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Novel Materials Can Radically Improve Whole-System Environmental Impacts of Additive Manufacturing

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Highlights

- Novel compostable / biodegradable, low-cost materials were 3D printed and assessed.
- The materials reduced printing energy 75% by bonding chemically.
- Embodied material impacts were 82% less than ABS plastic in ReCiPe Endpoint H pts.
- Material strength and print quality did not equal ABS; more research is required.

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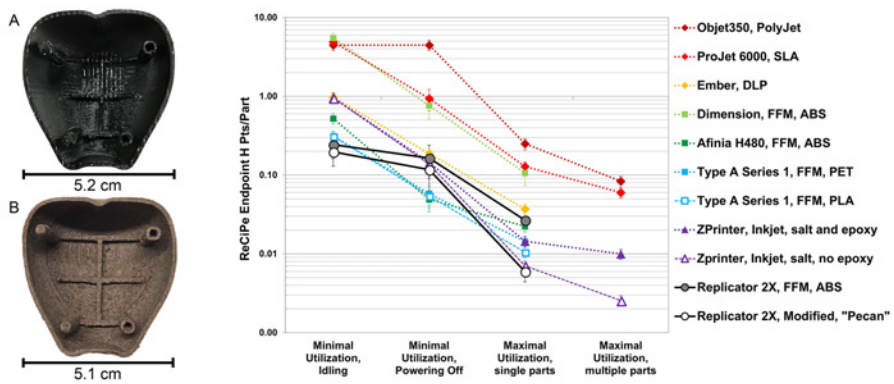
Abstract

Additive manufacturing often has higher environmental impacts per part than traditional manufacturing at scale, but new materials can enable more sustainable 3D printing. This study developed and tested novel materials for paste extrusion printing, and tested materials invented by others. Testing compared their whole-system environmental impacts to standard ABS extrusion, measured by life cycle assessment (LCA); testing also assessed material strength, printability, and cost. Materials were chosen for low print energy (chemical bonding, not melting), low toxicity, and circular life cycle (biodegradable, ideally sourced from waste biomaterial). Printing energy was reduced 75% (from 160 to 40 Wh/part), and embodied impacts of materials were reduced 82% (from 6.6 to 1.2 ReCiPe Endpoint H millipoints/part). Overall impacts per part were reduced 78% (from 27 to 6 ReCiPe Endpoint H millipoints/part), including embodied impacts of the printer itself, in a maximum utilization scenario. Results were also compared to previous studies of seven different 3D printers of various types. More than ten material recipes were tested, and pecan shell flour with sodium silicate showed the best print quality. Strength and print quality did not approach ABS, but material cost was cut by 50%. Thus, while further development is required, some materials show promise for greener additive manufacturing.



Keywords

Sustainable Additive Manufacturing; Green 3D Printing; 3D Printing Materials; Manufacturing Energy Efficiency; Industrial Ecology.

1. Introduction

Additive manufacturing (AM) is increasingly popular for manufacturing parts with complex geometries, product customization, small batch production, and prototyping. The use of AM for final part production has risen significantly since 2003, exceeding 50% of the market in 2015, and 60.6% in 2016 (Wohlers and Campbell, 2017). As the AM industry grows, analyzing and improving its environmental impacts is essential to help guide development of more sustainable manufacturing; researchers can benchmark, set priorities, and show industry what is possible.

Previous research has quantified the environmental impacts of AM, but most studies only investigate single issues, primarily printing energy use: Mognol et al. (2006) measured the power usage of three rapid prototyping systems; Baumers et al. (2011a) quantified the electricity use of two selective laser sintering (SLS) platforms and compared energy use across various major AM systems (2011b). Telenko and Seepersad (2012) compared the energy consumption of SLS to injection molding (IM) for nylon part fabrication. Sreenivasan and Bourell (2010) measured the power breakdown for SLS of Nylon-12 on two platforms. Not all studies target energy: Ford and Despeisse (2016) showed the material savings through waste reduction in laser material deposition. Toxicity of AM materials and particulate emissions have also been studied: Merlo et al. (2015) quantified the gaseous and nanoparticle emissions during fused filament modeling (FFM); Kwon et al. (2017) also characterized nanoparticle emission from FFM printers and tested control methods. House et al. (2017) studied respiratory problems associated with emissions from 3D printing. Yang and Li (2018) estimated the total volatile organic compound emission during stereolithography (SLA).

A few studies go beyond single issues, weighing energy use against toxicity or resource depletion, or including the materials and energy required to produce AM machines. This more comprehensive approach to AM impacts was first demonstrated by Luo et al. (1999) using the EcoIndicator single-score LCA method. Later, Kellens et al. (2011) used ReCiPe Endpoint H/A Europe LCA points to weigh multiple environmental impacts of an SLM machine against one another. Continuing in this vein, Faludi et al. (2015a) used ReCiPe Endpoint H/A World points to measure and compare impacts among a CNC mill and two AM machines; Faludi et al. (2015b) also compared impacts among several polymer-printing AM machines and metal printing (Faludi et al., 2016). These studies found printing energy to be the largest environmental impact of AM. While material impacts are smaller, the material choice determines printing process energy demand to a large extent (Faludi et al., 2015b): thermoplastics must be heated, photopolymers must be exposed to light, and so on.

Several "green" materials have been experimented with for AM. Kayser's "Solar Sinter" used sand, fused into glass by sunlight concentrated through a lens (Fateri et al., 2015). Klarenbeek and colleagues printed PLA bioplastic with a filler of mushroom mycelium growing in straw to create furniture (Fairs, 2013). The MIT Media Lab's Mediated Matter group's water-based robotic fabrication (Mogas-Soldevila et al., 2014), extruded biodegradable polysaccharides like chitin and sodium alginate that solidify at room temperature. Panda et al. (2017) developed a fly ash-based geopolymer mortar for extrusion-based printing as a green building material. Tran and colleagues (2017) fabricated biofilaments based on cocoa shell waste, a byproduct of the chocolate industry, for FFM printing at low temperature. Von Hasseln (2017) experimented with novel materials like sugar and dehydrated powdered fruit for 3D printed architecture. Rael and San Fratello (2018) produced several alternative AM material recipes for architecture based on locally available resources like sawdust, sand, clay, and salt, discussed later.

However, the "green" material experiments above have not quantified the impacts of their print energy or materials to demonstrate environmental improvement, nor have they quantified mechanical performance or cost to demonstrate market viability. This research extends previous studies by not only creating novel print materials, but also quantifying their whole-system environmental impacts, material strength, and material cost, as well as comparing the results to other AM materials and processing. Most 3D printing materials used for prototyping and manufacturing are thermoplastics, such as ABS, PLA, and PA12 (nylon), followed by thermoset resins that provide high detail and a variety of material properties (Wohlers and Campbell, 2017). As mentioned above, these material choices determine printing energy, the largest impact of AM; these materials are also often unrecyclable at end of life, often with toxicity from fine particles emitted during printing. Therefore, alternative materials should enable low-energy printing, circular economy material flows, and protect the health of workers, customers, and communities.

To address these priorities for sustainability, this research aimed to create radical improvements by 1) printing materials that bond or solidify at room temperature and pressure, for low-energy printing; 2) printing compostable biomaterials (ideally agricultural waste) for a circular economy; and 3) printing non-toxic materials. Ideally the materials would also mimic the mechanical properties, high finish quality, and low cost of ABS plastic, to be market-viable. Specifically, some materials tested included pine and oak sawdust, orange peel, rice starch, sugars, nanocellulose, sodium silicate, polyvinyl alcohol (PVA), cyanoacrylate (biodegradable, though not considered compostable due to slight toxicity concerns), and EcoPoxy (a bio-based epoxy, not considered compostable). The most promising results came from sodium silicate and pecan shell flour, a waste product from the pecan industry.

2. Methods

This section describes the procedure for assessing alternatives: print material formulations, printer modifications, printing process, mechanical tests, and LCA, as shown in Figure 1.

