



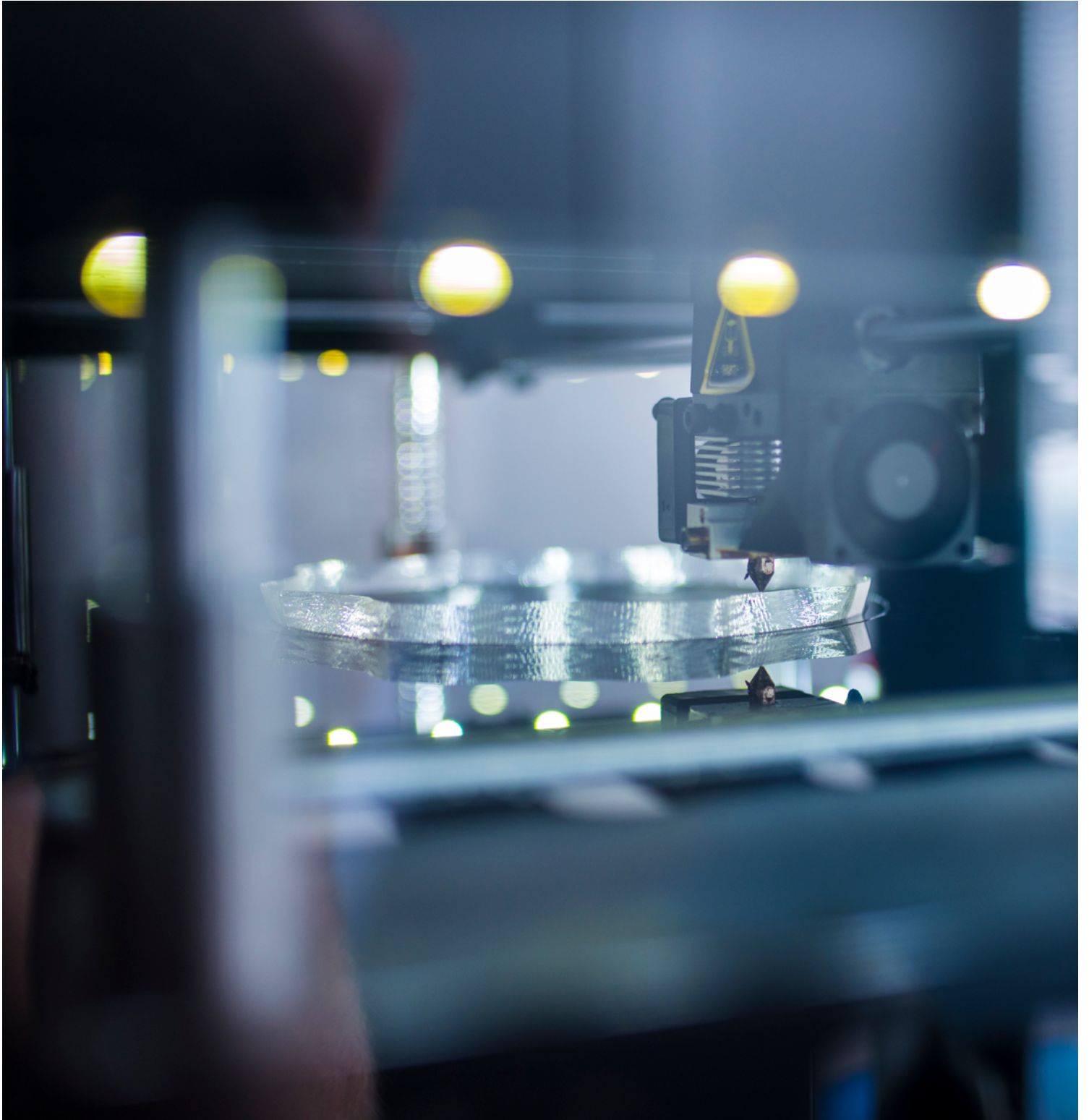
Certifying plastics for additive manufacturing

