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Trifol, Jon; Jayaprakash, Siddharth; Baniasadi, Hossein; Ajdary, Rubina; Kretzschmar, Niklas; Rojas, Orlando J.; Partanen, Jouni; Seppälä, Jukka V.

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3D-Printed Thermoset Biocomposites Based on Forest Residues by Delayed Extrusion of Cold Masterbatch (DECMA)

Jon Trifol,[⊥] Siddharth Jayaprakash,[⊥] Hossein Baniasadi, Rubina Ajdary, Niklas Kretzschmar, Orlando J. Rojas, Jouni Partanen, and Jukka V. Seppälä*



controlling the degree of curing, that takes some responsibility of the 3D printing from materials and as such can be used to 3D print otherwise unprintable materials. First, a masterbatch was produced by mixing a bio-based resin (bioepoxy) and sawdust and lignin. This paste was partially cured at room temperature until reaching an apparent viscosity suitable for extrusion ($\approx 10^5$ mPa·s at 1 s⁻¹). The system was next cooled (5–10 °C) to delay subsequent hardening prior to 3D printing. The printability of the biocomposite paste was systematically investigated and the merits of the delayed extrusion, via DECMA, were assessed. It was found that DECMA allowed the



revalorization of sawdust and lignin via 3D printing, as direct printing led to failed prints. Our approach afforded cost-effective, shearthinning dopes with a high bio-based content (58–71%). The bio-based 3D-printed materials demonstrated good machinability by computer numerical control (CNC). Overall, the benefits of the introduced DECMA method are shown for processing bio-based materials and for on-demand solidification during additive manufacturing.

KEYWORDS: 3D printing, DECMA, paste extrusion, thermoset, biocomposites, forest residues

INTRODUCTION

3D printing or additive manufacturing (AM) converts digital designs (CAD drawings) into three-dimensional (3D) objects via layer-by-layer addition of raw materials. The technology enables automatized and on-demand production of complex geometries while eliminating the need for tools/molds.¹ Utilization of 3D printers on an industrial scale allows production units to reduce material waste and optimize logistics and supply chain, thereby making it a more sustainable manufacturing approach. As such, the technology has matured considerably over the last decades and is currently utilized over a wide range of sectors including medical, architecture, automotive, food, and aerospace.²⁻⁸ One particular point of interest is the 3D printing of medium-to-large parts. For instance, concrete houses can be 3D printed at a low cost around 10 000 \$ in less than a day. 5,9-11 Companies and designers have also ventured into 3D printing of customized furniture.

Although nozzles with a small diameter give an acceptable resolution in fused deposition modeling (FDM), they limit the capacity or processing throughput. Similarly, selective laser sintering (SLS) relies on a laser-based power source to sinter polymer/metal powder/polymer composite¹² to create 3D objects and may not be the best option for 3D printing large

structures mainly due to their higher costs and limitations regarding material selection and working environment. Furthermore, stereolithography (SLA) generally requires support structures and postcuring, which may limit their large-scale applicability. However, paste extrusion/direct-ink-writing¹³ is a technique that uses high-viscosity resins and is a feasible option to print large structures. For example, concrete 3D printing utilizes this technique and is already advanced to create structures as large as a house. This opens up an opportunity for high-throughput extrusion in AM.

Paste extrusion/direct-ink-writing¹³ utilizes high-viscosity liquid materials that retain the shape after deposition and provides sufficient structural strength to withstand the load development upon layering. Ideally, the paste should be shear thinning to facilitate the flow of the resin during extrusion. Although this is relatively easy to achieve with concrete, this is not the case for thermoset resins—especially bio-based resins.

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A viscous thermoset resin can be achieved, for instance, via polymer composites (combining a polymer matrix with reinforcing particles, fibers, and nanomaterials).^{14–21} They solidify after deposition to exhibit suitable mechanical properties consequently withstanding several layers. Examples of these systems for 3D printing include polyurethanes filled with cellulose nanofibers²² and epoxy systems reinforced with nanoclays, carbon fibers, and silicon carbide whiskers.^{23,24}