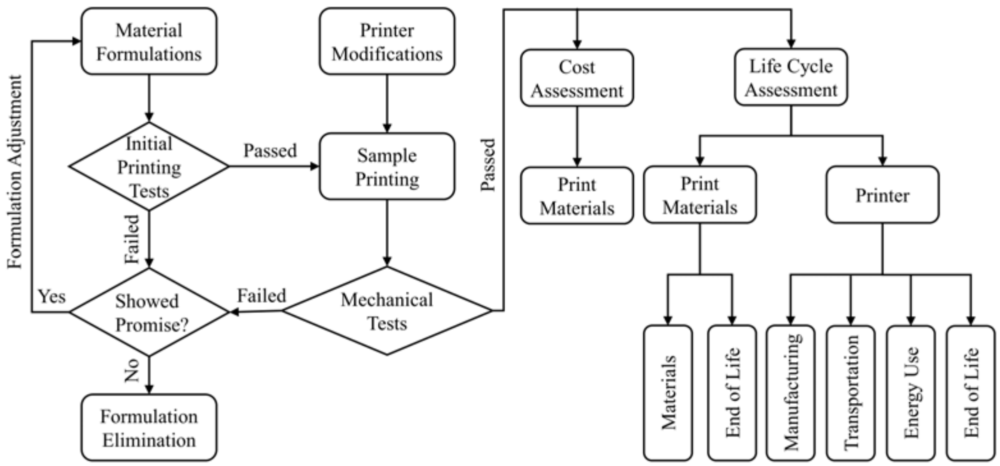


Figure 1. A flowchart of methods for material formulation and assessment.

2.1. Material Recipes

Figure 2 shows various materials tested; all were selected to avoid energy-intensive processes like heating, using compostable biomaterials, minimizing toxicity and cost, and ideally reusing waste. All recipes were pastes or gels comprising a filler bonded by a liquid matrix, solidifying through water evaporation or cross-linking reactions during and after printing. Some ingredients could act as either filler or matrix, depending on other ingredients. Early recipes replicated work by others to test mechanical properties, printability, and print quality, because of the lack of published data mentioned earlier. For example, the rice flour recipe was inspired by a powder bed printing recipe of Mark Ganter (2011); he also inspired the ingredient sodium silicate ("water glass"). Sawdust recipes were inspired by Ronald Rael (Rael and San Fratello, 2018); Ulrike Wegst suggested nanocellulose. Novel formulations were created later for originality, and to achieve better mechanical and environmental performance.

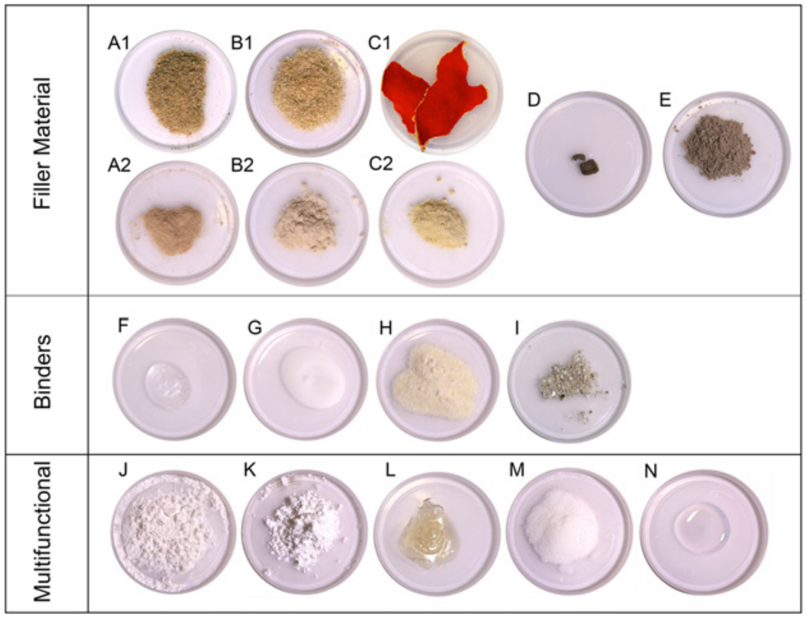


Figure 2. Recipe ingredients. Filler materials: oak sawdust, as purchased and filtered to 0.125 mm grain size (A1, A2); pine sawdust, as purchased and filtered (B1, B2); orange peel, whole and powdered (C1, C2); nanocellulose fibrils, dried (D); pecan shell flour (E). Binders: Sodium silicate liquid (F); polyvinyl alcohol (G); pine rosin powder (H); cyanoacrylate, dried with sediment (I). Multipurpose materials: superfine white rice flour (J); confectioners' sugar (K); gelatin (L); wheat dextrin (M); glycerin (N).

Table 1 lists ten variations of the three most notable recipes; others are omitted due to space limitations. Variations included different ingredients and different ratios of the same ingredients. The cyanoacrylate and epoxy variants were post-print treatments, due to difficulties printing with them.

Table 1. Three most notable recipes, with variants.

Recipe Name		Ratio multiples (unit)	Ingredient
Rice Flour Recipes	**"Rice+Wine"**	4.5x (g)	Superfine white rice flour
		1x (g)	Wheat dextrin
		1x (g)	Confectioners' sugar
		2.5x (ml)	Rice cooking wine
	"Rice+IPA"	4.5x (g)	Superfine white rice flour
		1x (g)	Wheat dextrin
		1x (g)	Confectioners' sugar
		2.5x (ml)	91% Isopropyl alcohol (IPA) and distilled water in 1:3 (volume)
	"Rice+NCF"	4.5x (g)	Superfine white rice flour
		1x (g)	Wheat dextrin
		1x (g)	Confectioners' sugar
		2.9x (ml)	2.1% Nanocellulose Fibrils (NCF) and 91% IPA in 3:1 (volume)
Pecan Shell Flour Recipes	**"Pecan"**	7x (g)	Pecan shell flour
		10x (g)	37% Sodium silicate liquid
	"Pecan+Oak"	7x (g)	Pecan shell flour
		10x (g)	37% Sodium silicate liquid
		0.5x (g)	Oak sawdust, 0.125 mm grain size
	"Pecan+Pine"	7x (g)	Pecan shell flour
		10x (g)	37% Sodium silicate liquid
		0.5x (g)	Pine sawdust, 0.125 mm grain size
	"Pecan+Epoxy"	Coating on "Pecan" prints	EcoPoxy by Entropy Resins
	"Pecan+Cyanoacrylate"	Coating on "Pecan" prints	Cyanoacrylate
Sawdust Recipes	**"Oak"**	1x (g)	Oak sawdust, 0.125 mm grain size
		7x (g)	37% Sodium silicate liquid
	"Pine"	1x (g)	Pine sawdust, 0.125 mm grain size
		10x (g)	37% Sodium silicate liquid

2.2. Printing Tests

Each recipe was first tested by hand extrusion and casting, followed by 3D printing if initial tests were promising. In initial tests, materials were mixed into a paste and extruded by hand through a syringe onto an acrylic surface to test flow behavior, self-adhesion and ability to self-support. Those performing well were then cast as an ASTM D638-14 Type IV dog bone in a silicone mold for material strength testing. Observations of cracking, curling or breaking also informed material choice, as they often occurred while pastes dried in the mold. Recipes failing initial tests were adjusted or eliminated from further consideration. Recipes that passed were then 3D printed into 30% infilled rectangular cuboids with two top/bottom surface layers, and 100% infilled ASTM D638-14 Type IV dog bones, both for mechanical testing. The final top-performing recipe was printed into a 100%-infilled thin-walled apple part with a single shell layer; this was the reference part for LCA and cost analysis. Support material was included where the part geometry exceeded a 60-degree overhang.

2.3. Printer Modifications

All parts were printed in a MakerBot Replicator 2X printer, which was first used to print in ABS and then modified to extrude pastes pneumatically rather than melt plastic filaments. The original extruder assembly equipped with two filament extruders was replaced with a custom assembly featuring a 3D printed ABS syringe mount and a 10cc syringe barrel with a pneumatic adapter. The syringe tip was 0.58 mm or 0.84 mm inner diameter, depending on the paste and desired results. A solenoid valve was added in-line with facility air, and an electronic valve control circuit replaced the original BotStep extruder driver. Finally, a 3.6 W fan was added to help dry materials during printing, and the enclosure panels and lid were removed to enhance air flow. Facility air was provided by a 5.6 kW screw-type compressor with 150 max psi (10.34 bar) at the tank, regulated to 90 psi (6.20 bar) at the network. Air pressure settings varied from 0.55 to 3.31 bar depending on the print material and the tip size.

MakerBot Desktop 3.10.1 software was used to operate the modified machine and create printing paths, adjusting layer thickness and printing speeds to accommodate material properties. Custom print profiles were created for printing at 0.4 mm layer height and 0.8 mm line width, at a consistent speed of 20 mm/s when using a 0.84 mm diameter extrusion tip. For smaller 0.58 mm tips, print profile settings were 0.3 mm layer height, 0.6 mm line width, and 30 mm/s speed across all features.

2.4. Mechanical Tests

Compression and tensile tests were performed to ASTM standard D638 with an Instron Universal Mechanical Test Frame model 4469, with 10mm/min and 3mm/min crosshead speed, respectively.

