

Polymeric Additive Manufacturing: Present Status and Future Trends of Materials and Processes

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Abstract – The additive manufacturing (AM) industry is predicted to maintain a strong growth rate over the next years, and exceed \$21 billion in sale of products and services by 2020, also thanks to its capacity of innovating and developing materials with better performance and broader range of applications. This paper provides an overview of the polymers currently used for AM, and the AM processes used with them. It also describes the polymers most likely to be developed in the short term, along with their future properties and process requirements.

Index Terms – Additive manufacturing, development, fused deposition modeling, innovation, laser sintering, material jetting, multi jetting modeling, polymers, stereolithography.

I. INTRODUCTION

The ASTM F2792 defines *additive manufacturing* (AM) as “a process of joining materials to make objects from 3D model data, usually layer upon layer, as opposed to subtractive manufacturing methodologies. Synonyms: additive fabrication, additive processes, additive techniques, additive layer manufacturing, layer manufacturing, and freeform fabrication”. AM is also known as 3D printing.

Some parts made by using AM, or *printed* parts, are pictured in *Figure 1*, where it is easy to appreciate the fine details and high degree of complexity achievable, which constitute some of AM’s strongest advantages.



Figure 1. Parts made from metal AM.

AM was officially born in 1986, when Charles Hull patented an “apparatus for production of three-dimensional objects by stereolithography” (US patent 4575330). In 1986, Hull founded the first company to generalize and commercialize this procedure, 3D Systems Inc., making

models that, while highly complex, were mostly limited to prototype parts because of the durability of the resins used. Also, since specialized tool path programming was not required, parts could be made much faster. This is how the term “Rapid Prototype” became the primary name used to describe all types of 3D printing for the early years. It was only after the printed parts become on a par with injection molding for quality and cost (at least for small batches) that the name AM would be used.

AM has grown over the last 25 years at a remarkable average rate of about 25% per year, and in 2020 the AM industry is expected to sell \$21.2B in products and services [4]. Knowledge about AM has long left the specialized circles to enter the mainstream media [5].

Different AM processes are commercially available, proving the intense and constant efforts to come up with new patents, and, therefore, the growing vitality of this type of technology. In fact, the graph in *Figure 2* displays the number of AM-related patent applications (higher column in each year) and granted patents (lower column in each year) in the period 1982-2012, and illustrates how the number of patent applications linked to AM has jumped in recent years, with patents concentrated particularly for healthcare applications, such as dental implants, medical devices, and bone implants. However, the number of granted patents has stabilized in most recent years.

ASTM F2792 has also categorized the AM processes into the following seven areas:

- *Binder jetting*: a liquid bonding agent is selectively deposited to join powder materials.
- *Directed energy deposition*: focused thermal energy provided by sources like laser, electron beam, or plasma arc, is used to melt the feedstock within a small area. This process is currently used for metal parts exclusively.
- *Material extrusion* (commonly known as *fused deposition modeling*): process in which material is selectively dispensed through a nozzle or orifice.

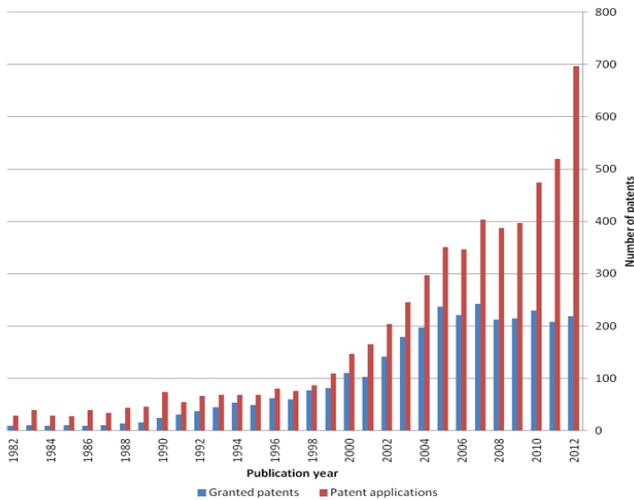


Figure 2. Patent applications (red) and patents granted (blue) from 1982 to 2012. Source: Intellectual Property Office of the UK [6]

- **Material jetting:** droplets of build material are selectively deposited. Example materials include photopolymer and wax.
- **Powder bed fusion:** thermal energy selectively fuses regions of a powder bed.
- **Sheet lamination:** process in which sheets of material are bonded to form an object.
- **Vat photopolymerization** (commonly known as stereolithography): a liquid photopolymer in a vat is selectively cured by light-activated polymerization.

Table 1 lists materials, and example companies for all AM processes described above.

Table 1. Materials, and examples of companies involved in the AM processes

AM PROCESS	MATERIALS	EXAMPLE COMPANIES
Binder jetting	Polymers, metals, foundry sand	3D Systems, ExOne, Voxeljet
Directed energy deposition	Metals	PM, Optomec
Material extrusion	Polymers	Stratasys, Maker Gear
Material jetting	Polymers, waxes	3D Systems, Solidscape, Objet, Arburg
Powder bed fusion	Polymers, metals	EOS, 3D Systems, Arcam
Sheet lamination	Paper, metals	Fabrisonic, Mcor, Solidica
Vat photo-polymerization	Photopolymers	3D Systems, Envisiontec

There are two distinct markets for printed parts: a) the industrial/production market, which includes medical, dental, aerospace, automotive and power generation; b) the consumer market which comprises home accessories, fashion and entertainment.

