa and tensile strength of 9.0 MPa while still having the environmental benefits of reducing print energy and reducing embodied impacts of materials (Faludi *et al.*, 2018), even though they do not upcycle agricultural waste or enable composting.

The question of this study is, to what extent shrinkage can be reduced and strength can be increased by using alternative binding agents, additional reinforcing fibers or fillers. Ingredients tested here included methylcellulose, cement, gypsum, salt, citric acid, corn starch and more. The overall hypothesis is that a well-chosen combination of such additives could reduce vertical shrinkage and increase compressive and flexural strength. To test this relatively general hypothesis, eight sub-hypotheses were formulated:

H1. Different ratios of water/methylcellulose/wood flour improve shrinkage and strength, respectively.

H2. Partly replacing wood flour with thermomechanical pulp increases flexural strength.

H3. Increasing cement content while reducing methylcellulose and wood flour decreases shrinkage and increases compressive and flexural strength.

H4. The combination of thermomechanical pulp and cement amplifies the effect named in *H3*.

H5. Replacing wood flour with non-hygroscopic sand decreases shrinkage.

H6. Adding salt decreases shrinkage because of crystallization during water release.

H7. Using cellulose powder as filler instead of wood flour increases flexural strength.

H8. Replacing methylcellulose binder with gypsum decreases shrinkage and increases compressive and flexural strength.

2. Methodology

The following sections list the material ingredients for all mixtures, the approach to vary the ratios of those ingredients for different mixtures, the process of mixing and printing the materials and the mechanical tests (shrinkage, compressive strength and flexural strength) to prove or falsify the hypotheses of optimized mixtures.

2.1 Ingredients

Mixtures were produced using different combinations of the substances listed in Table 1. The powders had previously been stored in a standard climate and were in an air-dry state.

Softwood flour, thermomechanical pulp and cellulose powder have a different chemical composition and anatomical structure, though they are all wood-based. Cellulose powder is produced by delignification of wood chips. This creates long and slim cellulose fibers that presumably improve tensile and flexural strength more than the broader, shorter wood flour fiber bundle fragments (*H7*) obtained from milling wood saw dust (Belani, 1940; Karinkanta *et al.*, 2018). Thermomechanical pulp has longer fibers still, but they are not slender like cellulose powder; rather, they are more volumetric chunks (Table 2).

2.2 Mixtures used for printing

To test the hypotheses, mixtures of the ingredients were chosen with different ratios. All 34 mixtures with their abbreviations and compositions are listed in Table 3. For time efficiency, an

Table 1 Substances used for the preparation of the tested mixtures

Substance	Description/supplier
Water	
Softwood flour	Lignobest C200, Holzmühle Westerkamp/Germany, particle size distribution see Table 2
Pine thermomechanical pulp (TMP)	Produced in a lab refiner (14 bar, 4 min, 3,000 min^{-1}, distance between grinding discs 0.15 mm)
Cellulose powder	Jelucel HM90, JELU-WERK J. Ehrler/Germany, particle size distribution see Table 2
Methylcellulose	Carl Roth/Germany, CAS No.: 9004–67-5, viscosity: 3660 mPa s
Maize starch	Mondamin, Unilever
Portland cement	Baumit/Germany, CEM I 32,5 R
Quartz sand	BCS Natur- und Spezialbaustoffe/Germany, particle size < 0.4 mm
Natural gypsum	toom – J.W. Ostendorf/ Germany
Citric acid	Dr Oetker/Germany
Sodium chloride	Carat/Germany

Table 2 Sieve residue on air jet sieve of softwood flour Lignobest C200 and cellulose powder Jelucel HM90 (manufacturer information)

Wood flour		Cellulose powder	
Mesh size [µm]	Proportion [%]	Mesh size [µm]	Proportion [%]
80	< 30	32	~ 25
125	< 1	100	~ 2
160	0	150	traces

iterative heuristic approach was used – not testing all variations of all variables in even increments, but cutting off lines of testing when mixtures were clearly performing poorly.

There were also different limits on the practical concentration ratios of different ingredients. Too much water leads to spreading of the material, too much filler to overloading of the extruder motor and cracking of the extruded material. To avoid phase separation of water and filler during extrusion, a certain amount of methylcellulose is required. A small admixture of methylcellulose was also necessary for the extrusion of gypsum (*H8*). A pure gypsum–water mixture is not extrudable (the same is true for mixtures of water with wood, pulp, cement or sand). Methylcellulose and citric acid were used to extend the time it takes for gypsum to solidify. The quantities required to extend the time to solidification from 6 to 40 min and more to enable printing of the test objects were determined in preliminary tests. Starch had to be used with sand as an alternative binder, because in preliminary tests, methylcellulose-sand-mixtures slumped, not holding their printed shape. In another set of preliminary tests, wood flour was partially replaced by thermomechanical pulp by 10, 20, 30 and 40%. On the basis of the results, it was decided to include only the first two variants (Pu1: 10% and Pu2: 20%) in the present study.

All mixtures were prepared the same way: first, the ingredients were weighed. Then, the powders were mixed manually. Then, the powder and the water were poured into a bowl and mixed manually. Immediately after mixing, the pastes were poured into the printer cartridge to prevent drying.

2.3 Printing

For printing the specimens, a standard Cartesian 3D printer (Zmorph, Poland) with a modified extruder toolhead was used. The modified paste extruder consisted of a cylindrical plastic cartridge with an internal diameter of 27 mm and a height of 120 mm, an outlet nozzle with an internal diameter of 8 mm and a length of 51 mm and a stepper motor, which moves a piston toward the outlet by means of a lead screw (Figure 1). The Voxelizer 1.4.18 software was used for slicing. Printing was carried out with a traverse speed of 1 mm/s. Layer heights for all printed parts were 4 mm, but with the first layer reduced to 3 mm for an improved adhesion to the printer bed.