2.5. Environmental Impact Assessment

LCA was conducted in SimaPro 8 software with data from the EcoInvent 3 database. Seventeen different ecological impacts were assessed and integrated into unified single-scores using the ReCiPe v1.12 World H/A methodology (Goedkoop et al., 2009). The scope is shown in Table 2; it excludes the use phase of printed parts, because it is assumed the prints would be used for general prototyping or other passive uses where impacts would be equivalent to printed plastic parts. Transport of print material was not considered, to keep consistency with earlier research (Faludi et al., 2015b). Machine impacts were amortized over the number of total parts that the machine is capable of printing in its lifetime; this lifetime was assumed to be five years, again in keeping with earlier studies.

Table 2. LCA scope.

Scope Category	**Coverage**
Print Material	Raw material extraction, processing (including filament extrusion), and end of life for material in printed part.
Print Waste	Raw material extraction, processing (including filament extrusion), and end of life for support material.
Replicator 2X Printer	Raw material extraction and processing of all materials comprising the printer, amortized per printed part.
Printing Process	Electricity use while starting up and printing; for certain low utilization scenario, this includes idling; for maximum utilization scenario, this includes tool changing, all amortized per printed part.
Printer Transport	Transportation of components comprising the printer from manufacturing sites to Dartmouth College, amortized per printed part.
Printer End of Life	Disposal of the printer, amortized per printed part.

To provide a realistic measure and an apples-to-apples comparison with previous LCAs, the functional unit was the ecological impact per part printed, for a specific reference part representing typical 3D printer use. Figure 3 shows a photograph of the ABS and "Pecan" prints. While the pecan print was successful, quality problems are visible: thicker walls caused by lower resolution, and the four cylindrical bosses lacking crisp definition.

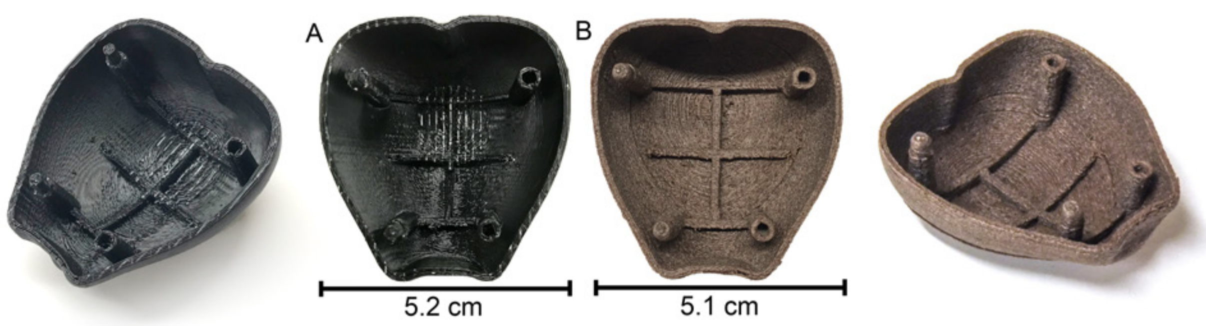


Figure 3. Thin walled apple part, (A) printed in ABS FFM by the standard Replicator 2X; (B) printed in "Pecan" paste extrusion by the modified printer.

2.6. Print Material and Waste

Only the "Pecan" recipe was used for LCA, due to its good printing performance. Amounts of print material and waste were determined by weighing them. Leftover material in syringes was not counted as waste because it would be used for subsequent prints in production. To model environmental impacts per gram of material use and waste, sodium silicate was available in the EcoInvent database; pecan shell flour was not, so a model of it was created based on research into its composition and processing. According to Nizio (2016), pecans in the shell are washed in ambient temperature water and then submerged in hot water for sanitation. Shells are a waste product, but are cracked, separated and ground into flour to sell as supplementary income. Because of the lack of EcoInvent data, sensitivity analyses of several comparable database items were made. Cellulose and lignin materials in the database were combined as a substitute for pecan shell because they are two major components in natural pecan shells (Nizio, 2016). The amount of washing water per kg of pecan shells and water temperatures were acquired from personal communication with the Southeastern Reduction Company. Washing and milling processes were modeled using "Washing, cold water/US", "Washing, hot water, 48 C/US", and "Milling, feed, at factory/US U". Multiple lignin materials and drying processes from the database were compared; choices with the highest and lowest impacts were used to model worst and best cases. The worst case represents an impact estimate that likely doubles processing impacts, as the database item used to represent lignocellulosic materials in this scenario already includes some processing. End of life for sodium silicate and pecan shell flour in printed parts and material wastes was modeled with "Compost {GLO}| market for | Alloc Rec, U".

2.7. Printer Manufacturing

A bill of materials (BOM) was not available for the Replicator 2X, so parts were measured to the greatest accuracy achievable without risking damage to the machine, a method developed by Diaz et al. (2010). Parts were removed and weighed where possible; some parts are the same as a previous version of the printer whose BOM and affiliated SolidWorks model files are available online (Thingiverse.com, 2012); these were used to determine exact part volumes and masses. Others were measured with calipers or rulers to determine their physical dimensions, their volumes calculated, and their masses determined using standard densities of materials (Engineering ToolBox, 2009). For composite or "black-box" components, specifications were referenced from manufacturers of similar, if not identical, parts, including cartridge heaters used in the two extruders (Watlow, 2013) and a silicone heating component used for the heated build plate, for which a silicone heater datasheet (Keenovo International Group Ltd., 2017) and standard flexible heater specifications (Tempco Electric Heater Corp., 2015) were referenced.

To check the accuracy of these estimations, the total calculated weight was compared to the actual weight listed by MakerBot Industries. An error of only 2.5% above the listed mass was found, so no further adjustments were deemed necessary.

Manufacturing processes for machine parts were determined based on materials, surface finish, the presence of tooling marks, and knowledge of common manufacturing methods. When a part appeared to require multiple processes, or the process could not be determined, an EcoInvent "average" of production processes was used. Motors were estimated to comprise 11% copper wire processed by "Wire drawing, copper {GLO}| market for | Alloc Def, U", 3% neodymium magnet using "Permanent magnet, for electric motor {GLO}| market for permanent magnet, electric passenger car motor | Alloc Def, U", and 85% steel using "Steel, low-alloyed {GLO}| market for | Alloc Def, U" processed by "Metal working, average for steel product manufacturing {GLO}| market for | Alloc Def, U".

To calculate impacts of the modified printer, all parts of the original extruder assembly, build chamber enclosure, build plate heater, insulation, and affiliated electronics were excluded. The weight of the main board was reduced by 15% to account for reductions in heating components, sensors, and temperature control circuits. Further precision was deemed unnecessary, because the machine impacts were not dominant in most scenarios.

2.8. Printer Transportation and End of Life

Transportation impacts for machine components were calculated for assembly occurring in Brooklyn, NY. Based on personal knowledge of MakerBot supply chain, electronics were modeled as shipped by air freight from Japan and all other components were trucked from a representative US Midwest location (Dayton, Ohio) to Brooklyn. This is a high estimate: some electronics likely came from southern China via ocean freight with lower impacts. Trucking was then measured from Brooklyn, NY to Hanover, NH for delivery to the end user at Dartmouth College. Transport packing utilization was assumed to be low because of 3D printers' relative rarity (Faludi et al., 2016), so transportation impacts were doubled by doubling distances. Unknowns about package sorting facilities/networks, multi-stop trucking, etc. were considered included in this overestimate. Due to the very low percentage of impacts from transportation in all scenarios, further precision was considered unnecessary.

End of life for the entire machine was conservatively assumed to be landfill, using the EcoInvent process "Municipal solid waste (waste scenario) {RoW}| Treatment of municipal solid waste, landfill |

Alloc Def, U". Since this was also a small percentage of overall impacts in all scenarios, further specificity was not sought.

2.9. Printing Energy Use

Electricity use was measured with the WattsUp Pro ES power datalogger and modeled as average US electricity grid mix. The manual removal of printed parts from the build platform with a razor blade or paint scraper did not consume electrical energy. Energy use from compressed air was modeled as "Compressed air, average installation, >30kW, 6 bar gauge, at supply network/RER S"; the volume of compressed air used was equal to that of material extruded, as there were no evident leaks.

2.10. Modeling Utilization Scenarios

Machine utilization can radically change the amortized ecological impacts per part. In this research, three utilization scenarios were defined based on different operation patterns. The scenario "Maximum utilization" modeled printing parts for 24 hours per day and 7 days per week, excepting 10% of the machine's lifetime for maintenance and repairs. The scenario "Minimum utilization, idling" modeled printing one part per week and sitting idle, powered on, the rest of the time. The scenario "Minimum utilization, powering off" modeled printing one part per week and turning the machine off the rest of the time.