A high dope viscosity may not be sufficient for effective 3D printing. For instance, curing is necessary to build up the mechanical strength needed to withstand the layering process. Curing is traditionally triggered by UV irradiation or by incorporating a second component in the resin. For instance, Kretzschmar et al. paste-extruded and concurrently UV-cured biocomposites of industrial relevance.²⁵ The issue with the UV-curing, however, is that the irradiation may not have a sufficient penetration depth, which limits large volume applications.²⁶ In a two-component approach, curing is initiated once the polymer resin makes contact with a second component. Here, the curing time, commercially described as "pot life", may range from seconds to days based on resin chemistry and the curing temperature. Depending on the material rheology and chemistry, fillers can be added either to the resin or hardener. The problem with two-component resins is tailoring the curing kinetics. If the curing happens very fast, then the resin will solidify inside the printer. If too slow, however, the bottom layer will not solidify. To tackle these issues, Lewicki et al. created an epoxy that gels in seconds but cures in minutes, making it an ideal system for 3D printing.²⁷ A CNT-reinforced combination of a thermoset and a thermoplastic has also been used for this purpose.²⁸⁻³³ Another strategy is the combination of nanoclays, carbon fibers, and silicon carbide whiskers/epoxy composites.²⁴ Unfortunately, the approaches considered to date are not widely applicable to bio-based materials.

Herein, we propose a new approach to tackle the challenges of traditional systems. This method is described as "Delayed Extrusion of Cold Masterbatch (DECMA)" and involves a temperature difference to optimize the curing kinetics for an ideal 3D-printing process. A slow curing resin is mixed with fillers, creating a masterbatch. The masterbatch is kept at a holding temperature until reaching a suitable viscosity for 3D printing and then cooled to slow down the reaction until they can be loaded conveniently into the extruder. In this approach, the improvement in printability is due to a processing method and not due to a material, which may make the 3D printing cheaper.

We report here a bio-based ink composed of bioepoxy, sawdust, and lignin. Indeed, the use of bio-based materials has become a relevant topic, and substantial effort has been made to develop materials for bio-based food packaging and sustainable building materials.^{34–36} Our DECMA method is shown for its potential for 3D printing of medium-sized objects. Finally, the latter were postprocessed with a computer numerical control (CNC) machine for hybrid manufacturing—a production process that combines additive and subtractive manufacturing.³⁷

EXPERIMENTAL SECTION

Materials. AMPRO BIO bioepoxy + slow hardener kit (Gurit Holding, Switzerland), herein the term "BE", low sulfonate alkali lignin (Sigma Aldrich), and hardwood sawdust (Germany), were used without further purification.

Ink Preparation. The resin and composites were prepared by gentle mixing of bioepoxy, hardener, and fillers in a disposable plastic coated cellulose cup using a disposable plastic stick. Table 1

Table 1. Composition of the Materials Used in This Study

sample	composition
BE	neat bioepoxy
BE/10	bioepoxy with 10% w/v sawdust
BE/20	bioepoxy with 20% w/v sawdust
BE/20-15	bioepoxy with 20% w/v sawdust and 15% w/v lignin

summarizes different formulations used in this study. The 45 mL of bioepoxy was mixed with 15 mL of hardener and the required amounts of sawdust and lignin. The formulation was then mixed gently for approximately 5 min to create the masterbatch.

The FTIR and TGA (Figures S2 and S3-left, and B) data show that the sawdust is composed of approximately 20-30% lignin and 65-75% polysaccharides. In contrast, lignin only contained a trace of polysaccharides. So, it can be estimated that BE/10 has 7% of polysaccharides and 3% of lignin, BE/20 contains 15% of polysaccharides and 5% of lignin, and BE/20-15 contains 15% of polysaccharides and 20% lignin.

Characterization. *Microscopy.* A field emission scanning electron microscope (FE-SEM, Zeiss Sigma VP) was utilized for high-resolution imaging of sawdust, lignin particles, and cross-section of 3D-printed samples. The samples were initially sputter-coated with an ultrathin layer (3 nm) of gold/palladium (Au/Pd) to make them electrically conductive. Sputtering used a Leica EM ACE600 high-vacuum table-top sputter coater. Afterward, the samples were mounted on the sample holder and placed in SEM at acceleration voltages (EHT) between 3 and 5 kV. The SEM images were then analyzed with ImageJ to obtain an average particle size based on at least 35 particles.