The number of specimens printed and tested per mixture was four for shrinkage, 12 for compressive and ten for flexural strength. A total of more than 750 specimens were tested.

2.4 Vertical shrinkage testing

Shrinkage was measured as shrinkage in the z-dimension, because it can be assumed that, due to the layered structure, there is more drying-induced deformation in the vertical direction than in the horizontal plane (x- and y-dimension). For the purpose of this measurement, a simple "tower"-shaped test specimen appeared sufficient (Figure 2): a single-walled, hollow cylinder with an external diameter of 40 mm, 11 layers high (limited by the cartridge volume of approximately 70 ml). The height of each tower was measured by a caliper, first, directly after printing was finished, and, second, after drying for a minimum of seven days to test long-term stability. The percentage decrease in specimen height was used as a measure of shrinkage.

Kariz and colleagues had observed material slump or flow of fresh 3D printed specimens (Kariz *et al.*, 2016). The pastes in this study, in contrast, are much more stable. For smaller objects, deformation due to gravity can be excluded. Instead, a relaxation of the material immediately after extrusion will actually result in a slight increase of the object height (Rosenthal *et al.*, 2018).

2.5 Strength testing

Compression specimens were printed as rectangular wall-like objects with a height of 20 mm, width of 10 mm and a length of 80 mm (five layers). After drying, they were cut into pieces and sanded. From each printed specimen, four compression test specimens with dimensions of $12 \times 8 \times 8$ mm were cut (Figure 3). The compression tests were carried out with a universal testing machine (TIRATEST 28100). Strength values were determined according to standard DIN 52185. If there was no stress decrease visible during the compression test, the stress value at 5% compressive strain was used as a measure of strength.

Table 3 Tested mixtures with ingredients and physical properties (mean ± standard deviation). "MC" = methylcellulose

Mixture Name	Ingredients [g]					Vertical Shrinkage	Density	Compressive Strength	Specific Compr. Strength	Flexural Strength	Specific Flexural Strength
	Water	MC	Wood	Pulp	Cement	[%]	[g/cm³]	[MPa]	[MPa•g/cm³]	[MPa]	[MPa•g/cm³]
Wo1	60.0	3.0	16.2	0	0	20.9 ± 0.8	0.37 ± 0.01	1.91 ± 0.10	5.16 ± 0.91	3.69 ± 0.36	9.97 ± 1.24
Wo2	60.0	2.0	19.4	0	0	15.1 ± 0.8	0.33 ± 0.01	1.36 ± 0.04	4.12 ± 0.89	2.12 ± 0.33	6.42 ± 1.19
Pu1	60.0	3.0	14.6	1.6	0	17.2 ± 0.9	0.36 ± 0.03			4.89 ± 0.78	13.58 ± 3.3
Pu2	60.0	3.0	13.0	3.2	0	17.7 ± 0.8	0.36 ± 0.04			4.59 ± 0.27	12.75 ± 2.17
Wo1	60.0	3.0	16.2	0	0	20.9 ± 0.8	0.37 ± 0.01	1.91 ± 0.10	5.16 ± 0.91	3.69 ± 0.36	9.97 ± 1.24
Ce1	59.7	3.0	16.0	0	1.53	19.6 ± 0.3	0.43 ± 0.01			4.33 ± 0.77	10.07 ± 2.02
Ce2	59.4	2.9	15.7	0	3.37	19.5 ± 0.5	0.46 ± 0.01	3.61 ± 0.20	7.85 ± 1.81	4.82 ± 0.74	10.48 ± 1.84
Ce3	59.1	2.8	15.4	0	5.66	19.3 ± 0.4	0.51 ± 0.01			4.81 ± 0.46	9.43 ± 1.09
Ce4	58.6	2.8	14.5	0	8.56	17.8 ± 0.9	0.55 ± 0.01	4.27 ± 0.21	7.76 ± 1.69	4.44 ± 0.67	8.07 ± 1.36
Ce5	58.0	2.6	14.4	0	12.4	16.0 ± 0.3					
Ce6	57.1	2.5	13.6	0	17.5	13.9 ± 0.5	0.65 ± 0.02	3.94 ± 0.47	6.06 ± 0.72		
Ce7	55.9	2.3	12.5	0	25.1	11.3 ± 0.4					
Ce8	53.9	2.0	10.8	0	37.0	8.6 ± 0.8	0.88 ± 0.03	4.98 ± 0.61	5.66 ± 0.69		
Ce9	50.3	1.4	7.6	0	58.6	9.2 ± 0.3					
Pu1	60.0	3.0	14.6	1.62	0		0.36 ± 0.03			4.89 ± 0.78	13.58 ± 3.3
PuCe1	59.7	3.0	14.4	1.60	1.53		0.42 ± 0.01			4.71 ± 0.42	11.21 ± 1.27
PuCe2	59.4	2.9	14.1	1.57	3.37		0.46 ± 0.01			4.85 ± 0.42	10.54 ± 1.14
PuCe3	59.1	2.8	13.8	1.54	5.66		0.50 ± 0.01			4.95 ± 0.31	9.9 ± 0.82
PuCe4	58.6	2.8	13.4	1.49	8.56		0.55 ± 0.01			4.80 ± 0.58	8.73 ± 1.21
	Water	Starch	Wood	Sand	Salt						
S0	100	10.0	27.0	0	0	23.0 ± 1.0	0.57 ± 0.01	5.19 ± 0.13	9.11 ± 2.33	7.94 ± 1.69	13.93 ± 3.21
Sn1	100	10.0	26.2	9.05	0	21.8 ± 2.3	0.64 ± 0.01	5.50 ± 0.25	8.59 ± 1.4	7.48 ± 0.76	11.69 ± 1.37
Sn2	100	10.0	24.9	23.3	0	19.8 ± 2.1	0.76 ± 0.02	5.53 ± 0.16	7.28 ± 1.04	7.26 ± 0.64	9.55 ± 1.09
Sn3	100	10.0	22.6	48.9	0	16.8 ± 1.7	0.93 ± 0.01	4.36 ± 0.19	4.69 ± 0.76	5.80 ± 0.62	6.24 ± 0.73
Sn4	100	10.0	17.2	109	0	9.7 ± 1.4	1.14 ± 0.02	3.76 ± 0.15	3.3 ± 0.69	3.81 ± 0.58	3.34 ± 0.57
Sn5	100	10.0	0.0	300	0	0.2 ± 0.2	1.41 ± 0.03	2.05 ± 0.08	1.45 ± 0.2	1.68 ± 0.13	1.19 ± 0.12
S0	100	10.0	27.0	0	0	23.0 ± 1.0	0.57 ± 0.01	5.19 ± 0.13	9.11 ± 2.33	7.94 ± 1.69	13.93 ± 3.21
Sl1	100	10.0	27.0	0	10.0	14.7 ± 1.3	0.58 ± 0.01	2.95 ± 0.22	5.09 ± 1.39	4.76 ± 0.86	8.21 ± 1.62
Sl2	100	10.0	27.0	0	20.0	11.5 ± 0.9	0.58 ± 0.03	2.61 ± 0.35	4.5 ± 1.96	2.72 ± 0.68	4.69 ± 1.42
Sl3	100	10.0	27.0	0	30.0	5.6 ± 0.5	0.56 ± 0.03	2.46 ± 0.33	4.39 ± 1.71	2.03 ± 0.41	3.63 ± 0.93
Sl4	100	10.0	27.0	0	35.8	0.1 ± 1.1	0.54 ± 0.04	2.10 ± 0.29	3.89 ± 1.84	2.00 ± 0.52	3.7 ± 1.24
	Water	MC	Cellulose	Gypsum	Citric Acid						
Gy0	50.0	2.50	18.8	0	0	20.3 ± 1.6	0.53 ± 0.01	3.17 ± 0.12	5.98 ± 1.05	8.13 ± 0.96	15.34 ± 2.1
Gy1	49.5	2.43	17.8	4.80	0.001	11.7 ± 1.7	0.53 ± 0.02	3.14 ± 0.09	5.92 ± 0.74	4.66 ± 0.27	8.79 ± 0.84
Gy2	49.0	2.35	16.9	9.60	0.002	7.9 ± 1.4	0.54 ± 0.02	2.47 ± 0.13	4.57 ± 0.73	3.52 ± 0.25	6.52 ± 0.7
Gy3	48.0	2.20	15.0	19.2	0.004	3.8 ± 0.6	0.60 ± 0.01	2.83 ± 0.05	4.72 ± 0.46	2.97 ± 0.19	4.95 ± 0.4
Gy4	46.0	2.10	11.3	38.4	0.008	1.6 ± 0.5	0.78 ± 0.01	4.51 ± 0.06	5.78 ± 0.62	3.67 ± 0.30	4.71 ± 0.45
Gy5	43.0	1.45	5.63	67.2	0.014	1.4 ± 1.3	1.07 ± 0.01	8.39 ± 0.32	7.84 ± 2.11	5.41 ± 1.20	5.06 ± 1.17
Gy6	40.0	1.00	0.00	96.0	0.020	-0.7 ± 0.4	1.35 ± 0.01	14.00 ± 2.15	10.37 ± 2.82	8.13 ± 0.90	6.02 ± 0.71