2.11. Uncertainty

Uncertainties of ±10% are typically the best case for environmental impact data (Ashby, 2012), so uncertainties in this study began with that baseline and grew when measuring or modeling uncertainty also existed, summarized in Table 3. Electricity use, ABS material use, and ABS waste were measured empirically with less than 1% uncertainty, therefore their impacts were assumed to have the baseline ±10% uncertainty. "Pecan" material uncertainty was calculated at ±49% based on the difference between best and worst cases modeled (see Results section). Machine transportation, compressed air, and end of life were assumed to be ±100% uncertain due to them being estimated rather than empirically measured; however, even these high errors would still make them negligible among overall impacts, so further precision was not sought. Uncertainties of machine hardware impacts were based on a previous study (Faludi et al., 2016): motors and wiring were assumed to have ±30% uncertainty due to estimation of material ratios; electronics were assumed to be ±60% uncertain due to modeling estimation; steel, brass, aluminum, plastic, and miscellaneous items were treated with an uncertainty of ±15% because measurement by physical dimensions instead of actual weighing might introduce error, though total calculated machine mass was within 2.5% of manufacturer specification.

Averaging those uncertainties with weighted contributions in ReCiPe Endpoint H points gave an uncertainty of ±42% for overall standard machine manufacturing, and ±43% for overall modified machine manufacturing (see Results for graph). The overall uncertainty of printing ABS in the standard printer was ±39% in low utilizations and ±12% in maximum utilization; printing "Pecan" in the modified printer had an overall uncertainty of ±42% in low utilizations and ±26% in maximum utilization. Though some uncertainties were high, this level of precision was adequate to show clear differences between scenarios for this printer, and to compare to others.

Table 3. Data sources and uncertainties of LCA impacts by category.

Item Category		**Data Source**	**Uncertainty**
Material Use and Waste	"Pecan" recipe	Measured, manufacturer data, literature (Nizio, 2016)	±49%
	ABS	Measured	±10%
Electricity Use		Measured	±10%
Transport of Machine		Calculated	±100%
End of Life		Assumed	±100%
Compressed Air		Assumed	±100%
Machine Hardware	Standard printer overall	(see below)	±42%
	Modified printer overall	(see below)	±43%
	Structural framing & other (steel, brass, aluminum, glass, plastic, etc.)	Dimensions	±15%
	Motors and wiring	Dimensions and specification sheets	±30%
	Electronics	Dimensions and specification sheets	±60%

2.12. Comparison to Previous Studies

Using previous LCAs (Faludi et al., 2015a, 2015b), the standard and modified Replicator 2X in this study were compared to eleven scenarios of seven other polymer-printing machines, printing various materials. These included three other FFM machines (the Dimension BST 1200 by 3D Systems printing ABS, the H480 by Afinia printing in ABS, and the Series 1 by Type A Machines printing in PET and PLA); three machines using ultraviolet light-activated thermoset resins (the Objet Connex 350 by Stratasys printing Fullcure 720, the ProJet 6000 by 3D Systems printing Accura "ABS White" SL 7810, and the Ember by Autodesk printing CPS 4D); and a 3D inkjet printer (the ZPrinter 310 by Zcorp modified to print with salt, developed by Ronald Rael in two variants: infused with epoxy in post-processing or not).

3. Results

This section first describes material strength and print quality of top-performing recipes. Then it describes environmental impacts of the recipe with best overall performance, comparing it with an ABS print from the unmodified printer and eleven different prints of the same object from the seven types of printers listed in Methods.

3.1. Material Strength, Printability and Print Quality

None of the prints achieved material strength or print quality comparable to ABS plastic, though some achieved quality acceptable for simple prop prototyping. Figure 4 shows results of several compression tests of half-cube molds/prints and tensile tests of dog bone prints. Table 4 shows ultimate strengths of both tests. See Table 1 for abbreviations used in them.

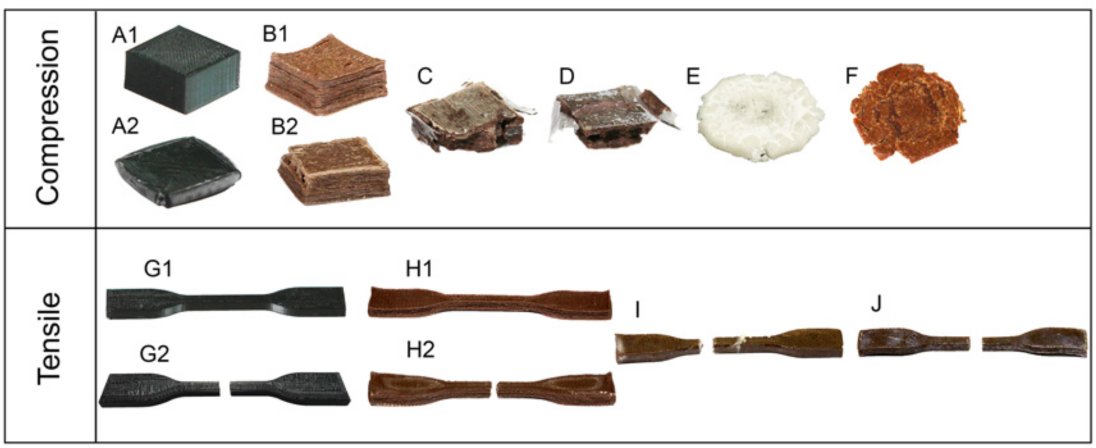


Figure 4. Compression tests on half-cubes: printed ABS before and after (A1, A2); printed "Pecan" before and after (B1, B2); "Pecan+Cyanoacrylate" after (C); "Pecan+Epoxy" after (D); molded "Rice+IPA" after (E); molded "Oak" after (F). Tensile tests on dog bones: printed ABS before and after (G1, G2); printed "Pecan" before and after (H1, H2); "Pecan+Epoxy" after (I); "Pecan+Cyanoacrylate" after (J).

Figure 4 shows some ductility in samples, since they squashed rather than shattered in compression, but they exhibited no necking in tensile tests, so they were largely brittle. "Pecan" parts were produced at half the resolution of ABS prints and had poorer surface finish, because of trade-offs between print parameters (line diameter, layer height, etc.) and print time/energy: thinner lines and layers cause longer print time and higher energy.

Table 4. Ultimate material strengths. Values determined from literature: [a] (MatWeb, n.d.), [b] (Engineering ToolBox, 2003). Values unable to be measured: [c] cracked while drying, [d] shrank and curled while drying, [e] unable to print.

Recipe	**Compressive strength of half-cube (MPa)**		**Tensile strength of dog bone (MPa)**	
	Molded, 100% infilled	**Printed, 30% infilled**	**Molded, 100% infilled**	**Printed, 100% infilled**
ABS	53[a]	37.5	40[b]	30.5
“Rice+Wine”	12.3	5.6	N/A[c]	N/A
“Rice+IPA”	116	10.0	N/A[c]	N/A
“Rice+NCF”	74.1	N/A[d]	N/A[d]	N/A
“Pecan”	4.5	5.8	3.3	9.0
“Pecan+Epoxy”	N/A	4.3	N/A	7.5
“Pecan+Cyanoacrylate”	N/A	5.1	N/A	5.1
“Pecan+Oak”	4.9	7.9	4.5	4.7
“Oak”	68.6	N/A[e]	11.8	N/A[e]

Table 4 shows that among all recipes, “Rice+IPA” achieved the highest compressive strength of molded 100%-infilled and printed 30%-infilled half-cubes; “Pecan” achieved the highest tensile strength of printed 100%-infilled dog bones. Some recipes were unable to print, or cracked or deformed while drying; several attempts to fix the latter problem were unsuccessful. “Pecan+Epoxy” and “Pecan+Cyanoacrylate” were not tested molded because they were coatings applied to the already-successful “Pecan” prints.

The “Rice+IPA” recipe showed promise in hand extrusion tests, but slumped under the weight of successive layers in print tests. The extrusion pressure was 2 bar, over twice that of “Pecan”, and prints took at least two days to dry at ambient temperature despite their alcohol component. Despite exhibiting the highest compressive strength, samples always cracked when drying, hindering tensile tests. The “Rice+NCF” was also relatively strong; however, samples shrank dramatically upon drying, ending at 1/4 the size of the original part, due to NCF’s high water percentage. Those were therefore excluded from further testing.