UL Solutions research on 3D printed polymer performance



Solutions

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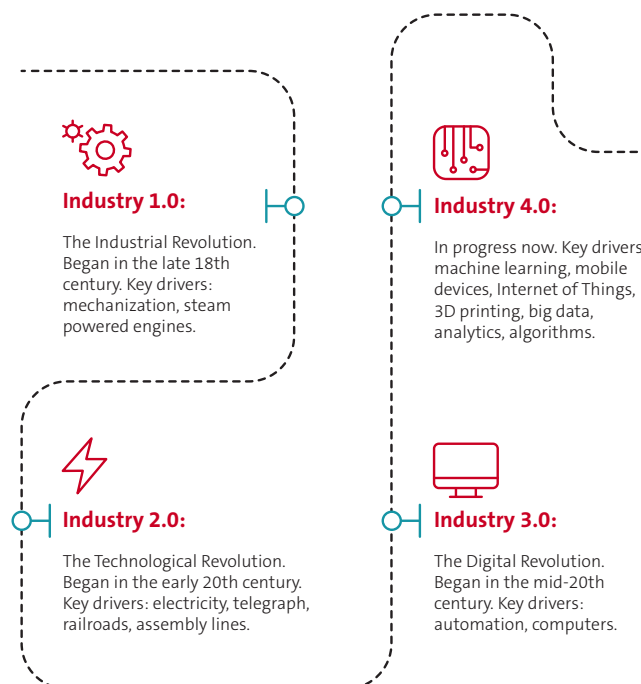


Executive summary

3D printing — or additive manufacturing (AM) — is quickly becoming one of the most disruptive technologies of the 21st century. Demand for 3D printed products is expected to grow to almost \$50 billion by 2025¹. As one of the building blocks of Industry 4.0, AM is at the forefront of a revolution in product development and manufacturing.

3D printing offers unprecedented versatility to manufacture complex parts and products directly from digital files. Printing parameters can be changed during the process, tailoring material properties to perfectly fit any given portion of a printed product. This incredible versatility, however, introduces a new level of complexity not seen in conventional manufacturing, which is yet to be well understood. Understanding how these process variations impact material properties and performance characteristics is a crucial aspect of product design and development. Confidence in 3D printed part performance is often cited as being necessary to increase the adoption of AM technology into serial production applications.

While 3D printing affords extraordinary design freedom to the product developer, it also carries the burden of a wide range of possible performance outcomes. These variable outcomes are directly a function of the interplay among the material selected, the printing process and the printer itself; thus underscoring the need for independent third party certification of product quality and safety.





UL 94, the Standard for Tests for Flammability of Plastic Materials for Parts in Devices and Appliances:

These requirements cover tests for flammability of polymeric materials used for parts in devices and appliances. They serve as a preliminary indication of their acceptability with respect to flammability for a particular application. They are intended to be used solely to measure and describe the flammability properties of materials used in devices and appliances, in response to a small open flame or radiant heat source under controlled laboratory conditions.

UL 746A, the Standard for Polymeric Materials – Short Term Property Evaluations:

These requirements cover short-term test procedures to be used for the evaluation of materials used for parts intended for specific applications in electrical end products. These investigations provide data with respect to the physical, electrical, flammability, thermal and other properties of the materials under consideration. The tests provide guidance for the material manufacturer, the molder, the end-product manufacturer, safety engineers and other interested parties.

UL Solutions introduced the certification program for Plastics for Additive Manufacturing (Blue Card) in 2017 to address the broad range of performance outcomes observed in 3D printed parts and products. This initiative recognizes plastics materials that are appropriate for use in 3D printing. More specifically, the Blue Card provides data to facilitate the pre-selection of 3D printed materials and components intended for use in various end-product applications from automotive to appliances and many others. It delivers confidence and trust across the supply chain — to both users and suppliers of 3D printed articles in terms of their quality, safety, consistency and performance. The Blue Card program defines UL Solutions requirements specifically for plastics intended for 3D printing. In addition, the Blue Card program provides any additional certification requirements that are needed for 3D printed products and offers independent auditing of service bureaus to help ensure ongoing compliance with UL Solutions requirements.

This white paper will:

- Describe how part performance differs depending on the method of production (3D printed versus injection molded)
- Provide an overview of our research study investigating the effects of 3D printing by material extrusion on safety critical performance properties
- Demonstrate how the lessons learned were implemented via UL Solutions Blue Card program
- Explain how the UL Solutions Blue Card program accelerates the adoption of 3D printing into serial production