Flexural specimens were printed as elongated rectangles with a height of 12 mm, width of 20 mm, and a length of 200 mm (three layers). During the drying process, they lay between two plane-parallel screens, which prevented warping. After drying, they were sanded to cuboids with dimensions of 9 × 18 × 200 mm (Figure 4). Flexural strengths were determined using the above-described universal testing machine, according to standard DIN 52186.

2.6 Density and specific strength

Because some applications do not only depend on strength, but specific strength (strength–weight ratios), the density was measured for each mixture, and specific flexural strength (flexural strength per unit density) was calculated. For calculation of the density, volume and mass of the test specimens were measured by a caliper and a laboratory balance. For calculation of specific flexural strength, the previously calculated flexural strength was then divided by density.

3. Results and discussion

3.1 Print quality and color

Print quality varied, though mixtures resulting in very poor quality in the preliminary experiments were excluded from testing. Table 3 lists all mixtures with their specific abbreviations and ingredients. Figure 5 shows a range of prints from the different categories of material mixtures. Note the differences in color and texture; while aesthetics were not considered in this study, some applications may be determined more by aesthetics than by mechanical properties. Most samples showed beige earth tones, with the darkest brown observed for the sand and starch mixture "Sn5," and the lightest gray for the gypsum mixtures, e.g. "Gy3." Surface textures were never smooth, but varied from softly grainy such

Figure 1 Modified paste extruder with stepper motor, cartridge, nozzle and connecting elements

Figure 2 Tower for vertical shrinkage measurement

as the wood flour/cement mixture "Ce4" to slightly lumpy such as wood and salt "Sl3" to dry and cracking such as wood only "Wo2."

Numeric results are shown in Table 3, followed by graphs in Figure 6. Note that Table 3 shows all mixtures, which could be printed with sufficiently high cohesive quality, and which preliminary tests suggested would perform well in mechanical testing. The table's data gaps are regimes, within prints were not tested, either because preliminary tests had shown that the mixtures perform poorly, or because trends could clearly be shown for testing the aforementioned sub-hypotheses before completion of tests (e.g. Ce1–Ce9).