“Pecan” was promising in both print quality and strength. The paste showed good self-adhesion, extrusion continuity, and flowability during printing, the latter credited to the rounded oval-shaped cells called sclereids in pecan shell; this enabled a low extrusion pressure (0.7 bar). Each layer dried quickly under a fan and supported subsequent layers without slumping. Molded samples gave poorer strength than printed ones, perhaps because of different drying process: molded samples dried in the mold over several days, while printed samples dried layer by layer during printing, ensuring the internal structure was completely dry. "Pecan+Epoxy" and "Pecan+Cyanoacrylate" showed poorer strengths, presumably because uneven diffusion and low permeability into the print surfaces (visible in Figure 4) caused stress concentrations.

"Oak" achieved high strengths in casting, but its elastic stretching during extrusion resulted in uneven deposition and failed print tests. The "Pecan+Oak" paste gradually hardened inside the syringe during printing, even at loads of oak as low as 3% by weight. This created inconsistent extrusion that required increasing pressure from 1 to 1.4 bar, causing discontinuously printed lineas.

Other materials tested were not considered good candidates for printing. Extruding pine sawdust with PVA resulted in a separation of liquid and solid components. Sodium silicate combined with orange peel powder formed a rubbery paste and brittle solid, since alcohols in orange peels crosslinked the sodium silicate to form an elastomeric polymer (Borgford and Summerlin, 1988). Blending sodium silicate and rice flour produced a taffy-like material, where rice starches gelled in the alkaline environment (Rashid et al., 2012).

3.2. Cost of Materials

For all recipes, the cost of materials used to print the apple part compared quite favorably to standard ABS filament, as follows:

- MakerBot ABS filament: $0.72
- "RF+Wine": $0.37
- "RF+IPA": $0.23
- "Pecan": $0.36
- "Pecan+Oak": $0.39
- "Oak": $0.58

Note that aside from ABS, these prices were for small amounts of material purchased retail; their cost would be even lower at industry scale. It is encouraging that most recipes are already roughly half the price of ABS filament.

3.3. Environmental Impacts

As described in Methods, LCA quantified environmental impacts per part printed using two methods: embodied energy in MJ to provide simplicity and precision, and ReCiPe Endpoint H/A World points to provide a comprehensive single score that measures seventeen kinds of environmental impact, including climate change, acidification, ecotoxicity, mineral depletion, land use, etc. Figure 5 shows embodied energy in MJ for three scenarios: “low utilization, off” (printing one part per week, turning the printer off between prints), “low utilization, idling” (printing one part per week, leaving the printer on between prints), and “maximum utilization” (printing 24 hrs/day for the entire life of the printer, minus 10% maintenance / repair time).

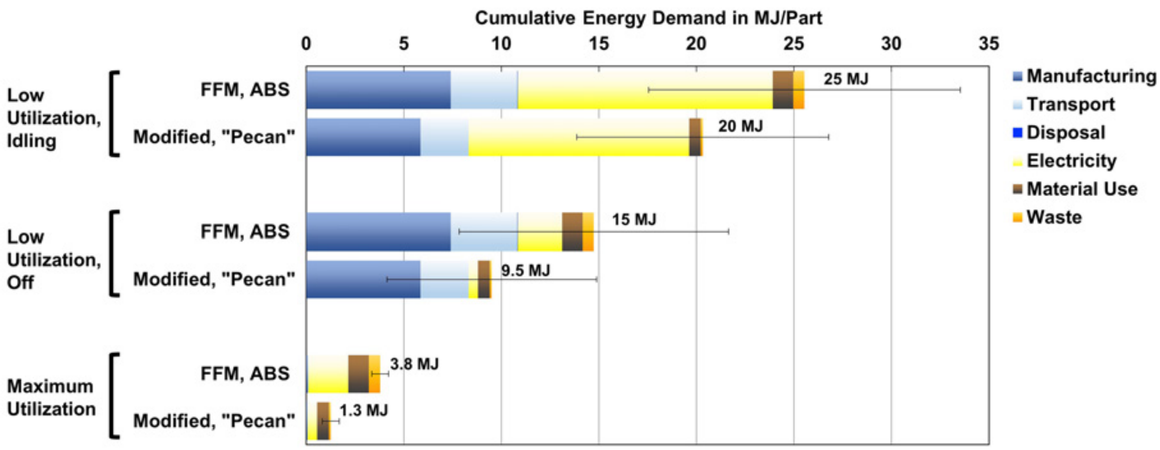


Figure 5. Embodied energy per part for the standard and modified Replicator 2X printing ABS and “Pecan” respectively, compared in three utilization scenarios. Error bars show accumulated error for all life cycle stages.

Figure 5 shows that at maximum utilization, the modified Replicator 2X printing “Pecan” reduced embodied energy per part by 67% compared to the standard machine printing FFM ABS, largely due to printing energy reduction. When printing in ABS, the printer heats filament to 230°C and the build plate to 110°C inside of an enclosed build chamber to prevent ambient temperatures from cooling parts too quickly and warping them. Ingredients in “Pecan” instead bonded chemically, requiring no heating energy, but required a solenoid valve to control compressed air for extrusion, and a fan to quicken the drying of extruded paste. Compressed air generation accounted for a minuscule percentage ($\sim 4.3 \times 10^{-5}$) of overall printing impacts. Thus, in total, modifying the printer and switching materials cut printing energy from 0.16 kWh for ABS to 0.04 kWh for “Pecan” paste (a reduction of 75%). The materials also had less embodied energy (from 1.04 MJ/part to .59 MJ/part, a 44% reduction), and the modified printer had fewer parts than the standard printer, reducing machine embodied energy 30%. For discussion of material and machine embodied impacts, see Material Details and Machine Embodied Impacts sections.

Figure 5 also shows that at “low utilization, off”, the modified printer and green material only reduces embodied energy by 35%, because the impacts of building the printer are not well amortized by the production of more parts. At low utilization and idling (left on between prints), embodied energy per part is only reduced 20%, because idle energy is similar for the modified and unmodified printers.

Comparing these to other printers printing the same reference part in previous studies provides a larger context for the environmental benefits of new materials enabling low-energy printing. Figure 6 shows a comparison in ReCiPe Endpoint H/A World points (embodied energy in MJ was not available from the previous studies). The two print processes here were compared to seven other printers; the Type A Series 1 and the ZPrinter 310 modified by Ronald Rael were both measured printing two different materials each, for a total of eleven printing methods. Each printer was assessed in the same three utilization scenarios described above, and some printers (not including the Replicator 2X) were capable of printing four reference parts at once in the same print time (thus amortizing energy use and machine impacts by a factor of four). This created a fourth scenario for these printers, “maximum utilization, multiple parts”. Figure 6’s results use conservatively high estimates for material impacts in cases where the uncertainty was significant (the Replicator 2X printing “Pecan”, inkjet printing with salt, PolyJet, DLP, and SLA).

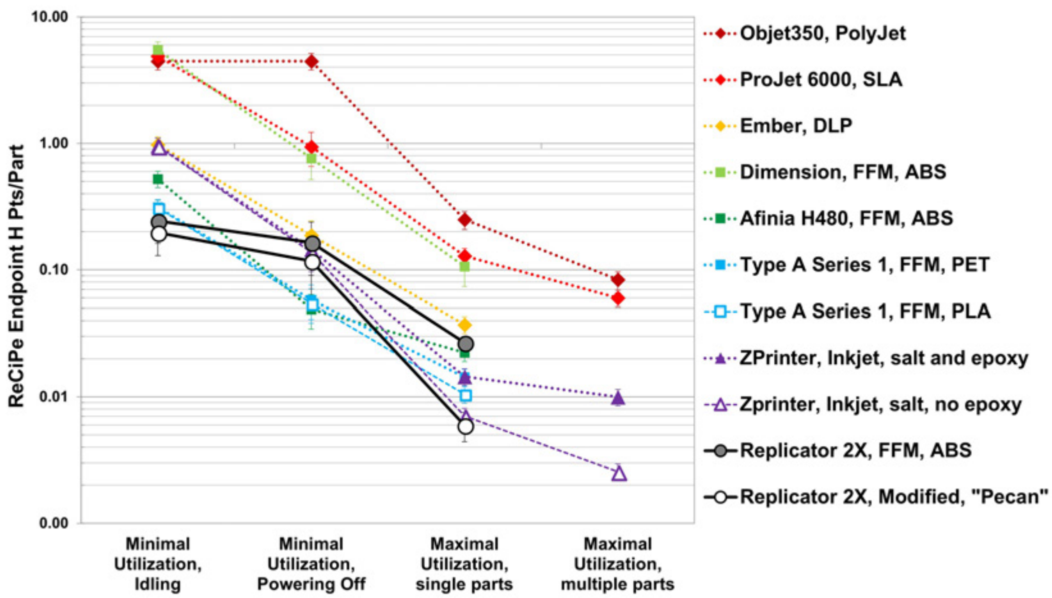


Figure 6. ReCiPe combined-score impacts per part for the standard Replicator 2X, the modified version, and several previously measured AM machines printing different materials, compared in four utilization scenarios.