Introduction

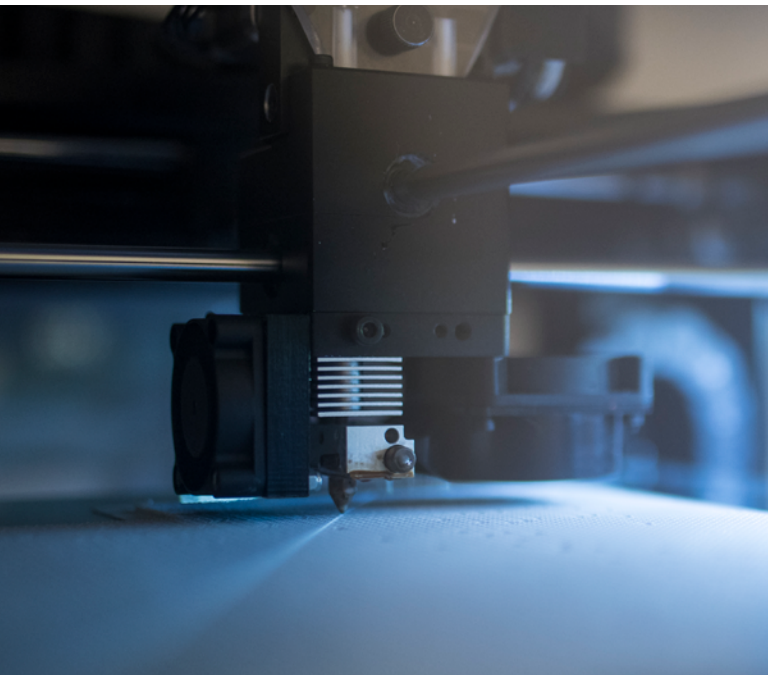
It is a well-known fact in the AM industry that mechanical properties of a material, such as tensile and impact strength, will vary considerably more when 3D printed than molded by conventional methods, such as injection molding. Less commonly understood, however, is that 3D printing may influence a material's safety-critical performance properties, such as ignition, flammability and dielectric strength.

UL Solutions plastics experts conducted a systematic research study to fill in the knowledge gap. To obtain the information needed, the team investigated the influence of various 3D printing and build parameters on safety-critical performance properties, especially those defined in UL 94 and UL 746A. Results were also compared to properties measured on injection molded specimens.

This research led to the creation of UL Solutions certification program for Plastics for Additive Manufacturing (Blue Card). The Blue Card program defines the requirements necessary to recognize the safety and suitability of plastics intended for 3D printing and 3D printed products. UL Solutions program independently certifies this critical information for the AM industry.

Plastics recognition: What is it and why do it?

To appreciate the necessity of this study, it is helpful to understand why UL Solutions' Plastics Recognition (Yellow Card) Program was originally developed.



UL Recognized Component Mark

The UL Recognized Component Mark is a Mark consumers rarely see because it is specifically used on component parts that are part of a larger product or system. The component recognition marking is found on a wide range of products, including some switches, power supplies, printed wiring boards, some kinds of industrial control equipment – and now also on 3D printed components. Recognized products and materials are permitted to claim compliance with the standards to which they were tested, within conditions of acceptability in the end application.

In the past, when a manufacturer had to verify a product's compliance with industry standards, they would need to submit each individual material used in the product to an independent third-party laboratory for testing and validation. Eventually, manufacturers questioned the need for having the same properties tested every time the material was used in a different product. This process was time consuming and costly. Manufacturers demanded a better way for getting their products to market safely and quickly.

In response to industry needs, UL Solutions launched the Plastics Recognition Program almost 60 years ago. The Plastics Recognition Program, informally known as the Yellow Card program, tests materials used in thousands of popular product types. Materials are evaluated for a variety of properties including mechanical, electrical, fire and ignition safety. Materials received a rating for each property, which was then published on yellow index cards that were distributed to industry.

Today, those yellow cards are digital and exist online in UL Solutions Prospector® and iQ™ material databases.

Since then, UL Solutions Yellow Card material recognition program has evolved to become the premier globally recognized polymeric materials safety program that helps demonstrate how plastic products have met a specific set of performance credentials. It provides trusted third-party performance certification for more than 47,000 materials and enables manufacturers to simplify their evaluation process by eliminating redundant performance testing of recognized materials used in their products.

This pre-selection process makes the entire product certification process easier, faster and more cost effective. In today's fast-moving competitive marketplaces with narrow windows of opportunity, that detail can make all the difference.



Our Plastics Recognition Program is a globally accepted tool that helps demonstrate how plastic products have met a specific set of performance credentials. These products are listed in UL Product iQ™ database, which is used by thousands of designers, engineers and suppliers to find materials that have already been evaluated and rated. This makes the entire product certification process easier, faster and more cost effective.



Polymer-entanglement theory describes how polymer molecules in a well-mixed state are physically tangled together, connecting in all unconfined directions. It is this entangled molecular structure that allows the transfer of mechanical stresses from one molecule to another, resulting in a structurally sound material. Polymer molecules that are not entangled can't transfer stresses efficiently and therefore result in structurally weak areas.

Who benefits from plastics recognition?

Material manufacturers: When your certified materials are added to UL iQ and Prospector databases, they are immediately visible to thousands of designers, engineers, purchasing agents and suppliers searching for a material or component provider who meets certain safety and performance requirements.