3.2 Vertical shrinkage

The values of vertical shrinkage varied between 23.0 and −0.7% (a slight expansion in the course of hardening of gypsum). In most of the test series, shrinkage was between 10 and 20%.

All mixtures with entirely bio-based ingredients, such as Gy0, S0, Wo1, Wo2, Pu1 and Pu2, showed 15% shrinkage or more, which aligns with results from other literature (Rosenthal *et al.*, 2018; Sanandiya *et al.*, 2018). Such high shrinkage is anticipated to be unacceptable for many applications, or, at the very least, requires design attention to accommodate for during manufacturing and hardening.

All mineral additives reduced shrinkage compared to mixtures with more MC or starch binder, even when the water content was unchanged, such as in Sn and Sl mixtures. The mixtures with the highest dimensional stability (shrinkage below 5%) were Gy3–Gy6, Sl4 and Sn5, all of which had high mineral content. In fact, Gy6 does not contain any cellulose, but methylcellulose binder only.

In case of Sl4, the high salt content could probably lead to precipitation and crystallization processes during drying (Mortimer and Müller, 2020), which would counteract shrinkage of the pasty mass in the course of water release (sub-*H6*), leading to the observed drying without shrinking. A similar explanation may be given for the Gy6 mixture. Here as well, crystals are formed during the hydration process. The crystallization nuclei grow into fine needles, which felt together and lead to a stiffening of the structure. The volume contraction, which initially sets in, is overlaid by an increase in volume as a result of dihydrate formation (Benedix, 2003; Karni and Karni, 1995).

Thus, a significant mineral content would be a valid means for achieving high dimensional accuracy. If compostability at end of life is a mandatory aspect, ingredients such as sand and gypsum are innocuous, in that they are non-toxic; however, their inert mineral nature could lead to low rates of decomposition in compost facilities and, thus, make them undesirable for use in large quantities. Therefore, further research is required to find bio-based ingredients to reduce shrinkage. An ongoing study indicates that a change in particle size may show positive effects. The wood flour used was very fine. If coarser wood particles were used, shrinkage could be reduced, unfortunately at the expense of decreased mechanical strength and workability.

3.3 Compressive strength

The values for compressive strength vary between 1 and 14 MPa. All purely bio-based mixtures revealed strengths of 1–5 MPa. This corresponds to the values determined by other researchers working with cellulose/xyloglucan and starch binders (Kam *et al.*, 2019; Kaufhold *et al.*, 2019). To benchmark against plastics, this is roughly 10% of the compressive strength of 3D printed ABS. The highest strength of 14 MPa was measured for Gy6, an almost pure mineral mixture with 1% methyl cellulose added. Due to this addition of methyl cellulose, the values are slightly higher than those of pure gypsum (Karni and Karni, 1995).

Table 4 shows that increasing wood and salt content reduced compressive strength. A higher wood content is associated with a lower content of the binder methyl cellulose in the case of test series Wo1 and Wo2. This could have caused a reduction in

Figure 3 Printed, sanded and cut specimens for compressive strength measurement

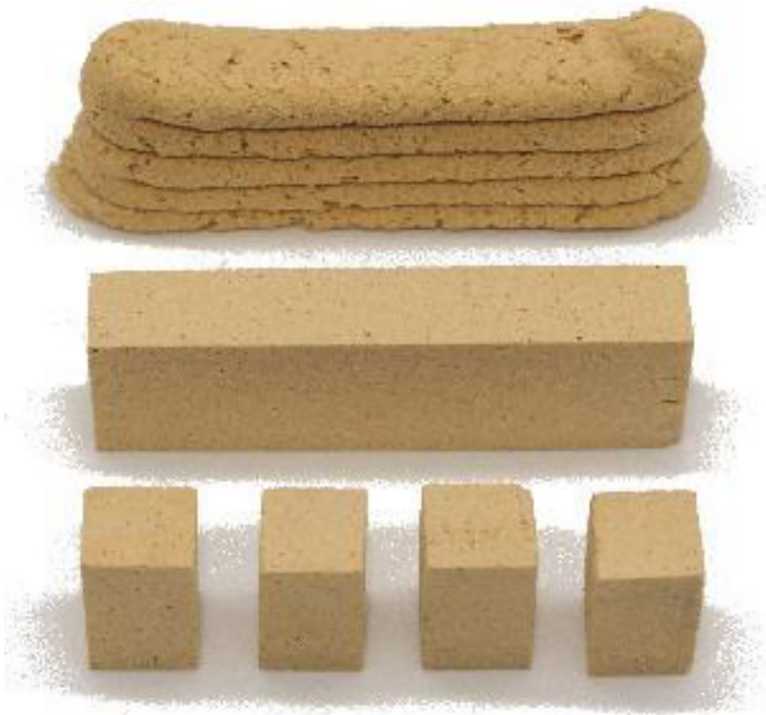

Figure 4 Printed and sanded specimens for flexural strength measurement

compressive strength. A higher salt content, in turn, possibly negatively affects the bonding strength between the wood flour and the starch binder. Probably, the presence of larger amounts of salt results in fewer hydrogen bonds being formed between wood flour and starch binder. Increasing cement content improved the compressive strength. As a function of sand content, the compressive strength first increased slightly and then decreased. The highest compressive strength was obtained with mixtures containing both sand and wood flour. On the one hand, sand particles themselves have a high compressive strength. On the other hand, the presence of more elongated wood particles (an ongoing investigation suggests that the wood flour used has a slenderness ratio of 2 to 3) could also have a positive effect on the internal cohesion of the composite. Furthermore, the bonding forces between starch and wood are probably higher than between starch and sand. In the case of gypsum, an initial decrease in strength was followed by an increase in strength as the gypsum content is further increased.