Thermogravimetric Analysis (TGA). Specimens (4-10 mg) were analyzed in a thermogravimetric analysis unit (TA Instruments TGA Q500) between 30 and 800 °C using a heating rate of 10 °C/min under a nitrogen atmosphere.

Rheology. The viscosity of epoxy and composites were measured with a rheometer (Anton Parr MCR 301, Austria) using 25 mm disposable parallel plates with a 1 mm gap between them at 25 °C. The paste was equilibrated at 25 °C (\pm 1 °C) for 2 min, and the test was performed using 0.05% strain and a shear rate of 1 s⁻¹ or a shear rate ramp. The shear rate-viscosity measurements were done in a cycle with a length of 5 min.

Dynamic Scanning Calorimetry (DSC). Specimens (4–10 mg) were analyzed in a TA DSC Q2000 (TA Instruments) from 0 to 90 °C using a heating/cooling/heating range of 10 °C/min under a nitrogen atmosphere (50 mL N₂/min) to determine the thermal transitions of materials. The curing kinetics was measured using 30–40 mg specimen under a nitrogen atmosphere (50 mL N₂/min) and isothermal conditions (25 °C). The degree of curing was obtained from integrating the area below the curve in the heat flow-time thermogram.

Mechanical Testing. The tensile properties of the samples were evaluated at 25 °C and 50% relative humidity using an Instron-4204 unit (Instron) equipped with a load cell of 2 kN and a crosshead rate of 5 mm/min. Each test was repeated four times, and the mean value \pm standard error of the mean was reported.

Moisture Absorption. Three samples were dried at 105 $^{\circ}$ C for 24 h and weighed. They were then equilibrated for 24 h in an atmosphere at 23 $^{\circ}$ C and 50% relative humidity (RH) and weighed again. The moisture absorption was determined as the weight difference between the dried and equilibrated samples divided by the dry weight.

Density. The material (approximately 5 g) was immersed in 25 mL of Milli-Q water in a graduated cylinder. The density was obtained by dividing the mass by the volume of water that was displaced.

Preparation of Cartridges for 3D Printing. The masterbatch was prepared as previously described in the ink preparation part.

Immediately after the mixing, the masterbatch was poured into a 25 mL syringe, which was consequently used to fill the standard replaceable 12 mL Luer lock plastic syringes. Then, a plastic nozzle is cut to an output of 2 mm diameter and attached to the syringe to make cartridges. The cartridges were sealed with parafilm and kept in a water bath at room temperature for 30 min. Subsequently, they were kept in a cold-water bath (5–10 $^{\circ}$ C) until their use for 3D printing.

3D Printing. The samples were 3D printed with an in-house developed piston-driven extrusion system (for a maximum print area of 200 mm × 200 mm) to guarantee a constant paste dispensing speed since any change in viscosity would otherwise limit the applicability of air-pressure-driven extrusion systems. A photo of the printer can be found in the Supporting Information (Figure S1). The printer frame performed Cartesian motion, and the extrusion itself was enabled by a downward pushing metal cylinder inside the Luer lock cartridge. The extrusion control (constant dispensing) was applied utilizing National Instruments DAQ and LabVIEW. A constant speed mode was utilized to facilitate a smooth and constant extrusion process considering the prepared paste (and its viscosity increase with time). Manual/modified G-code implementations enabled the extruder head movement in the x-, y-, and z-directions. The communication between the host computer and the 3D printer was achieved with the help of the Pronterface-GUI host for 3D printing. The paste extrusion process was performed at a piston speed (dispensing speed) for a total dispensing speed of 0.6 mL/min and a print speed of 200 mm/min. Objects were manufactured with a layer height of 1.5 mm utilizing nozzles 2 mm diameter.

Machining. The 3D-printed samples were post-processed in a CNC milling machine (Haas VF2, Haas CNC) using a spindle speed of 8000 rpm and a surface speed of 50 smm.

RESULTS AND DISCUSSION

Description of Delayed Extrusion Cold Masterbatch (DECMA) Approach. Figure 1 shows a schematic of the



Figure 1. Schematic of the Delayed Cold Masterbatch approach. In the present diagram, three layers are presented, albeit more layers were deposited as part of this study. Segments A–B: wetting of fibers, B–C: consolidation of resin, point C: start of 3D printing, point D: deposition of the second layer, point E: tack free, the moment at which the resin is so cured that its losses adhesion.