End-product manufacturers: You can save time and money when seeking certification for end products or systems by using UL Recognized plastics. These materials are also covered under UL Follow-Up Services — a product's ongoing certification assessment helps ensure products continue to meet UL Solutions Standards of safety and performance.

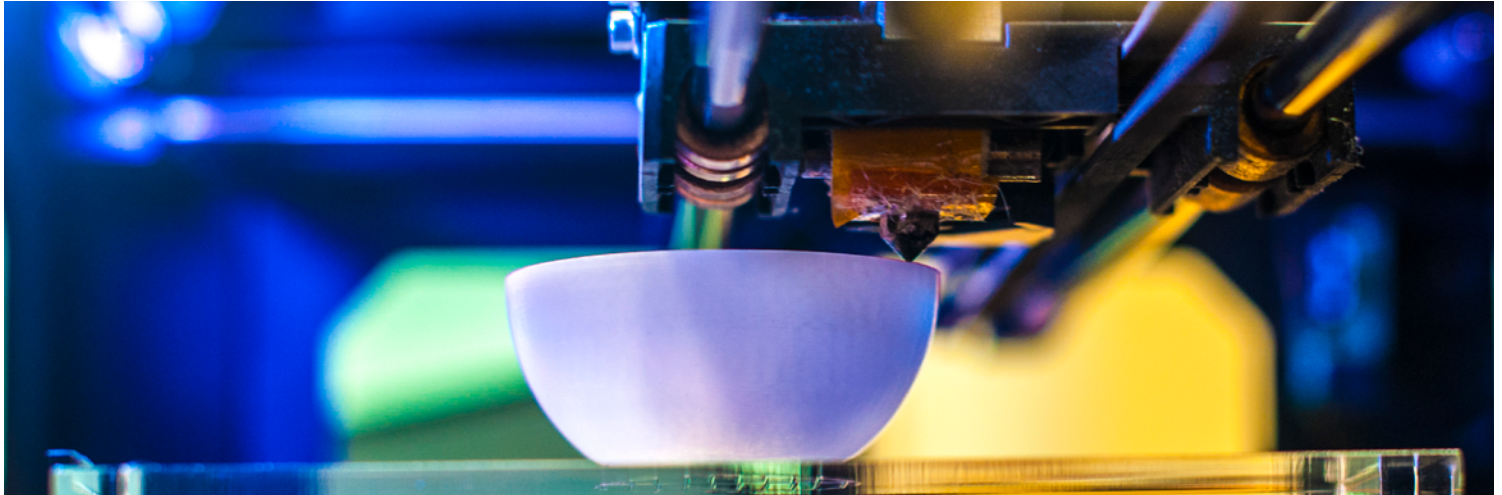
Molders and service bureaus: Use of UL Solutions AM certified materials enables market access for products requiring certification and helps ensure quality along the AM supply chain.

3D printing versus injection molding

The validity of plastics recognition is based on the premise that the pre-selection of material properties are representative of material properties expected in the final product. This implies that the test specimens used to generate the material properties reported in a plastics recognition were made by the same manufacturing process as the final product and are of comparable quality. This is to help ensure that there are no macroscopic differences between the representative materials and the final product as well as to confirm that the molecules in the representative materials are subjected to the same thermal and physical mixing history as the molecules in the final product.

When comparing two dimensionally equivalent parts, one injection molded and the other 3D printed by material extrusion, the injection molded part is uniformly dense throughout the sample whereas the 3D printed part is not. The 3D printed part can have voids and channels visible to the naked eye. These voids are created as part of the 3D printing process. Also, the injection molded part has a smooth outer surface attributable to the smooth mold cavity walls whereas the 3D printed sample does not — unless the 3D printed part is subjected to a post-processing step such as sanding or polishing to smooth the outer surface.

UL Solutions looked to polymer science, specifically polymer-entanglement theory, to understand how the molecules can differ when 3D printed versus injection molded and what this means for material properties of 3D printed parts compared to injection molded parts.



Injection molded samples are comprised of well-mixed polymer that is forced into mold cavities and then cooled to “lock” the entangled molecular structure together. In contrast, 3D printed samples, produced by the material extrusion process, are formed by extruding well mixed, molten polymer into a bead that is deposited alongside other beads. The polymer molecules within the bead are entangled — like in the injection molded samples — and can transfer stress along the bead, i.e., the raster direction. However, the polymer molecules at the interface between the adjacent beads may or may not be entangled depending upon molecular mobility and diffusion time. Other 3D printing processes have similar entanglement limitations, caused by their specific process technology.

