WHITE PAPER

Achieving Long-Term 3D Printed Resin Performance and Stability

Production-grade photopolymer resins provide enhanced strength, durability, and aesthetics over legacy resins

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3D SYSTEMS
Additive Manufacturing Solutions

The manufacturing world enjoys many benefits from additive manufacturing. These include faster development cycles for a shorter time-to-market, reduced product costs and lead-times, greater design flexibility, and countless opportunities for lighter, more robust products. There is also a wide variety of 3D printing technologies and materials to choose from, with more seemingly coming online each day.

Stereolithography and Projection-Based 3D Printing

One of the most capable and well-known 3D printing technologies is stereolithography (SLA), pioneered by 3D Systems' founder Chuck Hull more than 30 years ago. Together with its newer counterpart, the high speed, projection-based Figure 4® platform, these similar yet distinct additive manufacturing processes are an excellent solution for anyone who needs highly accurate 3D-printed parts in a range of advanced polymers.

Both technologies use ultraviolet (UV) light to cure sequential layers of photoreactive resin, a process known as vat polymerization. As the term implies, these epoxy, acrylic, or methacrylic monomer-based resins polymerize and harden when exposed to certain wavelengths of light. But where SLA uses a UV laser to draw each layer directly on the resin surface, Figure 4 employs a digital light source to project a series of images onto the photopolymer, curing each layer in an instant. This allows for print speeds in excess of 50 mm (2 in) an hour.

We'll discuss the merits and applications of each technology later in this paper, but first it's important to know that SLA is considered by many to be the undisputed champion of high accuracy prototyping, large format printing, and tooling applications. Figure 4, on the other hand, is generally the favorite for scalable, higher volume production of end-use polymer components.

3D Systems SLA 750 (left) and Figure 4® Modular (right) 3D printers

The Pros and Cons of Traditional Photopolymer Printing

Photopolymer materials have served as the foundation of 3D printing for decades, and only continue to broaden their capabilities with each passing year.

Photopolymers are liquid polymer resins that cure when exposed to light. They are a type of thermoset plastic. Unlike thermoplastics, which can be repeatedly melted and reformed into different shapes, the polymer chains within thermoset plastics are crosslinked or “cured” into a permanent form.

When describing these photopolymers, it is often preferred to reference engineering thermoplastics such as polypropylene (PP), acrylonitrile butadiene styrene (ABS), and polycarbonate (PC). These polymers are found broadly in machined, cast, and injection-molded parts, and are used in our everyday products. Photopolymers are generally formulated to replicate many of the properties of these “traditional” polymers.

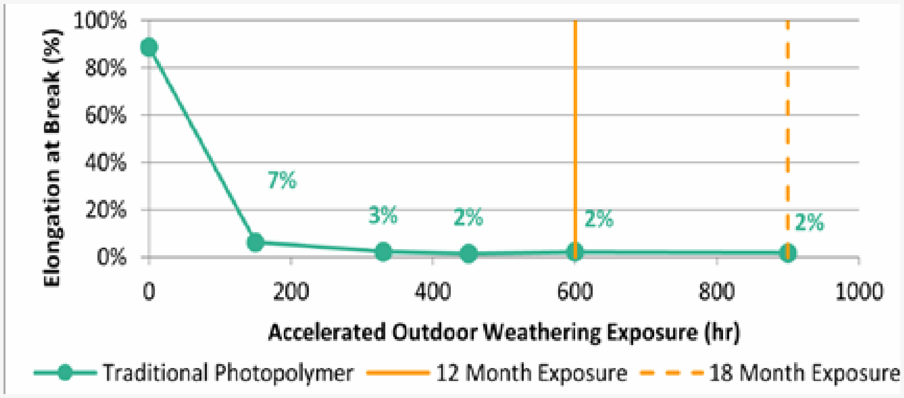
Photopolymer materials and the equipment they are 3D printed on provide excellent part quality, accuracy, and speed, with investment costs that are much lower than their conventionally produced counterparts. They provide a versatile, cost-effective path for a host of prototypes, low-volume parts, jigs, fixtures, and investment casting patterns for jewelry manufacturing. There’s just one problem: because the photopolymer resins used in 3D printing are cured with exposure to UV light, they have historically been susceptible to degradation with exposure to additional UV light—that is, sunlight—which has limited their applications for everyday commercial products

Depending on the amount of sunlight, whether it’s direct or indirect, and other environmental conditions such as humidity, white and gray parts will begin to yellow and eventually turn black. Clear parts will often turn yellow, then brown. To make matters worse, rapid polymer degradation results in cracking and extreme brittleness.