3.4 Flexural strength

The values for flexural strength range between 2 and 8 MPa. The lowest values are observed for the methylcellulose–wood mixtures and the mixtures with high sand or salt content. The highest values are found in the pure starch–wood mixtures and the mixtures with high cellulose or gypsum contents.

As in the case of compressive loading, a smaller proportion of wood or a higher proportion of binder also leads to higher strength values in the case of bending.

The partial replacement of wood flour by thermomechanical pulp increased flexural strength compared to Wo1. Cement mixtures showed nearly identical strength values across the range of mineral contents. The flexural strength is influenced not only by the compressive strength but also by the tensile strength of a material. Presumably, the improvement of the compressive strength alone was not sufficient to increase the flexural strength of the cement mixtures accordingly. For both cement and TMP, pre-tests were carried out with higher contents than shown in Table 3, but their performance was equal or worse, so they were not included in full testing.

For sand and salt mixtures, the increasing mineral content resulted in more brittle, yet not stronger mixtures; flexural strength decreased with increasing sand and salt content.

Mixtures with either zero gypsum (Gy0, all bio-based) or nearly pure gypsum (Gy6, zero cellulose) achieved the highest flexural strengths of all materials tested (8 MPa). This is about one-sixth of the flexural strength of 3D-printed ABS. Material tests with gypsum showed that the flexural strength can be considerably increased by adding fibers (Karni and Karni, 1995). This was not the case here. Intermediate mixtures achieved lower strength. At present, there is no convincing explanation for this.

Figure 5 Samples of prints: Wo2, Ce4, Sn2, Sn5, Sl3 and Gy3. For explanations of ingredients, see Table 3

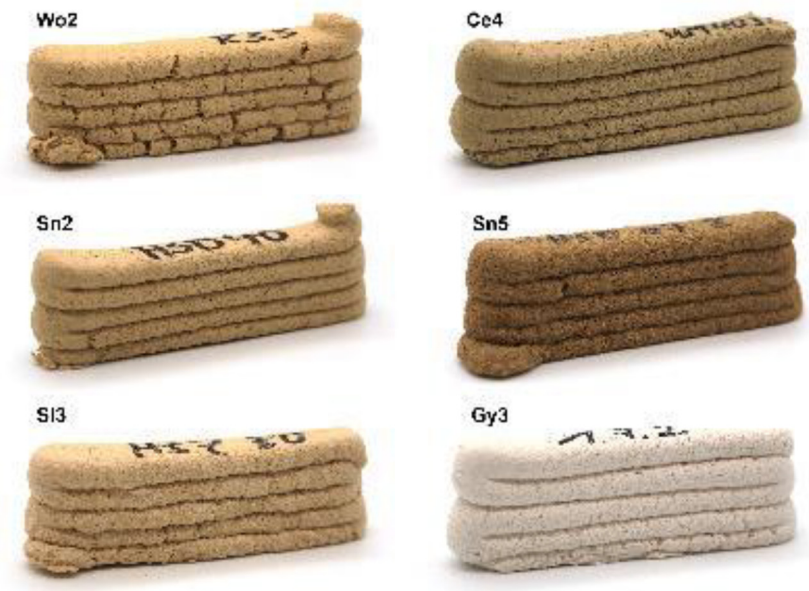

Figure 6 Compressive and flexural strength and vertical shrinkage of several LDM material mixtures, grouped by: (a) cement; (b) sand; (c) salt; (d) gypsum

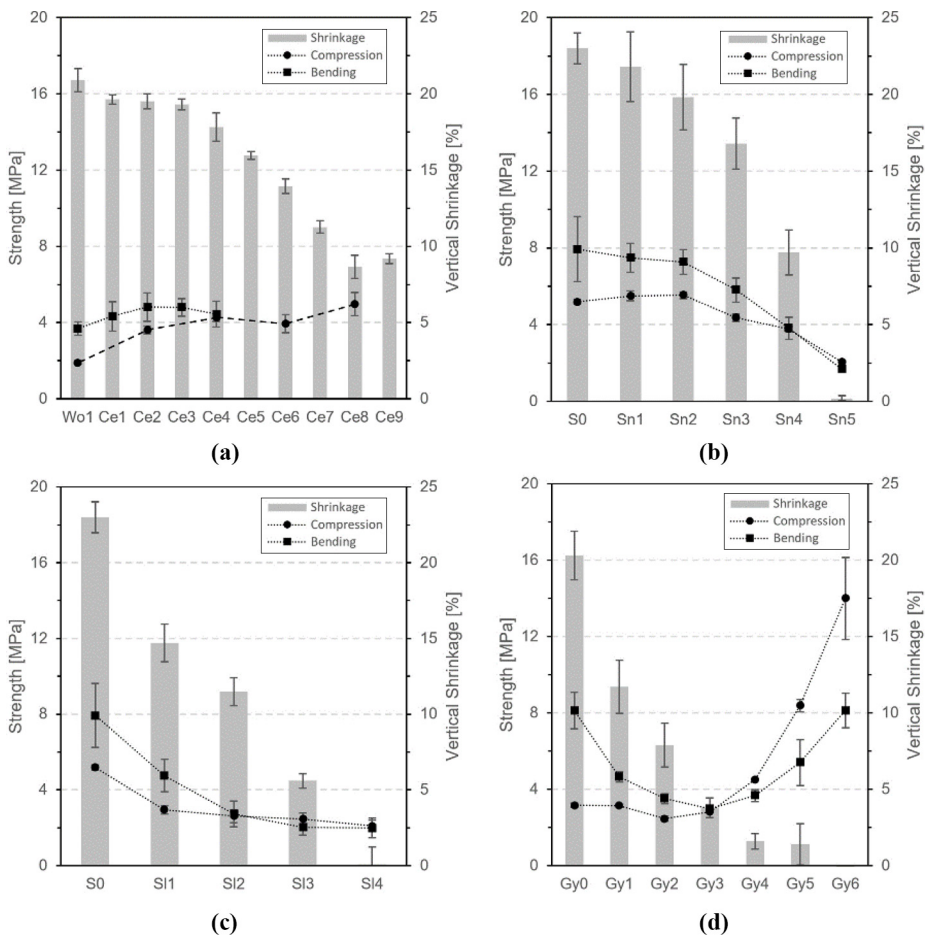

Table 4 Effect of a changed composition on the physical properties investigated (+ is increase, – is decrease)