AM is employed for: prototypes, models for form, fit, and function; presentation models; non-load bearing products; and increasingly for the fabrication of end-use products. The share of money spent on printing final products instead of

prototypes was 28% in 2012, and will grow to more than 80% by 2020, exceeding \$21bn in sales of products and services by 2020, as long as the AM technology maintains its pace in increasing the maximum volume of printable parts, and the printable rate of single parts.

The benefits associated with AM are the following:

- **Virtually unlimited design freedom at no additional cost,** being a method that is not constrained by design complexity, and allows for structurally efficient shapes similar to structures found in nature, e.g. bones, and plants.
- **Unparalleled degree of design complexity at no added cost** and without the need for complex multi-axis machining vs. no complexity
- **Minimized or eliminated need for assembly,** allowing for more highly integrated designs where part features can be fabricated as one piece rather than as a multi-part assembly
- **High “speed”** from a shorter overall process in case of limited quantities and applicable designs (materials, size: no tooling (mold, die), significantly reducing production ramp-up time, cost, and lead time, and simplifying the supply chains (lower inventories, etc.)
- **Relative affordability:** small production batches (even one item) are feasible and economical, and AM can be performed even from home, office, and classroom
- **Convenience:** AM can be done in-house, on your schedule. Furthermore, many service agencies are also available to build parts with a much broader selection of processes and materials. In most cases, instantaneous job bidding is available and parts are made in just a day or two.
- **Reduced waste,** for there is no material removal, like for instance with machining
- **Hedge against obsolescence.** In aerospace, it is very expensive to qualify a new product, and often a sole source is available. Many parts are needed infrequently and in relatively small quantities. Therefore, it is challenging to find suppliers that can provide the same parts, affordably over time.

One limiting feature of the AM processes is that the surface of current polymeric printed parts is less smooth than cut or molded plastic parts, requiring often post-processing operations. One way this shortcoming is being addressed is to develop techniques to predict the surface roughness of printed parts using different techniques and models [61, 62].

AM uses hundreds of materials, virtually covering their entire range: from polymers to metals, and ceramics, from concrete to chocolate, to biomaterials. Each material is designed to meet specific form, fit, and function needs. However, this paper will focus on polymeric AM for engineering applications, particularly on current and future polymers for AM. The AM applications are countless. David Leigh is the co-founder of Harvest Technologies (Belton, TX), a leading manufacturer of AM parts; he predicts that aerospace, automotive, and medical applications will be the most likely future application areas for AM, and the most likely future components made of AM polymers will be prosthetics (cranial and maxillofacial), aerospace

cabin and cockpit, engineered low pressure ducting systems for automotive and aerospace, automotive dash and trim (including under hood and headlight/tail light) pieces, testing and production jigs/fixtures [58].

Boeing has been using AM since the 1990's [8], when Douglas Aircraft Company operated a SLA machine from 3D Systems. [63], and is currently in the company of other large defense contractors, like Lockheed Martin, EADS, and Northrop Grumman. AM process has been adopted on a large number of military [51], and commercial aircrafts [52], as well as many unmanned aerial vehicles.

Plastic printed parts made by Boeing have been in flight operation for years. Examples of Boeing aircrafts featuring parts are F/A-18 Hornet [64], and 787 Dreamliner [65] for the defense and commercial side respectively.

II. STATE OF THE ART OF PROCESSES AND MATERIALS

A. Introduction

In general, the materials used often dictate the kind of machine needed to process them, therefore the former ones cannot be discussed without touching on the latter ones. The AM processes mostly used with polymers are:

- Selective laser sintering (SLS),
- Stereolithography (SLA),
- Fused deposition modeling (FDM),
- Material jetting.

B. Selective Laser Sintering

SLS printers lay down a thin layer of plastic powder. A laser heats the powder up, and fuses it with the previous layers, and bakes the particles together by only fusing powder particles in their "solid state", without melting the particles. After the laser has finished tracing one cross-section of the model, a new layer of powder is applied on top, and the process repeats. Since SLS requires a precise temperature control, the scanning strategy and laser energy-input are carefully controlled throughout the process [9]. The printer price range is \$0.3-1.3M (2014 prices).

Various polymers are utilized with SLS:

- Polyamide (PA), better known as nylon, used in carpets and women's stockings, is the workhorse for SLS. PA provides high impact resistance, elongation to break, and fatigue endurance, associated with moderate cost; therefore it can be used not only in prototypes, but also production parts. PA is available in:
 - Different grades, PA6, PA11, PA12
 - Carbon-filled PA12
 - Aluminum-filled PA12
 - Fire retardant PA (compliant with the flammability requirements for compartment interiors set by the Federal Aviation Regulation in the FAR 25.853)
- Polyether ether ketone (PEEK), a costly thermoplastic with excellent mechanical and chemical resistance properties retained to high temperatures, up to 464°F (240°C), excellent hydrolysis resistance, compliant with FAR 25.853, and the UL 94 V0 (Standard for Safety of Flammability of Plastic Materials). It also provides fire, smoke, and toxicity performance.

- Polystyrene (PS)-based materials:
 - Windform PS®, to produce complex investment casting patterns [11].
 - Prime Cast 101®, for fabricating patterns for investment casting, master patterns for vacuum casting, and lost patterns for the plaster and ceramic shell casting process [12].
- Polycaprolactone (PCL), a biodegradable polyester with glass transition temperature of about -60°C, used for parts not requiring heat resistance, such as scaffolds for bone regeneration. It has physical properties of a very tough, PA-like plastic, and melts to a putty-like consistency at only 60°C. It can be inserted in the human body, and reabsorbed in three years [13].