Although these effects may take years to manifest, photopolymer resins have nevertheless gained a reputation for unsuitability for long-term use. These polymers have therefore been relegated to the world of prototyping and non-functional parts despite their many positive attributes. This is particularly true of SLA technology.

With this being the case, an obvious question becomes: Why not 3D print these parts from one of the many thermoplastics used in fused filament fabrication (FFF) and selective laser sintering (SLS), or plastic injection mold them instead? As many additive manufacturers will attest, one or more of these has often been a good solution. However, like any technology, these come with their own set of unique benefits and drawbacks. With photopolymer printing, the advantages come down to part accuracy, surface finish, and speed.

OUTDOOR WEATHERING STABILITY



The rapid loss in mechanical properties as shown in the elongation at break curve is often accompanied by a significant change in color.

Example of the degradation seen with traditional photopolymers in outdoor weathering.

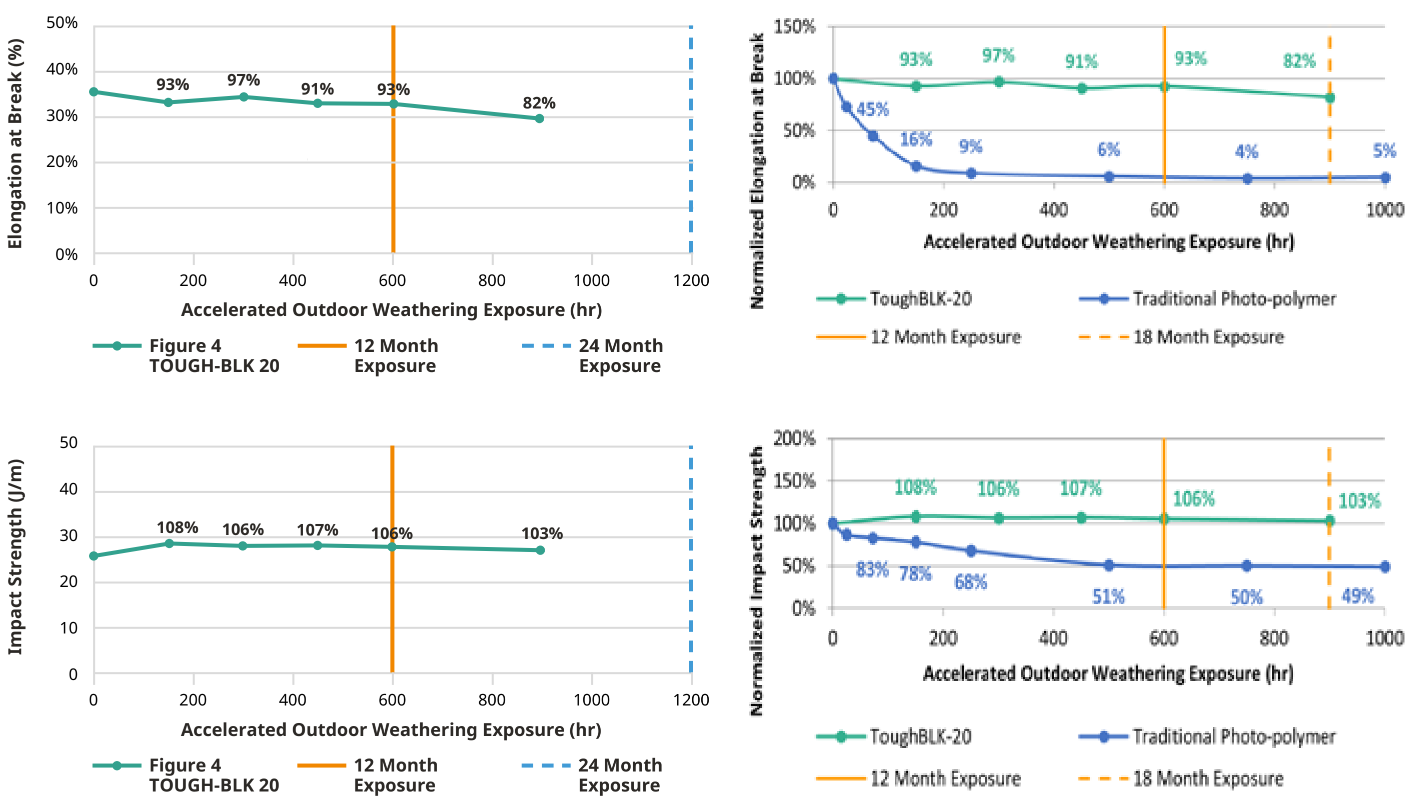
Color change in 3 mm thick coupon of a traditional clear SLA material. Images taken after the equivalent of 3, 6, and 9 months of accelerated outdoor exposure.