DECMA and a plot of the viscosity of the paste as a function of operation time. In DECMA, the scope is to shift the burden from materials to the processing method, so otherwise unprintable materials can be used for 3D printing. In this work, we have used this technique to revalorize two forest residues, sawdust and lignin, into 3D-printed parts, using a commercially available bio-based epoxy. Sawdust and lignin are two cheap, bio-based particles, which are generally regarded as pubs.acs.org/journal/ascecg

low-value-added waste materials. As such, making industrial parts via 3D printing using these fillers would be a very interesting way to revalorize these forest residues. However, and unlike what happens with other nanoparticles,²⁴ the incorporation of lignin and sawdust is not enough to provide enough consistency to an ink. In this context, the use of DECMA allows the printability of these residues. Additionally, improving the printability by means of a new processing method is interesting, as it is cheaper than using specialized materials.

During the time between points A and B, the twocomponent bioepoxy was mixed with fillers producing the masterbatch. At this stage, the resin has a low viscosity and facilitates the wetting of fillers (lignin and sawdust). The slow curing of the resin provided a time window (holding time) to properly mix the components. The fillers' role was to increase the viscosity and bio-based content and reduce the heating of resin during curing due to the presence of inert materials. After the materials were mixed, cartridges (five in this work) were filled with the masterbatch at point B.

In segment B–C, resin and fillers were already adequately mixed, and the aim was to reach the optimal viscosity for 3D printing. On one hand, this is viscous and cured enough to be deposited but still is liquid enough to provide layer adhesion. This is done by controlling the time-temperature conditions: 30' at 25 °C. Bioepoxies especially undergo highly exothermic reactions; thus, without proper temperature control, curing can get out of control, leading to the solidification of the resin. In this work, cartridges were kept in a water bath at 25 °C for 30 min until point C was reached.

At point C, the viscosity of the mixture reached $\sim 10^5$ mPa·s. The resin was then partially cured (making it suitable for 3D printing) but not to the extent to prevent the flow or stickiness (below tack-free time, point E). One of the cartridges was taken to the 3D printer to start the printing, while the remaining ones were kept in a water bath at 5-10 °C, e.g., to slow down the reaction. At this point, the resin was cured, and if cartridges were kept at room temperature, then the time window available for the printing was narrowed. A layer was then deposited. The next layer was deposited when it was consolidated (point D), i.e., when the deposited layer was sufficiently strong to withstand the subsequent layer's weight. The process proceeded successively, and the masterbatch resin was cured at point E losing the stickiness.

Characterization of the Fillers and Viscoelastic Properties of the Material. Figure 2A,B shows the fillers lignin and sawdust, respectively. As mentioned, lignin and sawdust were chosen as fillers as they are bio based, cheap, and are generally considered a waste. All of this makes them an ideal sustainable filler for 3D-printed composites. While sawdust had an irregular 3D micro-scaled shape, lignin particles were spherical. The particle sizes were 64 ± 35 and $189 \pm 104 \,\mu\text{m}$ for lignin and sawdust particles, respectively. As in this work, we will use a 2 mm diameter output; particles are considered to be small enough to create any clogging issue.

The FTIR and TGA (Figures S2 and S3-left, and B) data showed that the sawdust was composed of approximately 20–30% lignin and 65–75% polysaccharides. In contrast, lignin only contained a trace of polysaccharides.

In Figure 2C, we show the degree of curing over time for BE and BE/20-15. As shown, both curing kinetics were similar, and as such, it can be concluded that the incorporation of

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Figure 2. Characterization of materials (labeled as BE/sawdust%–lignin%). SEM images of (A) lignin powder, (B) sawdust, (C) curing kinetic of BE, and BE/20–15. (D) Loss factor (tan δ) of materials. (E) Evolution of the viscosity over time for BE and its composites. (F) Influence of the shear rate on material viscosity.

fillers did not substantially affect the curing kinetics of the bioepoxy.