Figure 6 shows that the modified Replicator 2X printing "Pecan" consistently reduced environmental impacts per part in all scenarios compared to the standard Replicator 2X printing ABS, similar to Figure 5. In the "maximum utilization, single part" scenario, it reduced total impacts 78%; in "low utilization, off" and "low utilization, idling" it reduced impacts 29% and 19%, respectively. It caused the lowest environmental impacts of all printers in the "maximum utilization, single part" scenario, reducing impacts 95% from the highest-impact printer, the Dimension BST 1200 FFM of ABS. This shows that choosing materials that enable low-energy printing processes can indeed reduce whole-system impacts of 3D printing.

However, Figure 6 also shows that the overall lowest impact per part is the ZPrinter printing salt without epoxy infusion in the "maximum utilization, multiple parts" scenario. This shows the power of maximizing utilization to amortize impacts. The power of utilization is also shown in the extremely large difference for all printers between impacts for their maximum utilization scenario and their "low utilization, idling" scenario: often twenty times, in one case forty times. Thus, a key recommendation is that 3D printers should be utilized to the maximum extent possible, with dedicated contract manufacturers performing jobs for many clients, not a 3D printer on every desktop. See Figures 7, 8, and 9 for more details on what causes these differences in impacts, and what life cycle stages are most responsible for impacts. Note also that the MakerBot data in Figures 7, 8, and 9 are the ReCiPe combined-impacts versions of the energy-only impacts in Figure 5.

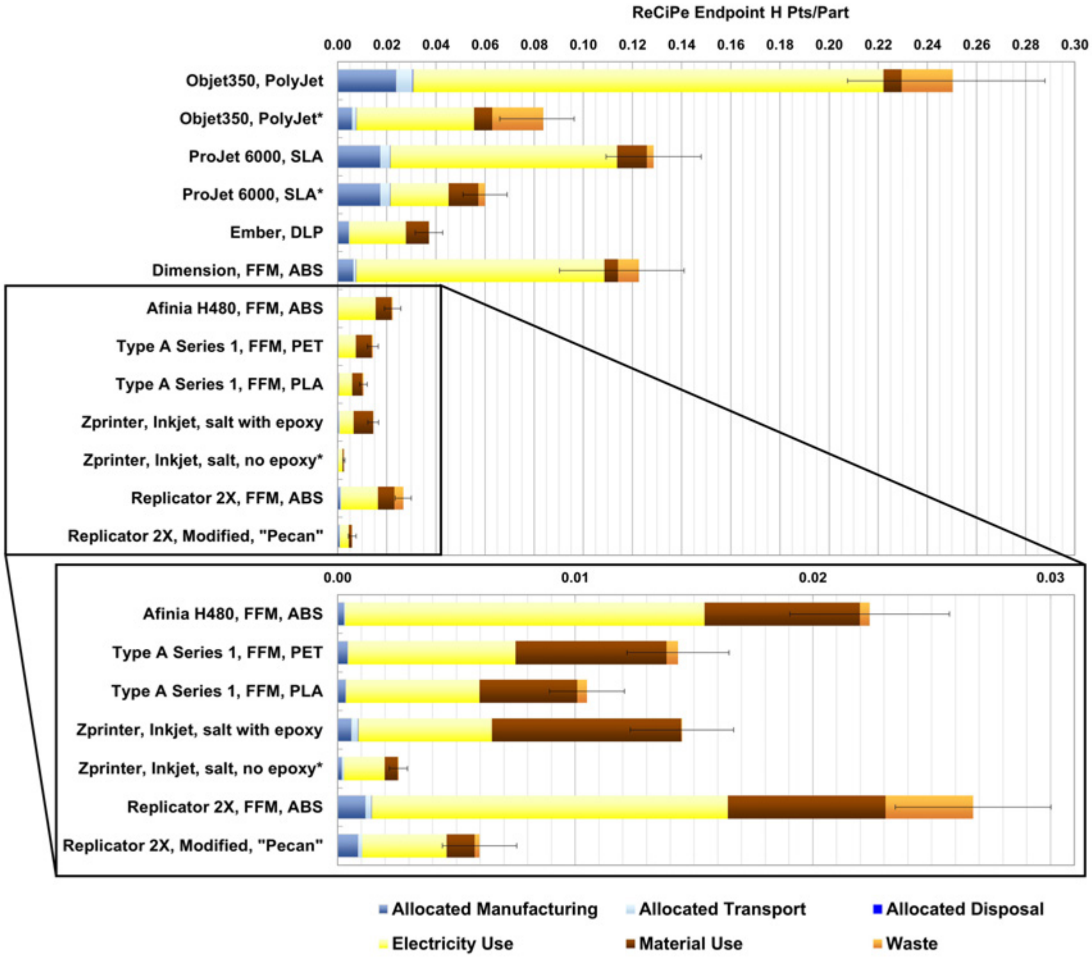


Figure 7. ReCiPe combined-score impacts per part in "maximum utilization, single part" scenario for all studied printers, and in "maximum utilization, multiple parts" scenario for those printers capable of it (denoted by *), broken down by life cycle stage. A detail is shown for low-impact machines.

Figure 7 shows that at maximum utilization, printing energy use was the greatest single impact for all printers, usually followed by material use. As mentioned earlier, switching the Replicator 2X from ABS to "Pecan" reduced printing energy by 75%. Compared to the Afinia H480 printing ABS, it was a similar reduction of 76%, and was 37% less energy than the Type A Series 1 printing PLA. The Series 1 printing PLA used less energy because PLA has a slightly lower melting point than ABS, and also does not use the heated build plate that ABS requires for dimensional stability. Inkjet printing in salt was another low-energy process, since its ingredients bonded chemically. Its efficiency was further improved by its ability to print multiple parts at once with little to no additional energy.

Figure 7 also shows the embodied impact of the “Pecan” material was 82% less than ABS filament material, even using conservatively high estimates for material impacts. This is because pecan shells are agricultural waste, not requiring the mining or as much refining as ABS. “Pecan” also embodied 70% less impact than PLA filament. The only other material with similarly low impacts from a previous study was inkjet printing in salt with no post-processing infusion; since the post-processing binder was an epoxy, its impacts were similar to materials used in SLA, DLP, and photopolymer jetting.

Finally, Figure 7 shows printer manufacturing contributed a small percentage of impacts per part at high utilization, as it is amortized over many parts in the printers’ lifetimes. Machine transportation and end of life were negligible for all printers studied. However, machine impacts were dominant in the scenario “low utilization, off”, shown in Figure 8.