Table 2 includes commercial polymers mostly used for SLS, along with their major physical-mechanical properties.

Table 2. Physical-mechanical properties of SLS materials

Supplier	LS Material	Young's Modulus, ksi	Tens. strength, psi	Hardness, Shore D	Impact notched IZOD, (ft-lb)/in	Heat defl. temp. @ 1.82 MPa, F	Density, g/cc
Solid Concepts	PA 12	246	6815	NA	4.12	187	0.95
FR 106, Advanced Laser Materials (ALM)	PA 11 flame retardant	1345	6700	NA	NA	158	1.07
PA 615-GS, Advanced Laser Materials (ALM)	Glass-PA	595	4500	NA	1.8	273	1.49
Duraform EX, 3D Systems	ABS & PP-like	220	6961	74	1.4	118	1.01
Windform XT	C-PA	1061	11288	NA	NA	348	1.01
Alumide, EOS	Aluminum-PA	551	6670	76	NA	291	1.36
Solid Concepts, PEEK HP3	PEEK	594	10700	NA	NA	482	1.25

The property values in Table 2 were plotted in Figure 3, and normalized to the lowest value for each property. The material price range is \$2-8/in³.

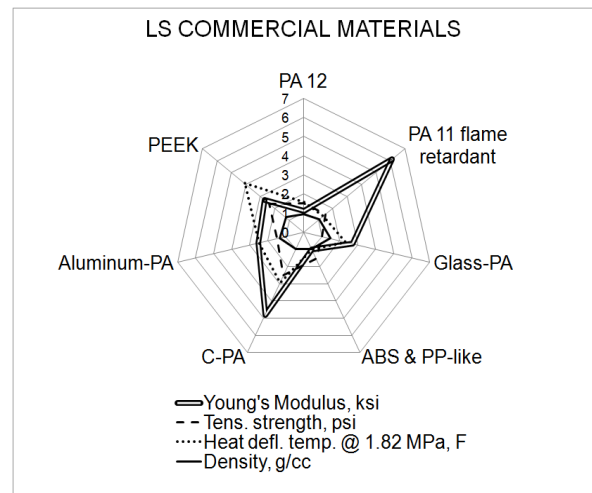


Figure 3. Plot of normalized material property values from Table 2.

Figure 4 displays some parts printed using SLS materials: PA (left) and PEEK (right).



Figure 4. SLS parts made of PA (left), and PEEK (right)

C. Fused Deposition Modeling

The FDM process uses small diameter round feedstock fed from reels. In the printer, the material is partly melted, and extruded through a heated nozzle, resting on a supporting platform if it constitutes the part’s first and bottom layer. The nozzle moves to produce a one-layer thick cross section of the part in x and y directions. The material hardens immediately upon extrusion from the nozzle [9]. When the layer is completed, the building board is lowered in z-direction and the next layer is built on top. In this way a 3D geometry is created one layer (*slice*) at the time. Nozzle and platform move according to 3D-CAD data defining the part geometry. Due to the thermal fusion, the material bonds with the layer beneath and solidifies, forming a permanent bonding of two layers. The printer price range is \$11,000-\$500,000 (2014 prices).

Polymeric materials for FDM are:

- Acrylonitrile butadiene styrene (ABS), a ubiquitous thermoplastic (from car bumpers to footwear, from Lego to luggage), with high impact resistance and toughness. It is selected for AM because its glass transition temperature is high enough to reduce unwanted deformation at slightly elevated temperatures, but low enough to be safely attainable with standard extrusion setups.
- Polycarbonate (PC), a durable material, with high impact-resistance, used with non-AM processes for compact discs, DVDs, and “theft-proof” plastic packaging
- PC-ABS
- Polyphenylsulfone (PPSF, or PPSU): a costly thermoplastic with outstanding heat resistance, good mechanical strength and resistance to petroleum and solvents
- Polyetherimide (PEI), an expensive amorphous thermoplastic with a great balance of thermal, mechanical and chemical properties. PEI has higher flexibility, and impact resistance than ABS. Particularly, the PEI Ultem 9085 (a PEI-PC blend) is preferred where high flame, smoke, and toxicity (FST) rating, and high strength-to-weight ratio are required
- Polylactic acid (PLA), a bioplastic produced from corn or dextrose. It is transparent, and in its characteristics resemble conventional petrochemical-based mass plastics, like polyethylene terephthalate (PET), PS or PE (polyethylene). Offered in soft (rubbery and flexible)

and hard grades, it is increasingly very popular as an alternative to ABS, due to higher maximum printing speeds, and lower layer height than the former, leading to smoother surface and higher geometrical resolution.

- Room temperature vulcanizing (RTV) silicone, a type of silicone rubber made from a two-component system that is base plus curative [53]
- PA, mentioned in section B
- PS, mentioned in section B.

Table 3. Physical-mechanical of FDM materials

Material	Young's Modulus, ksi	Tens. strength, psi	Hardness, Shore D	Impact notched IZOD, (ft-lb)/in	Heat defl. temp. @ 1.82 MPa, F	Specific gravity
ABS	236	3200	R105	2	169	1.05
PPSF	300	8000	M86	1.1	372	1.28
PC	330	9800	R115	1	261	1.2
PEI-PC	322	10400	NA	2	307	1.3

(*) redevondemand.com (Stratasys)

The properties values in Table 3 were charted in Figure 5, and normalized to the lowest value for each property. As for SLS materials, also FDM polymers offer a good range of property values, allowing some design freedom. The price of FDM materials ranges from about \$3 to \$6 per cubic inch.