Advancing Photopolymer Material Properties to Improve Longevity

3D Systems' chemists have taken on the challenge of overcoming the long-term stability issue in photopolymers, and have been able to revolutionize capabilities using both Figure 4 and large-format SLA, using novel chemistries not previously attainable with traditional resin materials. These chemistries have opened the door to the first true production-ready polymers for additive manufacturing.

Figure 4® TOUGH-BLK 20 was the first photopolymer offered by 3D Systems to be formulated with this patented UV-stability technology. This first-of-its-kind product offered long-term mechanical and color stability measured beyond 18 months' outdoor exposure. Figure 4 TOUGH-BLK 20's stability is demonstrated in the retention of mechanical properties such as tensile strength and modulus, elongation at break, and notched impact strength.

FIGURE 4 TOUGH-BLK 20



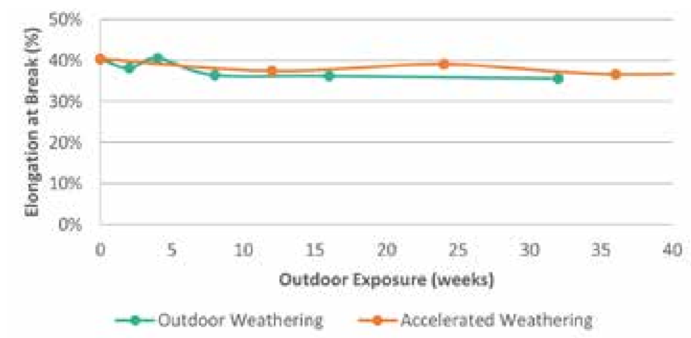
Outdoor weathering curves of Figure 4 TOUGH-BLK 20, an industry first photopolymer formulated for outdoor weathering resistance.

Material Properties and Accelerated Weathering Testing

Product designers and manufacturers must carefully analyze the properties of 3D printed materials to determine which ones will best meet their requirements, as well as which 3D printing processes will provide the accuracy, surface finish, and production speed needed for their project. Because paradigm-changing materials are being developed on a routine basis, it is also important that they stay current on these technologies.

Before exploring those developments, you might be wondering how to evaluate engineering-grade polymers, photoreactive or otherwise. Also, how are 3D printer manufacturers and materials suppliers determining a given polymer's expected lifespan? After all, each use case is different, and each part is unique. Who's to say how much sunlight, what temperature extremes, or moisture exposure a product will endure before failure, or until unacceptable levels of discoloration are reached?

ACTUAL VS. ACCELERATED WEATHERING



Comparison of accelerated outdoor weathering and actual outdoor weathering on a typical photopolymer's elongation at break.

USING ASTM TESTING METHODS

While evaluating outdoor stability, 3D Systems measured both natural outdoor weathering, over months and years, and industry standardized accelerated weathering in accordance with multiple ASTM and ISO standards. An important aspect of accelerated weathering is correlating the hours in the chamber to the effects of the natural weathering being simulated.