If a 3D printed sample was made such that there was insufficient time or thermal energy for the molecules to entangle across the interface, then the interface between adjacent deposited beads would be structurally weak relative to the well-mixed molecules along the bead. This could lead to mechanical failure at the interface.



Injection molded parts

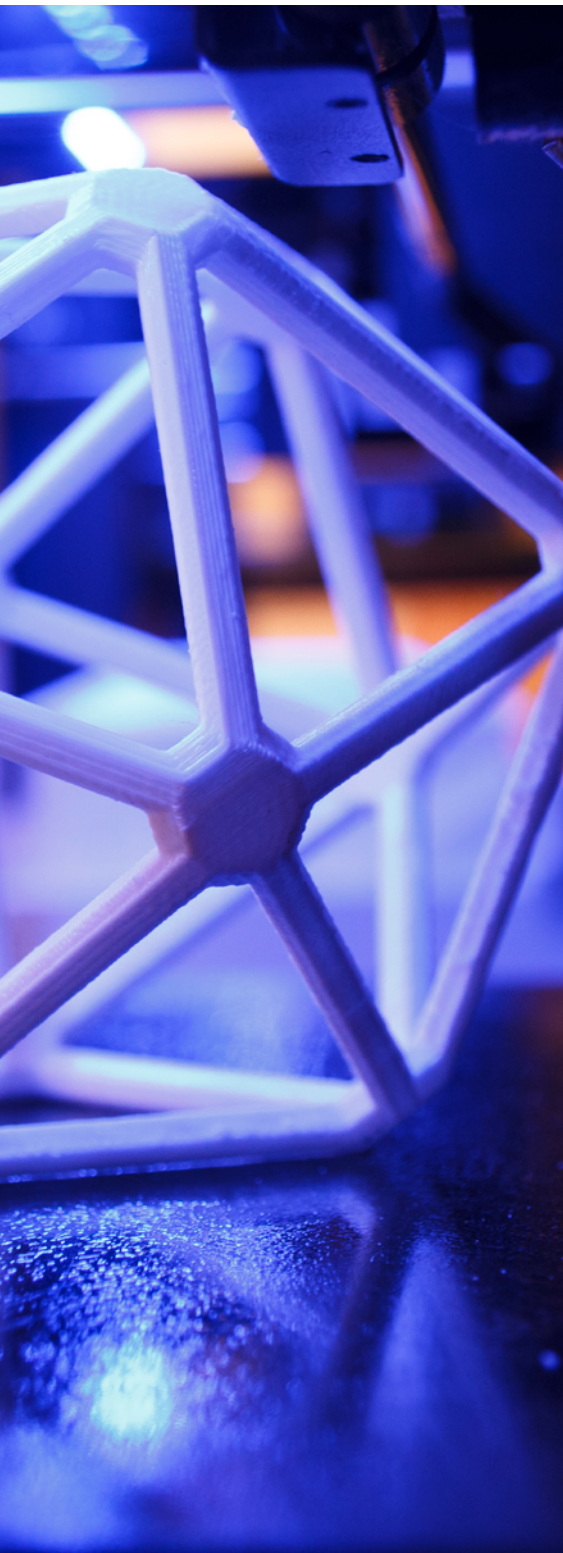


3D printed parts

Tensile strength variations and polymer entanglement

UL Solutions acknowledged how these voids and uneven outer surfaces could affect the mechanical properties and structural integrity of 3D printed materials. Previous research on this topic was already published in a 2002 Rapid Prototyping Journal issue. Findings from the study demonstrated that the tensile strength of an acrylonitrile butadiene styrene (ABS) polymer 3D printed by material extrusion could vary by more than fivefold depending upon the orientation of the printed raster — axial versus transverse — and be as much as an order of magnitude less than a dimensionally equivalent injection molded specimen².

These variations in tensile strength for 3D printed and conventional injection molded specimens can be readily explained by polymer-entanglement theory.



Variations in performance properties

Despite ample evidence of the influence of 3D printing on printed part mechanical properties, such as tensile strength, there was a lack of research on the influence of 3D printing on safety-critical performance properties. For example, injection molded specimens are solid throughout with minimal local density variations and smooth sides. Specimens that are 3D printed by material extrusion can have gaps and voids between adjacent deposited beads and an uneven surface stemming from the exposed bead edges. This difference can affect the performance properties of 3D printed materials in the following ways:

1. The air in the gaps and voids created by the 3D printing process have a different dielectric property than the polymer and could therefore act as an insulator to electric current.
2. These gaps could act as thermal insulation to heat exposure, effectively reducing the thermal mass of the exposed surface and increasing ignitability.
3. The 3D printed sample's greater surface area density could accelerate flame propagation and potentially lower the specimen's flame rating.
4. Vertically oriented channels could act like chimneys to redistribute heat along the inside of the printed specimen and introduce fresh air to further accelerate sample flammability.