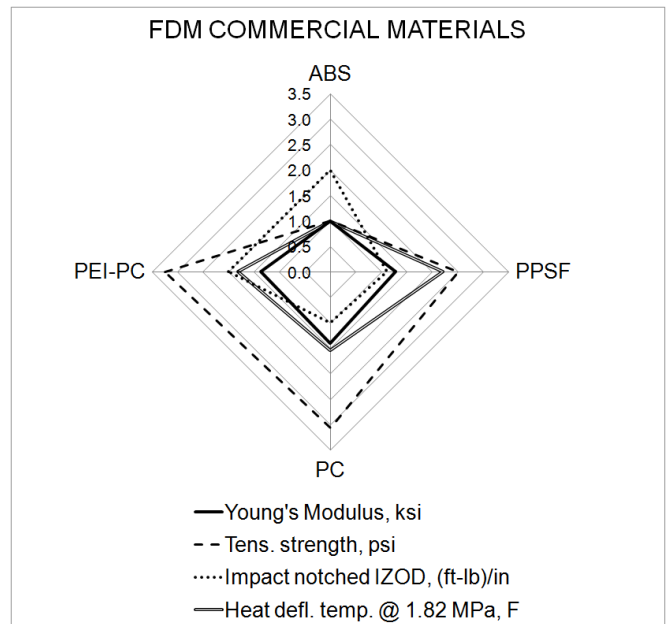


Figure 5. Plot of normalized material property values listed from Table 3

D. Stereolithography

The SLA process requires a photosensitive liquid polymer, filling a tank that also includes a platform movable in z-direction. At the beginning, the platform is located closely below the surface of the material. A UV-laser traces the cross-section of the part, causing the first and top *slice* of the resin to solidify in the respective area. Subsequently, the

platform is lowered into the resin basin by the thickness of one layer (~5 μm). A sweeper blade applies a new film of resin on top of the previously cured layer that is subsequently cured by the UV-laser again. This process is iterated and the following layer is fused to the solidified layer. Support structures are required because of the low stability of the part during the process. The part is tied to the platform, in order to avoid any motion of the part while the platform is lowered. The printer price range is \$250-575k (2014 prices).

Polymers employed in SLA are:

- Liquid photopolymers, that is UV-curable polymers such as epoxy resins, and polyether(meth)acrylate-based resins. They can feature mechanical properties similar to engineering plastics such as ABS, PA, PC, PE, polypropylene (PP), PP-ABS, high-density polyethylene (HDPE), in order to make functional prototypes, and end-use parts.
- Polyvinyl alcohol (PVA), a water-soluble synthetic polymer, used as a dissolvable support material or for special applications [54].
- PCL [55], mentioned in section B.

Table 4. Physical-mechanical properties of SLA materials

Supplier	Material	Young's Modulus, ksi	Tens. strength, psi	Hardness, Shore D	Impact notched IZOD, (ft-lb)/in	Heat defl. temp. @ 1.82 MPa, F	Density, g/cc
Somos 8110 UV	Epoxy	46	2600	77	1.6	129	1.11
3D Systems Corp Accura 25	like	235	5510	80	0.4	127	1.19
Somos Waterclear Ultra 10122	ABS-like	417	8000	86	0.46	121	1.13
3D Systems Corp Accura 60	like	420	9135	86	0.4	120	1.21
Huntsman RenShape SL 5530	HTR	532	7850	90	0.4	239	1.25
3D Systems Accura PEAK	HYMS	653	9800	86	0.45	255	1.36

HTR = high temperature resistance

HYMS = High Young's mod., high tensile strength

The properties values in Table 4 are represented in Figure 6, and were normalized to the lowest value for each property. Except for hardness and density, the range of property values provides users and designers with various options.

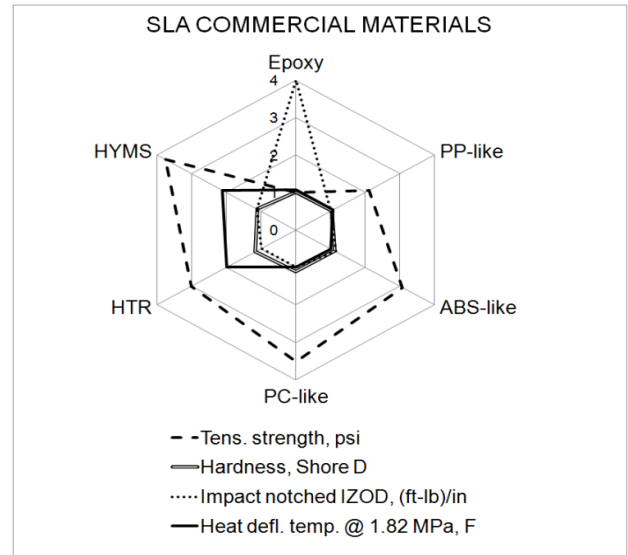


Figure 6. Plot of material property values from Table 4

In Figure 7 and Figure 8 the range of physical-mechanical property values from Table 2, 3, and 4 identified by printing process are plotted. SLS and FDM materials are thermoplastics, whereas SLA materials are epoxy-based thermosetting resins, and, therefore, feature a superior Young's modulus but inferior impact resistance and deflection temperature than SLS and FDM. However, in selecting the most suited AM material for a specific application, designers typically focus on a combination of cost and the material properties most relevant to the part service performance.