Prior to the launch of Figure 4 TOUGH-BLK 20, 3D Systems evaluated the natural outdoor weathering decay in mechanical properties of several formulations over the course of a year. These initial formulations represented the breadth of state-of-the-art chemistries at the time. Concurrently, samples were subjected to accelerated weathering to produce both natural and accelerated decay curves. Fixing the end points for each material based on tensile elongation at break, and solving each equation for fit, 3D Systems developed an acceleration factor for outdoor weathering. As new chemistries, technologies, and post-process techniques are developed, samples are routinely naturally weathered to validate this acceleration factor.

Figure 4 PRO-BLK 10 is one of 3D Systems' most popular production-grade materials,offering rigid, long-term performance.

Long-term outdoor stability can be defined by many measured properties. Discoloration or fading is the most obvious, and as previously mentioned, it represents significant challenges to photopolymers. Mechanical properties, more importantly the retention of “as printed” properties, are of equal importance. Properties of interest are typically:

- **TENSILE STRENGTH, TENSILE MODULUS, AND ELONGATION AT BREAK**

  Tensile properties are the most reported mechanical property when evaluating long-term performance. **Tensile strength** is the maximum stress that a material can withstand without incurring permanent damage. It is reported in megapascals (MPa) and often historically in pounds per square inch (PSI). **Tensile modulus**, also known as Young’s modulus or the modulus of elasticity, often refers to a material’s stiffness. It is calculated as the ratio of tensile stress to the amount of strain that initially occurs during tensile testing. **Elongation at break** measures a material’s ductility. It is defined as the ratio of the test coupon’s starting gauge length to its length upon breaking. Similarly, **elongation at yield** is the ratio of the test coupon’s starting length to the length at which permanent damage occurs. Both are measured as a percentage, with a higher value indicating greater ductility. 3D Systems tests rigid and semi-rigid polymers in accordance with **ASTM D638**, and elastomeric polymers in accordance with **ASTM D412**.

- **IMPACT STRENGTH**

  More commonly referred to as **Izod impact testing**. Whereas tensile and elongation testing apply force by pulling until breakage occurs, impact testing is performed by applying force onto notched and unnotched test samples by swinging what is essentially a precisely shaped hammer against the test coupons. Both notched and unnotched impact tests measure the energy required to break the coupon in Joules per meter (J/m) or foot-pounds per inch (ft-lb/in), and are an excellent indicator of a material’s impact resistance. For more information, refer to **ASTM D256**.

Figure 4 RUBBER-65A BLK is a mid-tear strength production-grade elastomer.

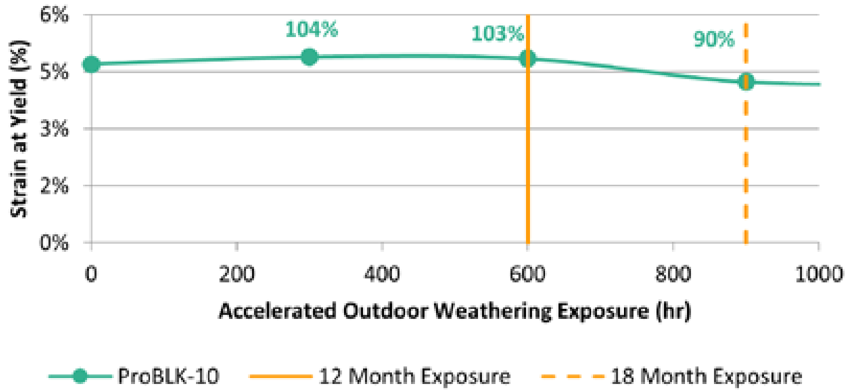
There are of course additional properties beyond these common properties. **Shore hardness** defines how deeply a needle or ball will penetrate a test specimen. Different hardness scales such as Shore A and Shore D are used for rubber-like materials or hard plastics, respectively. **Flexural strength** and **flexural modulus** in accordance with **ASTM D790** determine how much lateral force a test specimen can endure (as opposed to the axial force applied in tensile measurements). **Tear strength**, in accordance with **ASTM D624**, is also important for rubber-like materials and represents the force per thickness required to tear the material apart.