	Substance		Vertical shrinkage	Compressive strength	Flexural strength
Increasing the content of	Wood	leads to	–	–	–
	TMP		Not measured	Not measured	+
	Cement		–	+	No effect
	Sand		–	+/–	–
	Salt		–	–	–
	Gypsum		–	–/+	–/+

In other investigations with cellulosic materials, higher strength values were obtained (Sanandiya *et al.*, 2018). This leads to the expectation that values of about 15 MPa can be achieved by further optimization of the investigated compounds.

Table 4 qualitatively summarizes the trends for the different mixtures with increasing content of a specific component. Starting from the initial methylcellulose–wood mixture Wo1, the wood, TMP, cement contents were increased. Sand and salt contents were increased with respect to the starch mixture S0. And, the influence of increasing gypsum content was investigated starting from methylcellulose–cellulose mixture Gy0.

Note that modulus of elasticity was also measured for some, but not all, specimens, because it was not a key research question in this study. The values showed trends similar to flexural strength results. A high sand and gypsum content had a positive effect on the modulus of elasticity.

3.5 Strength to weight ratios

Specific flexural strength showed a clearer trend than flexural strength alone: almost all mixtures had higher strength-to-weight ratios for higher percentages of bio-based materials (particularly Sn, Sl, Gy). This is because even if flexural strength did not show clear trends, the mineral fillers increased material density to higher extent than increasing strength, which leads to a lower strength-to-weight ratio. For sand and salt mixtures, this was multiplied by the increased strength for higher wood content. In gypsum mixtures, the zero gypsum (all bio-based) mixture had almost triple the specific flexural strength of the nearly all gypsum (zero cellulose) mixture. As they had the same flexural strength, this could be a deciding factor to choose the bio-based mixture. One exception was the Pu and Ce test series. Here, specific flexural strength did not significantly change with cement or pulp content.

Specific compressive strength showed similar trends for most materials, for the same reasons. There was an increase in specific compressive strength in the Sn and S4l test series with increasing wood content, whereas the cement content showed no significant effect. However, for gypsum mixtures with low or zero percentages of gypsum (only bio-based materials), compressive strength was quite low, and the decrease in density was not pronounced enough to improve specific strength. The difference in bending versus compression may be due to the long fibers of cellulose-based materials versus the particulate shape of gypsum. A high fiber content increases tensile strength (one component of flexural strength) but not compressive strength. On the other side, a high content of mineral binders (cement, gypsum) increases compressive but not tension strength. The highest flexural strength values can be found in fiber-matrix-materials (plant cell wall, reinforced concrete). Thus, it is difficult to understand why Gy3 with a combination of cellulose fibers and gypsum matrix shows the lowest flexural strength. Maybe the binding between wood and gypsum is not good. Maybe the presence of higher cellulose and methylcellulose contents inhibits that gypsum solidifies chemically. Gy6 started to solidify after 40 min, Gy5 after 60 min and mixtures with lower gypsum contents solidified only during drying.

3.6 Hypothesis validation/falsification

Based on the results above, the hypotheses tested were supported or falsified as follows:

H1. *Different ratios of water/methylcellulose/wood flour improve shrinkage and strength, respectively.* This hypothesis is supported, as trends in shrinkage varied considerably with clear trends, and strength varied considerably in some cases, though trends were more mixed. But, the effects are contrary: an increase in wood content (at the same time, a decrease in methylcellulose content) improved the shrinkage performance (lowering from 20.9 to 15.1%) but worsened the strength properties (reducing flexural strength from 3.69 to 2.12 MPa and compressive strength from 1.91 to 1.36 MPa).

H2. *Partly replacing wood flour with thermomechanical pulp increases flexural strength.* This hypothesis is supported for replacing 10% of wood with thermomechanical pulp. This leads to a 33% increase in flexural strength (from 3.69 to 4.89 MPa). Additional replacing did not reveal any further effect.

H3. *Increasing cement content while reducing methylcellulose and wood flour decreases shrinkage and increases compressive and flexural strength.* This hypothesis is supported for shrinkage and compressive strength only, but not for flexural strength. The addition of a small amount of cement results in an 89% increase in compressive strength (from 1.91 to 3.61 MPa). A significant decrease in shrinkage was visible only at higher cement contents (Ce4–Ce9).

H4. *The combination of thermomechanical pulp and cement amplifies the effect named in H3.* This hypothesis is not supported. Increasing cement content of the pulp mixture did not influence the flexural strength.

H5. *Replacing wood flour with non-hygroscopic sand decreases shrinkage.* This hypothesis is supported. A clear decrease of shrinkage was observed (from 23 to 0.2%). The higher the sand content, the lower was the shrinkage. At high sand contents, on the other hand, the strength properties deteriorated considerably. However, the addition of a

small amount of sand reduces shrinkage by 14% (from 23 to 19.8%) without deteriorating compressive and flexural strength.