A real problem: How to evaluate and certify 3D printed materials?

These variations, and the industry's lack of understanding about them, posed a real problem. UL Solutions Plastics Recognition Program did not include information about 3D printed materials as information about the variations in 3D printing did not exist. How would manufacturers know if a 3D printed plastic was safe to use in their products? It was clear a solution was needed to mitigate risk and provide safety to users of 3D printed materials.

Considering that these processes had never been comprehensively tested and analyzed, there was no way of answering the fundamental question of product safety. It was obvious that a first-of-its-kind research study needed to be conducted to obtain the information required in order to create a new plastics recognition program for AM. That's where UL Solutions team of experts came in.



Finding answers

Recognizing this lack of knowledge about the impact of 3D printing on polymer material and performance properties, UL Solutions Dr. Thomas Fabian, an internationally known polymer and fire researcher, led a 14-month-long research study. The objectives of the study were to explore the influence of various 3D printing and build parameters on UL 94 and UL 746A material properties and compare results to properties obtained from conventional injection molding.

The study culminated in the publication of a 64-page technical report, titled “Influence of 3D Printing by Material Extrusion on UL 94 and UL 746A Material Properties.” Results from this report provided the preliminary knowledge necessary to develop guidelines for certifying polymer materials intended for 3D printing. The data was also used as a guideline to draft the requirements to address the difference in performance between 3D printed parts and conventional injection molded and extruded parts.



UL Solutions 3D printing research project

UL Solutions investigated the influence of the four material extrusion user-controllable print parameters and build strategies expected to most influence printed part performance. Two polymers commonly used in the electronics and electrical appliance market were printed using systematically different combinations of build orientation, air gap, build strategy, i.e., raster direction in successively printed layers, and layer thickness via printer tip size. The printed specimens were assessed for dielectric strength, volume resistivity, hot wire ignition (HWI), comparative tracking index (CTI), high-current arc ignition (HAI) and UL 94 V flammability performance. The two materials were also injection molded for material property comparison to the 3D printed specimens.

Materials

Test specimens of the two commercially available polymeric materials were made by conventional injection molding and 3D printing, including:

1. frABS: black color flame retardant poly (acrylonitrilebutadiene-styrene) filament with a 2.85 mm diameter; UL 94 V-0 rating claimed
2. PEI: natural color polyetherimide filament with a 2.85 mm diameter.

The frABS polymer specimens were printed on a popular desktop 3D printer used to make products submitted to UL Solutions for certification, whereas the PEI specimens were printed on a common industrial-grade 3D printer.

Material preparation: Thermal history

To help ensure that their research would yield the most accurate results possible, the team took an additional step in the preparation process. UL Solutions materials testing laboratory in Krefeld, Germany, made injection molded test specimens from the frABS and PEI filament by chopping and drying the purchased filament, and then molding them. This meant that the injection molded samples were made with the same original filaments as the 3D printed samples and therefore had the same thermal history prior to sample formation.

The findings explained

While this investigation was by no means all encompassing, particularly with regard to the limited number of materials, printer models, print parameters and build strategies, our team discovered several important findings, including:

1. Print quality was more consistent with the industrial grade printer than the desktop printer, presumably because of the industrial-grade printer's superior motors, actuators and measurement system as well as its enclosed temperature-controlled build chamber.
2. Print parameters and build strategies influenced results to the degree that the same material on the same printer yielded critically different performance.
 - Build orientation was the most influential of the four investigated print parameters and build strategies for most of the performance properties.
 - Air gap and tip size tended to have an interactive influence on performance properties, possibly by affecting void size and printed part density.
3. Dimensionally comparable 3D printed and injection molded test specimens did not yield the same performance results. 3D printed specimens yielded comparable or inferior performance, e.g., lower dielectric strength/resistance, worse flame rating and longer burning time — versus injection molded specimens, except for CTI.
4. CTI measurements of the grooved surface of 3D printed specimens appeared to yield misleading results because of a test method artifact. The surface grooves and any voids emanating downward from the test surface can wick the electrolyte test liquid away from the electrodes to artificially reduce the amount of electrolyte at the electrodes and promulgate higher CTI ratings than for a smooth, non-wicking surface.
5. UL 94 Flammability Test results were worse for 3D printed frABS than injection molded frABS, whereas 3D printed PEI was comparable or slightly better than injection molded PEI. This contrasting behavior suggests that the UL 94 Flammability Test response of 3D printed specimens is influenced by the print parameters and build strategy — presumably via influence on the physical characteristics of the test specimen — in combination with inherent material properties.