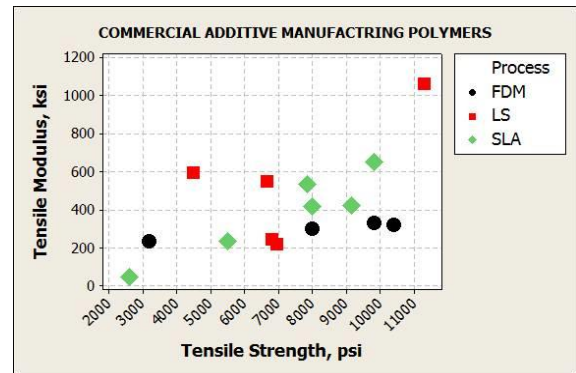


Figure 7. Comparison of values of tensile modulus and strength values of commercial additive manufacturing polymers used in SLS, FDM, and SLA

We also point out that the tensile yield strength is preferred to the tensile ultimate strength in designing functional parts, but the former value was reported only for a very few materials.

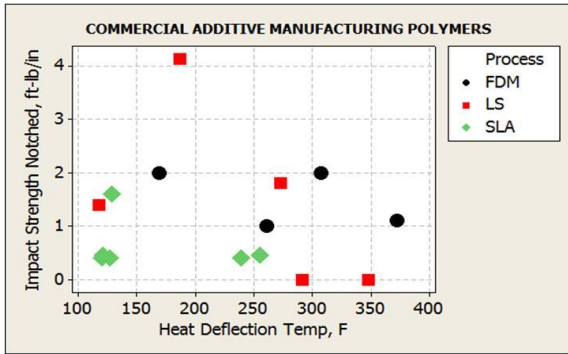


Figure 8. Comparison of values of impact strength notched and heat deflection temperature values of commercial AM polymers used in SLS, FDM, and SLA

Figure 9 compares the normalized price of the same part quoted by the same AM house using SLS, FDM, and SLA processes. The highest price for D80-ST is offset by the fact that this material possesses superior mechanical properties and is also stabilized to prevent premature thermal degradation.

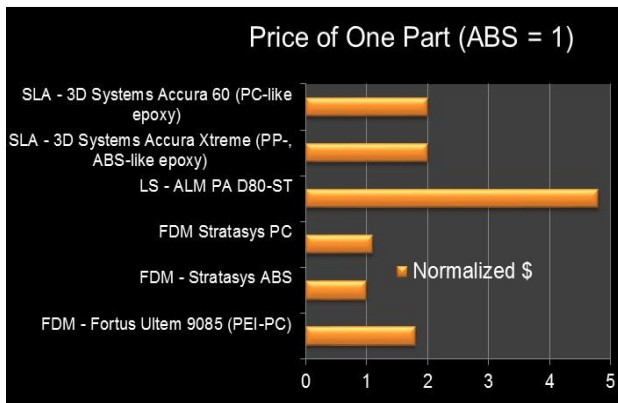


Figure 9. Normalized part prices across SLA, SLS, FDM for the same part quoted by the same 3D printing house

Figure 10, instead, illustrates the difference in the actual price of the same part to be 3D printed by the same vendor using FDM. Ultem and PPSF are the most expensive of the group, but they feature an unparalleled combination of mechanical properties, and heat and chemical resistance, that makes them the only available option for specific demanding application.

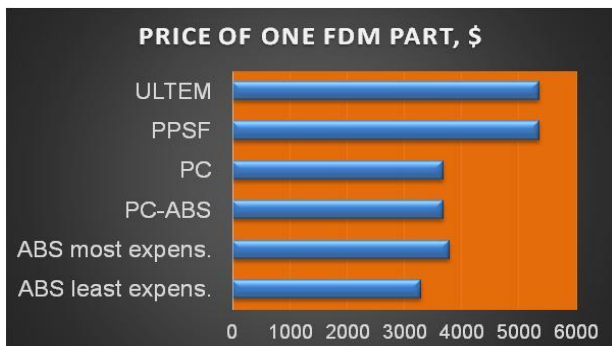


Figure 10. FDM prices of the same part for various materials provided by the same vendor

In the case of AM polymers, materials with higher property values do not necessarily result in more expensive parts, even within the same process. In fact, we compared the prices for the same part, whose mechanical properties most relevant to its service performance were rigidity and impact resistance. As Figure 11 to Figure 13 illustrate, using materials with the highest combination of Young’s modulus and impact strength, or highest Young’s modulus alone, or highest impact strength alone led to the most economical parts.

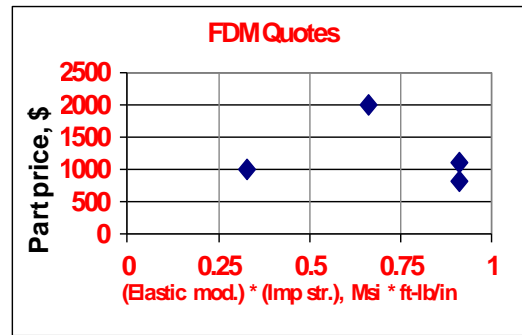


Figure 11. Part prices versus combination of elastic modulus and impact strength values

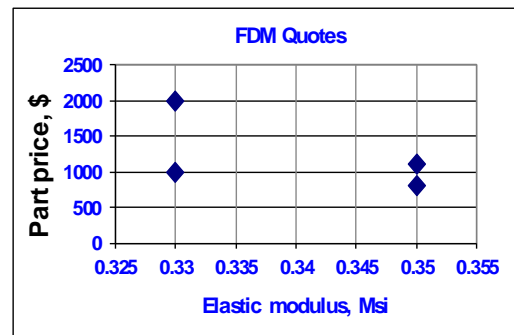


Figure 12. Part prices versus elastic modulus values



Figure 13. Prices versus impact strength values

E. Jetting

One example of the jetting process is the version patented by Objet, which is similar to inkjet document printing, but

instead of jetting drops of ink onto paper, the 3D printer jets layers of liquid photopolymer onto a build tray and instantly cures them with UV light. The fine layers build up to create a precise 3D model or prototype that requires no post-curing, and minimal post-processing. Along with the selected model materials, the 3D printer also jets a gel-like support material specially designed to uphold overhangs and complicated geometries, and easily removed by hand or water [16].