Figure 2D includes the gel point (where materials start to behave more as a solid than a liquid) of the BE and the composites. Different criteria can be used to determine the gel point: $\tan \delta = 1$, maximum of the $\tan \delta$ curve, point where $\tan \delta$ becomes independent of the frequency, intersection points of the two linear zones of G'', intersection point between the baseline and the tangent drawn from the turning point of G'curve, or point where the mixture reached predefined values.^{38,39} Therefore, it is difficult, especially for composite inks to determine it accurately. In this work, we have taken the gel point as the maximum of the $\tan \delta$ curve, a criterion that has been used in prepregs,⁴⁰ so it is likely applicable to our material. In 3D-printing applications, gelation ideally occurs at an early stage of the 3D printing so that a deposited layer will not flow and will keep the shape after deposition. The problem with fast gelation is that it probably will occur with fast curing leading to a narrow deposition time window—fully cured materials generally show low adhesion. Another possibility is dual-curing resins. Still, the latter method limits the cost efficiency or the bio-based nature of the material. Figure 2D shows that the BE took approximately 110 min to gel, while composites showed a little bit higher gel time (140 min). In any case, the difference is minor, and it is assumed that both materials gelidify similarly.

Figure 2E,F shows the viscosity of the bioepoxy and composites. The incorporation of fillers substantially increased the material's initial viscosity (Figure 2E). This is an essential requirement for 3D printing. The incorporation of sawdust

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Figure 3. (A) Failed attempt to print open cuboid without the DECMA approach, (B) open-cuboid object printed with DECMA, (C) 3D-printed open cuboid that was post-processed via CNC machining, (D) continuous line 3D printing, (E) printed long continuous line, (F) line 3D printing at six and four adjoining lines, and (G, H) lattice scaffold—honeycomb structure. Unless otherwise noted, printed parts are five layers high and one layer width.

dramatically increased the initial viscosity (from 1.6×10^3 mPa·s for BE, to 1.1×10^4 mPa·s of the composite with 10% of sawdust, and to 8.5×10^4 mPa·s for the composite with 20% of sawdust). The incorporation of lignin was less effective in this regard, the paste with 20% sawdust, 15% lignin showed 1.1×10^5 mPa·s. As such, it was concluded that the incorporation of lignin did not substantially affect the viscosity of the material. BE/20 showed a small peak around 20 min, being the only material not showing a linear behavior. This is likely due to the presence of some bubbles.

Finally, the influence of the shear rate on the materials' viscosity was evaluated (Figure 2E). Among other require-

ments, in an ink for 3D printing, the viscosity should be low at a high shear rate to make the pumping easier, but it should be high at a low shear rate so that the deposited material does not flow and keeps the shape. Figure 2E shows that for BE and BE 10% sawdust, viscosity values were similar regardless of the shear rate, making those materials suboptimal for 3D printing. However, BE 20% and BE 20–15% showed a substantial decrease in viscosity with an increased shear rate, which, as explained, makes them ideal materials for 3D printing.

3D Printing and Post-processing. Scalable geometries including open-cuboid structures, lines, and honeycomb

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Figure 4. General properties of the material (A) TGA and dTG, (B) moisture uptake, and (C) mechanical properties.

scaffolds were 3D printed to demonstrate the potential of DECMA. The output nozzle diameter was 2 mm for all cases.

- Direct extrusion (Figure 3A, no precuring, no consolidation time, five layers high, five layers per cartridge): in this approach, resin and fillers were mixed and immediately used for printing (mixing and printing preparation time around 5 min). An open cuboid was printed, and the consolidation time of layers (time between deposition of layers) was only a few seconds. A *z*-axis increase of 1.5 mm was implemented in the G-code, which was less than the nozzle diameter (*d*) used (2 mm). Previous paste extrusion studies showed that such a setting was desired for the better adhesion of printed layers.^{41,42}
- DECMA (Figure 3B-H, 30 min of precuring, 30 min of consolidation time, five layers high, one layer per cartridge, 1.3 mm high per layer): the fillers and resin were mixed and filled into the cartridge (a syringe + nozzle tip cut to 2 mm diameter) that was kept for 30 min at 25 °C and then at 10 °C until used for printing. A cartridge was loaded into the printer, and a single layer of all structures was printed (printing time approximately 20 min). After 25 min since the start of the deposition, a cartridge was collected from the water bath at 10 °C, placed into the 3D printer, and the *x*-, *y*-, and *z*-axes were repositioned. This was to minimize the positioning error associated with the cartridge installation (±0.5 mm approx.). All of the printed parts are five

layers high (2.5 h) and, since the gel time is also 2-2.5 h, after the deposition of the fifth layer, the first layer will be mostly solid and therefore can withstand a significant amount of layers. In other words, it is likely that this process could be continued until the limit where the material cannot withstand its own weight.