Using Datasheets to Match Materials with Applications

This information is clearly an important tool for any engineer searching for the best material to use in a given application. To support this need, 3D Systems publishes a thorough technical datasheet with a consistent display of properties. 3D Systems' datasheets provide a wealth of information to help guide the selection of the correct material for each application. Depending on the type of material, this might include: chemical resistance to industrial detergents and automotive fluids, biocompatibility and mechanical properties after sterilization, thermal resistance, isotropic properties, and sample applications for which the material will be suitable.

Returning briefly to the tensile strength and elongation described previously, design engineers should also pay attention to the stress-strain curve shown on many material datasheets. This is a graphic representation of a polymer's behavior under stress, providing valuable insights into how much stress the finished product will absorb in the real world, no matter how it's 3D printed. With the production-ready Figure 4 platform, more ductile and elastic polymers have been developed that were previously unachievable. This new generation of photopolymers have true tensile yield points resulting in more plastic-like deformation, such as necking and work hardening. The **tensile yield** point, as defined by a zero-point modulus, is the average maximum stress and strain the material can withstand before undergoing permanent deformation. Materials such as Figure 4® PRO-BLK 10 have a tensile yield point of 4.6% with an average elongation at break of 12%. This yield point allows for repetitive bending/straining of the material, as is seen when engaging and disengaging a clip or connector. After 1.5 years of accelerated weathering this yield point is retained at nearly 100%, whereas a traditional SLA polymer would typically have degraded before 3 months with a complete loss of all properties.

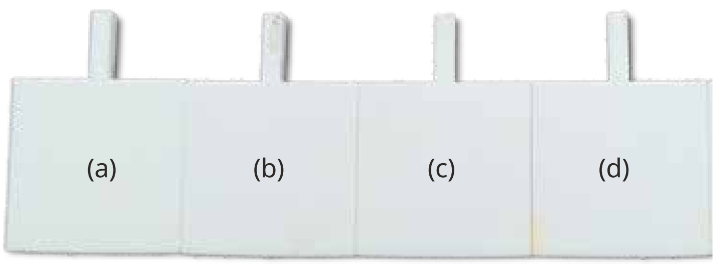
ACCELERATED WEATHERING



Outdoor weathering curve of the average strain at yield for Figure 4 PRO-BLK 10 measured past the equivalent of 18 months' exposure.

With 3D Systems' production-ready materials, these datasheets also provide information on long-term environmental stability. This paper began with the premise that the photopolymers used in projection-based printing and SLA have a reputation as "prototype only" materials due to their tendency to yellow and crack when subjected to light and other environmental conditions. Thanks to recent resin advancements at 3D Systems, this decades-old paradigm is shifting.

For example, for Figure 4® Rigid White, an opaque, biocompatible photopolymer used in medical applications, electronics enclosures, motor housings, and other small components, the datasheet indicates "good long-term environmental stability measured out to eight years indoor and two years outdoor." Similarly, yet with distinction, Figure 4® Tough 60C White enjoys long-term environmental UV and humidity stability, long-lasting white color, and injection molded-like surface quality. As such, 3D Systems recommends its use for "high mechanical load-bearing batch production medical parts that remain functional and stable for years."



Above: Accelerated outdoor weathering color samples: (a) control, (b) 6 months, (c) 12 months and (d) 18 months equivalent exposure.

Left: Outdoor weathering curves of Figure 4 Tough 60C White, a vibrant white, durable plastic that maintains its color for years.