We expect these findings to translate to other polymers and possibly other 3D printing technologies.

Experiment plan

frABS on \$4k desktop printer

PEI on \$45k industrial printer

DoE

Full factorial w/center DoE

- Build orientation
- Raster angle
- Air gap
- Layer thickness

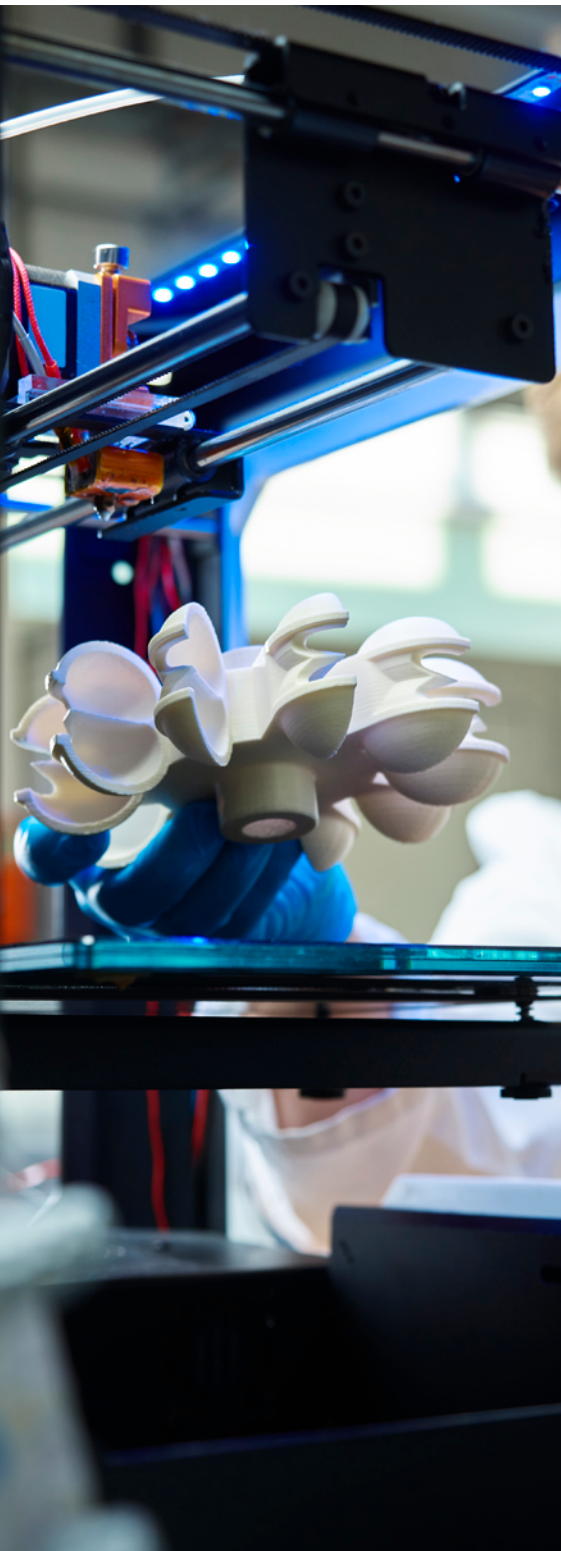
PLUS injection molded

UL 746 Tests

- Dielectric strength
- Volume resistivity
- CTI
- HAI
- HWI
- UL 94 flammability

What our research indicated:

- Injection molded sample dimensions were more consistent than 3D printed sample dimensions
- The industrial-grade printer yielded more consistent quality than the desktop printer
- Print parameters and build strategies significantly influenced the results
- The same material on the same printer can yield critically different performance
- No 3D printed build outperformed injection molded specimens — except for comparative tracking index (CTI)
- Some test methods and practices may need to be updated for 3D printed specimens



Applying lessons learned to end-use applications

Based on our technical report, we offer the following recommendations:

1. Material performance properties used to assess compliance of 3D printed components and products should be based on test specimens printed the same way as the 3D printed component or product and not on traditionally molded test specimens
2. Develop guidelines within the industry for assessing the “true” CTI of materials used in 3D printed components and parts
3. Investigate the influence of inherent material characteristics and physical characteristics of printed specimens on performance properties
4. Expand investigation on the influence of 3D printing to include long-term thermal aging effects as described in UL 746B
5. Expand investigation on the influence of 3D printing to other 3D printing technologies such as powder bed fusion and vat polymerization

A new program and a new card for a new technology

Product developers have long relied on UL Solutions’ Plastics Recognition Program (Yellow Card) to determine and verify material properties and performance characteristics of polymeric materials. Specifically, developers rely on the electrical, flammability, mechanical and thermal properties listed on the Yellow Card to select materials that comply with their product’s functional and safety requirements. Likewise, UL Solutions engineers rely on Yellow Card listed material properties to evaluate material suitability for use in products submitted to UL Solutions for certification.