H6. *Adding salt decreases shrinkage because of crystallization during water release.* This hypothesis is supported. A clear decrease of shrinkage was observed (from 23 to 0.1%). Similar to the decrease in shrinkage, however, the strength values also deteriorated.

H7. Different ratios of water/methylcellulose/wood flour improve shrinkage and strength, respectively.

H8. *Replacing methylcellulose binder with gypsum decreases shrinkage and increases compressive and flexural strength.* This hypothesis is supported for shrinkage, which was near zero for high gypsum percentages. It is also supported for compressive strength (increase from 3.17 to 14.0 MPa). However, flexural strength first decreased and then increased with increasing gypsum content.

It was also observed that the use of starch as a binder instead of methylcellulose reduces the wood content from 84 to 73%, but results in a 115% increase in flexural strength (from 3.69 to 7.94 MPa) and a 171% increase in compressive strength (from 1.91 to 5.19 MPa).

3.7 Outlook

The study included the most promising ingredients, mixture variations and print settings that the authors were aware of for furniture-related applications. Limited time required limits of how many mixtures were tested, resulting in the gaps in Table 3. Tensile strength was not tested because compressive and flexural strength are more important for the planned application in the furniture sector.

Regrettably, most additional ingredients improved only one physical property (either shrinkage or strength), while worsening the other. Small admixtures of fibers and cement were an exception. Here, both shrinkage and strength properties can be improved to a limited extent. Considerable improvements were only achieved with the addition of higher gypsum contents.

Overall, the printed mixtures that performed best for both shrinkage and strength were the least wood-based and the most gypsum-based. This is unfortunate from a sustainability point of view because wood flour and thermomechanical pulp offer much more opportunity for a circular economy. Both can be sourced from waste wood, and at their end of life, they could either be recycled into other wood pulp products, composted to grow new wood or burned for energy (avoiding the burning of fossil fuels).

This research represents a first exploration, which further research can build on. However, the results of this study already show that it will be very hard to achieve the physical properties of ABS plastics with wood-based LDM materials. Nevertheless, further improvements are possible: wood particles with higher density (hardwood instead of softwood) can increase strength (Rosenthal *et al.*, 2018). Bigger particles can reduce shrinkage (preliminary results of an ongoing study). Also, the improved strength of thermomechanical pulp and cellulose powder versus wood flour suggests that the geometry of cellulose fibers can improve performance significantly. Maybe other binding agents (e.g. sodium silicate liquid) can improve material properties. Because the performance of cellulosic-only materials studied here was lower than those mixed with minerals, future research might investigate which minerals improve strength but are still compostable (perhaps clay), or investigate which bio-based chemicals bind with cellulose with greater strength and less shrinkage.

Larger objects that were already 3D printed suggest that materials with flexural strengths of approximately 5 MPa and shrinkage between 10 and 20% could be used for some applications in the furniture, interior and packaging sector. Additionally, the possibility to use topology optimization in 3D printing technology (Christiansen *et al.*, 2015) could compensate for the disadvantage of relatively low strength. If the shape of a 3D object is optimized regarding its function, the material is concentrated at the positions where it is needed for mechanical reasons. In addition, with similar LDM studies having shown a 75% reduction in environmental impact and 50% reduction in cost compared to plastic printing (Faludi *et al.*, 2018), more material in thicker structures might be used while still reducing its impact. Thus, a larger quantity of the inexpensive and eco-friendly material can be an effective substitute for a stronger but more expensive and ecologically questionable material.

4. Conclusion

LDM is a promising approach for 3D printing wood-based materials. Yet, the physical properties of the material have historically not been satisfactory. The addition of alternative binding agents, reinforcing fibers and fillers could play an important role in solving this problem. In this study, numerous material variants were produced, and shrinkage and strength properties were measured. A heuristic approach was chosen, in which eight hypotheses about the relationship between material composition and material properties were tested. Five of the eight hypotheses were fully supported, two were partially supported (H3 and H8), and one hypothesis was falsified (H4).

In summary, shrinkage and strength, the most important physical properties of LDM materials, are influenced by additional binding agents, reinforcing fibers and fillers: The addition of cement, sand, salt and gypsum reduces shrinkage. Alternative binders as starch, cement and gypsum and the addition of fibrous particles can increase compressive and/or flexural strength.

Future material development should continue to follow the path taken. Making 3D printing "greener" is the ongoing challenge. The sustainability of the raw materials used and the processes must be kept in mind. On the other hand, further improvements in material properties are necessary to open up a broader field of application for environmentally friendly materials in AM. As trees and other organisms in nature build additively to form strong and beautiful structures that are parts of healthy sustainable ecosystems, it is clearly possible. It should only be a matter of time, effort and innovation for us to achieve these goals as well.

References

Belani, E. (1940), "Holzmehl", *Holz als Roh- und Werkstoff*, Vol. 3 No. 9, pp. 285-288.

Benedix, R. (2003), *Bauchemie. Einführung in die Chemie für Bauingenieure*, 3rd ed., Teubner, Stuttgart.

Christiansen, A.N., Bærentzen, J.A., Nobel-Jørgensen, M., Aage, N. and Sigmund, O. (2015), "Combined shape and topology optimization of 3D structures", *Computers & Graphics*, Vol. 46, pp. 25-35.

Dritsas, S., Halim, S.E.P., Vijay, Y., Sanandiya, N.G. and Fernandez, J.G. (2018), "Digital fabrication with natural composites", *Construction Robotics*, Vol. 2 Nos 1/4, pp. 41-51.

European Commission (2018), "A European strategy for plastics in a circular economy", No. 52018DC0028, European Commission, Brussels, available at: https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=COM%3A2018%3A28%3AFIN (accessed 8 May 2020).