FIGURE 4 TOUGH 60C White

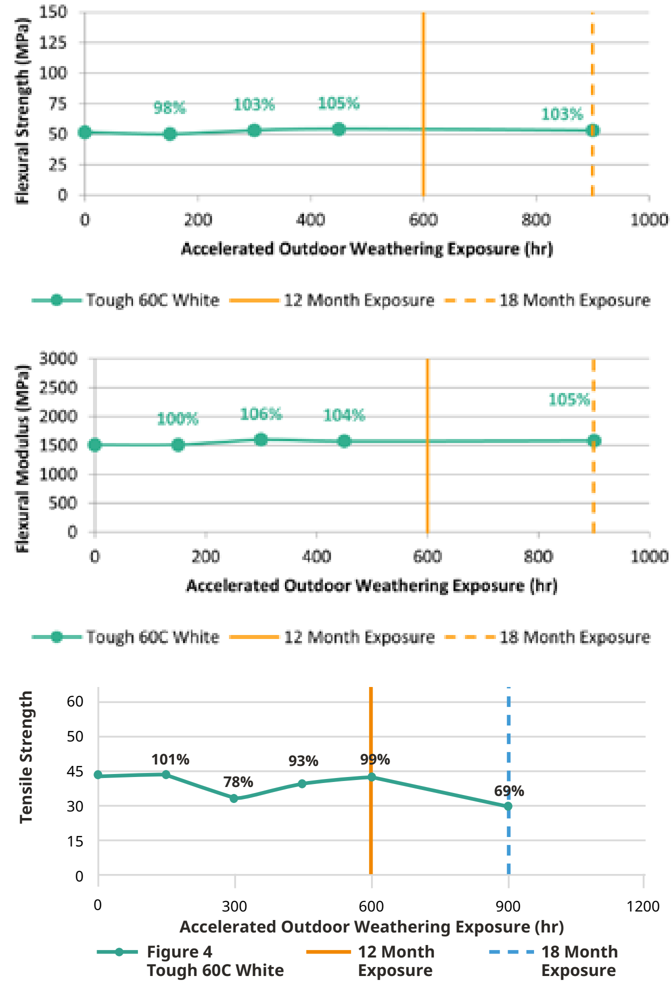
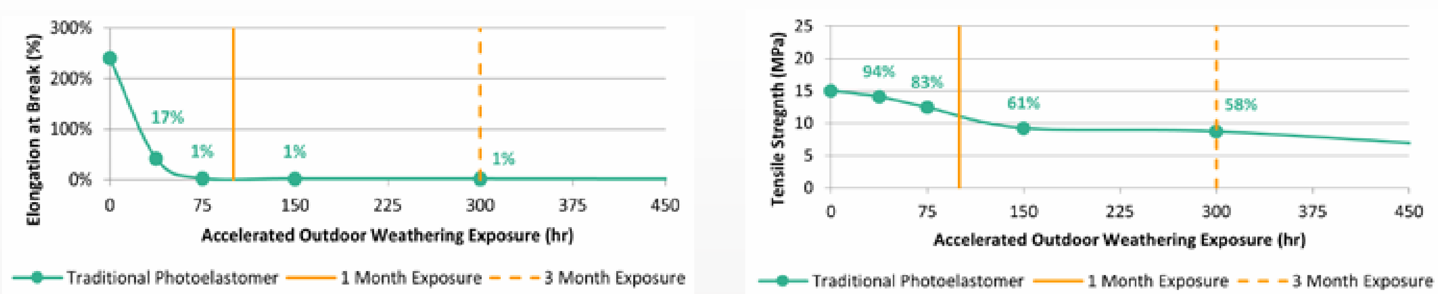


Figure 4® RUBBER-65A BLK is another example of how 3D Systems' advanced chemistry is solving decades-old problems. Traditional elastomeric photoset polymers are formulated to be under-cured, thus providing elasticity similar to a conventional elastomer. However this results in poor stability as the parts continue to slowly cure over time with exposure to light. Accelerated outdoor weathering of these traditional materials reveals complete loss of mechanical properties in less than the equivalent of 3 months' outdoor exposure.

FIGURE 4 RUBBER-65A BLK



Traditional photo elastomer accelerated outdoor weathering curves. Elongation at break quickly nears zero before the equivalent of 20 days' outdoor exposure.

In contrast, Figure 4 RUBBER-65A BLK maintains nearly all key mechanical properties at 18 months' outdoor exposure, such as tensile modulus, elongation at break, and Shore A hardness.