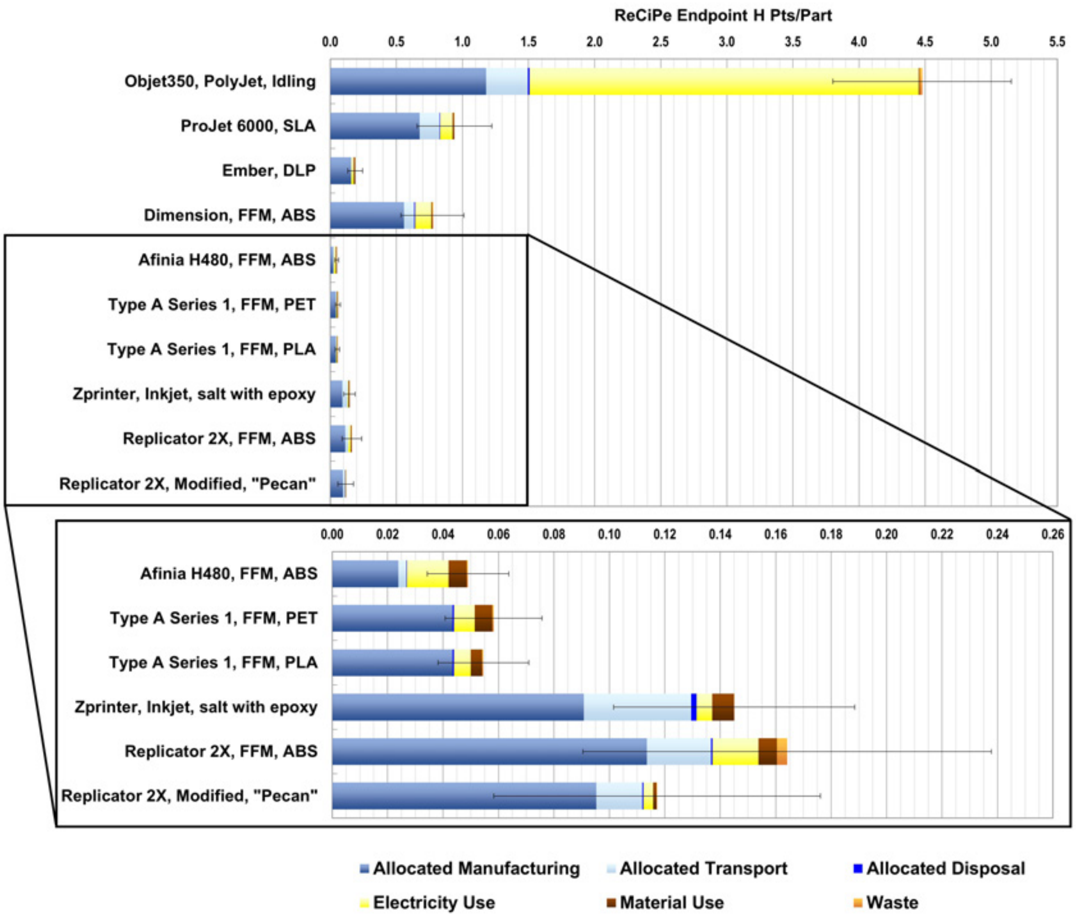


Figure 8. ReCiPe impacts per part in "low utilization, off" scenario, broken down by life cycle stage. A detail is shown for low-impact machines. Note the Objet350 is shown in "low utilization, idling" scenario.

Figure 8 shows that in this low utilization scenario, embodied impacts of the printers are not amortized away adequately, so they become dominant for most printers. This reinforces the point made earlier that for sustainable AM, printers should be shared in centralized locations instead of sitting on every desktop. The Type A Series 1 and Afinia H480 machines had lower embodied impacts than the Replicator 2X because they lack user interface electronics on board, instead relying on the user's computer, which was outside the scope of the LCA. Note that the Objet350 was modeled as idling on, because shutoff requires a fluid purging operation that operators prefer to avoid; users at different companies reported never powering off Objets unless planning to be idle for a month or more.

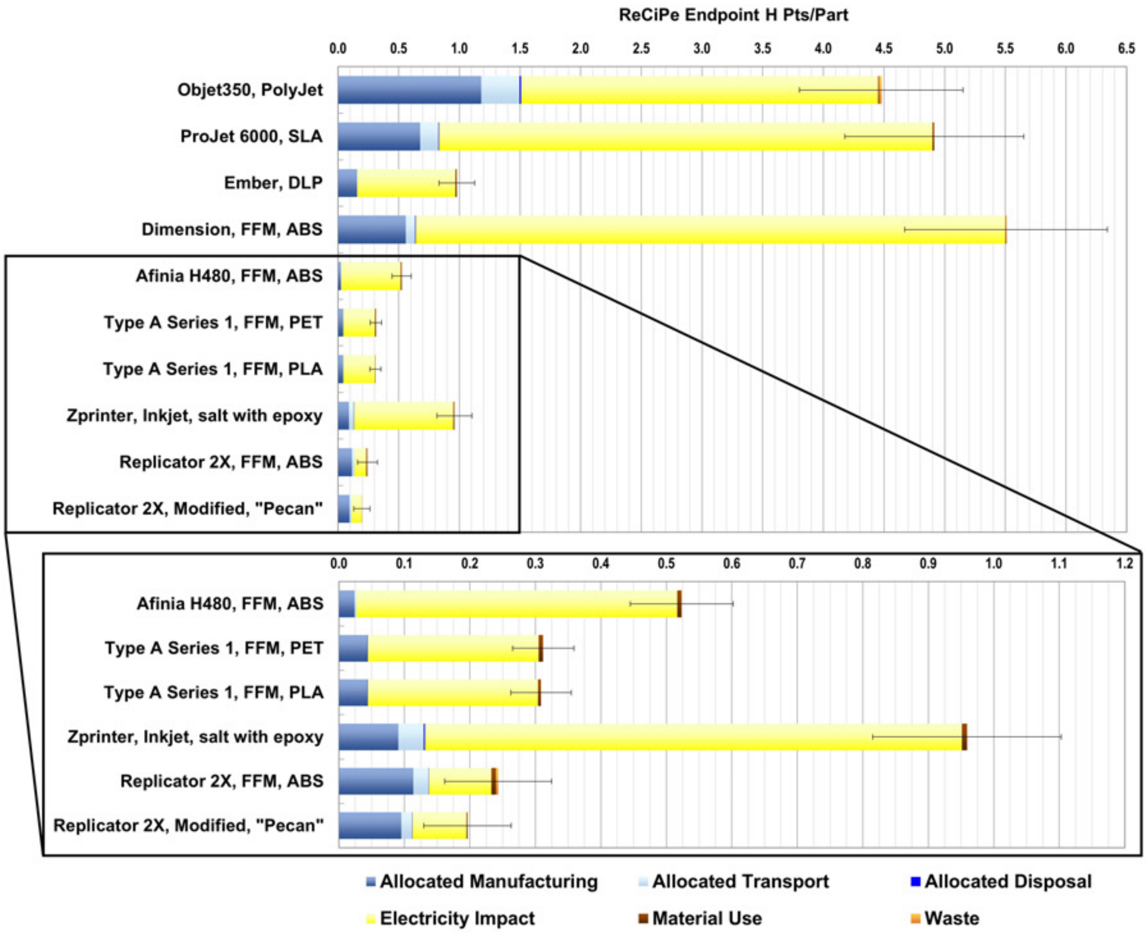


Figure 9. ReCiPe impacts per part in "low utilization, idling" scenario, broken down by life cycle stage. A detail is shown for low-impact machines.

Figure 9 shows that in the "low utilization, idling" scenario, energy impacts are again dominant, though in this case it is not primarily due to printing energy, but idle energy. This multiplies impacts per part drastically and is not advised. This is a rare scenario for some printer types, but common for others, such as the Objet350, as mentioned above.

Comparing the bottom two bars of Figures 7, 8, and 9 to Figure 5, the dominant impacts for ReCiPe and energy-only calculations are similar for every scenario, as are the ratios between impacts from different life cycle phases. This is because most impacts here relate to energy use rather than rare materials, land use, or toxicity.

3.4. Material Details

Printing in ABS and "Pecan" required supports that were constructed from the print material to produce the shelled apple part. The ABS apple used 15g of material: 64% for the part, 36% for support and the "raft" (additional base layers that improve plate adhesion). "Pecan" printing used 18.84g of material: 85% for the part and 15% for support, without needing a raft. Differences in these ratios are also due to part orientation: paste materials printed better when the model was oriented face-up, and ABS performed better with the model face-down. The LCA for ABS material was consistent with previous studies, accounting for the ABS polymer and processing, including filament extrusion.

As mentioned earlier, a high and low estimate for environmental impacts of the "Pecan" recipe was created. In the high estimate model, this recipe caused material impacts to account for 20% of total impacts in the maximum utilization scenario. Material processing of pecan shells accounted for the most variation between these two models, with a variable drying energy of 3.9×10^{-5} kWh per part minimum and 5.2×10^{-4} kWh per part maximum. The EcoInvent 3 database items chosen to substitute cellulose and lignin caused ~0 pts per part in the low estimate (assuming that all production impacts are allocated to the pecans instead because it is a waste product) and 3.8×10^{-4} pts per part in the high estimate ("Bark chips, wet, measured as dry mass {RoW}"). Database items were selected using sensitivity analysis discussed in Methods. Best-case and worst-case results are shown in Figure 10.

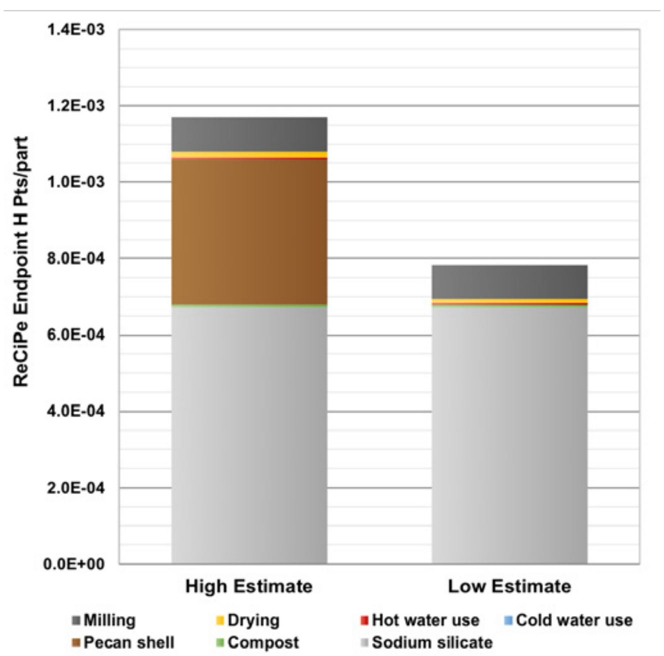


Figure 10. High and low estimates for "Pecan" material impacts per part, detailed by component and process.