Various polymeric materials are used for the jetting process. They are compatible with the acrylic-based photopolymer technology, and two materials can be jetted at the same time in specific concentrations and structures to generate tens of compounds, featuring a wide range of appearance (color, patterns, feel), and physical-mechanical properties, in order to meet the performance requirements of the end product. The hardness values range from Shore A 27 to A 95, to simulate various rubber products, but also various rigid materials, ranging from standard plastics, like PP, to the tough and temperature resistant materials, like ABS, or engineering-plastics like polymethyl methacrylate (PMMA). The heat deflection temperature can reach a maximum of 203°F after thermal post treatment [17].

The other material involved with a version of the jetting process called *multi jet modeling* [18] is wax, employed for casting mid-sized and large foundry applications, casting of fine-detail items, and dental prosthesis. Multi jet modeling, or *thermojet*, is a fast rapid prototyping process, employed to make models of wax-like plastics that are less accurate than SLA objects. The printer features multiple spray nozzles, spraying tiny droplets of melted liquid material which cool and harden on impact to form the solid object [19].

F. Advanced Polymers

Currently, the following polymers are less commonly used with AM equipment than those mentioned above, but they will be improved and become more widespread in the next future:

- *Functionally graded materials* (FGMs). They are materials with spatially varying composition or microstructure, ubiquitous in nature. One example is the cross-section of a palm tree, featuring radial density gradients resulting in bending stiffness varying across its height. FGMs are obtained through the computer control of the material distribution within a monolithic structure, resulting in continuous gradients, and structurally optimized designs with efficient use of materials, reduction in waste, and production of highly customizable features [20].
- *Shape memory materials*. They are made by mixing polymer fibers into the composite materials used in AM, resulting in the production of an object fixed in one shape that can later be changed to take on new shape [21]. The orientation and location of the fibers within the composite determines the degree of shape memory effects like folding, curling, stretching or twisting that can be controlled by heating or cooling the composite material. Another term for this type of material is *programmable matter* [22]: materials that can morph and self-assemble, or 4D printing, where the fourth

dimension is time, meaning that the printed objects change shape or self-assemble in response to movement or environmental factors, such as the presence of water, air, and/or temperature changes.

- *Bio-ink*. It comprises stem cells and cells from a patient, which can be laid down layer by layer to form a tissue. Human organs such as blood vessels, bladders and kidney portions have been replicated using this technology. With the bio-ink, stem cells are immersed in a biocompatible hydrogel ink, and the mix is then printed into their target form.
- *Bone-like material*. It contains silicon, calcium phosphate and zinc. In one experiment this material was integrated with a section of undeveloped human bone cells; in about a week, growth of new bone was seen along the structure, this new material dissolved eventually, and did not harm the patient.
- *Hot glue*. The greatest advantage of using the hot glue is the extremely low cost of its gun. In one setup, the hot glue gun can be connected to a XYZ computer controlled plotter, or a CNC router type machine [23]. In another setup, an engineering student designed and built a 3D printer using: a) LEGO NXT Intelligent Brick; b) hot glue gun; c) fan; d) VHS camera motor, powering the printer's extruder and build platform. NXT is basically a 32-bit microprocessor and flash memory equipped ports for attaching motors and sensors [24].

III. FUTURE MATERIALS

A. General Requirements

Predicting future polymers for AM is difficult, and can be most successful only in the short term, because new materials appear at extraordinarily fast pace, and companies are understandingly secretive about the materials they have in their pipeline. Tim Caffrey of Wohlers Associates, a consulting firm specialized in AM, agrees: "With 3D printing, we don't necessarily know where it's going."

Fortunately, some valuable indications to anticipate future AM materials have come from some reports prepared by AM experts from industry and academia [27, 28], that point out what topics should be addressed by future material research in order to meet additional requirements. Another source of information was papers on the latest academic research activities in AM polymers.

The handful of current AM polymers does not meet the requirements of the majority of commercial products, hence there is a demand for better materials to use as feedstock for AM. Indeed, materials are considered "the real issue and the biggest opportunity in AM" [29], therefore there are opportunities for new or improved materials. The market applications will direct the material research and development, with the medical field playing a major role due to its number of highly priced applications.

Broadly speaking, the effort to gain new applications will drive widening the range of AM polymers, and improving their physical-mechanical performance vs. the performance of the same polymers when used in conventionally fabricated counterparts.

More competition among materials providers will cause the price of standard AM polymers to drop, and the new materials should be competitively priced, unless their performance justifies a price premium. Reusable materials are already available. In fact PA not melt during the SLS process is already reused, and in fact the patent “Method and system for reuse of materials in additive manufacturing systems” was awarded to Stratasys in 2013. More sustainable materials including recycled, reusable, and biodegradable materials will emerge, further decreasing materials costs [30]. FGMs will be further developed, and represent a particularly high-value application for AM, enabling also graded geometries through the part’s volume, providing additional functionality [27].