FIGURE 4 RUBBER-65A BLK

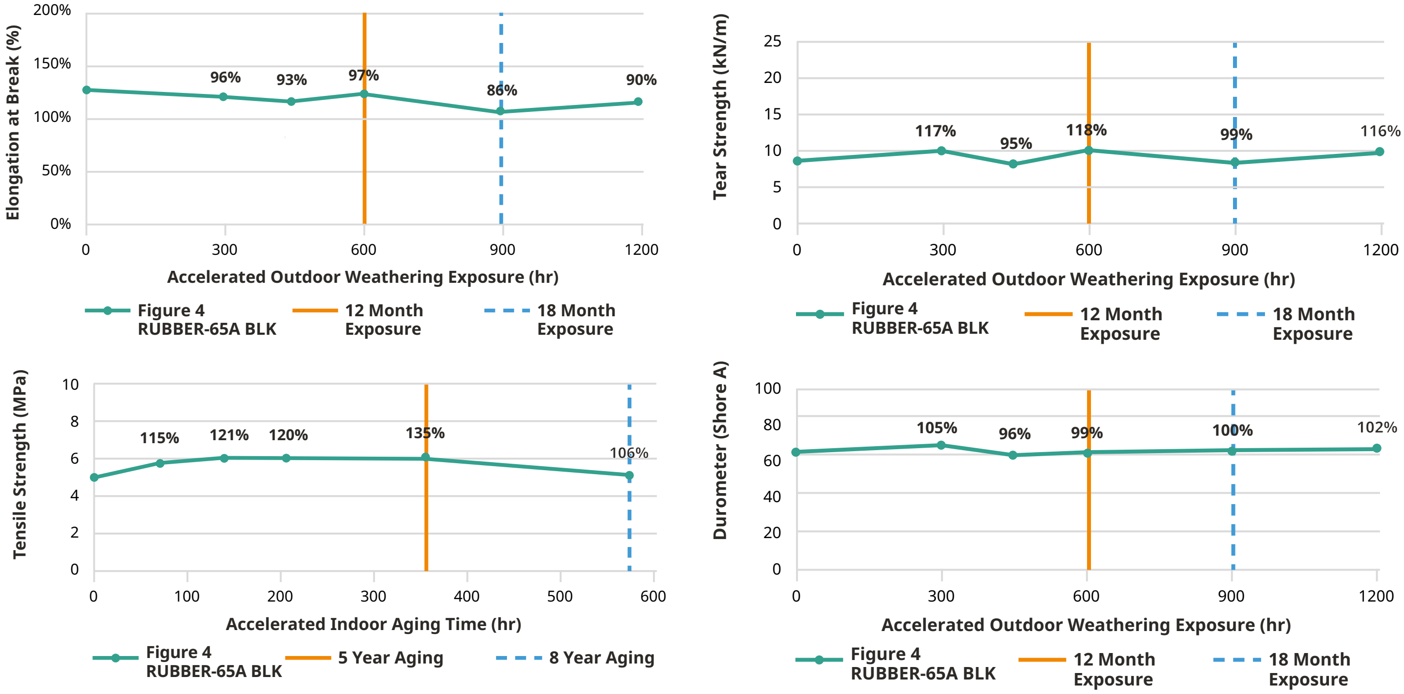


Figure 4 RUBBER-65A BLK is an industry-first elastomeric photopolymer with over 18 months of outdoor stability. It exhibits less than 14% reduction in key average mechanical properties, including tensile strength, elongation at break, Shore A hardness, and Type C tear strength.

Better Materials, Longer-Lasting Parts, Better Value

Why is this information important? As indicated earlier, SLA and projection-based Figure 4 3D printing provide superior aesthetics, accuracy, and mechanical properties. SLA is now suitable for large-format, production-grade end-use parts, particularly when using production-grade SLA resins such as Accura® AMX Rigid Black or Accura AMX Durable Natural. Figure 4 also produces production-grade parts and offers the speed needed for even high-volume applications. Thanks to the increasing number of strong, durable resins available for each technology, any concerns over longevity are quickly falling by the wayside.

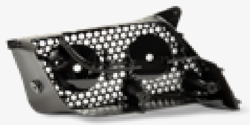
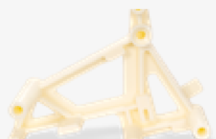
Knowing that a white or gray product will remain white or gray for years is an important benefit for any manufacturer, as is the knowledge that such products will remain functional.