Figure 10 shows that in both scenarios, sodium silicate caused the dominant impacts. Climate change and fossil fuel depletion comprised 67% of ReCiPe Endpoint H/A impacts of sodium silicate, with another 13% from particulates, so energy of extraction and refining is likely the dominant cause. However, 9% of sodium silicate's ReCiPe impacts were from human toxicity.

Since compostability is important in this research, health hazards of ingredients were investigated separately through a commercial Safety Data Sheet (PQ Corporation, 2013) and the Pharos chemical and material library (Lent, 2014). Sodium silicate is somewhat caustic due to its pH of 11 but shows low toxicity overall, indicating that it should be compostable in small quantities. It is inorganic, thus "persistent", but it quickly degrades into materials indistinguishable from naturally occurring silica. Its toxicity ratings in the Pharos library were notably lower than epoxies or cyanoacrylate, even the EcoPoxy tested. Precautions for workplace and environmental safety are still required due to its pH. Pecan shell flour was unable to be found in Pharos, but was deemed safe, with the caveat of potentially triggering nut allergies, despite being only the shell.

3.5. Machine Embodied Impacts

Manufacturing impacts of the Replicator 2X printer dominate in the "low utilization, off" scenario, so further discussion is needed. Figure 11 shows machine impacts of the standard and modified Replicator 2X.

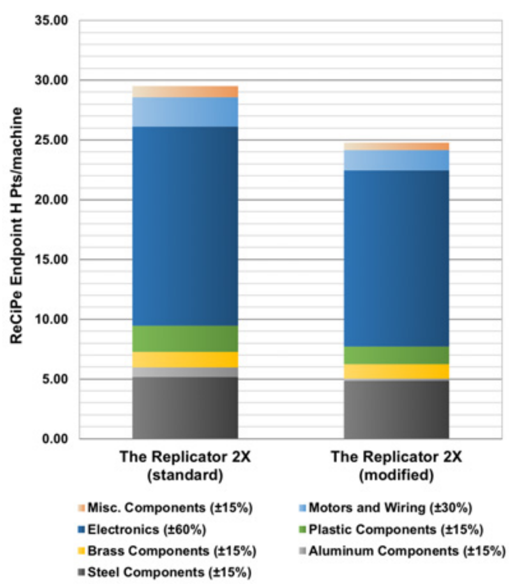


Figure 11. Embodied impacts of the standard and modified Replicator 2X, broken down by component type. Uncertainties are shown in the legend.

Figure 11 shows that the modifications to extrude paste rather than melt plastic reduced machine embodied impacts in all categories. The MakerBot Replicator 2X is a desktop machine with no auxiliary equipment, making its percentage of impacts from metal and plastic categories lower than its industrial counterparts. The electronics, including motors and wiring, account for roughly 2/3 of machine embodied impacts in both scenarios. Since electronics impacts had high uncertainty, further precision would be required for planning machine redesign, or other actions based on the "low utilization, off" scenario where machine impacts dominate.

4. Limitations and Future Work

One limitation of this study was simplifying assumptions made in LCA, as mentioned in Methods; these did not affect overall results noticeably, but in the scenario of "low utilization, off", the uncertainty in electronics impacts became significant; readers concerned with such scenarios would need more precise modeling.

The main limitation of the study was the strength and print resolution of materials not approaching ABS; thus, the materials are only a viable replacement for very limited applications. To address this, future research should improve the strength and rate of cross-linking in materials. This is challenging, as faster and stronger cross-linking of biomaterials traditionally increases toxicity. However, examples exist without toxicity, e.g., spider silk solidifying quickly based on a mild pH change and exposure to salt catalyst (Askarieh et al., 2010). Future studies are encouraged to test different material combinations and catalysts to increase cross-linking, while choosing materials to avoid toxicity hazards. Studies should also empirically test reusability / biodegradability / compostability for circular economy benefits. Finally, studies should formalize toxicity hazard assessments (e.g., GreenScreen) and provide ways to balance tradeoffs between toxicity and LCA scores.

5. Conclusion

Novel material choices can enable radical improvements in the environmental impacts of additive manufacturing. Here, water-based pastes that bonded chemically at room temperature enabled the removal of energy-intensive heating processes and hardware, as well as the materials themselves having lower embodied impacts and being compostable or biodegradable. Others have created similar print processes with other materials, but have not published quantitative comparisons of environmental impact, cost, or material strength. In this study, this paste (composed of pecan shell flour, water, and sodium silicate) reduced overall ReCiPe eco-impact points per part by 78% (from 27 to 6 ReCiPe Endpoint H millipoints/part) compared to the same machine unmodified and printing ABS at maximum utilization. This included a 75% reduction in printing energy (from 160 to 40 Wh/part) and an 82% reduction in material impacts (from 6.6 to 1.2 ReCiPe Endpoint H millipoints/part). This was also a 95% reduction in overall impacts per part compared to large commercial FFM printing of ABS at the same utilization. Note, however, machine utilization was also a very powerful factor: an inkjet machine from a previous study printing four parts at once in similarly low-impact materials produced the lowest environmental impacts per part of any printer measured.

Material cost was cut in half, from $0.72/part of standard ABS filament to $0.36/part of "Pecan". Pecan shell flour proved promising for 3D printing, because its slow reactivity with binder materials enabled extrusion, and it provided good flow properties. Sodium silicate is a strong and dynamic binder material, yet significantly less toxic than epoxies, even the EcoPoxy tested. The combination of pecan shell flour and sodium silicate provided good printability, including good shape retention and layer adhesion.

These findings imply that government or company policies could drive aggressive targets for improving AM environmental impacts, as large improvements are demonstrably possible, even at lower costs than ABS. However, these findings also demonstrated that challenges remain to providing adequate strength, stiffness, resolution, surface finish, and other print quality. Further research is required to develop AM extrusion materials that radically reduce print energy, provide circular resource flows, and minimize toxicity, while matching or exceeding the mechanical performance of FFM in ABS plastic. Most especially, more research is needed on cross-linking biopolymers without toxicity, to provide adequate strength with short print times. Such research, and policies that drive it, can ensure the coming additive manufacturing revolution benefits the world rather than harming it. Such benefits would also encourage governments and manufacturers to increase their rate of adoption of additive manufacturing, helping the industry as well.

Acknowledgments

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Figure Captions

Figure 1. A flowchart of methods for material formulation and assessment.

Figure 2. Recipe ingredients. Filler materials: oak sawdust, as purchased and filtered to 0.125 mm grain size (A1, A2); pine sawdust, as purchased and filtered (B1, B2); orange peel, whole and powdered (C1, C2); nanocellulose fibrils, dried (D); pecan shell flour (E). Binders: Sodium silicate liquid (F); polyvinyl alcohol (G); pine rosin powder (H); cyanoacrylate, dried with sediment (I). Multipurpose materials: superfine white rice flour (J); confectioners' sugar (K); gelatin (L); wheat dextrin (M); glycerin (N).

Figure 3. Thin walled apple part, (A) printed in ABS FFM by the standard Replicator 2X; (B) printed in "Pecan" paste extrusion by the modified printer.

Figure 4. Compression tests on half-cubes: printed ABS before and after (A1, A2); printed "Pecan" before and after (B1, B2); "Pecan+Cyanoacrylate" after (C); "Pecan+Epoxy" after (D); molded "Rice+IPA" after (E); molded "Oak" after (F). Tensile tests on dog bones: printed ABS before and after (G1, G2); printed "Pecan" before and after (H1, H2); "Pecan+Epoxy" after (I); "Pecan+Cyanoacrylate" after (J).

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Figure 9. ReCiPe impacts per part in "low utilization, idling" scenario, broken down by life cycle stage. A detail is shown for low-impact machines.

Figure 10. High and low estimates for "Pecan" material impacts per part, detailed by component and process.

Figure 11. Embodied impacts of the standard and modified Replicator 2X, broken down by component type. Uncertainties are shown in the legend.