David Leigh believes that custom formulations of existing PA (such as PA11, and PA12) and PEKK will be available for SLS in the short term, whereas in the longer term better formulations of PEEK, PEKK, PA, and blends including flame retardants and filled/fiber composites will be provided. He also expects that most of the future focus on material properties will be directed to medical grade and high temperature performance, and work on electrical properties will aim primarily at the development of hybrid printers that could fuse material with a laser and print conductive material with a print head [58].

According to Stephen Hanna, VP of Global Materials Sales and Marketing of 3D Systems, a large manufacturer of 3D printers based on FDM and polyjet technologies, the focus will continue to be on increasing the functionality of the materials, to extend the range of manufacturing application. “To achieve this,” he explains, “materials must meet the following design demands.

- *High stability.* We are focused on developing materials that are more stable over longer and longer durations, pushing the useful life of printed parts further and further. To do this, materials must be environmentally, mechanically and dimensionally stable over time. We have this in some materials, but not all. We believe that improvements in these areas will greatly increase adoption and applicability of 3D printing to manufacturing applications.
- *Improved mechanical properties.* We believe that improved properties will generate more applications. This is not just better properties, but also a wider variety of properties that can be addressed with 3D printing. 3D Systems offers a wide range of materials now that range from 1000 MPa to 10,000 MPa in flexural modulus! A huge range! But ranges of ductility, impact resistance, hardness are also important.
- *Other properties.* Special properties, be they electrical, medically related, chemical resistance or other, could be important for enabling new and emerging applications. 3D Systems carefully evaluated new application areas for 3D printing and will focus material developments to enable those where there is significant potential.” [59]

Many current SLA resins have softening temperatures under 100°C, and hence they have limited usefulness in high temperature applications. SLA polymeric formulations will be investigated that will meet the growing demand for an

AM resin type curable at a broader UV bandwidth, resulting in a wider range of softer to stiffer materials than the current options. To broaden the use, new SLA resins with improved performance, such as better mechanical properties and higher use temperatures, must be developed.

Common epoxy-based materials used for SLA are not suitable for medical applications due to the known irritating and cytotoxic (that is resulting in cell damage or cell death) effects on human cells, resulting mainly from uncured epoxies in the cured polymer prototypes [34]. The studies on non-toxic materials will continue, in order to overcome these severe problems of the biological incompatibility, and extend their applications.

Improvements in specific properties, like tensile strength, and elastic modulus, will be achieved not only in single materials for AM, but also in new combinations of materials, such as the current iron-ABS and copper-ABS for FDM [31] and PP-zirconia (ZrO₂) [32], and Al₂O₃-PP [33] for SLS.

There is large and qualified consensus [28] that the most likely AM polymers in the next future will comprise:

- Carbon-fiber-reinforced polymers (CFRPs), including carbon nanofiber reinforced materials
- Liquid-crystal polymers (LCPs)
- Biodegradable materials, such as polycaprolactone.

Currently, a few options exist for carbon-fiber parts made with AM. One challenge is material cost and production on a scale that enables commodity-priced carbon fiber PA.

B. Carbon Fiber-Reinforced Polymers (CFRPs)

A class of CFRPs comprises polymers reinforced with carbon nanomaterials, such as carbon nanotubes (CNTs), which are rolled-up one-atom thick sheets (called grapheme) of carbon. Adding nanomaterials is a way to reinforce and stiffen a “matrix” material compatibly with the AM layer-by-layer printing pattern that prevents laying a continuous reinforcement in the z direction across the part layers. CNTs constitute one area of development for AM polymers, and a comprehensive up-to-date overview of CNT applications to AM is provided in [35].

CNTs are already added to polymers to improve their mechanical, thermal, and electrical properties [36, 37]. Similarly, when added to SLA polymers, such as UV-curable epoxy resins, and SLS materials like PA12, they improve the mechanical properties of the printed part. Specifically, in the case of SLA, CNTs raise the tensile strength and fracture stress, but also increase brittleness compared to the unfilled resin [38, 39], therefore we expect in the next future material research directed at reducing the brittleness of the printed parts, without penalizing the tensile strength and fracture stress.

As to SLS, conventionally fabricated parts in pure PA12 have higher tensile modulus and impact strength compared to SLS parts in PA12/nanosized carbon black (CB) [40], hence work will be likely carried out with PA12 and CB to reduce or close the gap in mechanical performance between SLS parts and extruded or molded parts, aiming at possibly increasing the adhesion at the interface between PA and CB, and consequently making the load transfer between the two components more effective. Efforts will be also made to

find the optimal printing conditions for CB powder blended with PA12 powder, in order to improve mechanical properties such as the flexural modulus, and reduce the fraction of particles not melt during the process.

The surface quality of 3D printed parts depends on the specific process resolution, and “size” of the raw material, and for SLS the typical layer thickness is 60-200 μm , and the average roughness R_a can be as low as $R_a = 8.5 \mu\text{m}$ (DuraForm PA by 3D Systems). Surface quality is obviously important in applications where appearance is a requirement, such as presentation models, but also in others where the surface is functional, such as in the case of wind tunnel testing models, where the surface roughness significantly affects the drag coefficient [41]. Studies will be conducted to improve the surface finish of PA12/CNFs vs. PA12, focusing also on understanding the influences of parameters affecting surface roughness, and dimensional accuracy during fabrication.

Because varying the loadings of nanomaterials during the print enables to fabricate parts with graded material properties, graded materials will also be further studied.