Material properties published on UL Solutions Yellow Cards, however, are representative of test specimens formed through conventional manufacturing processes — like injection molding and film extrusion. Material properties measured on test specimens formed by 3D printing are not distinguished on the Yellow Card. As earlier noted, mechanical, flammability and other safety-critical performance properties of 3D printed materials have been demonstrated to vary significantly based on how test specimens are printed. These variations have proven to be substantially greater than those of conventional injection molded samples. AM represents an advancement in technology that demands an evolution in how materials are assessed, characterized and certified.

UL Solutions research on 3D printed polymer performance

Based on the recommendations from this study, UL Solutions introduced the certification program for Plastics for Additive Manufacturing (Blue Card). Serving as an extension of UL Solutions' Plastics Recognition (Yellow Card) Program, the Blue Card defines the additional requirements necessary to recognize plastics intended for 3D printing and 3D printed components and products. The card applies to AM processes such as material extrusion, vat photopolymerization, powder bed fusion, binder jetting and material jetting.

A Blue Card is issued when a material intended for 3D printing receives a UL Recognized Component Mark. Certified materials are added to the UL iQ™ and Prospector® databases, which are used by thousands of end-product manufacturers to find providers of certified materials and components.

An impactful marketing tool

The Blue Card demonstrates that a material is appropriate for a specific 3D printing technology in a compact, simple and easy-to-read digital format. This makes it the ideal recognition for manufacturers of materials and components to promote their products. The Blue Card showcases to the world that a manufacturer is using a tested and certified material, which facilitates access to global markets. It also enables manufacturers to give potential customers peace of mind, knowing that their products are being monitored at regular intervals by an independent test laboratory.

A key differentiator in a competitive market

Since UL Recognized materials are added to the UL iQ™ and UL Solutions Prospector® databases, Blue Cards are immediately visible to thousands of designers, engineers and suppliers searching for a material or component provider that can meet certain safety and performance requirements. UL Recognition also includes UL Follow-Up Service to help ensure that certified plastics continue to meet UL Standards for safety and performance, a key differentiator for end-product manufacturers. Products made using UL Recognized materials can move through certification both faster and less expensively than those that do not use UL Recognized materials.



Why trust UL Solutions?

UL Solutions history of testing plastics dates back to 1941 and UL Solutions currently provides service to all of the world's top plastics manufacturers. UL Solutions works closely with plastic industry stakeholders to maintain and enhance existing UL Standards, establish new Standards and develop certification and testing programs that address emerging technologies and product applications.

UL Solutions team of plastics experts consists of professionals from the AM space as well as experienced plastics testing engineers, and is led by an internationally known polymer and fire researcher. UL Solutions expertise, reputation and resources enable us to provide our customers with an important product differentiator in a crowded marketplace: communicating safety, performance and quality to original equipment manufacturers (OEMs), purchasers and regulatory authorities.

Summary and conclusion

When UL Solutions team of plastics experts recognized that the industry needed a new material certification program for materials used in 3D printing, they pioneered a 14-month-long research study to investigate the influence of various 3D printing and build parameters on UL 94 flammability and 746A material properties.

Results from the study indicated that 3D printing can result in significantly, even critically, different material performance depending on print parameters and print equipment. This meant that UL Solutions Yellow Card Program, which certifies materials designed to be used in conventional manufacturing, was not appropriate for the tremendous flexibility offered by 3D printing. At the time, a certification program specific to AM materials and 3D printed products did not exist within the industry.

To address this need, we leveraged information from our groundbreaking study to create a certification program for materials used in 3D printing: UL Solutions certification program for Plastics for Additive Manufacturing (Blue Card). The program presents the data necessary to prove the safety, integrity and usefulness of materials in 3D printed products. UL Solutions Blue Card program independently certifies this critical information for the AM industry.

Learn more at [UL.com/BlueCard](https://www.ul.com/bluecard).

Endnotes

1. <https://www.statista.com/topics/1969/additive-manufacturing-and-3d-printing/>
2. Ahn SH, Montero M, Odell D, Roundy S, Wright PK. Anisotropic material properties of fused deposition modeling ABS. Rapid Prototyping Journal. 2002; 8(4): 248-257.
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