Figure 3A shows that a direct printing approach was insufficient to make the 3D object upon deposition. However, the use of the DECMA approach (Figure 3B) led to good printing resolution, proving the efficiency of the technique. To fulfill the high-dimensional accuracy, which is usually required in industrial parts, the 3D-printed open-cuboid part was post-processed utilizing CNC machining (Figure 3C, SEM image available in Figure S4). The CNC machining operation also proved the potential of this strategy for hybrid manufacturing.

Adjoining (Figure 3F) and longer lines (Figure 3D,E) were printed using DECMA. The long lines (Figure 3D) show that despite the length and closeness of the lines (2 mm line width and a 2 mm gap as per the G-code), they did not merge due to resin flow (flattening) after deposition. To the best of our knowledge, the geometry will be very efficient in thermal insulation applications, where the air–solid–air configuration has been widely used. In adjoining lines, we found that the deposited material could be merged while avoiding gaps that could reduce the mechanical properties of 3D-printed structural parts. In other words, by combining optimizing printing conditions, we could print insulating and structural elements, which are of interest for buildings.

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In addition, a five-layer high honeycomb structure of a more complex geometry, shown in Figure 3G, was made using DECMA. Honeycomb structures are widely used in 3D printing because they provide good mechanical stability with minimal material consumption, which may be used for 3D printing of medium-to-large structures. The cured part was used to analyze the print quality at sharp angles and vertices. There was visual material overlapping at intersections, giving honeycomb links a dumbbell-like appearance. These imperfections were formed upon the double deposition of pastes and ensuing layer diffusion due to gravity.⁴¹

The SEM images of the 3D printed line cross-section (Figures S5 and S6) show that there was no separation between deposited layers proving that they adhered to each other. The SEM images of the cross-section had a triangular profile where the width after curing was narrower at the top and broader at the bottom. This is because the deposited layer laterally pushed out the material beneath. The sides of the cross-section showed typical extrusion, related bulges, and deformations. Small holes were observed at places where lignin particles resided, and no cracks were identified in cross-sections.

To summarize, the use of DECMA allowed 3D printing of a highly loaded bio-based and lightweight thermoset-based resin that was not possible otherwise without the need to modify the resin chemistry, curing kinetic, or incorporating nanoparticles. The proposed technique is likely to be suitable for an extensive array of resins.

Properties of 3D-Printed Materials. Figure 4A and Table 2 show the thermal degradation of bioepoxy and its

Table 2. Thermal, Tensile, and Moisture Uptake of Bioepoxy and Its Composites

${\mathop{(^{\circ}\mathrm{C})^a}\limits^{T_{\max}}}$	E (MPa) ^b	$\begin{array}{c} \text{fracture energy} \\ \left(kJ/m^2 \right)^c \end{array}$	density (g/cm ³)
332	1025 ± 130	245 ± 35	1.1
323/339	913 ± 107	28.8 ± 5.1	1.1
320/342	1089 ± 38	21.1 ± 6.1	1.2
320/352	917 ± 94	9.8 ± 2.9	1.1
	Tmax (°C) ^{c2} 332 323/339 320/342 320/352	$\begin{array}{c} T_{\text{max}} \\ (^{\circ}\text{C})^{\prime a} \\ 332 \\ 323/339 \\ 320/342 \\ 320/342 \\ 320/352 \\ 917 \pm 94 \\ \end{array}$	$\begin{array}{c} T_{max} \\ (^{\circ}C)^{\prime a} \\ 332 \\ 332 \\ 323/339 \\ 323/339 \\ 321 \\ 320/342 \\ 320/342 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 917 \\ \pm 94 \\ 928 \\ \pm 2.9 \\ 320/352 \\ 420 \\ $

^aTemperature at the maximum degradation rate (maximum of the dTGA peak). ^bYoung modulus at 25 °C and 50% RH. ^cFracture energy at 25 °C and 50% RH.