On the other hand, the diffusion of nanomaterials in AM applications has to overcome the following challenges [35], if improved materials are to be formulated:

- Enhancing dispersion of CNTs in the matrix has been a challenge for some time [42] and still is. Agglomeration of the particles makes the nanomaterials behave as a bulk, and lose their unique properties. To increase dispersion, nanomaterials can be functionalized with organic linker molecules keeping the particles away from each other, even when embedded into the printing media, ultimately improving the properties of the final parts.
- Because the cure depth of SLA parts can be adversely affected by the presence of nanomaterials due to their ability to absorb the UV light, finding the ideal wavelength that will solidify the polymer without being influenced by the nanomaterial will enable a cure throughout the part.
- Reducing the porosity of SLS parts, for example by synthesizing core-shell nanostructures, with the core made of nanomaterial, and the shell of the printing material, such as PA12, or PA11 [43]. Lower porosity translates into higher mechanical properties.

C. Liquid Crystal Polymers (LCPs)

One polymer family likely to be more common with AM is LCPs. LCPs are a class of aromatic polyester polymers, inert, and resistant to high temperature, that can be melted and molded. They exist in a state that has properties between those of conventional liquid and those of solid crystal. Upon melting, the polymer chains undergo parallel ordering in the direction of the flow, resulting in anisotropic physical, mechanical, and optical properties, with superior mechanical properties in the flow direction. LCPs are already used with SLA, and new liquid-crystal resins will continue to be developed [44, 45], with the goal to raise properties such as the glass transition temperature (and hence the maximum service temperature), and fracture toughness, and ultimately

gaining new uses like under-the-hood automotive applications.

A class of LCPs for SLA that will be still studied in the near future is the lyotropic liquid crystals (LLCs): a material is called lyotropic if it forms liquid crystal phases upon the addition of a solvent. LLCs have been recently studied to be used to control polymer structure at the nanometer scale and ultimately improve material properties [46].

D. Other Materials

One future material is bio-ink, which is already available, but requires further development, to overcome its key, opposing properties that make it complicated to handle. On one hand, bio-ink must be fluid enough to flow through the printing nozzle without damaging cells that are subjected to shear forces as they come out of the printer head. On the other hand, bio-ink must be stiff enough to hold its shape after printing to prevent the material from oozing into a shapeless mass.

Also on innovation watch list is AM of silicone nanostructure [47], and compounded polymers, such as the current ProPell™, a compound of thermoplastic PU, and polyether block amide (PEBA), introduced recently by Foster Corporation for improved medical catheters [48].

E. Future Polymer Properties

There is consensus that the future AM polymers will have to feature improvements in the following properties, opening a host of new applications, like commercial aircraft cockpit indoors [28]:

- Fire resistance
- Thermal conductivity
- Electrical conductivity
- Self-healing properties
- Recyclability.

Table 5 contains the predicted dates when LCPs and CFRPs will have frequent use in FDM and SLS [28].

Table 5. Predicted dates for frequent use of LCPs and CFRPs in FDM and SLS

MATERIALS	FDM	SLS
CFRPs	2017	2017
LCPs	2020	2020

F. Future Area of Study

The design of printed parts is at its early stage, and in fact design guides for printing parts have recently started by companies using AM and seeking to maximize its benefits. Therefore, investigating the failure mode of printed parts could provide designers with insightful information instrumental to take full advantage of material and part performance. The cross section morphology of polymeric printed parts is not exactly the same as that of parts produced through conventional processes, and hence the fracture surface analysis of printed parts may require some customization. In fact Figure 14 illustrates the significant porosity of a failed polycarbonate FDM part analyzed by Boeing BR&T Philadelphia.

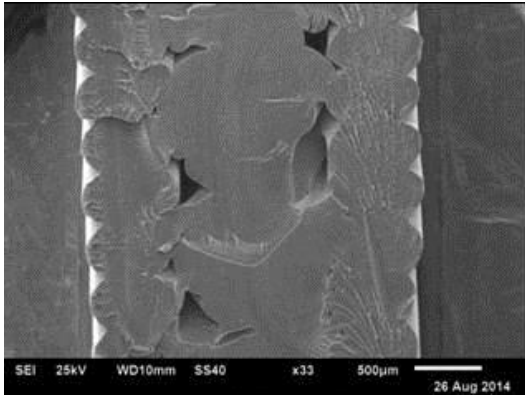


Figure 14. Fracture surface of polycarbonate 3D part for unmanned vehicle

IV. FUTURE PROCESSES

AM polymers are function not only of their chemical formulation, but also their printing process, therefore the future of AM polymers depends also on the future of printing processes. First, a better understanding of the physics of AM processes will be achieved to capture the complexity in the multiple interacting physical phenomena, and better exploit the capabilities of the materials. Understanding the material properties of AM materials after they have been processed to print the part is regarded by some as the most important aspect of any future improvement.

The AM processes will have to meet the following technology-specific requirements [28, 9]:

- Higher build-up rates, higher dimensional accuracy, and better surface quality
- Lower maintenance costs
- Lower machine acquisition costs.
- Larger build-chamber volumes
- High process stability
- Quality control process after job completion, and, even better, on-line quality control processes, that can be crucial for a broad application of AM in the future.
- Continuous certification for aircraft, automotive, and electronics manufacturing equipment
- Controlling the composition of the material of the printed part at the nano level. For example, using multi-material AM processes, we can print in the same part hard and soft materials resulting in a component with peculiar new structural behavior.

A current advanced development is complementing AM with subtractive and molding processes [49].

One accomplishment that if completed would multiply AM applications is available databases of the physical-mechanical properties and allowables of the AM materials. Unfortunately, comprehensive versions of such data bases are costly and lengthy; therefore collaborations among industry, academia, and government will be beneficial in order to reach this goal faster.

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