But these material advancements go beyond aesthetics. Longer-lasting parts mean a better shelf life and fewer warranty complaints. Functional prototypes more accurately represent the product's long-term viability. Not to mention, higher production speeds without sacrifices in accuracy open the door to lower manufacturing costs and a host of applications once dominated by plastic injection molding.

3D Systems' production-grade resin solutions provide all of this and more. Best of all, they work in existing ProX and ProJet SLA printers and Figure 4 printers with no equipment modifications. To Figure 4 users, this means batch runs of perhaps thousands of small, end-use parts in as little as 48 hours. Meanwhile, SLA users can rest assured that prototypes and low-volume parts will remain functional and attractive for years.

Summary of 3D Systems Production-Grade* Photopolymer Resin Plastics

*All materials in this listing feature long-term stability of mechanical performance, at up to 8 years indoor and 1.5 or 2 years outdoor, per ASTM testing methods.

	MATERIAL NAME	TECHNOLOGY	PROPERTIES	APPLICATIONS
	**ACCURA® AMX RIGID BLACK**	SLA	Rigid, Tough	Large size, high-impact production fixtures, end-use parts and functional prototypes.
	**ACCURA® AMX DURABLE NATURAL**	SLA	Durable, Tough	Large-scale, tough plastic parts, mandrel tooling for composites, end-use parts such as structural components, containers and enclosures, and functional prototypes.
	**FIGURE 4® PRO-BLK 10**	Figure 4	Rigid	Static, rigid end-use parts and functional prototypes including covers and housings.
	**FIGURE 4® RIGID GRAY**	Figure 4	Rigid	High contrast, static, rigid end-use parts and functional prototypes requiring texturing, lettering, painting and plating.
	**FIGURE 4® FLEX-BLK 20**	Figure 4	Durable	High-impact-resistant, polypropylene-like functional prototypes and end-use parts such as clips, enclosures and containers.
	**FIGURE 4® RUBBER-BLK 10**	Figure 4	Hard Elastomeric	Tear-resistant, malleable, functional prototypes and end-use parts such as grips, handles, bumpers, and strain-relief applications such as couplings and overmolds.
	**FIGURE 4® RUBBER-65A BLK**	Figure 4	Soft Elastomeric	Mid-tear strength functional prototypes and end-use parts such as grips, handles, gaskets, bumpers, seals, and vibration dampening components.
	**FIGURE 4® HIGH TEMP 150C FR BLACK**	Figure 4	Rigid, High Temperature, Flame Retardant	Rigid, UL94 V0 rated functional prototypes and end-use parts such as brackets, covers, and circuit board housings and covers.

Summary of 3D Systems Production-Grade* Photopolymer Resin Plastics

*All materials in this listing feature long-term stability of mechanical performance, at up to 8 years indoor and 1.5 or 2 years outdoor, per ASTM testing methods.

	**FIGURE 4® TOUGH 65C BLACK**	Figure 4	Rigid, Tough	Rigid, high impact production fixtures, end-use parts and functional prototypes such as clips, buckles and snap-fits.
	**FIGURE 4® TOUGH 60C WHITE**	Figure 4	Rigid, Tough, Biocompatible	Rigid, high impact production fixtures, end-use parts and functional prototypes such as clips, buckles and snap-fits requiring biocompatibility per ISO 10993-5 and ISO 10993-10.
	**FIGURE 4® RIGID WHITE**	Figure 4	Rigid, Biocompatible	Rigid, static handles, covers, enclosures and fixtures for medical applications that require biocompatibility per ISO 10993-5 and ISO 10993-10.
	**FIGURE 4® HI TEMP 300-AMB**	Figure 4	Rigid, High Temperature	Ultra-high temperature rigid plastic for use in applications requiring high heat resistance with a heat deflection temperature of over 300˚C.
	**FIGURE 4® RIGID 140C BLACK**	Figure 4	Rigid, High Temperature	Rigid, heat-resistant material for tool-less, direct plastics production including automotive under-the-hood and in-cabin parts, clips, covers, connectors, housings, and fasteners.

What's Next?

Interested in learning more about SLA and Figure 4 additive manufacturing solutions?

Please contact 3D Systems for more information

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