composites. All samples showed similar thermal stability these values were substantially above those required for conventional applications. One of the differences between composites and BE is that the latter showed a derivative TG curve (DTG) with a single degradation peak (at 332 °C). In contrast, composites showed a double-peaked thermogram attributed to the hemicellulose and cellulose⁴³ present in the sawdust. Furthermore, the thermal degradation of the composites started slightly earlier than that of the bioepoxy, which can be attributed to the hemicellulose that has a lower thermal stability than cellulose or lignin.⁴⁴ The composite with both sawdust and lignin revealed higher thermal stability (understood as the latest maximum degradation rate temperature) due to the presence of the highly thermally stable lignin.⁴⁴

Figure 4B shows the moisture uptake of BE and composites. The incorporation of filler increased the moisture uptake. Indeed, the incorporation of cellulose-based particles into biopolymers has been reported to increase water sorption.⁴⁵

The incorporation of lignin increased the moisture sorption because while lignin is a hydrophobic lignin, the one used in this work is hydrophilic.

Figure 4C and Table 2 show the mechanical properties of composites. Table 2 shows that the density of all of the materials was similar; thus, incorporating particles did not alter the lightweight nature of BE. No substantial changes were found in T_{α} (58–59 °C) due to the incorporation of sawdust and lignin. The incorporation of cellulose-based fillers has been reported to increase the T_{g} of polymers such as epoxies,⁴⁶ but this is not always the case.⁴⁷ The bioepoxy used in this study showed low tensile stress (Figure 4C) compared with other bioepoxies available in the literature, which have shown tensile strengths of up to 88 MPa.48 The incorporation of fillers substantially changed the material's mechanical behavior by decreasing the stress and strain at break. In other words, it made the material more brittle. This decrease in mechanical properties may be due to the presence of bubbles (some holes, presumably created by bubbles that can be found in the SEM of the cross-section in Figure S5) generated during the mixing of the resin. Kumar et al.⁴⁹ reported a reinforcing effect in epoxies; the incorporation of 7.5% sawdust increased stress at breaking (from 10 to 22 MPa), which supports the hypothesis that the decrease in mechanical properties is due to the presence of bubbles.

CONCLUSIONS

In this work, we have developed a new 3D-printing processing technique termed Delayed Extrusion of Cold Masterbatch (DECMA). This technique shifts the burden in 3D printing from materials to a processing method so otherwise unprintable materials can be printed. Briefly, in this technique, the degree of curing of the ink is controlled via time/ temperature conditions. Then, the resin is cooled down to stop the reaction and the printing is started. A bioepoxy-based ink containing a 20% of sawdust and 15% of lignin (with a total bio-based content of 58-71%) was developed. The incorporation of lignin and sawdust increased the starting viscosity of the mixture from 10^3 to 10^5 mPa·s and provided shear-thinning behavior without affecting the curing kinetic. It was found that the ink was not printable using the direct printing approach, but using DECMA, several parts (i.e., cuboids, adjoining lines, parallel lines, and honeycomb) were successfully printed. Additionally, 3D-printed parts could easily be machined, thereby showcasing potential for hybrid manufacturing.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c05587.

Setup and additional characterization of sawdust and lignin and additional SEM of the composites (PDF)

AUTHOR INFORMATION

Corresponding Author

Jukka V. Seppälä – Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland; Email: jukka.seppala@aalto.fi

Authors

Jon Trifol – Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland; © orcid.org/ 0000-0001-9447-1089

Siddharth Jayaprakash – Department of Mechanical Engineering, School of Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland

Hossein Baniasadi – Department of Chemical and Metallurgical Engineering, School of Chemical Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland; orcid.org/0000-0002-0463-337X

Rubina Ajdary – Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland

Niklas Kretzschmar – Department of Mechanical Engineering, School of Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland

Orlando J. Rojas – Department of Bioproducts and Biosystems, School of Chemical Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland; Bioproducts Institute, Departments of Chemical and Biological Engineering, Chemistry and Wood Science, University of British Columbia, Vancouver, British Columbia V6T 1Z3, Canada

Jouni Partanen – Department of Mechanical Engineering, School of Engineering, Aalto University, FIN-00076 Aalto, Espoo, Finland

Complete contact information is available at: https://pubs.acs.org/10.1021/acssuschemeng.1c05587

Author Contributions

[⊥]J.T. and S.J. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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