Faludi, J., Cline-Thomas, N. and Agrawala, S. (2017), "The next production revolution: implications for governments and business", *Ch.5: 3D Printing and Its Environmental Implications, Organisation for Economic Cooperation and Development*, OECD, Paris.

Faludi, J., Van Sice, C.M., Shi, Y., Bower, J. and Brooks, O.M. K. (2018), "Novel materials can radically improve whole-system environmental impacts of additive manufacturing", *Journal of Cleaner Production*, Vol. 212, pp. 1580-1590.

Gardan, J. and Roucoules, L. (2014), "3D printing device for numerical control machine and wood deposition", *Journal of Engineering Research and Applications*, Vol. 4, pp. 123-131.

Gardan, J., Nguyen, D.C., Roucoules, L. and Montay, G. (2016), "Characterization of wood filament in additive deposition to study the mechanical behavior of reconstituted wood products", *Journal of Engineered Fibers and Fabrics*, Vol. 11 No. 4, pp. 1-9.

Gibson, I., Rosen, D. and Stucker, B. (2015), *Additive Manufacturing Technologies: 3D Printing, Rapid Prototyping, and Direct Digital Manufacturing*, 2nd ed., Springer-Verlag, New York, NY.

Hernandez, R., Slaughter, D., Whaley, D., Tate, J. and Asiabanpour, B. (2016), "Analyzing the tensile, compressive, and flexural properties of 3D printed ABS P430 plastic based on printing orientation using fused deposition modeling", *27th Annual International Solid Freeform Fabrication Symposium, Austin, TX*, pp. 939-950.

Kam, D., Layani, M., Barkai Minerbi, S., Orbaum, D., Ben Harush, S.A., Shoseyov, O. and Magdassi, S. (2019), "Additive manufacturing of 3D structures composed of wood materials", *Advanced Materials Technologies*, Vol. 4 No. 9, p. 1900158.

Karinkanta, P., Ämmälä, A., Illikainen, M. and Niinimäki, J. (2018), "Fine grinding of wood – overview from wood breakage to applications", *Biomass and Bioenergy*, Vol. 113, pp. 31-44.

Kariz, M., Sernek, M. and Kuzman, M.K. (2016), "Use of wood powder and adhesive as a mixture for 3D printing", *European Journal of Wood and Wood Products*, Vol. 74 No. 1, pp. 123-126.

Karni, J. and Karni, E. (1995), "Gypsum in construction: origin and properties", *Materials and Structures*, Vol. 28 No. 2, pp. 92-100.

Kaufhold, J., Kohl, J., Nerella, V.N., Schroefl, C., Wenderdel, C., Blankenstein, P. and Mechtcherine, V. (2019), "Wood-based support material for extrusion-based digital construction", *Rapid Prototyping Journal*, Vol. 25 No. 4, pp. 690-698.

Krapež Tomec, D. and Kariž, M. (2022), "Use of wood in additive manufacturing: review and future prospects", *Polymers*, Vol. 14 No. 6, pp. 1174-1196.

Mortimer, C.E. and Müller, U. (2020), "Chemie", *Georg Thieme*, 13th ed., Stuttgart, New York, NY.

Ng, S., Song, B. and Fernandez, J.G. (2021), "Environmental attributes of fungal-like adhesive materials and future directions for bioinspired manufacturing", *Journal of Cleaner Production*, Vol. 282, p. 125335.

Pitt, K., Lopez-Botello, O., Lafferty, A.D., Todd, I. and Mumtaz, K. (2017), "Investigation into the material properties of wooden composite structures with in-situ fibre reinforcement using additive manufacturing", *Composites Science and Technology*, Vol. 138, pp. 32-39.

Rael, R. and San Fratello, V. (2018), *Printing Architecture, Innovative Recipes for 3D Printing*, Princeton Architectural Press, New York.

Rosenthal, M., Henneberger, C., Gutkes, A. and Bues, C.-T. (2018), "Liquid deposition modeling: a promising approach for 3D printing of wood", *European Journal of Wood and Wood Products*, Vol. 76 No. 2, pp. 797-799.

Sanandiya, N.D., Ottenheim, C., Phua, J.W., Caligiani, A., Dritsas, S. and Fernandez, J.G. (2020), "Circular manufacturing of chitinous bio-composites via bioconversion of urban refuse", *Scientific Reports*, Vol. 10 No. 1, pp. 4632.

Sanandiya, N.D., Vijay, Y., Dimopoulou, M., Dritsas, S. and Fernandez, J.G. (2018), "Large-scale additive manufacturing with bioinspired cellulosic materials", *Scientific Reports*, Vol. 8 No. 1, p. 8642.

Schunemann, E. and Silve, S. (2013), "Paste deposition modelling (PDM): a hybrid ALM/craft process", *Making Futures Journal*, Vol. 3, pp. 180-192.

Shabana, R.V., Santosh, N., Sarojini, J., Vikram, K.A. and Lakshmi, V.V. (2019), "Evaluating the mechanical properties of commonly used 3D printed ABS and PLA polymers with multi layered polymers", *International Journal of Engineering and Advanced Technology*, Vol. 8 No. 6, pp. 2351-2356.

Wohlers, T.T. and Campbell, I. (2017), Wohlers Report 2017, Wohlers Associates.

Wu, W., Geng, P., Li, G., Zhao, D., Zhang, H. and Zhao, J. (2015), "Influence of layer thickness and raster angle on the mechanical properties of 3D-printed PEEK and a comparative mechanical study between PEEK and ABS", *Materials*, Vol. 8 No. 9, pp. 5834-5846.

Corresponding author

Michael Rosenthal can be contacted at: michael.rosenthal@tu-dresden.de